

School of Civil and Mechanical Engineering
Department of Civil Engineering

Development and Utilisation of Bayer process By-products

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgement has been made. This thesis contains no material which has been accepted for any other degree or diploma in any University.



Evan John Jamieson

October, 2013

ABSTRACT

The Bayer Process is the hydrometallurgical treatment of bauxite ore for the extraction of alumina. Globally this process produces in excess of 64 millions of tonnes per annum of alumina (IAI, 2011). This extraction also results in a non-extracted residue called red mud. CSIRO (2011) report an estimated 120 million tonnes per annum of red mud production. This product is typically highly alkaline and needs to be contained in long-term secure storage facilities. It could however, be considered an underutilised resource.

Karl Bayer's original patent outlined many possible uses for bauxite residue (Bayer, 1889) and research has been conducted towards that outcome almost continuously since. In that time, very few products have entered the market and most are only of small volume.

This thesis assesses a variety of possible Bayer process by-products, and their subsequent utilisation. The focus is upon production of high volume commodity products that are made to specification and are suitable for multiple applications. This work includes pilot plant production and field demonstration trials.

This thesis reports on four key products that could make significant impact upon utilisation of wasted resources. These products are,

- Carbonated Red Mud and Alkaloam® - produced from the fine bauxite residue commonly termed red mud;
- Red Sand™ - manufactured from coarse bauxite residue;
- Red Lime™ - a by-product of liquor causticisation;
- Bayer-derived geopolymers - a cement replacement made from processed Bayer liquor.

These four products have been assessed and demonstrate significant benefit in their potential use.

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1 Peter 4:11

"If anyone ministers, let him do it as with the ability that God supplies, that in all things God may be glorified through Jesus Christ, to whom belong the glory and the dominion forever and ever." NKJV.

DEDICATION

To those that suffer from the hidden disease of the black dog:

I say never ever give up.

You can survive it.

The dog lies.

Get help.

Please!

I have commenced and completed this thesis while suffering the mental illness of anxiety and depression. I performed this task to show to my children and others that mental illness is an “Illness”. It is not a lack of cognitive function or rational thought.

LIST OF PUBLICATIONS ARISING FROM WORK

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LIST OF NOTATIONS

ALiAn	Alcoa Liquor Analyser
AMD	Acid Mine Drainage
ANC	Acid Neutralisation Capacity
ARPANSA	Australian Radiation Protection and Nuclear Safety Agency
ASLP	Australian Standard Leaching Protocol
ASS	Acid Sulphate Soil
Capex	Capital expenditure
CBR	California Bearing Ratio
CCWA	Conservations Council of Western Australia
CECP	Centre of Excellence in Cleaner Production
CIA	Concrete Institute of Australia
CSRM	Centre for Social Responsibility in Mining
CSRP	Centre for Sustainable Resource Processing
DAFWA	Department of Agriculture and Food, Western Australia
DEC	Department of Environment and Conservation
DEH	Department of the Environment and Heritage
DER	Department of Environmental Regulation
DOC	Dissolved Organic Carbon
DoE	Department of Environment
DSP	De-Silication Product
EBAM	Electronic Beta Attenuation Monitor
EIL	Ecological Investigation Level
ENV	Effective Neutralising Value
EPA	Environmental Protection Agency
ESA	Estimated Standard Axels
FC	Free Caustic
FWD	Falling Weight Deflectometer
GCRP	Geopolymer Concrete Recommended Practice
HIL	Health Investigation Level
ID	Internal Diameter
IAI	International Aluminium Institute
KIC	Kwinana Industries Council

LIMS	Low Intensity Magnetic Separation
LOI	Loss On Ignition
MMDD	Modified Maximum Dry Density
MRDWA	Main Roads Department Western Australia
NORMs	Naturally Occurring Radioactive Materials
NV	Neutralisation Value
ODD	Optimal Dry Density
OPC	Ordinary Portland Cement
Opex	Operational expenditure
PB	Parsons Brinckerhoff
PCR	Performance and Compliance Report
PER	Public Environmental Review
PRI	Phosphate Retention Index
PSD	Particle Size Distribution
QA/ QC	Quality Assurance and Quality Control
QEMSCAN	Quantitative Evaluation of Minerals SCANning electron microscopy
RILEM	Reunion Internationale des Laboratoires et Experts des Materiaux
RM	Resilient Modulus
SEM	Scanning Electron Microscopy
SGA	Southern Gateway Alliance
TA	Total Alkalinity
TC	Total Carbonate
TCA6	Tricalcium aluminate (Identified as katoite by XRD)
TCLP	Toxicity Characteristic Leaching Procedure
TGA	Thermo-Gravimetric Analysis
TOC	Total Organic Carbon
TS	Total Solubility
TSP	Total Suspended Particulates
WHIMS	Wet High Intensity Magnetic Separation
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

List of Chemical Symbols

Al_2O_3	Aluminium oxide, Alumina		
CaCO_3	Calcium carbonate, limestone		
CaO	Calcium oxide		
CO_2	Carbon dioxide		
Fe_2O_3	Iron oxide, hematite		
FeOOH	Iron oxyhydroxide, geothite, akagenite, lepidocrocite etc		
Ga_2O_3	Gallium oxide		
H_2O	Water		
K_2O	Potassium oxide		
$\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$	Jarosite		
KOH	Potassium hydroxide		
Na_2O	Sodium oxide		
NaOH	Sodium hydroxide		
OH	Hydroxide		
P_2O_5	Phosphorous oxide		
SiO_2	Silico dioxide, silica, quartz		
SO_3	Sulphur trioxide		
TiO_2	Titantium dioxide		

Ag	Silver	Mo	Molybdenum
Al	Aluminium	Na	Sodium
As	Arsenic	Nb	Niobium
B	Boron	Nd	Neodymium
Ba	Barium	Ni	Nickel
Be	Beryllium	P	Phosphorus
Bi	Bismuth	Pb	Lead
C	Carbon	Pr	Praseodymium
Ca	Calcium	Rb	Rubidium
Cd	Cadmium	Re	Rhenium
Ce	Cerium	S	Sulphur
Co	Cobalt	Sb	Antimony
Cr	Chromium	Sc	Scandium
Cs	Cesium	Se	Selenium
Cu	Copper	Si	Silicon
Dy	Dysprosium	Sm	Samarium
Er	Erbium	Sn	Tin
Eu	Europium	Sr	Strontium
F	Flouride	Ta	Tantalum
Fe	Iron	Tb	Terbium
Ga	Galium	Te	Tellurium
Gd	Gadolinium	Th	Thorium
Ge	Germanium	Ti	Titanium
Hf	Hafnium	Tl	Thallium
Hg	Mercury	Tm	Thulium
Ho	Holmium	U	Uranium
In	Indium	V	Vanadium
K	Potassium	W	Tungsten
La	Lanthanum	Y	Yttrium
Li	Lithium	Yb	Ytterbium
Lu	Lutetium	Zn	Zinc
Mg	Magnesium	Zr	Zircon
Mn	Manganese		

1 INTRODUCTION

1.1 Background

The Bayer process is the hydrometallurgical treatment of bauxite ore, for the extraction of alumina.

Alumina is used in many products but the main consumption is to produce aluminium. Globally, the Bayer process produces in excess of sixty four million tonnes of alumina per annum (IAI, 2011). The undissolved ore from this process is called red mud or bauxite residue. CSIRO (2011) reports the production of one hundred and twenty million tonnes of bauxite residue per annum. This bauxite residue is typically highly alkaline and requires containment in long-term secure storage facilities. These sites cover many hectares of land, which is an increasingly scarce resource near population centres.

Community concern over mining residues has changed over the last 20 years. To meet and address these concerns, residue storage facilities have had significant development to ensure safe long term storage and to reduce the overall footprint (Cooling, 2005a; Hond & Brouwer, 2011). There is now an increasing expectation that mining residue be utilised within construction and other industries.

Leading mining companies have understood the growing demands of the public “licence to operate” and have attempted to stay ahead of any public opinion. “Sustainability” is the new catch-cry, with many industries implementing a “re-cycle or re-use” policy. However, mining is the utilisation of a finite resource, so sustainability must centre upon the following areas:

1. The ability to recycle the target mineral. In this case, aluminium is very easily recycled and a significant recycle industry exists (IAI, 2012a);
2. The efficient use of energy (Van Berkel, 2007);
3. Maximise utilisation of mining products (Jamieson, 2008a).

Taken a step further, the goal of sustainable mining can be expressed as the ability to maximise the public benefit from the utilisation of a finite resource.

Bauxite residue should therefore be considered an un-utilised resource. Bayer (1894) recognised the potential for bauxite residue to be utilised in alternative products. Until recently, very few products have entered the market, and most are only of small volume.

1.2 Scope

The scope of this thesis is to provide a detailed description of the potential for Bayer refinery by-product utilisation.

Firstly, captured into one volume, is a significant review of the published work into Bayer residue by-products. The literature review provides a critical assessment of the ability to commercialise by-products; or to add value for the community at large.

Secondly, to highlight the considerable practical advances that have taken place over recent years. This thesis will review and discuss data from long term demonstration trials. The key performance indicator is the ability to maximise public benefit.

Finally, to provide a detailed evaluation on the development of new by-products (Bayer-derived geopolymers) that have the potential to revolutionise the industries of:

- Alumina refining;
- Commodity materials;
- Civil construction.

These new materials also have the potential to utilise other industry by-products in combination.

1.3 Objective and approach

The objective of this thesis is to highlight the development and utilisation of by-products from the Bayer process. To achieve this objective, the following approach has been conducted. Note some products such as carbonated red mud, Alkaloam®, sand and lime have commenced long term trials prior to the thesis, however, capture of the outcome and processing of that information is included.

- A critical literature review assessed for commercial and social application;
- A tailored research program to ensure by-product selection based upon commercial, social and environmental needs;
- An evaluation of long term utilisation trials of carbonated red mud as a soil ameliorant (Alkaloam^(R));
- Evaluation of the utilisation of carbonated red mud within an infiltration reactive barrier for water purification;
- Evaluation of the utilisation of coarse residue (sand) in road construction;
- Evaluation of the utilisation of coarse residue (sand) as construction fill;
- The evaluation of long term utilisation trials of lime residue as a soil ameliorant;
- The development and utilisation of Bayer geopolymer paste including reagent characterisation and reactivity assessment, mixing procedures product identification and characterisation and methods of cure.
- The development and utilisation of Bayer geopolymer mortar, including assessment of sand type and content.
- The development and utilisation of Bayer geopolymer concrete, evaluating mix design, reagent alternatives and admixtures.
- Assessment of geopolymer by-product performance against construction material standards.

1.4 Significance

This thesis provides a detailed summary of the development of some Bayer process by-products and their potential utilisation.

By encouraging market development, wastage of resources in tailings impoundments will be reduced and the public benefit from the consumption of finite resources will be enhanced.

Mining residues are resources that should be exploited, not abandoned. Utilisation of by-products can replace virgin natural resources, greatly extending their availability to future generations and perhaps removing their need altogether.

1.5 Thesis outline

This thesis has been broken into a series of chapters described below, but can also be represented diagrammatically in Figure 1-1.

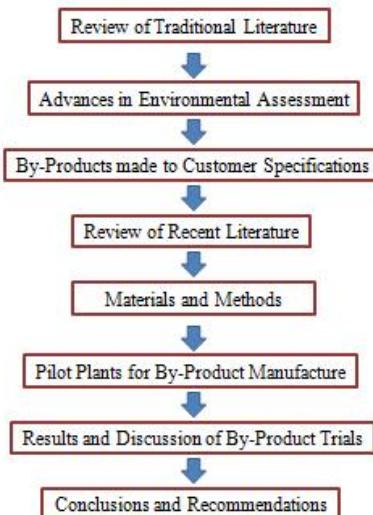


Figure 1-1. Thesis outline.

This process is idealised, as several sections were conducted outside the thesis time line. The author's involvement with this field significantly predates the doctoral

studies so Figure 1.2 clarifies the new material from what is historical. It also demonstrates why Chapter 8 (Bayer-Derived Geopolymers) is the largest chapter, containing a majority of the new information developed during the thesis.

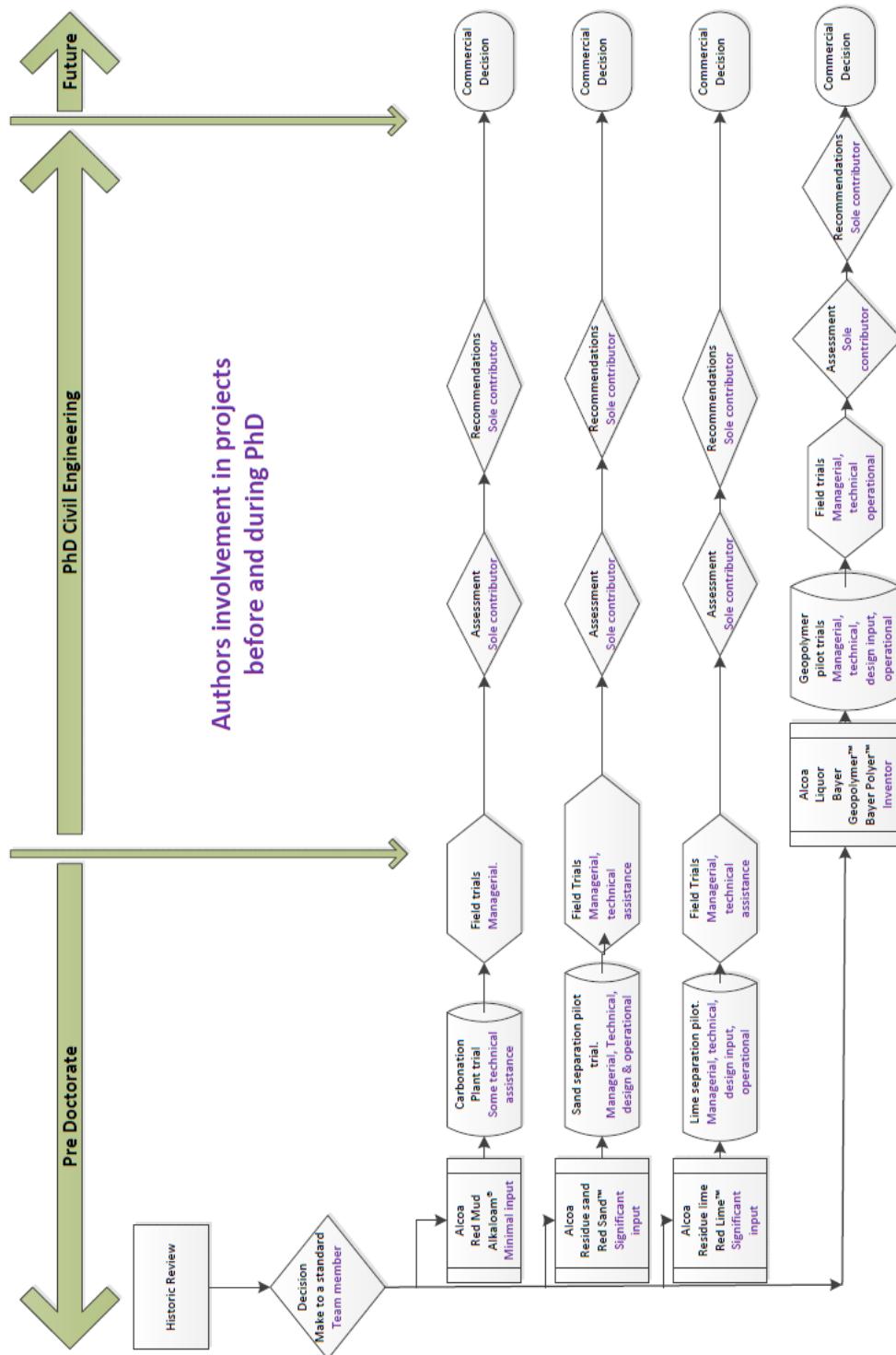


Figure 1-2. Author's involvement in historical development and doctoral studies.

Chapter 1 (Introduction) provides background to the opportunity facing the alumina industry and mining in general.

Chapter 2 (Literature Review) provides a detailed literature review of the historic attempts to develop by-products from bauxite residue. It highlights the recent advances in environment assessment that will enable confidence in the utilisation of by-products. This confidence assists the change in attitude from the historic ‘take it or leave it’, to a new phase of manufactured by-product, made to customer specifications. Finally, the recent literature evaluating the ‘fit for purpose’ by-product is reviewed.

Chapter 3 (Materials and Methods) documents the experimental procedures used and describes how some of the techniques were modified to assess the products in use.

Chapter 4 (From Waste to Resource) Transition in treating residue as a waste to a potential resource, requires the move from laboratory to pilot plant production. This chapter concentrates on refinement of pilot plant products suitable for utilisation demonstrations.

Chapter 5 (Carbonated red mud and Alkaloam®) Alkaloam® is the trademark used, when carbonated fine bauxite residue is applied as a soil ameliorant. Alcoa has investigated this application for many years and this thesis reports on some new long term studies. It also looks at alternative uses of carbonated red mud, such as within an infiltration reactive barrier for water purification.

Chapter 6 (Sand) reports on a variety of product opportunities derived from coarse bauxite residue. This thesis reports on the product derived from the sand pilot plant, as well as demonstration in-situ performance analysis.

Chapter 7 (Lime) reports on the development of a unique product derived from carbonate removal from the Bayer process. Pilot plant derived material is assessed and then utilised in potential applications including, a long term soil ameliorant trial.

Chapter 8 (Geopolymers) reports on the development of Bayer-derived geopolymers and seeks to utilise several other by-products in its formation. Several applications for products are reported upon including preparations for demonstration trials. This field of development is unique and has the potential to bring many different by-products together in new ways. As demonstrated in Figure 1-2, Chapter 8 will form a significant proportion of this thesis.

Chapter 9 (Conclusions) summarises the knowledge gained during this thesis particularly with respect to product application.

Chapter 10 (Recommendations for further work) describes areas of work that require further investigation or pose significant opportunities.

Chapter 11 (Appendices) additional information is stored on CD due to size. This includes experimental error evaluations and assessment data.

Chapter 12 (References) contains a list of all cited material used within the text.

2 LITERATURE REVIEW

This chapter looks at the historic application of by-products which exclusively represented methods of utilisation of bauxite residue. The review then reports on more recent changes towards production of genuine by-products and some of the advances that have taken place as a result.

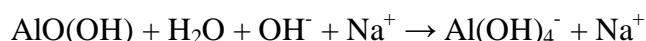
2.1 The Bayer process

The Bayer process was first patented in the United States of America by Bayer (1894). Today it is widely used for the production of alumina from bauxite ores containing minerals such as gibbsite and boehmite (Equations 2-1 & 2-2). Descriptions of the process can be found widely including IAI (2013) and the Red Mud Project (2011).

The process shown in Figure 2.1 involves mining the bauxite ore and crushing it to a typical particle size less than 2 mm in diameter. This is to allow efficient extraction of gibbsite or boehmite from the unwanted background minerals such as iron oxides and quartz. The bauxite slurry is mixed with a highly alkaline solution (sodium hydroxide, $\text{Na}^+ \text{OH}^-$) then heated in a digestion process. During this digestion process the hot caustic liberates the aluminium in the form of aluminium hydroxide, to produce a sodium aluminate ‘liquor’.



Equation 2-1. Gibbsite Dissolution



Equation 2-2. Boehmite Dissolution

The sodium aluminate solution is still mixed with the gangue residue at high temperature and pressure; until ‘blow off’ or ‘blow down’ is achieved through a series of depressurisation chambers. Once the slurry reaches atmospheric pressure the liquor is separated from the non-dissolved gangue materials. The larger sized residue particles are the first to be separated. This residue sand is relatively easily removed.

One such removal process uses a series of counter rotating screws called rakes. The large sand-like material is counter current washed to recover the valued sodium aluminate solution and then sent to residue storage facilities.

The remaining fine mud solids are separated from the aluminate solution in a thickener (clarifier) with the aid of flocculants. The underflow from the thickeners is washed in a series of counter current washers to recover caustic and also render the fine solids suitable for disposal. The dense underflow slurry (now termed red mud or bauxite residue) is distributed over drying beds to allow for atmospheric drying and to allow any entrained liquor to be recovered through an underdrain system.

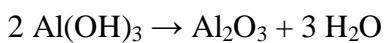
The aluminate liquor from the thickener overflow is relatively free from impurities, but must still undergo polish filtration to remove any remaining bauxite residue.

The clean aluminate liquor is then pumped to precipitation and mixed with gibbsite seed to aid crystallisation. The solution is held in a series of tanks maintained at specific temperatures with relation to their aluminate concentration. This aids the precipitation process; other chemical additives may also be applied. The precipitation reaction is the reverse of the digestion reaction (Equation 2-3).



Equation 2-3. Precipitation of hydrate

The precipitated material (hydrate) is separated from the caustic aluminate liquor, with a portion of the fine hydrate being recycled to be used as seed. The bulk of the hydrate is recovered as product. It is then dried and calcined to produce alumina (Equation 2-4).



Equation 2-4. Calcined Alumina

The remaining liquor from the precipitation process is recycled in the Bayer circuit. A side stream may be treated for impurity removal while the bulk is heated to drive off excess water. The liquor is then available for further digestion of bauxite ore.

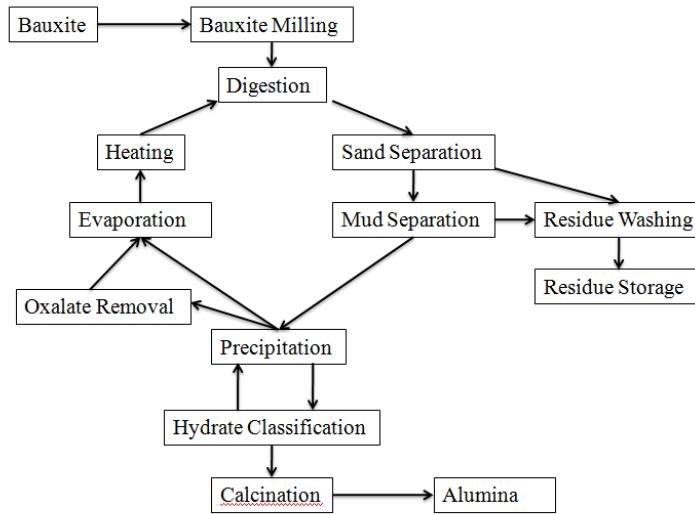


Figure 2-1. The Bayer Process.

Some bauxite deposits contain a significant amount of organic material, some of which dissolves in the liquor adding to the impurity load. These organic species are known as 'Total Organic Carbon' (TOC). The presence of TOC and other impurities in Bayer liquors reduces productivity largely through two effects.

Firstly, organic compounds can act like acids and combine with free caustic. This reduces the caustic available to dissolve alumina from bauxite ore. The high solubility of various organic species ultimately reduces the overall concentration of caustic in the liquor circuit and the amount of aluminate it can carry, so that less hydrate product is made for each cycle of the liquor.

Secondly, some organic compounds can reduce the hydrate precipitation rate by acting as precipitation poisons. Others, such as oxalate, can co-crystallise and cause impurity issues with the product as well as create fines as they burn within the calciner. Ultimately, the organic species are partially oxidised within the Bayer circuit to form sodium oxalate which must be removed from the process and maintained below the critical precipitation limit. Some organics may be fully oxidised to form carbonates which are removed by a causticisation process.

Other impacts associated with the presence of organic compounds in the Bayer process include an increase in the amount of soda in hydrate product, increased liquor viscosity, increased liquor foaming and decreased hydrate agglomeration.

Inorganic impurities are also dissolved during the digestion process and have two main impacts on the Bayer circuit.

Firstly, inorganic species such as iron, calcium, sulphate and fluoride in combination, can co-precipitate with gibbsite, resulting in product purity issues.

Secondly, inorganic impurities can recirculate within the Bayer circuit holding onto their hydroxide counter-ions reducing the hydroxide available for alumina dissolution. This effect will reduce the precipitation yield for each circuit of liquor. Inorganic species can also increase the apparent solubility of aluminate, reducing the precipitation yield.

Many inorganic impurities can be removed by the desilication process. Reactive silica from the bauxite dissolves readily in liquor and reacts with caustic and alumina to form a sodium alumina silicate, so called DeSilication Product (DSP). DSP can remove sulphate and other impurities from the circuit but since it consumes caustic and alumina, this is an expensive process. DSP also needs to be removed from the process and so becomes part of the bauxite residue (figure 2-2). Reactive silica can even be added to increase impurity removal.



Figure 2-2. Kwinana residue storage area. (Google Maps, 2011)

Red mud is the main residue from the extraction process and considerable work has centred on its processing and storage best practice (Cooling, 2005b). Bauxite residue is a mixture of minerals such as goethite, hematite, quartz, gibbsite, boehmite, anatase, calcite, tricalcium aluminate, muscovite and DSP (Thornber & Hughes, 1986). Residual calcium oxide is also potentially present along with a variety of trace minerals and amorphous products such as sodium aluminium carbonate and aluminium hydroxide, which are undetectable by XRD.

Bauxite residue is classified as a hazardous waste because of the high pH from the residual entrained caustic solution. It is thus required to be securely stored. However, once neutralised, red mud loses this hazardous nature, becomes easier to handle and can be processed into further potential products.

2.2 History of residue use

Karl Bayer's original patent for a process to produce alumina described the resulting sediment as being able to be filtered and washed. He suggested that *As the residue contains a high percentage of iron and a comparatively small percentage of alumina, it can be worked up as a by-product, or it can be mixed with iron ore and utilized in the production of pig iron* (Bayer, 1894).

Research has been conducted into the utilisation of the sediment/residue almost continuously since. This is partly because of the recognised potential value as a commodity and also because of the significant volumes that are continuously produced. Li *et al.* (2009) summarises this argument by stating that Bayer residue is a ... *waste of secondary resources*.

2.2.1 Bauxite residue for iron and metal production

Iron oxides are the main component of red mud and much research has been focused into their beneficiation and liberation. Thakur & Sant (1983) provide a detailed list of the potential liberated metals in a holistic approach. Piga *et al.* (1993) summarised the state of the art with stylised flow sheets and Klauber *et al.* (2011) adapted one for multi element separation shown in Figure 2-3.

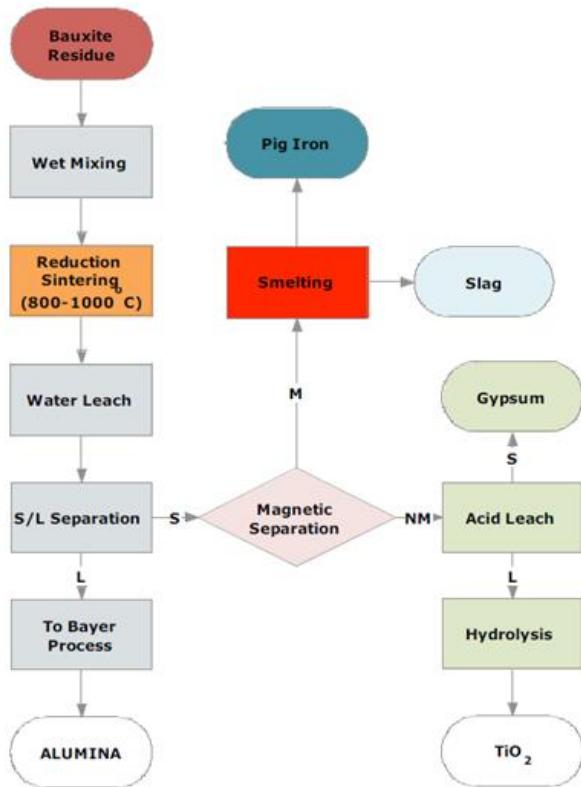


Figure 2-3. Multi element recovery flow sheet (adapted by Klauber *et al.* 2011).

Klauber *et al.* (2011) reported that there are at least 42 patents related to iron recovery from red mud, but to date no significant iron production has taken place.

The patents and published literature can be summarised into three main areas.

1. The reduction of the iron oxide minerals, to aid magnetic separation (Liu *et al.* 1995; Xiang, *et al.* 2001; Liu *et al.* 2009; Li *et al.* 2009);
2. The more traditional smelting of pig iron in a furnace smelting process (Logomerac, 1976, Ercag & Apak, 1997);
3. The potential for direct reductive smelting or an adaption (Romenets *et al.* 2011) of the Romelt process (Pokhvisnev *et al.* 2002).

All three processes suffer from the same issues when handling red mud as a feedstock.

- The fine nature of red mud creates handling and flow issues;
- Red mud is wet and requires drying prior to processing;
- The high caustic nature of red mud can be a significant impurity to the process;
- The low grades of iron result in high power and materials consumption;
- The multiple trace elements in red mud can cause iron purity issues;
- The high level of quartz creates waste issues in their own right;
- Utilisation requires multiple complex processes;
- Utilisation requires significant capital requirement and operational expense;
- It is still cheaper to utilise lower grade iron ore in existing facilities rather than construct new infrastructure.

The economic argument is the key to further development, as recognised by Piga *et al.* (1993), Mishra *et al.* (2001; 2002), Agrawal *et al.* (2004) and Kumar *et al.* (2006). They propose that extraction of multiple metals value is the key to success; such as high value titanium, vanadium, aluminium etc. While the opportunities may arise for specific sites and markets, it is the author's opinion that the significant cost of capital and the abundance of cheap alternative feedstock will ultimately prevent widespread uptake of this by-product utilisation - a view shared with Klauber *et al.* (2011).

For example, Xenidis *et al.* (2009) used a reductive roast of Greek red mud at 500°C, followed by wet magnetic separation to achieve a product of 36 wt% iron (only marginally better than the original red mud). There is a drying step prior to the roast and another after magnetic separation, both with a significant amount of materials handling. Yet since iron ore is typically graded at 60 wt% iron, the chances of competing with direct mine product is very low.

Ercag & Apak (1997) proposed a flow sheet for the extraction of metal values from red mud. One of the goals for the process was the consumption of large volumes of wasted bauxite residue. Yet the flow sheet claims 117 g of waste for each 100 g of red mud used. Whatever the economic outcome, that is not a sustainable process.

Balomenos *et al.* (2011a, 2011b) claim that their process utilises an innovative electric arc furnace to turn untreated red mud into pig iron and a slag suitable for rock wool production (figure 2-4). They also claim that the process effectively doubles the "energy efficiency" of the bauxite ore utilisation. This may be, but an evaluation of the economics would surely still favour utilisation of standard iron ore. That is, the use of red mud would require alternative drivers such as lack of iron ore, prohibitive transportation costs or direct political intervention.

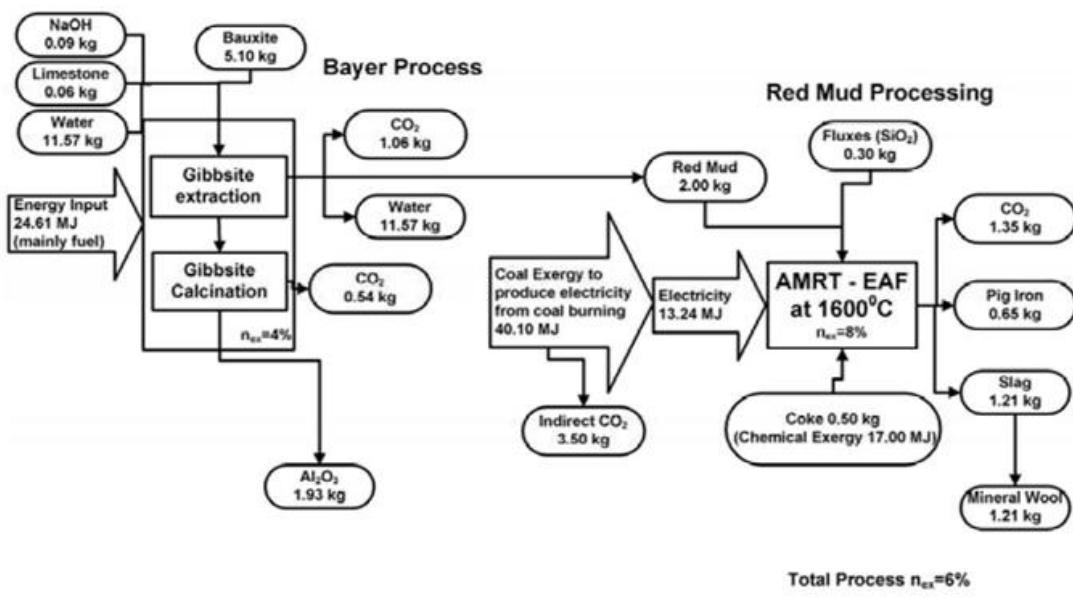


Figure 2-4. Flow diagram for production of pig iron, as proposed by Balomenos *et al.* (2011a).

A key to the efficiency claims of Balomenos *et al.* (2011a, 2011b), is the production of a material that would supposedly be utilised as rock or mineral wool (figure 2-5). This author has doubts that 'public perception' has been tested on utilisation of this material, or that a significantly large enough market would exist locally. However, this author feels that a mixture suited to rock wool manufacture would also be potentially suitable for manufacture of geopolymers; which would have a suitable market size and potential public support.

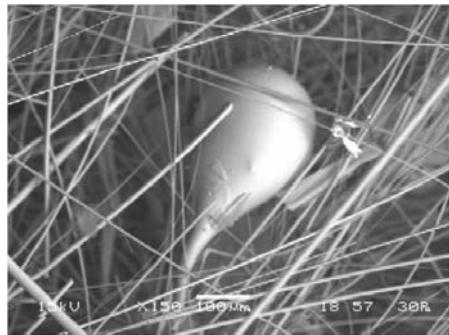


Figure 2-5. SEM of inorganic fibres made for furnace slag (Balomenos *et al.* 2011a).

2.2.2 Bauxite residue as soil amendment

The use of bauxite residue as a soil ameliorant is by far the most studied application. This is because it has the most beneficial application for the resource, requires the least processing, and has the largest potential market by volume.

Phosphate removal from water by application of red mud was demonstrated by Shiao & Akashi (1977). Thereafter, the beneficial application of bauxite residue to sandy soils has been reported widely (Barrow, 1982; Puskas & Gergely, 1992). Sandy soils are very poor soils for crop production due to their rapid leaching of soluble fertiliser. Iron and aluminium oxides from bauxite residue mixed with soil act as temporary adsorption sites (akin to ion exchange) for ammonium and phosphate (Ward, 1986; McPharlin *et al.* 1994; Summers, 2001). This allows plants to have sustained access to those nutrients. Alumina has also been proposed as a phosphate control soil ameliorant in its own right (Lynch *et al.*, 2003).

Significant agriculture is conducted on the poor sandy soils of Western Australia's 'South West', with regular application of artificial fertilisers. These highly soluble phosphate fertilisers are not retained in the sandy soils and are leached away rapidly. Transportation of fertiliser to water tables and waterways results in pollution (Summers *et al.* 1993; Hodgkin & Hamilton, 1993). There is also the potential to generate significant algal blooms in water bodies (Summers & Smirk, 1992) as shown in Figure 2-6. Some blooms are toxic to marine creatures but most reduce the available oxygen when they decay (Summers & Pech, 1997).

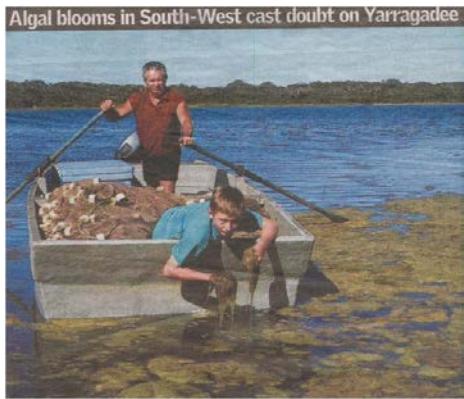


Figure 2-6. Algal bloom (The West Australian, 2006).

There are several options to combat the resulting pollution. One method is the attempt to physically clean the water body of algal growth (WARC, 1998). This is expensive, generates large volumes of waste with its own disposal issues and ultimately is ineffective. The alternative is to stop the fertiliser at its source and prevent the excessive growth events (DEH, 2006). One method of achieving this outcome is the application of sparingly soluble fertilisers. For this application to be effectively implemented there needs to be a transformation of entrenched farming practices and fertiliser manufacturing processes. This would seem an unlikely outcome and it still leaves the soil “unproductive” in the long run. It would also be ineffective upon the existing nutrients currently making their way through the system towards the water body.

The best option appears to be amelioration of the agricultural soil to absorb soluble nutrients for subsequent slow release. To achieve this aim, an ameliorant would need to have a high surface area of iron and aluminium oxides for cation exchange (Grubinger *et al.*, 1986). It would need to have small particle size to allow mixing into the sandy soil with high capacity for phosphate absorption. Bauxite residue would appear to meet these criteria, as shown by Kayaalp *et al.* (1988) utilising a local Bassendean sand.

Bauxite residue is a naturally derived material that has had the alumina extracted at high temperature through an industrial process, leaving a high residual pH. This process sterilises the residue making it environmentally safe for agricultural use (i.e. weed and disease free). Once the pH is neutralised to non-hazardous levels, then

bauxite residue is little more than crushed gravel with some liberated and entrained salt.

However, most of the minerals and elements from the original bauxite remain in the red mud. These trace elements have raised concern because regulations are based on composition limitations. The mere presence of these elements can be perceived as a risk, even if the elements are completely mineralogically bound. This results in public mistrust, even though the red mud will actually reduce heavy metal content in crops grown in amended soils. This was demonstrated by Robertson *et al.* (1992) who were able to show that heavy metals such as chromium, nickel, lead and cadmium were not taken up by carrots grown in residue ameliorated soils. The levels of lead and cadmium in roots decreased with increased soil amendment. While this was attributed to the pH of the amended soil, mineral adsorption could have also played a role.

Ward (1983) demonstrated that excessively high applications of bauxite residue did not cause accumulation of heavy metals in legumes. The high application rate changed the soil pH to a point where foliar analysis indicated a manganese deficiency and an excess of molybdenum from the added fertiliser. The highest addition rates of red mud (1680 t/ha) resulted in a slight decrease in yield. Alternatively, similar application rates of gypsum amended red mud resulted in increased crop yield. Both these impacts can be attributed to the amended soil pH.

2.2.2.1 Excessive application.

The high alkalinity of red mud can be a benefit for acidic farm soils, particularly those in South Western Australia. However, high application rates may result in localised pH elevation and this will damage plants. This issue can be overcome with use of lower rates of amelioration, the breaking up of red mud and allowing atmospheric carbonation, or through neutralisation by the addition of gypsum.

Ho (1989) highlighted that red mud had issues with high pH, high salts and sodium activity. He was able to demonstrate that neutralisation of red mud was possible through the addition of gypsum or copperas. It was shown that addition of 4 wt%

gypsum to red mud, decreased the pH to less than 9 and replaces the sodium in ion exchange sites with calcium. This provided the option to allow a leach treatment to remove the excess salt and sodium. (See also Ho *et al.* 1989 and Wong & Ho, 1995)

Gypsum in Western Australia can be sourced as a by-product from fertiliser production facilities. When this residue is utilised, there is a potential for a five fold sustainability benefit.

1. Wasted red mud is utilised;
2. Wasted gypsum is consumed;
3. Phosphate within the gypsum becomes a fertiliser for plant growth;
4. The pH of the bauxite residue is reduced to non-hazardous levels;
5. Calcium replaces sodium absorption, protecting plants against sodium burn.

More recently the neutralisation of red mud with gypsum has been replaced by carbonation (depending upon application). The carbonation can take place through atmospheric absorption or direct carbon dioxide injection (Cardile, 1993; Galarraga *et al.* 2002).

Snars *et al.* (2004a) demonstrated in glass house trials of rye grass that the phosphate content of grass was lower for plants growing in red mud ameliorated soil (0-20 t/ha amelioration equivalent). However, the total yield between treatments was not significantly different. Similar results were reported by Robertson *et al.* (1997), for the growth of carrots in amended soils at up 240 t/ha amelioration rates. While total phosphorous in carrots was lower, the yield was unchanged. There was complete retention of phosphate within the soil. They proposed that the captured phosphate remained available for carrot growth over a longer period, enabling similar yields. While these results demonstrated a reduction in phosphate leaching, the constant yields are in contrast to field trials reported by Summers (1994, 2001) where dry matter productivity gains of up to 25 wt% were achieved, depending on initial soil conditions (20 t/ha amelioration rate). Summers *et al.* (2002) also demonstrated increased clover pasture growth of 25 wt% was achieved for field amended soils with up to 200% improvement in ideal conditions. It was thus thought that the initial application of 240 t/ha was excessive.

Ward & Summers (1993) and Summers *et al.* (1996) demonstrated bauxite residue application did not give a linear benefit response per unit of residue added (Figure 2-7). They were able to show that the majority of benefit was in the range of 10 – 20 t/ha. This rate worked best without the inclusion of gypsum.

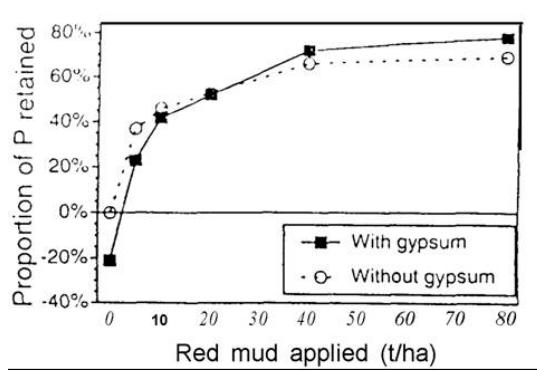


Figure 2-7. Proportion of phosphate retained (compared to control) against rate of ameliorant application (Ward & Summers, 1993).

As a result of the data above, Summers *et al.* (1996) proposed the use of low amelioration rates. This recommendation was incorporated into the Department of Agriculture Code of Practice (DOA COP, 2002) for use of bauxite residue (Alkaloam^(R)). Application rates were recommended between 5 and 25 t/ha. This gave moderate phosphate adsorption while ensuring pH was not highly elevated. It also ensured minimal impact from salt and sodium release.

2.2.2.2 Added benefits from amelioration with bauxite residue

Vlahos *et al.* (1989) demonstrated water retention was significantly improved through high rates of red mud applied as a soil ameliorant. Rates of amelioration at 200 and 2000 t/ha increased water retention by 14 and 50 wt% respectively. While the bauxite residue was amended with gypsum or copperas (ferrous sulphate), the level of total salt was believed capable of impacting pasture growth in the initial years following application. By contrast, Summers *et al.* (1996) reported that the best application rate for the reduction of phosphate leaching was in the order of 20 t/ha. At this level gypsum amendment is not needed and the phosphate retention benefit was maintained for at least 5 years. Unfortunately the low application rate is unlikely to significantly impact upon wet-ability or water retention (Ward & Summers, 1993).

Subsequent applications may improve soil water retention as the total red mud content increases, without the impact of the first season flush of salt.

Snars *et al.* (2004b) was able to compare the lime effect on acidic soils of bauxite residue from various locations. While they were able to show that the bauxite residue has a high pH and neutralising capacity, this was dependent on the treatment of the bauxite residue. Factors that determined its effectiveness included the level of free caustic, sodalite and calcite.

Finally, Summers *et al.* (2000) reported on the application of phosphate fertilisers coated in red mud. The trials were successful in showing that the leaching of phosphate was reduced by half with a red mud coat of 30 wt%. Plant uptake of phosphate was improved and plant growth bolstered over non coated trials. A commercial product was later trialled and marketed under the name “Red Coat Super”, though without market success.

2.2.3 Bauxite residue in road construction

Road construction would seem an ideal application for bauxite residue as a benign fill. Road construction consumes significant volumes of fill for sub-base, sub-grade and embankment design. Hence it would be expected to be a significantly reviewed application. However, this is not the case, with very few published works in the area. It can be assumed that this work has been conducted but, for various reasons, not been reported. Some of those reasons may be presented below but it is the author's belief that the need to neutralise red mud and wash it free of entrained salt has proven to be an economic hurdle too high in comparison to cheap alternatives.

Thakur and Sant (1983) reviewed a series of red mud applications and reported that a key issue in utilisation was the detrimental impact of sodium on residue's structural strength properties. They reported that substitution with calcium would improve the structural integrity of the residue. This is very similar to soil amelioration structural issues reported by Ward (1986). Martinent-Catalot *et al.* (2002) appeared to overcome the problem with incorporation of fly ash to act as a binder. They

successfully utilised mixtures of ash and mud for embankment construction and for sub-grade road construction.

Kehagia (2008) reported a trial of red mud stabilised with addition of fly ash and blended with a natural ‘virgin’ high grade fill. The trial utilised heavy truck traffic to simulate the impact of high volume loadings as seen in Figure 2-8. After five years the embankment trials were reported as having settled about 1 cm. Despite the description of the amended red mud as plastic, the deformation was very limited. Presumably this was a result of the confined nature of the application. A foundation to the successful trial was the realisation that red mud alone is too plastic and required treatment or reprocessing to reach a required minimum standard.



Figure 2-8. Trial section of road (Kehagia 2008).

By contrast, internal bund walls in residue impoundment areas are frequently made from dried red mud and these same bund walls are frequently utilised by internal traffic without deformation. This should not be considered a successful trial as the traffic load is minimal and the walls are frequently confined to prevent their deformation.

Recent trials have taken place in Jamaica where red mud was reportedly utilised in geopolymmer formation for road construction at St Elizabeth (Jamaica Observer, 2010). No further details have been located.

It would appear that red mud is a suitable material for road construction, particularly in confined applications or in combination with other materials. Issues with pH and entrained salt are likely to require processing to prevent localised contamination and this alone may be prohibitively expensive.

2.2.4 Bauxite residue in brick manufacture

Red mud is regularly considered for use in brick manufacture because of its abundance, fine nature and soda. The entrained low levels of soda (as sodium hydroxide or carbonate) aid glass formation during the brick firing process. The level of glass formation has a direct correlation to brick structural properties and durability (Jamieson, 1987).

While high temperature firing of products is an obvious method of brick development, many opportunities exist for low temperature block manufacture. These processes utilise the chemical interaction of sodium silicates, lime, cement and more recently geopolymers. Klauber *et al.* (2011) found some 14 patents related to this by-product application in their well rounded review.

2.2.4.1 Fired bricks and ceramics

The evaluation of red mud for utilisation in fired brick production is dominated by researchers wanting to maximise red mud content. Frequently the research aims at 100 wt% red mud bricks and methods of achieving suitable products. This approach is being superseded by those who see red mud as a component to brick manufacture. Brick formation is a complicated process of matching clay and soil types with appropriate characteristics to give a blend that will produce a uniform product. Red mud, while being a fine material ($> 80 \text{ wt\%} < 10 \mu\text{m}$), is still quite coarse ($50 \text{ wt\%} > 1 \mu\text{m}$) in terms of brick manufacture. Hence those attempting to manufacture pure red mud bricks encounter the need for elevated temperatures to achieve suitable strengths such as Kara & Marmara (2000). This is in contrast to the expectation that the entrained soda will lower firing temperatures. The solution is to utilise red mud as a component of a brick and mix with genuine clays. This approach was utilised by Bayer *et al.* (1975) who determined that as little as 10 – 30 wt% clay was required to

assist with brick firing. The same approach was utilised by Dass & Malhotra (1990), who reported that commercial production was to take place "shortly". Unfortunately no further records can be located suggesting commercialisation did not take place to any significant extent.

Other fired ceramic products are possible with Balasubramanian *et al.* (2000) suggesting incorporation of red mud into the production of tiles. Yalcin & Sevinc (2000) made high value (but low volume) glazes utilizing 37 wt% red mud. A review by Pontikes *et al.* (2011) looked at several possible ceramic options but was unable to report any large scale application. This is likely a result of the negative public perception of red mud as a waste product, and the relative ease of supply of competing reagents.

The changing economic climate can also have a significant impact upon innovation. Indebar of Spain constructed a plant for the production of thermal heater bricks utilising red mud from the local Alcoa San Ciprian Refinery (Figure 2-9). These bricks were utilised as a thermal mass storage for home heating. Customers could buy off peak power and heat the mass blocks. When power reached peak tariff, then the heated blocks would be used to heat the house. Production started in 2007 with a batch process at a consumption rate of about 300 cubic metres per day. Production was to increase with automation to about 11,000 tonne per annum (Europe Press, 2004). However, the Spanish Government removed the peak power tariff system and this effectively removed the business model. The plant is now idle.



Figure 2-9. Indebar heater brick production facility at San Ciprian, Spain.

Satpathy *et al.* (2011) reported on the construction of a pilot plant to produce 10,000 bricks for assessment and trial marketing. The bricks contained between 60 and 80 wt% red mud, yet achieved compressive strengths in the order of 11-28 MPa. House bricks typically range from 15 to 30 MPa, so the trial was deemed successful. They also believed the process is viable from their "techno-economic" assessment. While the strength was suitable, the authors noted that the cold water absorption was *slightly high* at 22 wt%. This figure and the leaching of caustic in distilled water are troubling and the authors should undertake further investigations, particularly a sulphate salt test. Nevertheless, this report is encouraging and a simple process correction to enhance glass formation will close pores and improve results.

The evaluation of thermal behaviour and glass formation during firing of clay products and red mud can be read elsewhere (Jamieson, 1987, Sglavo *et al.* 2000; Zhang & Yan, 2000; Ekerim, 2004; Atasoy 2005; Agarwal & Shashikanth, 2008).

2.2.4.2 Blocks utilising silicate solutions

There have been some widely reported trials utilising red mud to make blocks for house construction in Jamaica (Glanville, 1991; McLeod, 1998b). The blocks of pressed and dried mud were immersed in sodium silicate solution, then allowed to dry. The economic opportunity for by-product utilisation was caused by the scarcity of building materials and the need for affordable housing. Glanville (1991) concedes that large scale commercialisation is unlikely (presumably due to transport costs), however, localised and remote production could deliver considerable savings.

McCarthy *et al.* (1992) looked at the social considerations to the uptake of bauxite residue blocks in Jamaica. They listed a series of issues preventing large scale uptake which are summarised below:

- Long term structural integrity;
- Potential leaching issues;
- Public conservatism in favour of concrete blocks;
- Potential issues with radon;
- Cost is not significantly cheaper than concrete blocks.

Newton (1993) reported that sodium silicate stabilised Jamaican red mud bricks were safe and similar to conventional fired bricks. The strength was derived from the drying silicates reacting with aluminate species. However, they are still not as strong as their fired counterparts. Newton (1993) also reports that the radon is reduced by the silicate treatment and that the bricks meet international standards for radiation. He reported that these bricks are half the cost of fired products. Unfortunately the cost of cement blocks was not discussed. This is believed to be similar to the silicate blocks.

McLeod (1998b) reported sodium silicate stabilised block strengths of around 5 MPa. This is not a great result for structural materials and the project was dropped when the cost of silicate solution tripled.

2.2.4.3 Blocks utilising lime, cement and geopolymers

Red mud blocks can also be stabilised with other binders such as ordinary Portland cement (OPC), pozzolanic cement or even geopolymers.

Popovics (1990) reported on the use of pozzolanic cement, where a mixture of 7 wt% fly ash with red mud would result in a brick having an unconfined compressive strength of 3.5 MPa. Utilisation of 15 wt% OPC binder produced bricks with strength of 35 MPa. There was a significant impact upon strength depending on the type of red mud used and also other additives. For example, strength was improved when gypsum was included, presumably due to calcium precipitates.

Ikeda (1992) utilised red mud, gypsum and portlandite (lime) to make cement mixtures with compressive strengths ranging from 8 - 19 MPa. Best mixes appeared to have almost equal amounts of each.

McLeod (1998b) reported that gypsum and hydrated lime act as activators to enhance cementation (Figure 2 - 10). Mixtures of red mud (40 - 45 wt%), fly ash (35 - 40 wt%) with added gypsum and lime (not stated), produced blocks of up to 5.17 MPa.



Figure 2-10. Red mud pozzolanic cement blocks (McLeod 1998b).

McLeod (1998a) reported on an OPC stabilised red mud brick demonstration building shown in Figure 2-11. The formula was 50 wt% red mud, 43 wt% sand and 7 wt% OPC. The bricks had individual compressive strength of 4.7 MPa. This is in comparison to quality fired clay products that have unconfined compressive strength in the range of 15 - 35 MPa (Boral, 2011). Nevertheless, McLeod (1998a) reported that after 11 years of service, the bricks showed no signs of peeling (water damage) or cracking (in spite of some small earth quakes), had demonstrated a resistance to fungal growth, and good mortar bonding. This is a significant result and should have been the beginning of a significant industry. However, McLeod (1998a) stated: *Investigations carried out in the building over a period of time have given early assurance that there is no inordinate risk of radiation exposure if such a building is used as a permanent dwelling.* While the message was probably meant to assure people of the materials safety, the terminology used certainly would not.



Figure 2-11. Demonstration of cement stabilised red mud bricks (McLeod, 1998a).

Martinent-Catalot *et al.* (2002) reported on the application of Bauxaline^(R) (processed red mud) and fly ash blocks, for construction of artificial reefs to improve fish

habitats. These pozzolanic stabilised blocks appear suited to purpose as shown in Figure 2-12, but no information was reported on the composition or strength (Pechiney, 2002).



Figure 2-12. Artificial reef made from red mud blocks (Pechiney, 2002).

It would appear the utilisation of red mud in brick and block construction is possible, but that the material must be processed to become a more suitable feedstock to this industry. It should also be utilised to enhance the formulation rather than dominate it.

2.2.5 Bauxite residue in water purification

Water purification utilising red mud as an absorbent has been well documented (Klauber *et al.* 2011). Rather than be considered a waste, bauxite residue is shown to be a by-product of demonstrable value, though of small volume.

George & Poirier (1985) utilised red mud for the cleaning of heavy oil/bitumen emulsions from water. While successful, the process created a residue of high volume which was difficult to handle.

Ho *et al.* (1992a) demonstrated the ability of sand (coated with up to 30 wt% red mud) columns to strip phosphorus and nitrogen from sewage effluent. Greater than 90 wt% of the phosphorus was removed and between 40 and 70 wt% of the nitrogen, depending on use of secondary or primary effluent. The difference is due to ammonium/ammonia conversion, since ammonium is absorbed but ammonia is not. Ho *et al.* (1992b) utilised red mud coated sand in a ground water recharge site to clean sewage effluent. Trials were able to show that greater than 80 wt% of the phosphorus was removed by adsorption. Up to 45 wt% of the nitrogen was removed

through the nitrification/de-nitrification process. In addition, they found increased faecal coliform removal through bacterial die off caused by longer contact, increased filtration and absorption. This would suggest reactive barriers may be a suitable application for red mud.

Phillips (1998) reported that red mud amended sandy soils were able to decrease the availability (water mobility) of nitrogen (as ammonium), phosphorus and heavy metals such as copper, lead and zinc.

Lopez *et al.* (1998) aggregated red mud with 8 wt% gypsum to form a granular material that could be used in batch and column absorption processes. The aggregated red mud removed phosphorus, copper, zinc, nickel and cadmium. They were also able to utilise a column of granulated red mud to clean secondary effluent from an urban sewerage treatment plant. While not all metals were removed, their adsorption suggested that contact area and engineering may compensate for slow absorption.

Apak *et al.* (1998) demonstrated the removal of copper, lead and cadmium onto red mud and fly ash. The metals appeared to be bound as they were not released by subsequent carbonic acid or bicarbonate solution attack. This is consistent with agricultural applications where the heavy metals were not available to plants. Apak *et al.* (1998) recommended that the loaded red mud and fly ash be incorporated into construction materials with cement to ensure long term environmental safety.

Pradhan *et al.* (2006) utilised activated red mud to remove nickel from water. Up to 90 wt% of the divalent nickel was removed in batch experiments. Unfortunately raw or carbonated red mud was not used for comparison, as these results would be more applicable to the nickel scenario described in their introduction. Little consideration was given to the significant cost of activation of the red mud, nor of its subsequent disposal. A similar complaint can be made about Pradhan *et al.* (1999) when they also used an activated red mud to remove hexavalent chromium from solutions. While a technical success, it is very unlikely to be a commercially viable application. The activation process involved acid dissolution of red mud and precipitation using ammonia, followed by drying at 110°C.

Rubinos *et al.* (2005) reported that arsenic (V) was removed from water utilising red mud, but went further to determine that the majority of arsenic was associated with the aluminium and iron oxides/hydroxides. They also reported that only a small minority (up to 5 wt%) of the arsenic was exchangeable, though this increased as the loading increased, presumably occupying secondary binding sites.

Li *et al.* (2006) claim that activated red mud is "extremely suitable" for absorption of phosphate species from water, particularly waste water from a fertiliser plant. Unfortunately their product is unlikely to be implemented in the field because of economic considerations. They believe that red mud is considered a waste and hence is cheap. However, their subsequent processing includes acid neutralisation and thermally treatment (200 – 1000 °C). The cost of this processing would make any product uncompetitive compared to naturally occurring alternatives, including carbonated red mud. The same is true for Altundogan *et al.* (2002) who reported similar activation experiments successful in enhancing red mud's ability to absorb Arsenic III and V cations.

Gupta *et al.* (2004) proposed the utilisation of red mud as an alternative to activated carbon for extraction of chlorophenols, with near complete removal of some species in column studies. Tor *et al.* (2006) reported that neutralised red mud was capable of removing phenolic compounds from water.

These reports demonstrated the ability of red mud to remove carcinogenic phenolic compounds, and also provided the possibly that other ionic organic compounds (such as pesticides) may similarly be removed from solution. This was indeed demonstrated by Ozcan *et al.* (2011) in laboratory batch experiments and subsequently on field collected samples. This technology is still in its infancy but looks very promising. One point that still troubles this author is the disposal of a now contaminated inorganic mass. A method for natural uptake and conversion is required as physical removal is not an option.

Greenburg *et al.* (2011) have demonstrated that bauxite residue will also disinfect waste water. Addition of a small percentage of iron (metal) enhanced the process and

pilot column trials are continuing. They hope to utilise the residue as a final disinfection step for the product of engineered wetlands.

Cho *et al.* (2011) similarly utilised metallic iron to reduce waterborne nitrate to ammonium ions, allowing their removal by the iron oxides of red mud. This technology would appear to be a significant improvement in water purification technology but would require the regular replacement of the metallic iron and absorbing material.

Sea water neutralised red mud.

Sea water neutralisation of red mud has been practiced by industry for many years. It is a product that has more recently been heavily reported and commercialised, hence is covered separately below. In many cases the neutralised product is referred to by the trade name Bauxsol^(TM).

McConchie *et al.* (2002) described the neutralisation of red mud with seawater to form the product Bauxsol^(TM). The chief reactions are the precipitation of brucite $\{\text{Mg}_3(\text{OH})_6\}$ and hydrotalcite $\{\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_6 \cdot 4\text{H}_2\text{O}\}$. They then utilised this product for the treatment of acid waters. A “before and after” analysis is reproduced in Table 2-1. Note the elevation in pH that may be driving the process. The fourth column is the results of a Permeable Reactive Barrier (PRB) utilising Bauxsol^(TM).

Table 2-1. Before and after Bauxsol^(TM) treatment of water from Captains Flat, New South Wales, as reported by McConchie *et al.* (2002).

Component	Before treatment	After direct addition	Using a PRB
pH	2.8	8.2	8.4
Aluminium	12,340 µg/L	4.8 µg/L	3.1 µg/L
Cadmium	94 µg/L	0.3 µg/L	0.2 µg/L
Copper	314 µg/L	4.4 µg/L	1.3 µg/L
Iron	38,120 µg/L	0.9 µg/L	0.8 µg/L
Manganese	10,000 µg/L	1,027 µg/L	31 µg/L
Nickel	60 µg/L	22 µg/L	1.4 µg/L
Zinc	122,400 µg/L	18 µg/L	6.3 µg/L

Lin *et al.* (2002) were able to demonstrate that Bauxsol^(TM) immobilised a series of heavy metals in a soil solution. They published a list of preferential removal being,

Pb>Fe>Cr>Cu>Zn>Ni>Cd>Co>Mn. In addition there was shown to be significant buffering capacity of the soil pH. The pH is known to have a large impact upon metal speciation and subsequent absorption.

Genc-Fuhrman *et al.* (2004) activated Bauxsol™ to increase the hydroxyl surface active sites. The Bauxsol™ is refluxed with hydrochloric acid then re-precipitated with ammonia. It is washed, dried and then calcined to 500 °C for 2 hours. The resulting product was shown to be more effective than Bauxsol™ alone. However, they do not appear to explain why the red mud needed to be neutralised with seawater prior to being acid refluxed. The seawater treatment would seem to be redundant. Neither is there a comparison to utilising a waste iron product as the starting material to produce the activated sorbent. Nevertheless, Genc-Fuhrman *et al.* (2004) were able to demonstrate that activated Bauxsol™ removed arsenic species from water. Genc-Fuhrman *et al.* (2005) further utilised activated Bauxsol™ to create arsenate removal demonstration columns by coating the reagent onto sand. They make no reference to disposal once absorption surfaces are saturated.

Virotec Global Solutions (2011) now offer a series of Bauxsol™ and similarly derived products for treatment of stormwater, sewerage effluent, acid mine drainage and other like solutions. While the range of products is large and the potential applications are large, as yet there still appears to this author to be low volume uptake of this technology.

2.2.6 Bauxite residue for catalysis

The use of red mud for catalysis has been reported for various uses for a significant amount of time. However, the majority of applications are of low volume and the author is unaware of any significant uptake in this technology. Some of the more promising developments are discussed below.

Eamsiri *et al.* (1992) utilised activated red mud for the liquefaction of coal and model aromatics. While the process was successful, the reagent was not as active as the commercially available materials.

Mastral *et al.* (1995) looked at the use of red mud for conversion of coal to liquid components. Catalysis centred on the finely divided iron oxides. While promising, this technology requires activation of the red mud which negates the initial low cost. It is also less efficient than standard catalysts hence the economic drivers of any process would tend to preclude an inefficient catalyst even if it were cheap.

Sushil & Batra (2008) provided a significant review of the use of red mud as a catalyst. They compared the utilisation of red mud against the performance of iron oxides and other standard catalysts. They state *Its (red mud) properties such as iron content in the form of ferric oxide (Fe_2O_3), high surface area, sintering resistance, resistance to poisoning and low cost make it an attractive potential catalyst for many reactions.* They summarise that red mud can act as a catalyst for many reactions, but that the performance is inferior to pure iron oxides and commercial catalysts. Given that iron oxides can be sourced cheaply, it is difficult to foresee the use of red mud in place of iron oxides. Sushil & Batra (2008) concluded that modifications can be made to red mud to enhance the catalytic properties but this author believes these options are likely to be cost prohibitive.

Wang *et al.* (2008) reviewed various options for bauxite residue reuse including the various catalysis processes. Of particular note was the observation that *Moreover, leaching and eco-toxicological tests indicate that red mud does not present high toxicity to the environment before or after use.*

Mangrulkar *et al.* (2010) demonstrated that the finely divided mixture of metal oxides in red mud were able to photo-catalyse the generation of hydrogen from water. While the efficiency of the mixture was only about 10 - 15% of the commercially available alternative, red mud is relatively inexpensive. Conceptually the process could be utilized in large areas and volume, however, this would create significant practical issues such as hydrogen collection.

While showing some promise for large scale applications, catalysis is usually a critical part of a refinery's process and using a lower grade catalyst is not a practical option.

2.2.7 Bauxite residue in cement and concrete manufacture

Bauxite has been a component of cement manufacture for some time, hence it would be natural to ask if bauxite residue could be utilised in its place.

Pera & Momtazi (1992) calcined red mud and then added it to Ordinary Portland Cement (OPC). Mortars made of the blended products containing up to 30 wt% calcined red mud achieved suitable compressive strength. Red mud was found to be most reactive when calcination was conducted at 600°C for 5 hours. Coimbra *et al.* (2004) used similar conditions (8 hour calcination), but only recommended a replacement of OPC cement of 5 - 10 wt%. This discrepancy may be due to variation in red mud composition.

Singh *et al.* (1996) assessed a wide variety of red mud, gypsum, fly ash and bauxite combinations to form clinker at temperatures ranging from 1150 - 1350°C. They found that up to 35 wt% red mud could be successfully utilised at the higher calcination temperature.

Tsakiridis *et al.* (2004) also determined that red mud was a suitable raw material for clinker and cement manufacture. They were able to show that there was no detrimental effect upon the cement performance. However, the raw material mix only contained 3.5 wt% red mud and still contained further 3 wt% bauxite. Nevertheless this is a good demonstration of product substitution.

Balasubramaniam & Kumar (2008) demonstrated that replacement of low grade bauxite with red mud for cement production was possible. They rather triumphantly claim that the *waste has been turned into a wealth....* The key to their proclaimed success would appear to be the high sulphur (3 wt%) in the coke burnt for roasting the clinker. The sulphur reacts with the entrained soda and sodalite (or DSP) to form sodium sulphide, which they claim assists in cement cure. Product parameters are given in Table 2-2.

Table 2-2. Cement made utilising red mud, Balasubramaniam & Kumar (2008).

Parameters of Cement	Spec as per BIS 43 Grade OPC	Analysis of Cement Produced without Red Mud	Analysis of Cement Produced with Red Mud
Compressive Strength (Mpa) day 28.	43	59.8	59.9
Fineness m ² /kg	225	310	310
Initial Set (mins)	30	120	110
Final Set (mins)	600	190	180

Pontikes *et al.* (2011) utilised pressure filtered red mud as part of the clinker and cement raw material. They demonstrated that cement made with 5 wt% red mud (probably a full replacement of bauxite) achieved compressive strengths of 58.4 MPa (day 28 after cure). Results also tended to suggest high early strength. It was concluded that red mud could be utilised in cement manufacture as part of the standard blending process and would normally range about 3 wt%. This author believes the pressure filtration allowed the creation of a product more suited to the proposed application as it contained less sodium aluminate solution. The application of steam filters could potentially lower the entrained aluminate solution further.

Ribeiro *et al.* (2011a) was able to demonstrate that red mud added to concrete delays the onset of steel reinforcement corrosion and may even slow the corrosion rate. Ribeiro *et al.* (2011b) demonstrated that red mud added to mortar (cement and sand mix) could replace the cement due to the pozzolanic action of the red mud. Mortar strength was impressive, as seen in Figure 2-13. Of some issue is the effect of red mud on water availability and mortar plasticity. For a fixed water content, the water absorption of red mud resulted in an early cure.

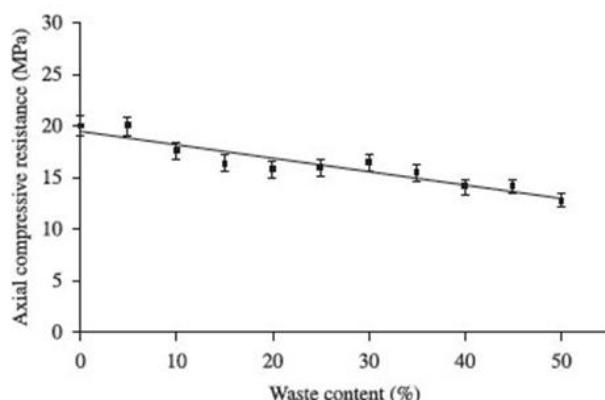


Figure 2-13. Compressive strength of a mortar as red mud replaces cement (Ribeiro *et al.* 2011b).

2.2.8 Bauxite residue for acid sulphate soil and acid rock remediation

Bauxite residue contains entrained soluble and solid alkaline components. There have been several attempts to use red mud to neutralise Acid Mine Drainage (AMD) and Acid Sulphate Soils (ASS). Inevitably, the majority of research would rediscover that red mud only holds a small proportion of alkaline agents, and thus will be relatively expensive compared to traditional agents such as limestone, especially once the transport costs are factored in.

There are some examples of dual purposes for the red mud that do appear to be economically rational. One dual application is the need to ‘fill’ or ‘seal’ acid generating mine sites. The plug of red mud would act to neutralise any generated acid, while also significantly reducing oxygen ingress to the active sulphide minerals (Duchesne & Doye, 2005). It has also been claimed that mixtures of red mud with lime kiln dust reduce the viability of the bacteria responsible for oxidation of sulphides.

Glenister & Thornber (1885) reported possible methods for blending of acid waste and red mud. In particular was the ability to blend waste gypsum and red mud to act as a soil ameliorant. Lin *et al.* (2004) remediated AMD and ASS for vetiver grass growth through amelioration with red mud, though suffered from over liming. This is an issue that amendment with gypsum would prevent.

Varnavas *et al.* (2005) demonstrated that red mud amelioration of ASS was capable of reducing the pore water concentrations of heavy metals, effectively remediating the soil for vegetative cover.

McConchie & Clark (1996) utilised seawater neutralised red mud for treatment of ASS, and Davies-McConchie *et al.* (2002) did likewise for AMD, while Rubinos *et al.* (2011) utilized carbonated red mud for AMD decontamination. It is clear that red mud can be utilised no matter which form of initial pH reduction is utilised.

Maddocks (2009) conducted field trials for remediation of cover sites over acid rock using Bauxsol^(TM) (sea water neutralised red mud), lime and clay covers, amended with bio-solids. All three treatments performed well, with strong eucalypt tree growth compared to the control site. One species of eucalypt did struggle in the Bauxsol^(TM) but this was probably due to an intolerance of chloride.

Another dual advantage to utilising red mud is the adsorption and immobilisation of heavy metals, particularly from AMD or ASS. Typically these polluted sites also contain dissolved iron species. As heavy metals are precipitated due to neutralisation, they generally co-precipitate with the iron species. Since red mud has a significant concentration of high surface area iron oxides, it can act to seed nucleation sites for precipitation of the iron and other heavy metals. These precipitates tend to be more ordered and more resilient to subsequent pH change. This is in agreement with Ciccuzzi *et al.* (2003) who highlighted that pH alone is not the only factor immobilising heavy metals from contaminated soils. Absorption onto surface sites, such as silico-aluminates and unburnt carbon in fly ash, played a key role.

Maddocks (2009) used a sequential extraction technique to indicate that greater than 95% of absorbed heavy metals in Bauxsol^(TM) must be bound within the iron and magnesium oxides.

Whichever iron, aluminium, silicon or magnesium hydroxide, oxyhydroxide or oxides, the heavy metals become bound within (probably a combination), they do appear to be strongly held and resistant to later re-acidification. This is a significant advantage to remediation and amelioration projects.

2.2.9 Bauxite residue in other applications

There has been a host of products suggested for the utilisation of bauxite residue, though they are less developed than those already discussed. The majority of these products utilise the residue as benign filler. Others rely upon key properties of bauxite residue in order to solve specific problems.

Hofstede (1992) utilised the physical and chemical properties of red mud to provide synergistic improvements to the composting of organic wastes. The bauxite residue provides some bulk structure to the compost and its fine nature aids soil wetting and moisture retention. The red mud alleviates odour generation through elevation of the pH (Hofstede & Ho, 1992) and may trap ammonium compounds, a useful fertiliser for plants. Volatile ammonium compounds are a significant contributor to odour release during the composting process. The iron and aluminium adsorptions sites also lock up many heavy metals that may be released from the organic decomposition process (Hofstede, 1994). Other benefits are the slight pH elevation that prevents soil acidification and the formation of clay-organic complexes that significantly increase the life of the compost.

Summers & Ellis (1992) demonstrated that pigments could be extracted from red mud. They extracted various iron oxide grades and colours. While pilot plant batches were made, competition with existing products appears to have prevented market uptake. Karasu *et al.* (2005) appears to have had similar technical success but with no known commercial utilisation.

Martinent-Catalot *et al.* (2002) and Pechiney (2002) report the use of red mud as filler in the production of plastic. They noted that thermoplastics processed at 300°C require the pre-treatment of red mud so as to prevent residual gibbsite decomposition. They also added red mud to recycled rubber used for padded flooring. The red mud provided filler, as well as a *friendly* colour, as seen in Figure 2-14. The application of red mud to cement and to paint has also claimed a suitable colour generation. To date there does not seem to be widespread commercial application of these by-products.



Figure 2-14. Sample of plastic with 15 % red mud filler.

Lombi *et al.* (2002) reported on a chemical assessment for utilisation of red mud to fix metal contaminated soils. The goal was to mix red mud into a contaminated soil and have the absorbing power of the mud fix mobile metal species. They found that the red mud reduced heavy metal concentrations of soil pore water, and appeared to prevent the metals subsequent release when the soil was acidified. Presumably this was through a chemical bonding to the iron oxides present.

Deveson (2003) filed a patent to utilise red mud to extract magnesium and calcium from sea water, improving the subsequent production of salt. This would appear to be the other-side-of-the-coin to using sea water for the purpose of neutralising red mud.

While the potential applications for utilisation of red mud may be endless, the vast majority are considered niche markets at best and do not provide a significant market volume to commence commercialisation. Alternatively the residues produced from utilisation are more difficult to handle and store than the unused red mud.

2.2.10 Remediation of bauxite storage facilities

The historical philosophy for bauxite residue management is secure impoundment. Long term management strategies have embraced the need for a site cover. Typically this has taken the form of vegetative rehabilitation for the creation of refuge parkland (Courtney & Harrington, 2011). To achieve this aim, impoundment remediation has become a significant area of research. Capitalising on the ability to utilise red mud for amelioration of sandy soils, researchers have looked into methods of surface transformation.

Harrison (1996) suggested that even with significant re-use of residue and by-products, the vast amount of residue currently in storage had a very low probability of ever being used. In an effort to remediate the current residue storage areas, various problems need to be overcome as summarised below:

- The wet lakes need to be dried and thickened to support plants etc;
- The high pH needs to be reduced to a level tolerated by plants;
- Excessive salt needs to be removed or nullified;
- Bauxite residue has low porosity that needs to be amended;
- There is no organic matter in the residue area;
- There are no nutrients in the residue area;
- There can be an absence of calcium in residue.

Many of these issues can be overcome and the following review is a selection of some of the notable efforts made towards site remediation.

Wong and Ho (1991) reported the impact of gypsum and sewage sludge amendment on bauxite residue. The sewage sludge added organic matter and also significantly reduced the bulk density (by 25 wt% for 144 t/ha). They claim the sludge increased total porosity by 8 wt%. The sludge and gypsum contributed to soil hydraulic conductivity increasing from 1.3 to 24×10^{-5} m/s. Wong & Ho (1992) utilised similar mixtures to successfully grow pasture grasses, including Bermuda grass.

Bell & Ward (1992) evaluated coastal limestone vegetation zones to select plant species naturally tolerant to high salt and pH. The selected species were tested in glass house trials then progressed onto field trials. They were able to demonstrate that several species had 100% survival on soil above pH 8.

Pechiney (2002) claim that Bauxaline® mixed with 10 – 20 wt% organic waste (presumably animal manures) can improve agronomic results.

Menzies *et al.* (2004) claim that seawater neutralisation of red mud not only reduces the pH and sodium content of the residue but adds significant levels of calcium,

magnesium and potassium. However, they report that in-situ remediation would be difficult due to gelatinous precipitates potentially blocking the drainage system. In addition the product remained too saline to support significant plant growth without leaching.

Courtney & Timpson (2005) utilised 25 wt% coarse bauxite residue (sand) to improve soil structure of amended red mud (gypsum, biomass and nutrients). The sand allowed improved leaching of the amended mud and lowered plant impact of sodium.

Ippolito *et al.* (2005) ameliorated red mud with gypsum, acid gypsum, sulphuric acid, and elemental sulphur. Some mixtures included wood chips to add organic matter and to break up the clay-pan structure. Leach assessment indicated the acidic gypsum lowered the pH the greatest; while leaching the highest levels of sodium, calcium and magnesium (consistent with soda reactivity and sodium displacement). The sulphur had least impact on pH probably due to insufficient time for it to oxidise. The sulphuric acid was not as effective at lowering pH probably because of its aggressive nature attacking soluble and less soluble alkali alike.

Xenidis *et al.* (2005) made a significant effort to ameliorate red mud. They found that gypsum reduced the pH, electrical conductivity and the concentrations of sodium and aluminium. Sewage sludge was found to improve the soil structure as well as provide nutrient. They also found that calcium phosphate added to the above mixtures enhanced plant growth.

Krishna *et al.* (2005) were able to grow the high pH tolerant microbes, *Aspergillus Tubingenesus*, on red mud amended soils. The microbes were able to reduce the pH from 10 to 7 on a mud-to-soil ratio of 75 wt%. The key lesson is that to transform red mud back into a soil requires more than mixing a few chemicals together. This echo's the successful use of gypsum and sewage sludge by Wong and Ho (1991).

Wehr *et al.* (2006) reported a case study from the Alcan Gove refinery in the Northern Territory, Australia. Due to a lack of suitable materials for red mud amelioration, soil capping was utilised for remediation. The soil capping of wet

disposal areas resulted in water-logging during the wet season and salt scald from capillary rise during the dry. The key to plant survival was the fresh water content of cap soil during the long hot dry season. Established vegetation cover appeared to reduce capillary rise of salt and soda from the underlying residue. In addition, the red mud tended to crack into blocks (drying and consolidation) allowing root penetration into lower sources of moisture. The plants obviously needed to be highly tolerant to salt and alkali.

Maddocks (2009) used Bauxsol™ (sea water neutralised red mud) for construction trials of reactive in-situ covers over acid tailings. Four 400m² test cells were constructed to compare a control with Bauxsol™ plus biosolids, lime plus biosolids and soil capping alone. He found that the Bauxsol™ treated site had much larger root penetration of up to 1.6 m when the cap was only 0.5 m thick. This impact was not observed with the lime treated site, however, there was no statistical difference in tree growth between these test cells over the time span of monitoring.

Phillips (2010) reported on the impact of gypsum incorporation depth and impact of irrigation. Irrigation was found to significantly increase above ground biomass but not impact diversity (Figure 2-15). Plant performance was independent of gypsum depth, probably because the “shallow” and “deep” incorporation both covered a large portion of the root zone. However, root growth did tend to be associated with higher gypsum zones; hence shallow incorporation would leave plants more susceptible to drought stress.



Figure 2-15. Native plant growth on rehabilitated residue area (Phillips, 2010).

A review published by Jones & Haynes (2011) reported that the integrated use of gypsum, organic amendments, nutrients, and inoculation of saline and sodic tolerant plants was preferential. That is, the re-establishment of soil type conditions. They noted that much work has been devoted to establishing vegetation, with little work on subsequent self propagation.

Patil *et al.* (2011) reported on some successful re-vegetation trials. While the specific soil amendments were not mentioned, the vegetation selection was. This author noted the significant change in selection process to favour local valued crops. This included grass and tree species for both fodder and for fuel wood. In essence a transformation of the impoundment site to a resource that supplied valued products to the local community. This would seem to be a more sustainable long term outcome.

Not all areas need to be converted to natural bushland to aid community benefit. The goal should be to maximise the potential applications for future generations to choose. For example, the State Government of Western Australia resumed a heritage residue disposal area from the Kwinana refinery of Alcoa of Australia Limited. The wet residue disposal lake was drained and compacted to allow construction of parking and marshalling areas for the Kwinana Motorplex shown in Figure 2-16. Built in 2000, the complex has taken advantage of the industrial location and transport network.



Figure 2-16. Kwinana Motorplex service areas built on top of a compacted heritage residue storage site.

Perhaps this is the simplest form of remediation. Stabilisation and use in whatever format future generations choose. These sites are usually located close to key road networks and sometimes have rail hubs and ports. There will be significant power supply nearby and a ready workforce. The opportunity to turn stabilised residue areas into future industrial sites would seem to be as large an opportunity as the use of the residue itself.

2.2.11 Sodium oxalate utilisation

Sodium oxalate is an organic impurity produced by the oxidation of organic materials during the Bayer process cycle. Sodium oxalate needs to be removed from the circuit to prevent it from precipitating with alumina. This would cause a significant increase in fines production as well as a co-precipitated product.

The removed sodium oxalate can be reacted with calcium oxide (lime) to precipitate calcium oxalate and return the sodium to circuit, or stored in impoundment sites.

Sodium oxalate can be utilised in the production of vanadium pentoxide. Sodium oxalate is used to leach vanadium from iron oxides at a temperature of around 1100°C. A concentrate is precipitated and then roasted to produce sodium vanadate precursor.

In 1999, Vanadium Australia Pty Ltd built a \$200 million plant for extraction of vanadium at Windimurra in Western Australia. The plant was commercially supplied with sodium oxalate from Alcoa of Australia's Kwinana and Wagerup refineries. Almost 14 million tonne of high quality vanadium pentoxide was produced before a drop in price closed the plant in March 2003 (Chemlink, 2012).

2.2.12 Obstacles to reuse

With so much research by quality scientists producing significant numbers of potential applications over many years, it would be expected that economic commercialisation would be a reality. In fact it is not.

Hamada (1986) listed a series of obstacles for the commercialisation of residue utilisation. They are summarised as:

- Products are not economically viable;
- Inability for use of residue to compete with traditional raw materials;
- High cost of processing residue;
- High cost of dewatering;
- Complexity of some products;
- Issues surrounding handling of residue.

While this was true at the time, much has changed in the modern Bayer process and processing of residues has made major advances (Hond & Brouwer, 2011). Residues are now dry and easy to handle once carbonated. Process costs have also come down with the scale of production, while the cost of traditional land use for wet disposal has increased significantly. Many academic papers still persist with the art of the possible but more now incorporate economic assessments as part of their research. The cost of traditional resources has increased as their availability has decreased. Transport costs now play a pivotal role in economic models, creating further opportunity. With so many changes potentially favouring residue and by-product utilisation, what other factors need to be addressed?

Gambrell *et al.* (2002) proposed a dual use application for bauxite residue. They proposed that the red mud be utilised for restoring Louisiana coastal marshlands. Glass house studies determined that red mud amended with soil or mulch generally resulted in good plant growth, even freshwater species. In addition the metals contained within the red mud were environmentally bound and were not rapidly released to the surrounding environment. They concluded that ... *comprehensive laboratory, greenhouse and controlled field plot experiments showed potential for use as a substrate to enhance or restore deteriorating coastal marshes*. This is a positive outcome and their claim is the result of significant scientific vigour. However, Gambrell *et al.* (2002) then spent the next three-quarters of their conclusions chasing *precautionary points*; one even raised by a journalist. Not that these concerns aren't valid but they would be better served as a paragraph within the text, rather than be raised and clarified in the conclusion. This over-sensitivity to

potential criticism (a natural part of the scientific method) can lead the casual reader away from the significant results that were reported.

Pappu *et al.* (2007) wrote, *The scientific advancement in recycling and using industrial and agricultural processes for utilizing wastes will lead to better use of the world's resources*. They went on to claim that the utilisation in building construction could lead to lower construction costs, improved resource utilisation and potential lowering of greenhouse gas production. They claim that there needs to be encouragement for entrepreneurs and construction agencies to use these materials. But how do you do that? What is the factor that is holding development back?

Klauber *et al.* (2011) list four reasons why the more than 700 patents on bauxite residue utilisation have not been implemented. They are summarised below.

- Volume: the annual production volume of residue is daunting, let alone the historic stored volume. Most ventures would result in only trivial percentages of residue being consumed and hence their value can be overlooked;
- Performance: bauxite residue often needs pre-treatment to allow handling and beneficiation. Even then, the product grade tends to be on the poor side in comparison to natural ore bodies;
- Cost: the expense of any project is usually encumbered with start-up capital, pre-treatment and impact costs upon the alumina refinery. In comparison the alternative of secure impoundment, cover and maintenance are future costs; discounted to net present value, making economic arguments alone difficult;
- Risk: partly this is the "what if?" scenario. What are the possible adverse impacts from utilisation compared to the safe continued storage? A significant portion of risk is simple public perception of by-products.

From above, there appears to be a different driver required to make projects happen. There is a tangible belief that any risk is wrong, a complete misunderstanding of the term "risk". There is also a systemic under-representation of the risk of doing nothing i.e. stasis. Public sentiment is changing; while "waste" is disliked, "wasted opportunity" is despised. That is the true risk to the public licence to operate.

Harris (2007) in a review of regional synergy of industries in the Kwinana industrial area of Western Australia summarised the impact of current regulatory and policy settings. *This study found that although current regulations do not function as direct barriers per se, the current regulatory framework does not encourage or support regional synergy developments. Therefore, in the short term, the most immediate policy support requirement to foster further resources synergies is the development of standards and guidelines for reuse.*

While the work of Harris (2007) relates to a specific location, country and time, his findings could be translated to almost any location and reuse opportunity.

Attiwell (2013) noted that the only countries that recycled and utilised mining residues (e.g. Holland) were those counties that had legislation and standards in place as a driver. Hence the emphasis was changed from "Prove why residues should be utilised" to "Prove why residues cannot be utilised". The resulting change in emphasis has seen significant enhancement of public benefit from consumption of limited resources.

2.3 Environmental assessment

The environmental assessment methodology for testing by-products is a significant factor in the further development of reuse technologies. In Western Australia, the Kwinana Industrial Council identified several synergies between local industries and wanted to explore options for improving by-product utilisation. They commissioned the Centre of Excellence in Cleaner Production (CECP) to evaluate the potential for by-product utilisation within the area and to look at barriers and drivers to assist the process. A significant number of valued synergies were identified (Harris, 2007). It was reported that the need for a formalised framework of by-product assessment was essential to allow companies to show that they have met or exceeded regulatory requirements. Without this ability, industries were unwilling to invest significant funds in by-product development.

Attiwell (2013) reported a major review of by-product utilisation assessments. She observed that countries with significant by-product utilisation were those where

assessment scenarios were well established and documented. Likewise, countries with no firm assessment framework had correspondingly very little utilisation of by-products. Attiwell (2013) continued with a summary of the environmental agencies available in Australia and how each State regulates by-product utilisation. It was noted that a national approach for assessing contaminants in fertiliser (of which industrial residues could be a subcategory) was in preparation. These national guidelines typically over rely upon compositional assessment, leading to *overly conservative estimate of risk*. These assessments often refer to a measure of the ability of a species to be adsorbed from solution, K_d . Hence a higher K_d should reflect a high level of solubility and impact. Unfortunately this term does not take into account the significant changes to solubility, due to soil types and pH, and so is open to incorrect interpretation.

A variety of different leach testing methods have been put forward by various countries, in an effort to gain a better understanding of the actual impact a product has upon its environment. These have been reviewed below and a summary by Attiwell (2013) is shown in Table 2-3.

Table 2-3. Comparison of leach extraction procedures for granular materials from Attiwell (2013). Note L/S is the liquid to solid ratio.

Leach test	Extractant	L/S ratio	pH	Extraction time	Reference
'Availability' test	Deionised water with addition of nitric acid	1 st step 100:1 2 nd step 100:1	Controlled 1 st step 7 2 nd step 4	1 st step 3hr 2 nd step 18hr	(Nordtest, 1995)
Sequential Extraction Leach test	1 st step: acetic acid	1 st step 40:1	No pH control	1 st step 16hr	(Ure <i>et al.</i> , 1993)
	2 nd step: Hydroxylammonium chloride	2 nd step 40:1		2 nd step 16hr	
	3 rd step: ammonium acetate Demineralised water	3 rd step 50:1		3 rd step 16hr	
Australian Standard Leaching Protocol (ASLP)	Demineralised water, sodium acetate buffer solution	20:01	No pH control	18hr	(Australia Standards, AS 4439.3)
Toxicity Characteristic Leaching Procedure (TCLP)	Sodium hydroxide and sodium acetate buffer solution	20:01	No pH control	18hr	(US EPA, 1992)
pH dependent leach test	Demineralised water, nitric acid and sodium hydroxide	10:01	pH range 4-12 or controlled at selected pH	48hr	(CEN 2005).

2.3.1 Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP is a procedure designed to assess the leachate from industrial wastes that are deposited into acidic landfill. This is the basis of the United States Environmental Protection Agency method 1311 (US - EPA, 1992). Generally, the extracting liquor is prepared with an initial pH of 2.9, 5.0 or 9.0 then added to the mixed waste extraction. The test method does not take into account the final pH of the mixture, which could easily be changed by a buffered reagent. Nevertheless, this is the preferred leach testing method adopted widely.

2.3.2 Australian Standard Leaching Protocol (ASLP)

The Australian Standard Leaching Protocol (ASLP) is similar to the TCLP method but allows for utilisation at the natural equilibrium pH of the test material. While this test is arguably better for the assessment of mining residue by-products, the TCLP is

still recognised and accepted by a wider variety of government agencies within Australia.

2.3.3 pH dependence leach assessment

There is a significant variety of different methods and complexing agents that can be used for leach assessment. It has been shown that solution pH has the greatest influence over solubility (Brunori *et al.* 1999, Van der Sloot, 2002). Thus it is very important to identify both the natural pH of the reagent and the pH of the region that will receive the material. This is essential to understand what is actually going to happen, rather than merely theorise. For the pH dependence leach test, samples are assessed across a range of pH values where the pH is stabilised and reported once equilibrium has been reached within the time parameters of the test.

Van der Sloot & Djikstra (2004) reported on the method of using sequential extraction across a variety of pH units particularly for soils and sediments and Van Zomeren *et al.* (2005) reported the prediction of long term leaching from landfill containing inorganic waste. Dijkstra *et al.* (2006) used pH dependence leach testing to enable equilibrium geochemical modelling using ORCHESTRA® upon coal bottom ash samples.

The European Union leach assessment protocol (CEN, 2005) adopted pH dependence methodology and Van der Sloot *et al.* (2006) successfully applied the technique to granular materials such as concrete waste. Carter *et al.* (2005) utilised pH dependence leach testing to characterise the leaching behaviour of bauxite residue. Attiwell (2013) extended this work to a range of different residue materials and their application to various soils, firstly as a predictive tool and secondly in practice. This allowed her to assess the reagent impact and compare against the predicted level utilising geochemical modelling.

2.3.4 Geochemical modelling

The pH dependence leach testing provides a range of information including the total concentration available to leaching and the leaching experienced at any pH.

Applying this information to geochemical modelling software, such as Leach XS™, allows the determination for controlling mechanisms and speciation within the original sample. Hence it is possible to determine which minerals are available for leaching and, from first principles, determine what their environmental impact will be. Figure 2-17 shows the leaching of iron from bauxite residue called Alkaloam®.

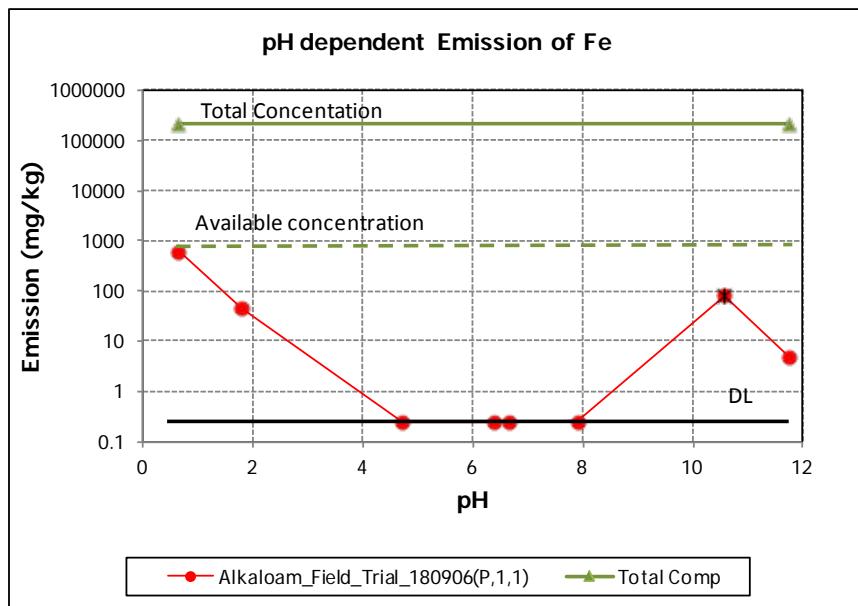


Figure 2-17. pH dependent leaching of iron from Alkaloam® (Attiwell, 2013).

Attiwell (2013) utilised this data, in conjunction with Leach XS™, to determine the controlling leaching process and associated mineral species (Figure 2-18). This allows for a thorough assessment of any potential environmental impact. The data set below shows the ferric iron (Fe^{3+}) in solution at a given pH, then the proportion of the soluble iron species. It also highlights which mineral products are leaching. It demonstrates that the majority of iron in solution chemistry is dominated by Dissolved Organic Carbon (DOC) absorption, while the mineral species at play are predominantly ferrihydrite (a short order iron oxyhydroxide, Jamieson (1995)) and clay bound iron (Figure 2-18).

It is hoped that this powerful tool can be utilised to encourage the use of by-products; both by allowing manufacturers to understand any risk, and by allowing governing bodies a methodology for assessment.

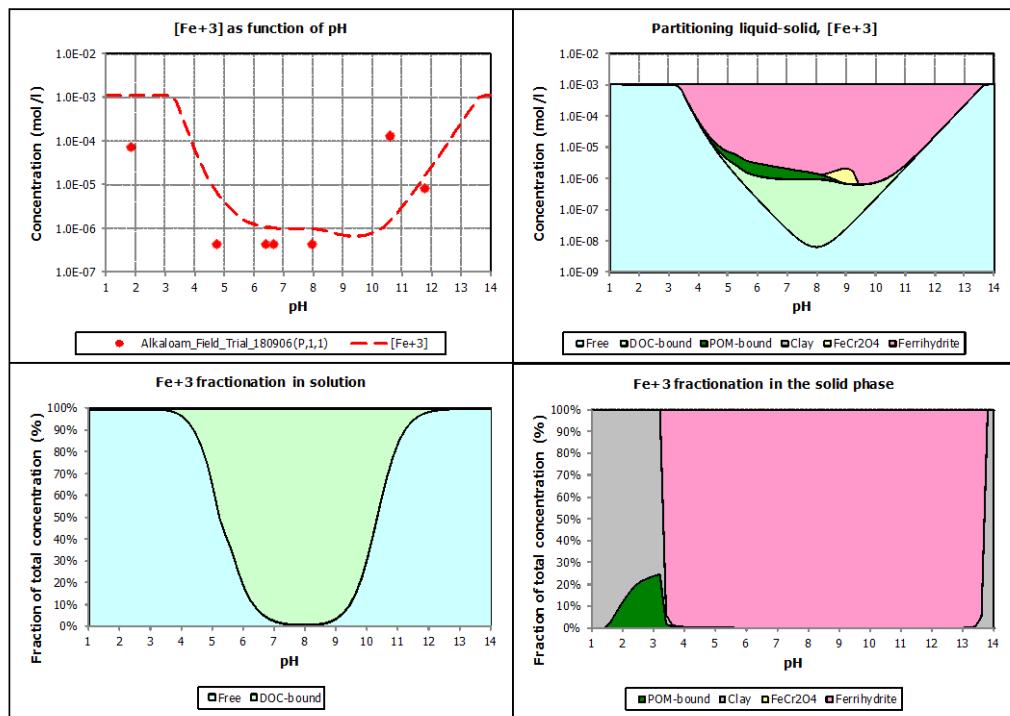


Figure 2-18. Geochemical modelling for iron in Alkaloam® (Attiwell 2013).

2.3.5 Monolith testing

It has been shown that the application of compositional testing can be overly conservative thus preventing many safe by-product reuse applications. In addition the use of K_d data (which does not take into account either the reagent pH or the receiving environment pH) can also prevent many safe applications. A further complication is that the majority of leach assessment protocols involved the use of granulated material, much of which is broken or crushed prior to assessment, exposing fresh surfaces and providing inaccurate long term data. This is particularly true for products that are used with binding agents for construction purposes such as concrete and geopolymers. In response, a series of monolith testing protocols and factors have now been established (Van der Sloot & Dijkstra, 2004) which need to be disseminated globally to enable wider uptake of by-product utilisation. These protocols have recently been endorsed by the United States EPA office as LEAF 1315 (2009). The method is designed to provide release rates of inorganic elements from both monolith and compacted granular material. This test utilises diffusion controlled release and is recorded as a function of time. The leaching water is replaced nine times during the process and the mass of the solid recorded. The pH

specific conductance and trace elements are plotted against time to show control mechanism as well as a cumulative function.

It seems appropriate to utilise LEAF 1315 (2009) guidelines for by-product assessment. Specifically this method will be applied to monolith samples of geopolymers that are utilised for block application (e.g. footpath, curb, pavement slab etc). It may also prove suitable for aggregate assessment.

2.4 Change from 'end of pipe' to 'product specifications'

“Waste is a product made to poor specifications” (Jamieson, 2008a).

Alumina is produced by the Bayer process to meet customer specifications. Failure to meet the specifications could result in the product being rejected or penalised. The Bayer process is run to a strict set of quality control and quality assured criteria to ensure that the alumina produced will meet the required specifications. The same will be true for by-products. By-products need to be produced to agreed specifications to ensure market acceptance and uptake, as shown in Figure 2-19.

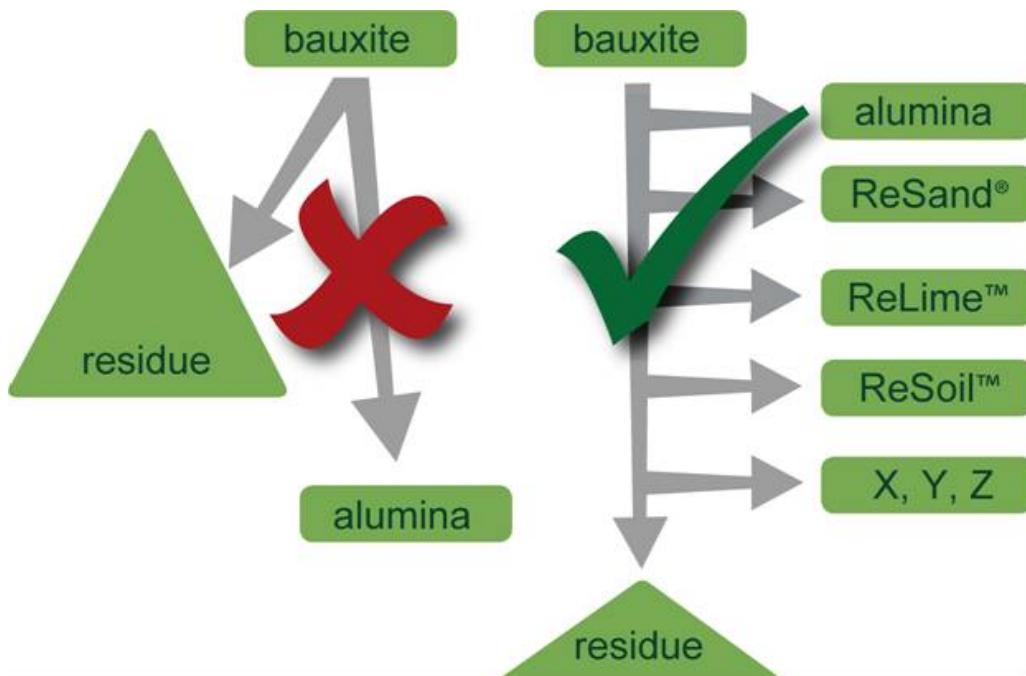


Figure 2-19. Co-products are made to accepted specifications (Jamieson, 2008a).

Alcoa of Australia Limited was one of the first alumina industry participants to recognise this approach and has made considerable efforts to achieve co-production of alternative products. This process underlies the philosophy of sustainability to the mining industry. Mining is a consumption of a finite resource. As such, sustainability is defined in terms of maximising the public benefit of that consumption. This is reflected by Rankin (2011) in his discussion of mineral and metals sustainability chapter on “Towards zero waste”.

Roach (1992) foreshadowed the need to “process to a specification” when in a review of potential by-products from bauxite residue, he stated economic recovery of products including soda would be: *assisted greatly if simple beneficiation processes could be found for the potentially valuable minerals in the fine red mud.*

This chapter seeks to highlight recent developments in beneficiation.

2.4.1 Introduction

The development of by-products has taken many years to progress. This is partly due to the conservative nature of the mining and construction industries and partly due to the successful development of safe environmentally secure impoundment technologies. It is also influenced by fear of the unknown. The “what if” scenario! What if a by-product used in construction, fails? What if a by-product leaches into the environment? Thankfully, these scenarios can be addressed by utilising the scientific method and the principle of balancing risk. Risk is assumed in all construction materials; performance standards are made to ensure the risk is minimised and controlled. The same is true for by-products. Ensure that a by-product meets standards and it becomes a commodity like all others. The recent development of pH dependence leach testing and mineralogical assessment has also minimised unknown environmental risks associated with utilisation.

This process can be summarised as a change in philosophy from “end of pipe” to “products made to a specification”.

The development of this process has involved a fundamental approach as outlined below.

- Firstly, separate the residue into as many different components as is technically and economically possible.
- Evaluate separated components against appropriate existing product standards. By-products that meet industry standard become products.
- Determine modification to processes to meet standards if applicable.
- Assess re-combinations of components to meet alternative product specifications and modify the production process if applicable.
- Conduct bench scale assessments of technical feasibility.
- Ensure all technical, environmental and legal requirements are met.
- Follow a stage gate process to determine final feasibility and economic assessment.

During this process, potential products are assessed in use for their proposed application. Laboratory, bench and field applications are conducted as required.

Often an overlooked part of by-product development is the need to identify a market for the product. The existence of a process and a product that meets specification does not mean that it is going to be successful. Factors that need consideration include:

- The secondary product process needs to be able to adapt to primary product process production rate changes;
- Product demand needs to be able to support planned production;
- Transport methods, nodes and costs need consideration;
- Competitor response needs evaluation;
- Customer requirements and demand cycles need to be forecast;
- Storage methods, supply methods and locations need evaluation.

These considerations need to be met to aid the development of by-products but typically a driving force is needed, either an individual or corporate.

2.4.2 Separation technology

This review focuses on the novel application of new and existing separation techniques to the unknown product of bauxite residues. It also attempts to comment upon the potential for each technique to be utilised in a commercial framework. Bauxite residue is a unique material and has significantly different properties to those materials that the separation equipment was designed for.

The majority of published research on bauxite residue separation techniques relates to the preparation of iron and other metal ores, as has been reviewed in Chapter 2.2. Very little has been published surrounding other alternative by-products.

Picaro (1997) patented a method of mechanically grinding desilication product (DSP), a component of red mud, to allow subsequent dissolution with water. Examples were provided with extraction efficiencies of between 40 and 60 wt%, while also extracting 10 - 20 wt% of the remaining alumina. This process is akin to the carbonation problems encountered with red mud. Unless CO₂ is held in excess with red mud to allow DSP to react over time, subsequent washing away of the bicarbonate solution would allow pH reversion. The mechanical activation reported here appears to enhance the reaction rate, though at a significant cost. In addition, DSP formation in refineries is typically managed by bauxite grade control to ensure a balance between excessive DSP formation and the impact of impurity removal. Destruction of the cage-like structure of DSP liberates soda and alumina, but also silica and any bound impurities such as sulphate. The resulting solution is also likely to be of low concentration requiring evaporation at significant cost.

Picaro *et al.* (2002) utilised 50 mm hydro-cyclones and multi gravity separators in an attempt to beneficiate desilication product (DSP) and titanium dioxide (TiO₂) fractions. Their results were mixed. The separation of DSP only achieved a beneficiation factor of 1.1 - 1.3. This is due to the fact that DSP can be in discrete balls or surface precipitated onto other minerals. The poor beneficiation would suggest the majority of DSP is either surface precipitated or strongly surface absorbed to other minerals. The separation of TiO₂ rich minerals was encouraging with beneficiation ratios between 3 and 5. The final grade of TiO₂ was a very

respectful 20 – 36 wt%. Unfortunately the recovery was less than 10 wt% of the total titanium available. This is due to the distribution of the target mineral throughout the bulk matrix of iron minerals. While a recovery of this level may still represent significant yearly tonnage, it is a poor outcome of having to run a mountainous building full of 50 mm hydro-cyclones. The capital expenditure (Capex) and operational expenditure (Opex) would be very high.

The following published works were managed and overseen by this author while acting in the role of Bauxite Residue Program Manager for the Centre for Sustainable Resource Processing (CSRP). The work can be broken down into the separation and processing of coarse particles (sand) and the separation and processing of silt and clay. The following definition of sand, silt and clay is provided by ANRA (2012).

- *The sand fraction is made up of those particles that have a diameter between 2 and 0.02 mm.*
- *Silt-sized particles are those with diameters between 0.02 and 0.002 mm.*
- *Clay-sized particles are those with diameters < 0.002 mm.*

2.4.2.1 Sand

Kimber (2004) utilized bauxite residue sand having a PSD from about 80 μm through to 1.2 mm with a D_{80} of 800 μm . She processed this material by both wet and dry magnetic separation. The average grade of iron oxide (Fe_2O_3) rose from about 25 wt% to 45wt% with a maximum achieved at the highest field strength of 65 wt%. Similarly a quartz rich fraction of above 96 wt% was achieved at the highest field strength. Unfortunately, the procedure also produced a large middle fraction of particles mostly consisting of quartz particles coated with red mud, as shown by Jones (2011). Kimber (2004) was able to achieve some success in leaching the sand prior to electrostatic separation to enhance recovery and grade, however, these pre-treatments would be cost prohibitive.

Down (2005) attempted to separate glass standard sand from bauxite residue sand. He evaluated a series of separation techniques but also encountered issues utilising the mud coated sand. Best results were 90 wt% quartz using a Wilfrey table. Attrition cleaning of the sand was beneficial but did not achieve the required grade.

The work of Kimber (2004) and Down (2005) demonstrated that the drying of red sand with even small proportions of red mud results in a product that was very difficult to beneficiate. This has significant impact upon current bauxite residue management practices where up to 15 wt% mud can contaminate the sand fraction. Until this procedure is modified to remove all mud, existing sand production will not be capable of future beneficiation.

To determine if high quality glass sand was achievable, fresh bauxite residue sand was washed clean of red mud and carbonated before drying. Strickland (2006) was unable to beneficiate quality glass sand through gravity separation alone. This was explained by Jones (2011), who reported that the sand is not just quartz and hematite, but a collection of iron, silicon, aluminium and calcium minerals. A further complication is the wide particle size distribution of all minerals. Nevertheless, Strickland (2006) was able to remove a heavy mineral concentrate similarly to Low Intensity Magnetic Separation (LIMS). Strickland (2006) proposed a LIMS/WHIMS (Wet High Intensity Magnetic Separation) combined flow-sheet shown in Figure 2-20. This combination produced a quartz fraction in excess of 95 wt% and he believed that subsequent processing would achieve the required purity.

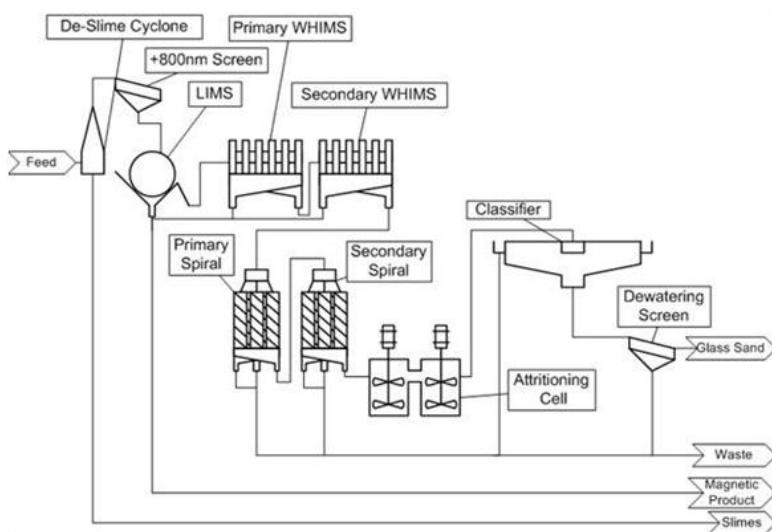


Figure 2-20. Flow diagram for beneficiation of glass quality sand (Strickland 2006).

Skender (2006) reported on the separation of iron sand from coarse bauxite residue using spirals. She was able to significantly upgrade an iron fraction from 31 to 43

wt% as Fe₂O₃ at a maximum recovery of 50 wt%. While disappointed at the outcome, spirals were shown to be very effective and could work in combination with other techniques.

Hawks (2008) investigated dry magnetic separation of clean red sand. His aim was to determine the moisture content of red sand that would allow dry magnetic separation because wet separation was considered too problematic. He reported that sand moisture needed to be below 2.6 wt% to prevent agglomeration and to allow the free flow action within the magnetic separators. He proposed the combined use of solar and fluidised bed drying as precursors to a two step magnetic separation.

2.4.2.2 Silt and Clay

“Soils ain’t soils” as the saying goes and mud isn’t mud. As shown previously, bauxite residue contains a range of particle sizes. While sand is relatively easy to separate, separation of silt and ultrafine clay is more difficult. However, large opportunities exist for both silt and clay if the separation process is technically and economically efficient.

Kim (2004) used a Mozley hydrocyclone (50 mm ID) to separate the silt from the ultra-fines (<10 µm). He utilised high intensity wet magnetic separation, froth flotation and the Knelson gravity concentrator in an attempt to concentrate more valuable components. Unfortunately results were poor due to the similarities in density between the target and gangue minerals. Density similarity and the fine particle size made high separation with high recovery very difficult.

Sunnassee (2006) utilised settling rates to collect fines/clay from bauxite residue. By application of Stokes’ Equation, he was able to calculate the time needed to allow >20 µm material to settle. This simple method proved effective at separation of finer sand, silt and clay. Unfortunately subsequent magnetic separation (wet and dry) proved difficult. As with sand, it may be that using fresh residue samples will aid full particle size differentiation and subsequent magnetic separation.

Bloomfield (2005) attempted to utilise wheat starch for selective flocculation of the Bayer residue slimes (clay). The flocculent appeared to be pH sensitive and at best only increased iron concentrations by 2 wt%. As a concept it demonstrated that such a process is possible and that further evaluation is required. Bloomfield (2006) pursued her earlier investigation to optimise flocculation performance. She reported that the use of wheat starch was unable to significantly increase iron concentrations to a level that would encourage economic interest.

Down & Lozyl (2006) used sodium oleate to enrich the iron content of red mud by froth flotation. Results were marginal. It appears that the major issue relates to the residues significantly wide particle size distribution (PSD). Even though the material was screened, the combined effect of a wide PSD across all minerals impacts upon the flotation performance. Sankey (2006) used froth flotation from a different angle. Her aim was to selectively remove a high alumina fraction for possible recycle back into the Bayer process. It was shown that any available alumina (i.e. available to caustic extraction) was associated with a significantly high level of fine quartz. The quartz would react during the digestion step consuming both liberated alumina and caustic, making the process unviable.

2.4.3 Product Specifications

Klauber *et al.* (2009) stated that:

Ensuring sufficient soda removal and/or neutralisation prior to downstream processing would enable residue to be transported and handled as a non-hazardous material and to be properly designated as a by-product.

This is correct but even the word by-product seems to attract negative connotations within some parts of the community. Hence it is the downstream processing that should remove all connotations of these products being inferior and confirm that they are made to a standard like all others.

The basic premise for production is to produce a commodity to a specified standard. Fortunately the bulk of commodities that can be produced from Bayer by-products have existing Australian standards and performance criteria. These standards are

listed below so the reader can be aware of the significant depth and wide range of existing performance standards.

2.4.3.1 Lime

The standards for lime tend to be based upon composition and sometimes can include particle size distribution. This is to allow for reactivity to be evaluated particularly when the lime agent is to be used for agricultural purposes. The appropriate standards are Australian Standard AS 4489.0, Test methods for limes and Limestone.

- 4489.1.1 September 1997 Method 1.1: Sample preparation —Quicklime and hydrated lime
- 4489.2.1 September 1997 Method 2.1: Fineness—Wet sieving
- 4489.3.1 September 1997 Method 3.1: Slaking—Dewar flask
- 4489.4.1 September 1997 Method 4.1: Soundness—Pat
- 4489.4.2 September 1997 Method 4.2: Soundness—Le Chatelier
- 4489.4.3 September 1997 Method 4.3: Soundness—Autoclave
- 4489.5.1 September 1997 Method 5.1: Chemical composition—Quicklime and hydrated lime
- 4489.6.1 September 1997 Method 6.1: Lime index—Available lime
- 4489.7.1 September 1997 Method 7.1: Loss on ignition—Quicklime, hydrated lime and limestone
- 4489.8.1 September 1997 Method 8.1: Free moisture—Convection oven
- 4489.9.1 September 1997 Method 9.1: Solid content—Convection oven
- 4489.10.1 September 1997 Method 10.1: Bulk density —Quicklime and hydrated lime

In Western Australia, Lime WA (Inc) has produced a set of minimum criteria for product assessment which is called The Code of Practice (Lime WA, 2013). This code requires a minimum composition analysis, neutralising value, and the particle size distribution. Additional information such as effective neutralising value may be included on the reverse side but is not mandatory.

2.4.3.2 Sand and Aggregate

Aggregates can be used for concrete as well as for road base and other construction applications. Standards relating to the application are described in Australian Standard AS 1141, Methods for Sampling and Testing Aggregates.

- 1141.0 List of methods
- 1141.1 Definitions

- 1141.2 Basic testing equipment
- 1141.3.1 Sampling—Aggregates
- 1141.3.2 Sampling—Rock spalls, boulders and drill core
- 1141.3.3 Sampling—Preparation of stabilized pavement materials
- 1141.4 Bulk density of aggregates
- 1141.5 Particle density and water absorption of fine aggregate
- 1141.6.1 Particle density and water absorption of coarse aggregate —Weighing-in water method
- 1141.6.2 Particle density and water absorption of coarse aggregate—Pycnometer method
- 1141.7 Apparent particle density of filler
- 1141.8 Water soluble fraction of filler
- 1141.11 Particle size distribution by sieving
- 1141.12 Materials finer than 75 µm in aggregates (by washing)
- 1141.13 Material finer than 2 µm
- 1141.15 Flakiness index
- 1141.16 Angularity number
- 1141.17 Voids in dry compacted filler
- 1141.18 Crushed particles of coarse aggregate derived from gravel
- 1141.19 Fine particle size distribution in road materials by sieving and decantation
- 1141.20 Average least dimension of aggregate by direct measurement
- 1141.21 Aggregate crushing value
- 1141.22 Wet/dry strength variation
- 1141.23 Los Angles value
- 1141.24 Aggregate soundness—Evaluation by exposure to sodium sulphate solution
- 1141.25.1 Degradation factor—Source rock
- 1141.25.2 Degradation factor—Coarse aggregate
- 1141.26 Secondary minerals content in basic igneous rocks
- 1141.27 Resistance to wear by attrition
- 1141.28 Ball mill value
- 1141.29 Accelerated soundness index by reflux
- 1141.30 Coarse aggregate quality by visual comparison
- 1141.31 Light particles
- 1141.32 Weak particles (including clay lumps, soft and friable particles) in coarse aggregate
- 1141.33 Clay and fine silt (settling method)
- 1141.34 Organic impurities other than sugar
- 1141.35 Sugar
- 1141.36 Sulphur in metallurgical slag, crushed rock or other pavement materials
- 1141.37 Iron unsoundness
- 1141.40 Polished aggregate friction value—Vertical road-wheel machine

- 1141.41 Polished aggregate friction value—Horizontal bed machine
- 1141.42 Pendulum friction test
- 1141.50 Resistance to stripping of cover aggregates from binders
- 1141.51 Unconfined compressive strength of compacted materials
- 1141.52 Unconfined cohesion of compacted pavement materials
- 1141.53 Absorption, swell and capillary rise of compacted materials
- 1141.70 Lime or cement content of uncured stabilized pavement materials (EDTA method)
- 1141.71 Lime or cement content of stabilized pavement materials (EDTA method)
- 1141.72 Cement content of cement stabilized materials

In addition other standards may also be appropriate including Australian Standard AS 2758 Aggregates and Rock for Engineering Purposes.

- 2758.0 Part 0: Definitions and classification (this Standard)
- 2758.1 Part 1: Concrete aggregates
- 2758.2 Part 2: Aggregate for sprayed bituminous surfacing
- 2758.4 Part 4: Aggregate for gabion baskets and wire mattresses
- 2758.5 Part 5: Asphalt aggregates
- 2758.6 Part 6: Guidelines for the specification of armour stone
- 2758.7 Part 7: Railway ballast

2.4.3.3 Concrete

Australian concrete is assessed by a series of performance standards and not composition. Composition standards for concrete are particularly limiting and could result in the prevention of industry development and growth. Performance standards allow for alternative binding agents to be developed including geopolymmer technology. The standard is Australian Standard AS 1012 Methods of Testing Concrete.

- AS 1012.1-1993 Methods of testing concrete - Sampling of fresh concrete
- AS 1012.10-2000 Methods of testing concrete - Determination of indirect tensile strength of concrete cylinders (Brasil or splitting test)
- AS 1012.11-2000 Methods of testing concrete - Determination of the modulus of rupture
- AS 1012.12.1-1998 Methods of testing concrete - Determination of mass per unit volume of
- AS 1012.12.2-1998 Methods of testing concrete - Determination of mass per unit volume of hardened concrete - Water displacement method

- AS 1012.13-1992 Methods of testing concrete - Determination of the drying shrinkage of concrete for samples prepared in the field or in the laboratory
- AS 1012.13-1992/ Amendment 1-1993 Methods of testing concrete - Determination of the drying shrinkage of concrete for samples prepared in the field or in the laboratory
- AS 1012.14-1991 Methods of testing concrete - Method for securing and testing cores from hardened concrete for compressive strength
- AS 1012.16-1996 Methods of testing concrete - Determination of creep of concrete cylinders in compression
- AS 1012.17-1997 Methods of testing concrete - Determination of the static chord modulus of elasticity and Poisson's ratio of concrete specimens
- AS 1012.18-1996 Methods of testing concrete - Determination of setting time of fresh concrete, mortar and grout by penetration resistance
- AS 1012.19.1-2000 Methods of testing concrete - Accelerated curing of concrete compression test specimens - Hot water method
- AS 1012.19.2-2000 Methods of testing concrete - Accelerated curing of concrete compression test specimens - Warm water method
- AS 1012.2-1994 Methods of testing concrete - Preparation of concrete mixes in the laboratory
- AS 1012.20-1992 Methods of testing concrete - Determination of chloride and sulfate in hardened concrete and concrete aggregates
- AS 1012.21-1999 Methods of testing concrete - Determination of water absorption and apparent volume of permeable voids in hardened concrete
- AS 1012.3.1-1998 Methods of testing concrete - Determination of properties related to the consistency of concrete - Slump test
- AS 1012.3.2-1998 Methods of testing concrete - Determination of properties related to the consistency of concrete - Compacting factor test
- AS 1012.3.3-1998 Methods of testing concrete - Determination of properties related to the consistency of concrete - Vebe test
- AS 1012.3.4-1998 Methods of testing concrete - Determination of properties related to the consistency of concrete - Compatability index
- AS 1012.4.1-1999 Methods of testing concrete - Determination of air content of freshly mixed concrete - Measuring reduction in concrete volume with increased air pressure
- AS 1012.4.2-1999 Methods of testing concrete - Determination of air content of freshly mixed concrete - Measuring reduction in air pressure in chamber above concrete
- AS 1012.4.3-1999 Methods of testing concrete - Determination of air content of freshly mixed concrete - Measuring air volume when concrete dispersed in water
- AS 1012.5-1999 Methods of testing concrete - Determination of mass per unit volume of freshly mixed concrete
- AS 1012.6-1999 Methods of testing concrete - Method for the determination of bleeding of concrete

- AS 1012.8.1-2000 Methods of testing concrete - Method of making and curing concrete
 - Compression and indirect tensile test specimens
- AS 1012.8.2-2000 Methods of testing concrete - Method of making and curing concrete
 - Flexure test specimens
- AS 1012.9-1999 Methods of testing concrete - Determination of the compressive strength of concrete specimens

In addition other assessments may also be relevant such as Australian Standard AS HB79 - Alkali Aggregate Reaction, and Australian Standard AS 1379 (2007) – Specification and Supply of Concrete.

It is apparent that with existing performance standards in place for a range of commodity products, Australia is well placed with a significant advantage to progress by-product or co-product development. As a leader in mining and mineral processing technology, it would be advantageous to be a world leader in maximising the community benefit from the harvesting of resources.

2.5 Alcoa bauxite residue as a by-product (Alkaloam®)

As highlighted in the historical review, bauxite residue or red mud has been shown to be a suitable soil ameliorant (Figure 2-21). Carbonated red mud produced for soil amelioration at Alcoa is called Alkaloam®.

Of all the bauxite residue by-products, Alkaloam^(R) has been the only product to be utilised in significant quantity by Alcoa. It was also the first by-product to be substantially modified to suit customer specifications. Raw red mud is a hazardous material because of the high residual pH (Grafe *et al.* 2011) and so is difficult to transport and handle. Atmospheric or forced carbonation was used to reduce alkalinity and remove any hazardous nature.



Figure 2-21. Application of Alkaloam® for broad acre soil amelioration.

2.5.1 Peel-Harvey catchment amendment

The West Australian Department of Agriculture, now called Department of Agriculture and Food, Western Australia (DAFWA), had been given an objective to decrease the amount of phosphorus that ran off land and entered the Peel-Harvey estuary. This fertiliser run-off was causing significant algal blooms and pollution within the inland waterways. After 15 years of research on a variety of pollution control and soil amendment reagents, the Department had settled on a reagent that they believed would enable widespread application and site remediation. This reagent was bauxite residue. It was described as finely ground bauxite and ironstone gravel from the Darling Scarp, where most of the alumina had been extracted. The residue mainly consisted of iron, aluminium and silicon oxides, but it is the iron and aluminium oxides that had the capacity to bind pollutants such as phosphate. In 1993 the West Australian Department of Agriculture sought approval from the Environmental Protection Authority to conduct widespread agricultural and horticultural trials within the Peel-Harvey catchment area. A Public Environmental Review (DOA PER, 1993) was prepared to enable the Environmental Protection Agency to assess the proposal and to allow a public discussion (Figure 2-22).



Figure 2-22. Public Environmental Review (DOA PER, 1993).

The Public Environmental Review (DOA PER, 1993) provided a detailed description of the proposal, the benefits and the impacts of bauxite residue application. There was also a significant summary of previous trials, potential applications and a detailed literature review. The proposal listed a series of recommendations for the use of bauxite residue. These recommendations are summarised below.

- Standard health and safety precautions should be taken during transport spreading and handling of bauxite residue because of its caustic nature.
- Recommended dose rates below 100 t/ha will prevent the need for gypsum addition for pH control. Additional rates of between 20 and 80 t/ha were considered to be the most economic as they did not require incorporation into the soil or the added expense of gypsum. These rates would also have minimal dust impact.
- A maximum rate of 80 t/ha is to be incorporated in domestic garden applications and well mixed to prevent staining of exterior surfaces from boot transport.
- A maximum application of 250 t/ha can be used for horticultural soils with adequate mixing.
- Rural site soil mixing of low application rates could rely upon natural mixing by stock and rain.
- The use of bauxite residue should be regulated for infiltration barriers to allow adequate flow.
- Site testing for pH and buffering capacity is required to avoid over liming particularly with well-drained sandy soils.

The Minister for environment approved the project, subject to conditions, on 4th February 1994. One of those additional conditions was that the project be

“substantially commenced” within a period of five years. During this time Alcoa sought a deed of indemnity from the Government of Western Australia, for any unforeseen consequences arising from the use of bauxite residue, in accordance with the conditions set by the EPA. This was granted in September 1999 requiring DAFWA to apply for a further five-year extension for the project from the EPA in June of 2000 (AWA, 2000). The extension was granted and a code of practice (Figure 2-23) was published in December 2000 (DOA COP, 2002).



Figure 2-23. Code of Practice (DOA COP 2002).

In the summer of 2002, bauxite residue was released for broad scale catchment trials. However, following several adverse media articles, including one in the Sydney Morning Herald titled “The Great Red Mud Experiment that went Radioactive” (Ryle 2002), Alcoa stopped the supply of Alkaloam®.

DAFWA issued a Performance and Compliance Report (PCR) in November of 2006 (DAFWA, 2006) in which it sought to update the project and outline the overall environmental performance. It also sought to clear all outstanding project requirements. A key finding outlined in the executive summary states: *Related environmental monitoring and research programs have been undertaken by DAFWA since 1994 and research and monitoring to date has indicated that no detrimental environmental impacts have occurred from the application of Alkaloam®* (DAFWA 2006).

This finding is in accord with numerous previous publications (Summers et al. 2004a, Summers et al. 2004b). In addition the Department of the Environment and Heritage, Canberra, (DEH 2006) state that a key recommendation for the reduction in

phosphate leaching is: *Undertake soil amendment on sandy soils. Using soil additives or conditioners such as ‘yellow sand’ and ‘red mud’ to help absorb phosphorus is very effective in stopping it leaching into the Peel-Harvey waters.*

A Water Quality Improvement Plan by the EPA (2008) accepted literature that found that use of bauxite residue had an immediate and marked ability to reduce nutrient leaching. They reported that: *Consultation must now commence with stakeholders to overcome barriers to the use of soil amendments such as bauxite residue. Once barriers are overcome a four-year demonstration program can then commence. If it is shown that after the four year period uptake is low then a regulatory approach may be necessary.* (EPA 2008).

2.5.2 CSRP review of Alkaloam®

Given the environmental need and potential benefit of utilising bauxite residue for soil amelioration in the West Australian agricultural industry, the Centre for Sustainable Resource Processing (CSRP) conducted a risk analysis and a cost / benefit study (Figure 2-24). This included engaging all the stakeholders. The CSRP commissioned environmental consultants URS and the Centre for Social Responsibility in Mining (CSRM), to evaluate sustainability assessment for the use of Alkaloam® as a soil ameliorant. The scope was summarised as follows.

The key tasks of this review were to provide a risk and sustainability assessment of the use of bauxite residue (Alkaloam®) in the Peel-Harvey catchment by undertaking community consultation, a consolidated safety and technical review (of research and assessments conducted previously by others), and an indication of the potential benefits and costs with commercial use of bauxite residue (URS, 2010).



Figure 2-24. Bauxite Residue (Alkaloam®) Sustainability Assessment (URS, 2010).

The assessment reviewed available data and found that ... *there is no reason to suggest that Alkaloam®, when applied to broad acre agricultural land, is unsafe at the application rates approved by the EPA of 20 t/ha.* This is in agreement with the report by DAFWA (2006).

The sustainability review went on to compare the chemical analysis of Alkaloam® against a range of guides and regulations, and found that rates up to 80 t/ha would not exceed recommended maximum concentrations for most WA sandy acidic soils. Some soils could utilise up to 800 t/ha when such applications were supported by leach analysis.

An economic assessment was based only on the Peel Harvey catchment zone with benefits coming from productivity increase to farming, reduced fertiliser use and reduced fertiliser run off. The estimated benefit was reported to be \$70 million over 25 years.

The review also provided a series of recommendations that can be used to provide further confidence in the product. Two of which are listed in truncated form below from URS (2010).

- *There is no evidence in the literature reviewed to suggest Alkaloam® is detrimental to health of livestock under the proposed application conditions to agricultural land. However, further tests over longer time periods would strengthen the results.*
- *Western Australia requires a framework that clearly authorizes the use of industrial by-products where the safety and benefits have been demonstrated.*

2.5.3 NORMS and Alkaloam®

A NORM is a Naturally Occurring Radioactive Material and bauxite, like nearly every other natural material, contains them. Unfortunately the mere mention of the term “radionuclide” is enough to incite fear in the general public. Thus a dispassionate, science - based assessment is essential.

It is evident from the literature that red mud has been assessed as safe. McPharlin *et al.* (1994) reported red mud addition to soil at a rate of 256 t/ha (mix with top 20 cm) met the required safety standards. Cooper *et al.* (1995) were able to show that vegetables grown in red mud/gypsum amended soils had no significant increase in radionuclide uptake. In fact the use of red mud amelioration actually reduced the uptake of radioactive “fall out - ^{137}Cs ” in cabbages, a consideration of the times.

Attiwell (2013) reported:

... the radionuclide concentration and specific radionuclide activity of uranium in Alkaloam® is comparable to that of the Darling Range soil. Thorium concentration and the specific radionuclide activity of thorium in Alkaloam® varied depending on the refinery it was sampled from, with levels being lower than the Darling Range soil when sampled from Kwinana refinery and higher when sampled from Wagerup refinery.

A comprehensive assessment including exposure pathways was reviewed and reported by URS (2010). The risk and sustainability review reported the following about radionuclides. *Research has shown that there is a linear relationship between the amount of Alkaloam® applied and the resultant gamma radiation emission (Summers *et al.*, 1993). The research showed that the 1 mSv/yr effective dose would only be reached at very high rates of over 1,500 t/ha of red-mud-gypsum (RMG) application and with 100 per cent occupancy (meaning that the person would have to live on the treated land for every hour of an entire year). Therefore, at the suggested application rate of 20 t/ha, there would be no risk and over 75 repeat applications would be required to reach a level of potential concern for humans URS (2010).*

Note The Summers reference is included here as Summers *et al.* (1993b).

Hence while it is important that radionuclides should be monitored to ensure safe limits are never exceeded, a degree of rationality is required. Most construction products and soil ameliorants contain radionuclides and bauxite residue should be treated in similar manner. For a comparison of everyday radioactivity exposure, see Metting (2010).

2.6 Sand residue as a by-product (Red SandTM)

Bauxite from the Darling Range in Western Australia has high quartz content. Crystalline quartz is a very hard material to grind in semi-autonomous mills and so bauxite residue has a large proportion of coarse material (nominal particle size >90 µm). This coarse material should be considered as medium-grained sand and was first called Red SandTM by Cooling and Jamieson (2004).

The Bayer process utilises high concentrations of caustic to dissolve the alumina from the bauxite ore. Lime (CaO) is also added to the process to remove carbonate, with the solid waste added to the process residue. Unprocessed red sand has a residual pH >10 and contains solid alkalinity (lime residue solids) that dissolves in fresh water to keep the pH high. To determine if processing this coarse residue sand would produce a potential saleable product, the market first needed to be identified.

Golder & Associates (2003) found that there was a significant market for residue sand in the applications of construction, general purpose fill, and in concrete. These applications are reviewed below.

2.6.1 Recent history of sand

Jamieson *et al.* (2005) reported that coarse bauxite residue could be processed to remove the alkalinity and meet ‘inert landfill’ environmental requirements.

A plant process design was needed to meet the accepted criteria. To remove the coarse bauxite residue (sand) it was decided to intercept it prior to joining the mud residue disposal lines. In addition, separation efficiency of fines from sand needed to

be increased. Stages of washing and carbonation reduced the residual pH and salts to accepted levels. This design was utilised to build bench scale ‘proof of concept’ trials (Jamieson, 2007) and eventually a 10 t/hr pilot plant as reported in Chapter 4.3.

Alternative processes were investigated for the utilisation of existing stockpiled sand. The process selected for trial involved the use of wet vibration screening to remove oversize product, as well as an attempt to wash off fines from the sand. This was conducted as part of the CSRP project 3B2 and reported by Davies *et al.* (2005). It was shown that while the screening process did remove the oversized material as well as the majority of fines through washing, the product still contained ultra-fine mud adsorbed onto the sand surfaces. While not impacting particle size determinations, nor adversely affecting physical performance, wet applications tended to have an associated ‘bleed’ of red water shown in Figure 2-25. This was deemed to be aesthetically unacceptable, hence would need resolution as a new criteria.



Figure 2-25. Cleaning Red Sand™ dried with mud.

The cleaned stockpile sand met physical specifications and further assessment in applications was conducted and reported below. Many of these assessments were conducted as part of the CSRP 4A7 student projects program where this author was

the adjunct supervisor. They were also part of the CSRP Bauxite Residue Program where this author was program manager.

2.6.2 Utilisation in concrete

Serrao (2004) assessed Wagerup refinery washed stockpile sand for use as fine aggregate in steam cured cement. His initial assessment of the sand indicated that *Though the chemical properties are significantly different between natural and red sands the physical properties are not.* Serrao (2004) also noted that the use of red sand resulted in a lower level of slump and hence lower concrete workability. In order to achieve consistent slump and workability, more water had to be added to the mix with additional cement. This immediately made the concrete more expensive and less likely to be utilised. Fly ash was added to improve workability, but no advantage was observed.

Watson (2004) utilised red sand to replace fine aggregate in concrete and also partially replaced Portland cement with fly ash. All the fine aggregate sand was replaced with red sand and up to 25% of the cement was replaced with fly ash. The results for concrete dimensional stability and compressive strength were similar to current materials. Watson (2004) was able to conclude that the replacement of fine aggregate with red sand was able to produce concrete of suitable performance but the workability or slump of the mix failed to achieve specifications.

Wahyuni *et al.* (2006) reported low concrete workability when utilising Red Sand™ as fine aggregate. They noted that this poor workability probably caused high porosity and high chloride diffusion, observed for the concrete. It was also reported that leach assessments on the concrete made with Red Sand™ met New South Wales (Australia) EPA guidelines.

2.6.3 Utilisation as residue remediation cover

Red Sand™ has been used to rehabilitate Alcoa residue storage areas as the primary growth medium for vegetative covers. Phillips and Chen (2010) reported that typical

coarse residue is highly saline, is alkaline, has high sodium content and is deficient in trace elements required for plant growth. Vegetation did grow once fertiliser was added and the salinity and pH lowered.

Jones *et al.* (2010) evaluated the amendment of coarse bauxite residue with a variety of organic materials. They concluded that the organic amendments improved the water holding capability and the microbial content allowing the sand to be a suitable growth medium. They did note that soluble salts originating from the organic amendments may require leaching prior to sowing of plant seeds.

Anderson *et al.* (2011) reported that the addition of fine bauxite residue (red mud) improves the soil-like character of coarse bauxite residue (red sand). This was particularly true if the red mud had been treated to remove the adverse impacts of high pH, sodium content and general salinity. Fertiliser was also needed.

Jones *et al.* (2011) looked at the impact of organic waste and red mud residue added to coarse bauxite residue. They concluded that the addition of residue mud to the sand induced aggregation and the beginnings of soil structure. These structures were improved further with the addition of poultry manure, where it was found that the fine residue appeared to aggregate and protect the organic matter from rapid decomposition, allowing significant microbial activity to build up. This is similar to the findings of Hofstede (1994).

The reviewed literature indicates that coarse bauxite residue can be utilised as a growth media but requires the addition of fine particles to improve moisture-holding capability and organic matter to improve the soil-like structure to provide suitable microbial activity.

2.6.4 Use in pavement

Kudla (2004) investigated the use of fly ash and lime to stabilise Wagerup refinery washed stockpile sand for use in pavement design. He reasoned that the sand had potential as pavement material but was more likely to be utilised as embankment fill

and as sub-grade fill. These applications are significant but are of low value, hence are limited to a transport-based economic window. Kudla (2004) proposed to stabilise red sand so as to replace more valuable crushed rock or limestone. Based upon dry compressive strength, a mixture of 65 wt% sand, 30 wt% fly ash and 5 wt% lime was utilised. While this may look expensive, it was price competitive with the alternative rock or limestone. Results from Kudla (2004) are summarised below and in Figure 2-26.

- Stabilised red sand was found to be non-plastic.
- Stabilised red sand was found to have an un-acceptable linear shrinkage of 0.1%. (Possibly incomplete reactions).
- The Californian Bearing Ratio (CBR) for sand and stabilised sand was found to be 47% and 108% respectively (100% is crushed rock equivalent).
- Unconfined Compressive Strength (UCS) was found to increase significantly with time and temperature of cure for the stabilised sand. This is typical of pozzolanic reactions.
- The stabilised sand was considered to be a "bound" material for pavement design classification. UCS was 7.6 MPa at day 56 for samples cured at 40°C. Ambient cure achieved above 3 MPa for the same period.
- Stabilised sand was found to have a resilient modulus (28 day, 22°C, 3000 cycles) of 11237 MPa with an ultimate modulus of 1319 MPa.

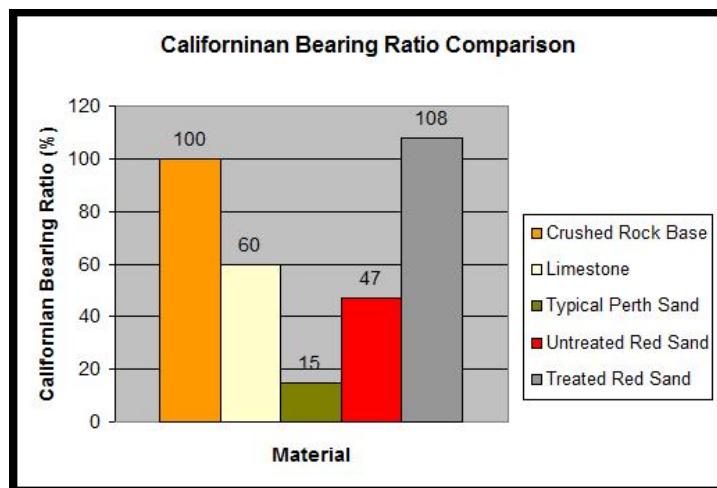


Figure 2-26. Comparison of CBR of stabilised red sand against standard materials (Kudla, 2004).

Ultimately Kudla (2004) found that the fatigue performance of the stabilised red sand was lower than crushed rock, and made further recommendations to address the criteria.

Hirsiger (2005) attempted to use fly ash and Lime Kiln Dust (LKD) to stabilise the high quartz component of magnetically separated Wagerup coarse residue. His attempt was to make concrete replacement rigid pavement design. Best mixtures were found for a blend of 65 wt% sand, 30 wt% fly ash and 5 wt% LKD. The results of direct shear, CBR and UCS, were all inferior to stabilised Red Sand™. Hirsiger (2005) suggested that the high quartz sand was not sufficiently strong to be used in rigid pavement, however, it is more likely that the high quartz content did not assist with pozzolanic reactions during cure.

Jitsangiam (2007) reported his investigation into the use of coarse bauxite residue (Red Sand™) for use as road base, embankment fill and also seawall fill. This early version of Red Sand™ retained a layer of red mud (Figure 2-27) and was not fully neutralised. These factors were important for the attempt to stabilise the sand using pozzolanic reactions with fly ash.

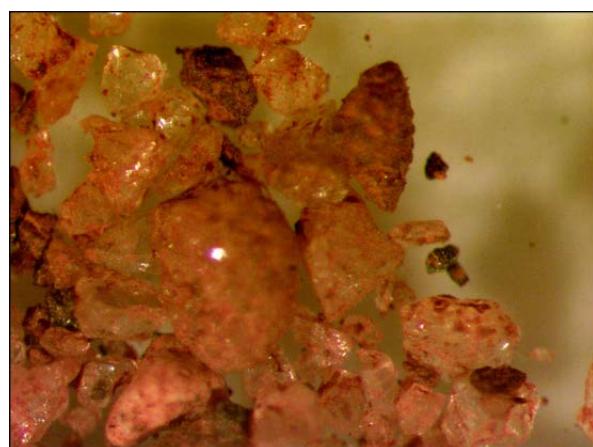


Figure 2-27. Red Sand™ with fine coating of Red Mud (Jitsangiam 2007).

Jitsangiam (2007) concluded that Red Sand™ was only suitable for seawall fill in its current state. These results were utilised in the design of the Red Sand™ pilot plant described in Chapter 4.3. Other conclusions were that residue sand could be

stabilised and that product was well suited for road base (Jitsangiam *et al.* 2007a) and for embankments (Jitsangiam *et al.* 2007b; 2008). As shown in Figure 2-28, stabilised sand was significantly superior to gravel and crushed rock when tested by Californian Bearing Ratio (CBR).

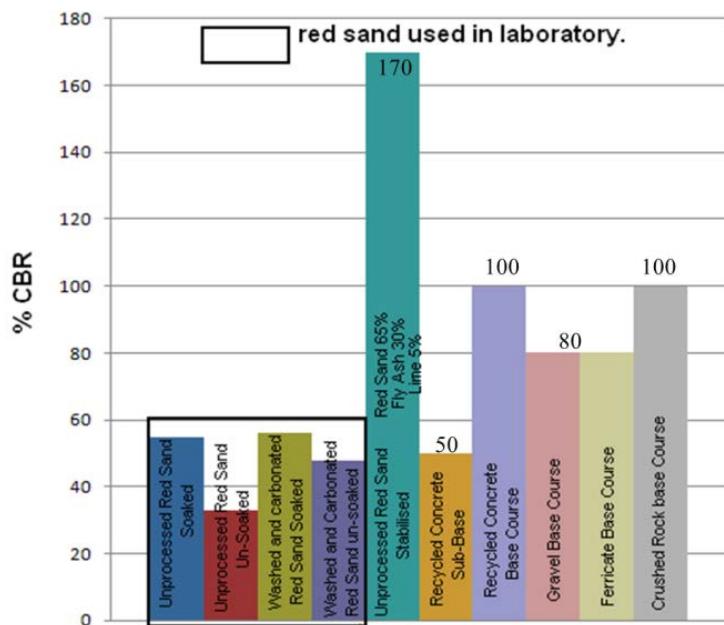


Figure 2-28. Californian Bearing Ratio of various red sand products and mixtures against standard materials (Jitsangiam, 2007).

2.6.5 Magnetic separation

A microscopic investigation (Figure 2-29) has shown that red sand exists as discrete particles of quartz and iron oxides. Hence it should be relatively easy to separate the sand and improve grades.

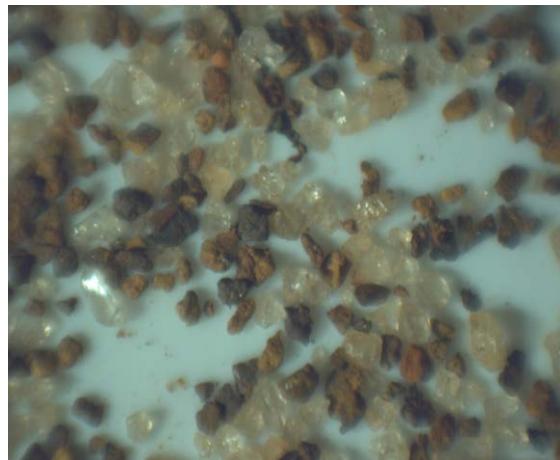


Figure 2-29. Microscope image of Red Sand™.

Typical red sand has been shown to have 26 wt% as Fe_2O_3 (Jamieson *et al.* 2005) and can be upgraded to 62 wt% utilising Wet High Intensity Magnetic Separation (WHIMS).

In a demonstration trial, Jamieson *et al.* (2006) reported that an iron rich fraction could be separated utilising Low Intensity Magnetic Separation (LIMS) achieving 63 wt% Fe_2O_3 (Figure 2-30).



Figure 2-30. LIMS unit removing magnetic fraction of bauxite residue (Jones, 2011). In this trial, the LIMS unit could not be utilised (due to size) in conjunction with WHIMS. Subsequently the WHIMS unit only achieved 65 wt% Fe_2O_3 , at a recovery of 35 wt% (Figure 2-31). This result is believed to be caused by para-magnetic material in the residue (that should be removed by pre-treatment with LIMS) “holding up” non-magnetic residue within the WHIMS and blocking proper separation. Nevertheless, this material was further upgraded with a caustic digestion

of alumina to achieve 77 wt% as Fe_2O_3 (Jones, 2011). Further investigation is warranted.

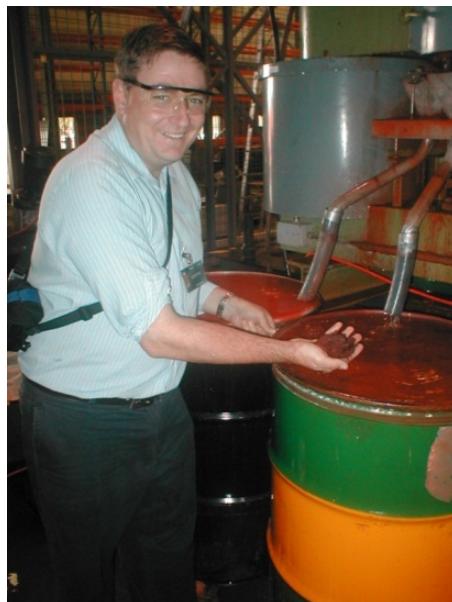


Figure 2-31. The author with high iron sample post WHIMS separation.

2.7 Lime residue as a by-product (Red LimeTM)

During the Bayer process, the recirculating caustic liquor is continuously contaminated with CO_2 , which reacts to form sodium carbonate. This reduces the efficiency of the process as the carbonate does not dissolve aluminate from bauxite. To regenerate the lost reactive caustic, quicklime is added in a process called causticisation. The reaction forms a series of solid phase alkaline products that can be separated and have been called Red LimeTM (Figure 2.32).



Figure 2-32. Red LimeTM.

The solid residues from the causticisation process are calcium carbonate (CaCO_3), tri-calcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$), called TCA6, and tri-calcium aluminate monocarbonate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$), called monocarbonate. If the process is not operating correctly, or there are issues with particle size, then un-reacted calcined lime (CaO) and quicklime (Ca(OH)_2), could also be present. An XRF chemical analysis is provided below in Table 2-4.

Table 2-4. Lime composition as reported in Clarendon *et al.* (2010).

Treatment	Key Contents	Neutralising Value (%)
Alcoa Lime Residue	65% CaCO_3 , 30% $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$	73.6
Alkaloam®	36% Fe_2O_3 , 23% SiO_2 , 17% Al_2O_3 , 3.9% CaO	14.5

Cooling and Jamieson (2004) recovered coarse causticiser residue as a prerequisite for the recovery of residue sand at Alcoa's Kwinana refinery in Western Australia. Rather than treat the solid alkalinity, it was decided to intercept the coarse lime residue prior to mixing with bauxite residue. During the investigation they determined that the lime solids could be a valued by-product in its own right as a liming agent. These causticiser residue solids were called Red LimeTM.

Further testing of the by-product revealed that it had a significantly high neutralising value of 75-80% (compared to pure calcium carbonate) and as such was considered a high grade agricultural lime. Some similarly-used products, such as crushed limestone, were shown to have neutralising values between 60 and 90%. Cooling and Jamieson (2004) suggested that, as Red LimeTM had a very fine particle size (compared to agricultural lime) and contained a mixture of agents of varying reactivity, it would be much faster acting in the agricultural environment. They believe that it would typically react within the first flushes of rain. Current agricultural lime agents are known for their slow action, with a return on investment taking years to be achieved.

Red LimeTM is also expected to have a high Phosphate Retention Index (PRI) due to the aluminium oxides present. Weaver and Ritchie (1987) reported that lime-based

amendments were more efficient at phosphorus removal from piggery effluent than red mud. Hence it is likely that the use of Red Lime™ will have the dual benefit of pH elevation as well as phosphorus control making it a valuable ameliorant.

2.8 Geopolymers

The discovery of a new class of inorganic materials, geopolymer resins, binders, cements and concretes, resulted in wide scientific interest and kaleidoscopic development of applications (Davidovits, 2008).

2.8.1 What is a Geopolymer?

The term “geopolymer” was first used in the public domain by professor Joseph Davidovits in 1979 (Davidovits, 2005). Geopolymers are inorganic aluminosilicate polymers (i.e. mineral polymers), where the backbone chains consist of aluminate and silicate units. Geopolymers can also be described as alkali-activated alumino silicates due to the high caustic concentration required for dissolution of the reactants. The polymerisation and precipitation of the X-ray amorphous aluminosilicate is generally considered to operate via a condensation process. Barbosa *et al.* (2000) (Figure 2-33) and Davidovits (2005) (Figure 2-34) have published representations of the backbone chains and links as shown below.

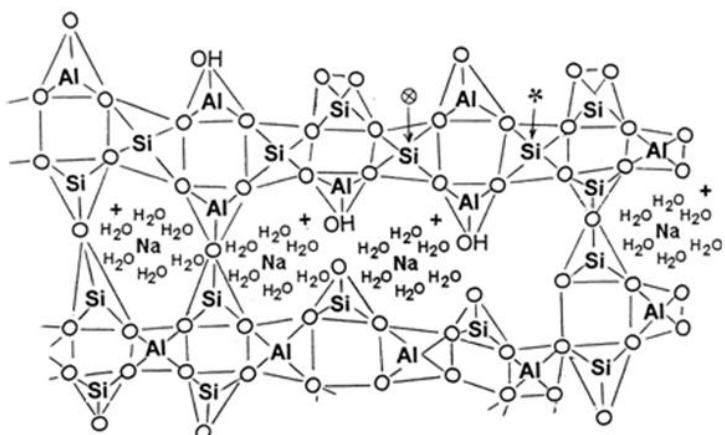


Figure 2-33. Proposed schematic for Na–polysialate polymer (Barbosa *et al.* 2000).

Barbosa *et al.* (2000) favoured this structure because it allowed for greater structural disorder and the ability to incorporate hydrated sodium ions. They reported that incomplete geopolymserisation resulted in efflorescence of caustic that subsequently carbonated with the atmosphere. Since complete geopolymserisation did not effloresce, caustic must be accommodated within the structure.

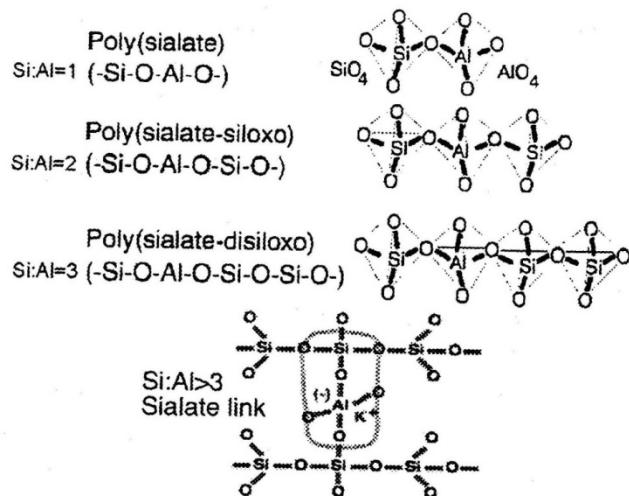


Figure 2-34. Aluminosilicate chains and terminology (Davidovits, 2005).

The mineral polymer chains harden with significant cross linking to form a material with high strength. Further discussion on the proposed structures of geopolymser bonding is limited here but is discussed elsewhere (Provis *et al.* 2005; Davidovits, 2008; Zhang *et al.* 2008; Provis & Van Deventer, 2009).

2.8.2 Geopolymer Formation

It has been reported that the alkali cation affects most stages of the geopolymserisation process. However, upon studying a series of fly ash samples no predictive preference could be found (Van Jaarsveld & Van Deventer, 1999a). Potassium and sodium worked preferentially with different sources of fly ash.

Xu & Van Deventer (2000) investigated a range of minerals for their suitability as feedstock for geopolymser formation. They reported a series of generalisations which are summarised below.

- Increased causticity increases mineral dissolution;

- The minerals studied dissolved preferentially in sodium hydroxide than potassium hydroxide with the exception of sodalite;
- Silica content is higher than alumina for geopolymers.

Lee & Van Deventer (2000; 2002a) reported that inorganic salts could affect geopolymers as they change the electrolytic concentration of the dissolving solution. Curing rate and compressive strength appeared to be impacted.

This author speculates that a concentrated salt caustic solution, including ionic organic species (e.g. in Bayer liquor), would have significant impact on geopolymers cure and properties because of the lowered activity of water.

Yip & Van Deventer (2002) studied the effect of the mineral source of calcium upon the geopolymers process. They were able to demonstrate that the addition of calcium improves the compressive strength of the geopolymers and that the mineralogy of the calcium plays a significant role. At a low caustic content, fast-dissolving calcium sources (amorphous) produced superior results over crystalline forms. This advantage was reduced as the caustic content increased.

Lee & Van Deventer (2002b) reported that the addition of sodium silicate to caustic increased dissolution of fly ash and subsequent geopolymers. They were able to show that when the soluble silica was low in concentration, dissolution was hindered by precipitates forming on the fly ash surface. This was later supported by Lee & Van Deventer (2007) who reported that additional silicate in the activation solution was critical for dissolution of silicate species from aggregate surfaces, creating an alumina-rich interfacial zone.

Shvarzman *et al.* (2003) reported dissolution of sources of alumina into caustic solutions can be difficult, with non-crystalline or amorphous forms favoured by high caustic concentrations. Yong *et al.* (2005) reported that to activate the polymerisation process, at least the surfaces of the aluminosilicate must dissolve. Sata *et al.* (2012) reported finer fly ash gave better geopolymers indicating greater dissolution.

Hart *et al.* (2006) investigated a series of industrial by-products from the Kwinana area of Western Australia. Key factors were found to be the impact of relative humidity, drying temperature and the ability to form a geopolymers in a sealed vessel. All these factors seem to indicate that the dissolution polymerisation and precipitation of geopolymers is heavily dependent upon the available water content.

Sperinck (2012) used computational methods to provide atom level insight and noted: *The Al-terminated surfaces in metakaolin demonstrated the greatest level of interaction with water compared to Si, causing a surface puckering effect that resulted in a widening of the surface layers. The results indicate that water plays an important role, as the presence of water in the reaction mixture combined with high levels of structural disorder in the source materials increase their susceptibility to the caustic attack involved in geopolymserisation.* (Sperinck, 2012). The importance of water would indicate that liquids with low water activity (due to high entrained salt content) may have issues with geopolymers formation. This may impact on the use of Bayer liquors which are known to have extreme concentrations of dissolved species.

The activity of water and its role in dissolution was highlighted by Duxson *et al.* (2007a). They noted that the dissolution of solid aluminosilicate source materials was by the process of alkaline hydrolysis and a conceptual model is shown in Figure 2-35. Impurities such as calcium and iron were believed to add additional reaction pathways, causing changes to the resultant properties such as strength, slump, and cure rate, etc.

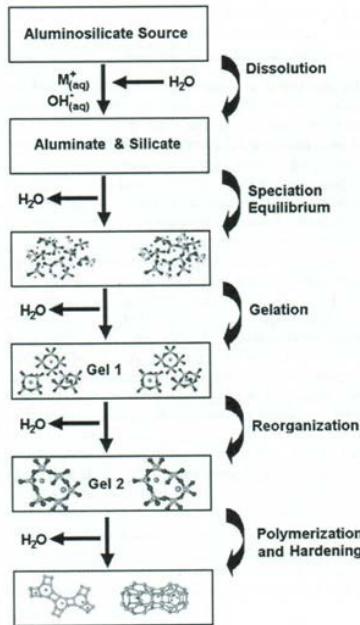


Figure 2-35. A conceptual model for geopolymers. (Duxson *et al.* (2007a).

Duxson *et al.* (2007b) reported on the impact of the silica to alumina ratio overlaid by changing the caustic metal cation (Figure 2-36). As shown below, mixed alkali produces a higher strength product. They postulated that the increased strength may be related to the different microstructures observed from the alkali cations as the silica to alumina ratio changes.

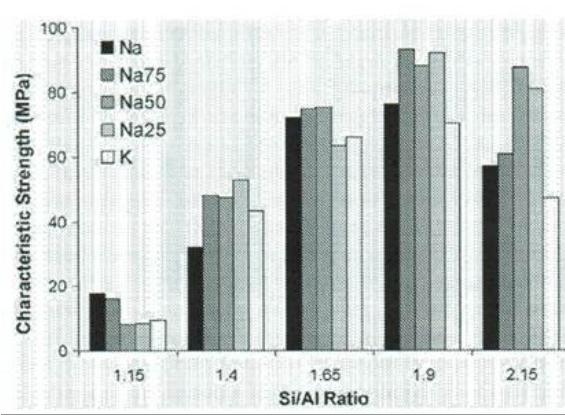


Figure 2-36. Strength of metakaolin geopolymers (Duxson *et al.* 2007b).

Rovnanik (2010) reported that the effect of temperature during curing had a significant impact upon compressive strength development for metakaolin-based geopolymers. It was shown that the higher the temperature (up to 80°C), resulted in rapid early strength development. However, the higher temperatures appear to

increase pore size and cumulative volume, which is used to explain the lower strength compared to slow cure polymer after 28 days. It is also likely that the dehydration prevented further dissolution of reactants and encouraged precipitation of short order polymeric chains. This is consistent with Hart *et al.* (2006).

Chen-Tan (2010) reported that different beneficiation methods applied to fly ash resulted in geopolymers with different properties. Hence if a particular property is required, then careful selection of the source materials or their beneficiation can be utilised to achieve the desired outcome. This enhances the ideal that geopolymer formation can have Quality Assurance and Quality Control (QA/QC) by applying such procedures upon the source materials. With QA/QC comes predictive production.

2.8.3 Properties of geopolymer

There are several texts reporting the beneficial properties of geopolymers comprehensively (Davidovits, 2008; Provis & Van Deventer, 2009). This chapter is a summary of geopolymer characteristics reported in literature.

2.8.3.1 Strength

The significant compressive strength of geopolymers is widely reported and will be only briefly reviewed here. Some level of comparative data may assist in evaluating the meaning of the results. For example footpaths generally have a compressive strength of up to 15 MPa, house pads in Western Australia (single story) aim for 24 MPa to guarantee 20 MPa and sea wall armour has a minimum criterion of 50 MPa.

Palomo *et al.* (1999) reported that fly ash based geopolymer is a cement of the future. They reported mechanical strengths in the order of 60 MPa after curing alkali activated fly ash at 85°C for only five hours. The curing time and temperature has subsequently been shown to be critical to strength development by Rovnanik (2010).

Barbosa *et al.* (2000) reported geopolymers as having Mohs hardness greater than 7, Vickers hardness of 54 and compressive strength of 48 MPa, while Nugteren *et al.*

(2009) made a matrix of geopolymers from fly ash, blast furnace slag and potassium silicate solution. Some samples reached compressive strengths in excess of 100 MPa.

Lloyd and Rangan (2010a) reviewed a formula for estimation of the tensile strength from the compressive strength. They report that the tensile strength is equal to 0.6 (+0.1) times the square root of the compressive strength. This is a significant finding and highlights the growth of geopolymer technology from reactive assessment towards predictive assurance.

Sarker (2011) reported that fly ash based geopolymers have a much stronger bond to steel reinforcing than OPC, as measured by the “pull out” test ASTM A944 (2010). He reported that the mode of failure was a splitting of the test block and that as geopolymers have a higher tensile strength to OPC, they proved superior in this test.

High compressive strength has been demonstrated in the literature, but there are many other factors that are of significant importance.

2.8.3.2 Early strength development

The early cure strength development of geopolymers has been known for some time (Davidovits & Sawyer, 1985). Significant hardening or “first set” of a geopolymer is usually obtained within one hour of mixing, depending on the silica to alumina ratio, the lime content and the curing temperature.

Skvara *et al.* (2006) reported early strength development with continued improvement over 1 year for paste, mortar and concrete samples. They achieved paste strength of 164 MPa after 12 months of aging. They noted that the microstructure of fly ash based geopolymers was unchanged as it approached aggregate surfaces. This is in contrast with OPC interaction with aggregates. The question is now raised about the bonding to the aggregate. Is the aggregate a mere inclusion or do surface sites react creating a significantly stronger material? Graves (2006) describes the impact of grading, shape and surface texture upon concrete properties with surface texture having an impact upon strength. However, the impact of geopolymers upon aggregate binding appears to be unanswered.

2.8.3.3 Ecological footprint

One ecological advantage of geopolymer is the ability to use waste or under-utilised by-products. The utilisation of materials such as fly ash, metakaolin, finely ground metakaolin, blast furnace slag, stainless steel slag, mining residues and various feldspar materials has been reported. (Granizo *et al.* 2000; Mathur *et al.* 2001; Xu & Van Deventer, 2002; Comrie, 2005; Corder *et al.* 2009; Lloyd & Rangan, 2010b).

Another ecological advantage over cement is the carbon footprint or embodied energy. That is the energy consumed to make the product.

Davidovits (1994b) reported that conventional cement had a considerable carbon dioxide footprint. Cement is made from the calcination of limestone. The production of 1 tonne of cement directly releases 0.55 tonne of carbon dioxide from the calcination of mineral limestone. An additional 0.4 tonne of carbon dioxide is generated from fuel consumption. Hence it is generally quoted that 1 tonne of cement has a footprint of 1 tonne of carbon dioxide. Through a series of comparisons and product equivalents, Davidovits (1994b) demonstrated that the geopolymers produce somewhere in the vicinity of 10 to 20% of the carbon dioxide (CO_2) footprint of ordinary Portland cement. This data was reported as an example within Davidovits & Davidovits (2005) US Patent 0172860.

Tempest *et al.* (2009) assessed the energy required to form 1 cubic metre of 70 MPa concrete from OPC and from geopolymer. As with all these calculations, it is the assumptions that are very important to the process. In this instant, the energy requirements for collection of fly ash and silica fume are ignored as they are considered waste products. Also the transport component for raw materials of both geopolymer and OPC are ignored by suggesting that both are likely to be similar. In addition, admixtures are ignored due to relative small size and likely to be used in both scenarios. It is this author's opinion that such assumptions are a suitable starting comparison as they minimise site specific anomalies. However, case studies must be calculated on specific circumstances. Tempest *et al.* (2009) calculated the energy requirement for caustic soda and for manufacture of sodium silicate solution with

further assumptions on energy requirements. The composition of geopolymers is critical since the selection of reagents and curing conditions all have different energy costs. For example, an ambient cure material would not need heating, but the additional use of lime would have energy footprints. Tempest *et al.* (2009) chose to use a mixture that required 2 days of heating at 75°C. This comparison demonstrated that geopolymers concrete only required 70% of the energy needed for manufacture of OPC concrete. The important note is that the largest input to the geopolymers concrete footprint was the embodied energy of caustic.

Wimpenny (2009) summarised the findings of a UK Government Environment Agency study (Carbon Reduction Fund) to identify low CO₂ alternatives to OPC concrete. Specifically the concrete was to be used for flood mitigation schemes. In this report the comparison is made on a kilogram carbon dioxide per cubic metre of concrete basis (kg CO₂/m³). Unfortunately a specific compressive strength target does not appear to be reported. They report that a cubic metre of conventional OPC concrete would release a total of 248 kg of CO₂ compared with 78 kg of CO₂ for geopolymers concrete. This represents a 70% reduction in carbon footprint, more in line with the findings of Davidovits (1994b).

Weil *et al.* (2009) also utilised a life cycle analysis and demonstrated that geopolymers concrete could have a *global warming potential* in the range of 70% lower than OPC concrete. They noted that individual applications are all different and all have varying footprints. They concluded that the critical contributors to the footprint are the sodium silicate, the caustic and the energy used for curing. Stengel *et al.* (2009) concluded that geopolymers concrete had only 26 - 45% lower global warming potential compared to normal cement (note, cement contained fly ash replacement of OPC). They concluded that the manufacture of sodium silicate represented about 50% of the ecological footprint of geopolymers and that caustic was about 30%.

Habert *et al.* (2010) reported that some geopolymers formulations achieved a 60% reduction in carbon dioxide emissions. They noted that sodium silicate and sodium hydroxide solutions were the largest factors for carbon dioxide production in geopolymers formation. A similar finding was reported by McLellan *et al.* (2011) for

an Australian context. In addition, the cost of transport made each individual case study different.

2.8.3.4 Fire resistance

Davidovits (2002) reported fibre-reinforced geopolymers capable of resisting 1200°C.

Rahier *et al.* (2007) studied metakaolin-derived geopolymers at temperatures up to 1200°C. They were able to show the loss of structural water up to 400°C. Between the temperatures of 950 and 1100°C, they also observed the formation of a nepheline phase as confirmed by high temperature XRD.

Duxson *et al.* (2007c) investigated metakaolin geopolymers with silica to alumina ratios between 1:1.15 and 1:2.15 for their thermal behaviour up to 1000°C. Shrinkage was observed to increase with higher ratios and to start at lower temperatures.

Kong, *et al.* (2008) reviewed 30 geopolymers based on metakaolin calcination temperature, the silica to alumina ratio, the activator to metakaolin ratio, curing temperature and the alkali cation type, for impact upon specimens exposed to temperatures of 800°C. An assessment of compressive strength (Figure 2-37) coupled with thermo-gravimetry and scanning electron microscopy studies demonstrated that geopolymers with higher silica to alumina ratios in excess of 1:1.5 suffered lower strength loss. In addition it appeared that potassium-based activators performed better than sodium.

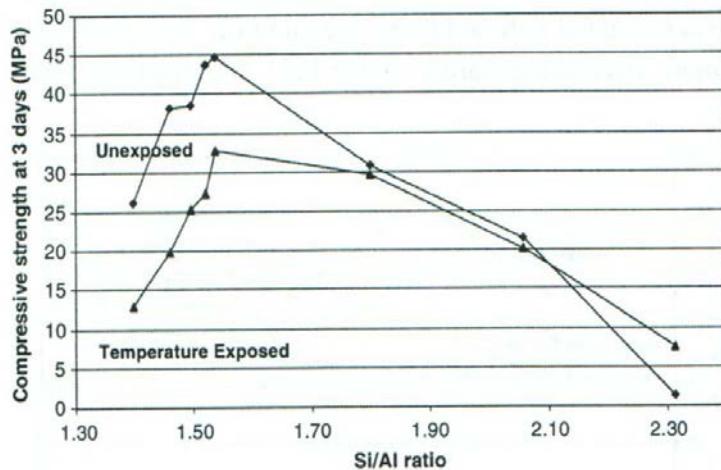


Figure 2-37. The effective silica to alumina ratio on temperature exposed compressive strength (Kong, *et al.* 2008).

Van Riessen & Rickard (2009) provide a review of the thermal properties of metakaolin and fly ash based geopolymers. This work demonstrates the superior nature of geopolymers over OPC concrete in this field.

Pan & Sanjayan (2009) reported compressive strength assessed at temperature. Their results show that geopolymer strength increased with temperature to about 560°C, where glass transition begins and strength drops rapidly.

It is anticipated that Bayer-derived geopolymers will also perform better than OPC concrete, however, the high carbonate and carbon content may prevent them from achieving the outstanding results seen for silicate activated geopolymers.

2.8.3.5 Acid resistance

Bakharev (2005) reported the results of acetic and sulphuric acid (5 wt%) attack on fly ash based geopolymers. They found that geopolymers had superior acid resistance compared to OPC, however, some formulations (such as those activated by mixed caustic - Na and K) still lost significant strength. Utilisation of sodium hydroxide and elevated cure temperatures resulted in best resistance.

Wallah *et al.* (2005b) assessed the resistance of fly ash based geopolymers to sulphate and sulphuric acid attack. Specimens soaked in 5 wt% sodium sulphate showed excellent resistance to the sulphate environment. Likewise resistance to 0.5 wt% and 1 wt% sulphuric acid were excellent. However, submersion of the geopolymer samples in solutions for 12 weeks at 2 wt% sulphuric acid resulted in reduced compressive strength.

Allahverdi & Skvara (2006) reported that acid attack under mild conditions (pH 2) appeared to follow a path of ion exchange of geopolymer counter ions Na^+ or Ca^{2+} with H^+ or H_3O^+ . This allowed the electrophilic attack of the acid upon the silica oxygen alumina bonds. They also reported that once shrinkage cracking occurred, sulphate tended to form gypsum with calcium.

Sathia *et al.* (2008) assessed a series of fly ash based geopolymers ranging in compressive strength from 10 to 60 MPa and compared their acid resistance (3 wt% H_2SO_4) to similar strength OPC samples. Table 2.5 highlights the advantage of geopolymers compared to similar strength OPC.

Table 2.5. Mass loss after 90 days in 3 wt% sulphuric acid. OPC mix and geopolymers are in pairs of equal strength. (Sathia *et al.* 2008).

Concrete	% Wt Loss
OPC mix NC20	25
Geopolymer G2	0.5
OPC mix NC40	18
Geopolymer G8	0.47
OPC mix NC60	22
Geopolymer G9	0.4

Thokchom *et al.* (2009) exposed a series of fly ash based geopolymer mortars to 10 wt% nitric or 10 wt% sulphuric acid for up to 24 weeks. Samples were shown to have minor surface erosion and weight loss of less than 2 wt%. They also claim that because the mortar still contained significant strength (30 MPa), the geopolymer mortars were highly resistant to both sulphuric and nitric acids. While this is not disputed, given the significantly aggressive test environment, the strength of some

samples was only 30% of the original 100 MPa. This author holds concern for the impact of starting with much lower strength mortar more suited to general use.

Wallah *et al.* 2007 concluded that after 3 months immersion in 5 wt% sodium sulphate solution fly ash geopolymers demonstrated no observable impact upon strength, mass, length etc.

2.8.3.6 Caustic resistance

Sindhunata *et al.* (2008) reported that the immersion of fly ash based geopolymers in carbonate or hydroxide solution up to pH 14 resulted in very little leaching of the geopolymer framework. Immersion of samples for up to 1000 hours in 8 M sodium hydroxide cause some damage to the framework, however, small quantities of crystalline zeolites were also found suggesting that immersion results in a continuation of the original geopolymerisation process.

Temuujin *et al.* (2011a) immersed fly ash based geopolymers in 14 M sodium hydroxide for up to 5 days and found a 20 wt% mass loss. This compared to a 10% mass loss over the same period when immersed in 18 wt% HCl. These results from very extreme caustic conditions agree with those findings of Sindhunata *et al.* (2008). Temuujin *et al.* (2011b) also reported that calcination of the geopolymer to 600°C reduced compressive strength by 30% but subsequently prevented caustic or acid attack. This was probably due to pore closure.

2.8.3.7 Permeability

Davidovits (1994a) patented the utilisation of geopolymers for the rapid stabilisation and immobilisation of toxic waste materials. The advantages listed included stability in acid and long-term binding capacity (that is low permeability).

It has been reported that geopolymers can incorporate or encapsulate metal contaminants (Van Jaarsveld & Van Deventer, 1996; 1999b; Van Jaarsveld *et al.* 1999). They report that copper and lead are not only encapsulated but also appear to affect both the chemistry and morphology of the geopolymerisation process. The

cations do not appear to impact upon the basic silica/alumina backbone but do appear to be chemically bound impacting phase formations. As such they noted that there appears to be a limit to how much metal impurity can be incorporated into a geopolymers structure before the matrix fails to cure.

Olivia & Nikraz (2011a) evaluated the durability of fly ash based geopolymers in seawater environments. It was found that chloride penetration and corrosion of embedded steel was faster for some paste formulations (compared to OPC concrete), while other geopolymers concretes performed better. It appears that the nature of the geopolymers paste heavily influences the chloride penetration and corrosion, hence needs to be well understood and controlled within this environment.

Olivia & Nikraz (2011b) assessed water absorption and strength of fly ash geopolymers concrete. They concluded that water absorption of less than 5 wt% provided a “low” classification. They also reported that water absorption was decreased by increasing the solids to water, aggregate to solids and alkalinity to fly ash ratios. The concrete samples were shown to have “average” water permeability and void content. This would imply geopolymers concrete is capable of being made to meet existing concrete performance standards.

2.8.3.8 Toxic metal containment

Bankowski *et al.* 2004 proposed converting fly ash into geopolymers as a method of trapping and encapsulating the fly ash, to allow for disposal as inert landfill.

Khale & Chaundhary (2007) proposed that geopolymers are a cost-effective solution for the containment of hazardous residue. They concluded that the geopolymers immobilises 90% of any toxic materials within the matrices, outperforming ordinary Portland cement. Metals assessed included mercury, arsenic, iron, manganese, zirconium, chromium, cobalt, lead, copper, vanadium, and magnesium.

Aly *et al.* (2008) investigated the leaching of metakaolin based geopolymers with the aim to optimise formulations for the immobilisation of nuclear waste. They reported

that the capture of caesium appeared to be within the geopolymer matrix while strontium was both captured as well as incorporated, with some strontium carbonate precipitation being noted. Formulations were found that met deep storage as well as near surface storage criteria based upon ASTM/PCT-B. They reported that geopolymers may be “serious candidates” for immobilisation of nuclear waste.

2.8.3.9 Creep and drying shrinkage

Wallah & Rangan (2006) and Rangan (2008) reported on the creep and drying shrinkage of geopolymers. Two samples were placed under 40% of the compressive strength for 1 year. The specific creep (defined as “creep strain per unit of sustained stress”) was found to be half the value of that accepted for OPC concrete in Australian Standard AS3600. In addition drying shrinkage samples were also measured over 12 months. These values were found to be 5 to 8 times better than the micro-strain produced using OPC concrete. In contrast Mukhin *et al.* (2007) reported significant and unacceptable geopolymer concrete shrinkage and a host of other potential issues. They noted that aggregate moisture content was critical and also that significant efflorescence was an issue. Efflorescence is a sign of incomplete geopolymerisation and hence their results must be considered in that light. Wimpenny *et al.* (2011) used Australian Standard AS1012.13 to assess linear shrinkage of fibre reinforced geopolymer used for tunnel segments in a commercial application. The field trials demonstrated that geopolymer concrete had as little as half the micro-strain of OPC equivalents. Aldred & Day (2012) reported 40 MPa geopolymer concrete with shrinkage of only 230 micro-strain and that geopolymer concrete is now being assessed for load bearing as well as non-load bearing products.

Wallah *et al.* (2005a) reported that low calcium fly ash geopolymer concrete had low creep and very little drying shrinkage. Wallah (2010) assessed a series of fly ash based geopolymers of various strengths. After one year of loading, creep ranged from 15 to 29 micro-strain for samples of compressive strength from 67 to 40 MPa. In general, the creep coefficient was about half of that predicted for OPC. From these results it was concluded that fly ash based geopolymer concrete has low creep.

2.8.3.10 Steel corrosion

Shi *et al.* (2006) reviewed literature on chloride diffusion, a method believed to indicate susceptibility to steel corrosion. The review indicated that alkali-activated slag cement gave lower diffusion coefficients for chloride than OPC.

Sathia *et al.* (2008) evaluated the open circuit potential for a series of fly ash based geopolymers and comparable strength OPC concrete utilising Australian Standard ASTM C 876. They noted that it can take years for stable potentials to develop but still reported that after 90 days of testing, the geopolymer concretes in each strength class were as well as or better than comparable OPC concrete.

Olivia & Nikraz (2010) used a constant impressed current of 5 and 30 V to steel embedded in fly ash based geopolymer concrete samples and compared to steel embedded in OPC concrete. Alkalinity, Chloride penetration and half-cell voltage were also measured. After 28 days, the geopolymer steel samples had lower current and higher resistance than the OPC concrete. They concluded that the geopolymer concrete samples had good corrosion and performed better than the OPC concrete samples.

2.8.4 Historic geopolymers?

There has been some confusion surrounding the term geopolymer because of its linkage by Davidovits & Davidovits (2001) to construction of ancient monuments such as the pyramids. Certainly there are many people (such as this author) who believe mankind significantly underestimates the intelligence of ancient civilisations and hence are predisposed to accepting evidence on face value. Others however, struggle with ancient civilisations having access to such technology. Davidovits' (2008) interpretation of Egyptian hieroglyphs and the apparent obsession of Egyptian society with the "eternity" of stone may help explain their advancement in this area (Figure 2-38). Certainly the Egyptian understanding of chemistry was well advanced as demonstrated by the complex formation of the pigment "eternal blue" or Egyptian Blue (Tite, 1987) and their knowledge of electroplating.

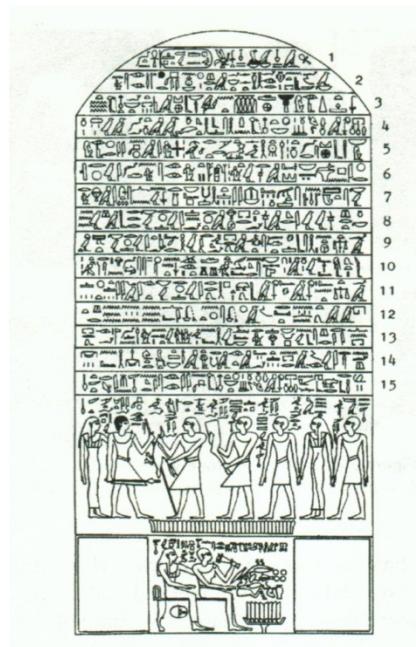


Figure 2-38. Hieroglyph interpreted as stone manufacture (Davidovits, 2008).

Now while the debate between synthetic stone and quarried stone is intense, the chemistry involved should not be confused with the modern interpretation of the term "geopolymer". Barsoum *et al.* (2006) provides supporting evidence of the synthetic stone hypothesis, however, noted that the chemistry involved is quite different. Hence there have been a significant number of authors utilising alternative descriptions such as mineral polymers or alkali activated minerals, etc.

Xu *et al.* (2008) evaluated slag concretes activated with carbonate and carbonate/hydroxide that were cast between 1964 and 1982 in the Ukraine. The activated slag concretes have survived difficult climatic conditions (-20 to +20°C) where comparable OPC products have failed prematurely (3 years). These products have been shown to form amorphous gels of calcium silicate hydrate that are polymerised to a high degree with low permeability. These products have actually increased in compressive strength after more than 30 years of service. While these materials are also alkali activated cements, their chemistry is also sufficiently different from alumina-silicate chemistry and should possibly not use the term geopolymer.

So until a definitive description is accepted, this author will use the term geopolymer but clarify it to be an alkali-activated alumino-silicate.

2.8.5 Geopolymer application in general construction

The uptake of geopolymer technology in the construction industry has been slow but appears to be growing steadily (Duxson & Van Deventer, 2009). Scientists have attempted to improve uptake with better science, greater mechanistic understanding and by establishing a set of production criteria. However, most conclude that the slow acceptance by industry is mainly due to the entrenched position of ordinary Portland cement concrete (Komnitsas & Zaharaki, 2007). While the industry is known to be conservative in nature it should also be realised that it is extremely competitive. Hence any material that can give a competitive advantage, particularly with respect to cost or performance, can have a real impact in a rapid timeframe.

Gourley & Johnson (2005) demonstrated the use of geopolymer concrete for the production of railway sleepers (Figure 2-39), wall panels and acid resistant sewer pipes (Figure 2-40) for Rocla. They report that the products meet or exceed performance criteria.



Figure 2-39. Geopolymer railway sleepers after 7 years service (CIA-GCRP, 2011).



Figure 2-40. Geopolymer pipe, 1500 mm diameter (Gourley & Johnson, 2005).

A team of scientists led by Professor Vijaya Rangan utilised field methodologies at Curtin University in Western Australia to test geopolymers structures. In a series of publications, a fly ash based geopolymer concrete was utilised to construct structural beams with steel reinforcing. This work is widely referenced and should be seen as a significant contribution towards commercialisation of this technology. A selection of work is listed here but can also be found online at Curtin University espace (<http://espace.library.curtin.edu.au>). (Hardjito, 2005; Hardjito & Rangan, 2005; Rangan, 2006; Wallah & Rangan, 2006; Sumajouw & Rangan, 2006; Sumajouw *et al.* 2007; Rangan, 2007; Rangan, 2008.) A pictorial review of their field scale demonstrations is provided below in Figures 2-41 to 2-45.



Figure 2-41. Steel reinforcing in place (Sumajouw & Rangan, 2006).



Figure 2-42. Reinforced geopolymer beams (Sumajouw & Rangan, 2006).



Figure 2-43. Geopolymer beams being tested (Sumajouw & Rangan, 2006).



Figure 2-44. Reinforced geopolymer columns (Sumajouw & Rangan, 2006).

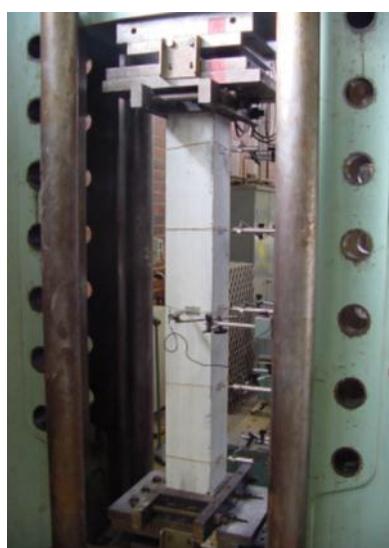


Figure 2-45. Geopolymer column being tested (Sumajouw & Rangan, 2006).

The work of Sumajouw & Rangan (2006) concluded that the draft Australian Standard for Concrete Structures (AS 3600, 2005) was applicable for assessment of geopolymers. In addition, the Australian Standard for Concrete Structures AS3600 and American Concrete Institute Building Code ACI318-02 were suitable for assessment of reinforced geopolymers concrete columns. That is, the performance standards used for OPC construction materials can be used directly for geopolymers products. Chang (2009) & Chang *et al.* (2009) reported that existing methods for assessing OPC concrete beams also worked for geopolymers concrete, while Sarker (2009) needed only small modifications to use existing stress-strain models for the prediction of geopolymers column load deflection behaviour. Rahman & Sarker (2011) assessed geopolymers columns under axial load and biaxial bending and reported that Bresler's formulae (used for designing OPC concrete columns) worked equally as well for geopolymers. These reports are very important as they suggest current performance and design standards work for both materials.

2.8.6 Geopolymer in niche applications

The following is an eclectic mix of publications that are worth noting for their specialist application of geopolymers technology.

Fletcher *et al.* (2005) looked at the range of silica to alumina ratios between 24 and 300 found a product with elastic behaviour when heated (100 - 250°C). The product was stabilised dehydration foam, with the potential application for insulation.

Hu *et al.* (2009) utilised geopolymers paste to bind light weight aggregate to make a refractory concrete. Their product was a highly porous structure where the geopolymers coated the aggregate and allowed point to point contact binding. The primary factor influencing the heat resistance of the concrete was found to be the thickness of the geopolymers coating. The aggregate (Haydite shale) apparently releases vapour that will shatter the structure if the geopolymers is too thick. With too little geopolymers, the aggregate will not bind together. However, even structures that retained their shape were shown to have lost almost half their strength. This author wonders why a better aggregate was not utilised, or why the aggregate was not abandoned altogether.

Bortnovsky *et al.* (2010) reported on the incorporation of metal cations. Their study attempted to add alternative metal ions into the geopolymer structure for the manufacture of catalysts as well as anti-bacterial coatings.

Cerny *et al.* (2010) added up to 44.5 wt% graphite to meta-kaolinite geopolymers to create electrically conductive materials. The high graphite content was probably the maximum inclusion rate before structural integrity failed.

Williams & Van Riessen (2011) reported production of a mineral polymer utilising alkali activated borosilicate (in place of aluminosilicate). They report compressive strengths of up to 56 MPa making the material suitable for structural use, with particular emphasis on the application as a neutron shield.

Finally, Vaidya *et al.* (2011) poured a 1 cubic yard fly ash based geopolymer with compressive strength of 43 MPa. They observed that the block achieved uniform temperature of 42°C (well above room temperature) and only lost temperature at a rate of about 2°C per day. This will have implications for mass-poured blocks and heat transfer, particularly with items such as dams, etc.

2.8.7 Geopolymer standards and codes of practice

From the early literature it is apparent that scientists have utilised ordinary Portland cement-based concrete test methods and protocols (Davidovits, 1994b). It is the ability to utilise the same assessment methods and meet or exceed OPC performance that has generated much excitement in the scientific fraternity. Unfortunately, composition standards will not be met, creating an effective barrier to market in countries using these standards.

The acceptance of geopolymer concrete into the conservative construction industry has been slow but is gaining momentum as prescriptive standards are replaced with performance standards (Duxton & Provis, 2008). Duxton & Van Deventer (2009) provide a good summary of the opportunities and obstacles for commercialisation of geopolymers with emphasis upon the need for standards.

The US Department of Transport Federal Highway Administration (USDT-FHA, 2010) issued a Tech-Brief on the use of geopolymer concrete for transport infrastructure. Their review listed the current technology limitations as being workability and sensitivity to cure conditions. Hence they suggested limiting applications to pre-cast conditions. However, the strength, resistance to chemical attack, heat and water ingress, coupled with very low alkali aggregate reactivity make the material of great interest. They concluded that once user friendly geopolymers are developed with similar character to Portland concrete, then *The production of versatile, cost effective geopolymer cements that can be mixed and hardened essentially like Portland cement would represent a “game changing” advancement, revolutionizing the construction of transport infrastructure.* While the USDT-FHA (2010) requirement for geopolymer formation conditions may be overly simplistic (i.e. mimic OPC) they did identify that geopolymers have the potential to revolutionize construction industries.

The Concrete Institute of Australia has also released a Geopolymer Concrete Recommended Practice (CIA-GCRP, 2011). This recommended practice guide outlines the ...*mix design, transport, placement, workability, curing and safety. Environmental benefits from reduced CO₂ emissions and industrial by-product utilization are also discussed.* CIA-GCRP (2011) make the following comparison between geopolymer concrete and Portland cement concrete. Geopolymer concrete has:

- *Very superior chemical resistance, particularly acid resistance;*
- *Very superior fire resistance;*
- *Very superior bond to reinforced steel;*
- *Superior tensile strength;*
- *Superior durability in naturally occurring environments (e.g. marine performance);*
- *Rapid, but controllable setting rates (the ability to gain full long term strength within one or two hours of heat curing).*

In addition CIA-GCRP (2011) claimed that these properties make the product very competitive for precast work, as well as in-situ casting once correct training has been made for specialised placement, curing and finishing.

An ASTM conference (ASTM, 2012) evaluated the need to change the American Standards for concrete, which are composition based, for standards that would allow competition of geopolymers and other concretes on a performance base. To date the ASTM committee is still in discussion.

RILEM (*Reunion Internationale des Laboratoires et Experts des Materiaux, Systemes de Construction et Ouvrages* -French: International Union of Laboratories and Experts in Construction Materials, Systems, and Structures. <http://www.rilem.net/>), have a Technical Committee 224-AAM (Alkali activated materials) that is due to release a state of the art report by Mid 2013, but no report has been issued to date. RILEM (2012) have a clear goal to prepare: *a set of recommendations for the use of national Standards bodies, whereby performance-based requirements for alkali-activated materials will be laid out in such a way as to enable reliable specification of these materials by architects and engineers, similar to the current status of traditional cements.*

There are several commercial operations now providing geopolymer concrete to a strength standard with further information available from the following:

Zeobond (2013). www.zeobond.com/products-e-crete.html

Wagner (2012). <http://www.wagner.com.au/capabilities/efc/>

Hyssil (2012). <http://www.hyssil.com/geopolymerrooftiles/>

Banah (2012). <http://www.banahuk.co.uk/faqs/index.html>

Halcrow(2012). <http://www.halcrow.com/Where-we-work/Australia/Fibre-Reinforced-Geopolymer-Concrete/>

Rocla (2012).<http://www.pipe.rocla.com.au/News.php?id=40>

Even structural elements are being designed from geopolymer as shown in Figure 2-46 to 2-49.



Figure 2-46. A pre-cast geopolymer suspended structural concrete floor beam, at the Global Change Institute building at University of Queensland (Aldred & Day, 2012).



Figure 2-47. E-Crete™ concrete at Thomastown Recreation Centre (Zeobond, 2013).



Figure 2-48. Geopolymer tunnel lining sections (Wimpenny & Chappell, 2013).



Figure 2-49. Graves, capstones and lids by Austeng & Rocla (Rocla, 2012).

2.8.8 Bayer geopolymers

Drechsler & Graham (2005) reported on explorations of synergy between the alumina industry and construction products such as geopolymers for the utilisation of Bayer sand and bauxite residues. The primary goal was to utilise residual caustic values within red mud.

Dimas *et al.* (2009) utilised an alkali silicate solution at high caustic concentration to polymerise red mud within a metakaolin geopolymer. The attempt was to make structural elements for the construction industry. During optimisation they found that dissolution of silica was fundamental to the formation of a geopolymer of suitable strength, in this case 20 MPa. Unfortunately dissolution studies demonstrated that very little alumina and only some silica was supplied by the red mud. Hence 15 – 20 wt% metakaolin must be added. The products achieved significant compressive strength but not flexural strength or freeze/thaw resistance. Workability was not reported but was probably poor due to the water absorption capacity of red mud.

Giannopoulou *et al.* (2009) reported similar results for red mud geopolymers to Dimas *et al.* (2009). Evaluations of caustic concentration, silica concentration, etc, still failed to achieve suitable compressive strengths for red mud polymers. Utilisation of ferronickel slag was found to improve compressive strength achieving in excess of 100 MPa.

Zaharaki & Komnitsas (2009) added 20 and 50 wt% red mud to a slag based geopolymer. Results indicated that both additions significantly reduced compressive strength by at least 60%. Surprisingly, the lower concentration of red mud performed worst with a 75% reduction in strength. This is in contrast to Abhishe & Aswath (2012) who reported an immediate decrease in strength with only 10 wt% red mud addition.

Zhang, *et al.* (2010) reported utilisation of red mud to fly ash in ratios of 80, 50 and 20 wt%. Samples were polymerised with sodium silicate solution but still achieved compressive strength of only 7 – 13 MPa. Clearly the high surface area of the red mud requires significant binding agent for coverage.

Nanoaims (2012) report an interest in utilisation of red mud in geopolymers formation, citing the Hungary mud lake rupture as a driving force for utilisation. They state that the red mud residual caustic and high alumina and silica content makes it ideal for geopolymers production. Clearly they have not assessed the caustic solubility of these fractions in the mud.

He *et al.* (2013) attempted to use red mud with rice husk ash to make geopolymers. They encountered results that did not follow trend and mentioned rheological issues may be to blame. This is probably correct as the red mud (if dry) would significantly reduce water availability for flow and for reagent dissolution. It is this author's experience that red mud is little more than filler and a poor one at that.

Phair and Van Deventer (2002) demonstrated the formation of geopolymers utilising pure solutions of sodium aluminate as an alternative to sodium silicate solution. They mentioned the potential to utilise bauxite residues (red mud) as a possible source of caustic credits. Specifically, no one appears to have noted that the use of concentrated Bayer liquor for geopolymers production would provide an impurity bleed for the alumina refinery. Jamieson (2007) took a very different approach to Bayer residues, seeing them as a resource (see also Jamieson *et al.* 2008; Avraamides *et al.* 2009; 2010a; 2010b). This approach was utilised to develop a product suitable as feedstock for geopolymers formation, rather than attempting to blend residue into a product. Jamieson (2008b) realised that enhancing Bayer liquor to be suitable as a geopolymers activator would result in the export of liquor from the refinery. The liquor export would act as an impurity removal process as the liquor is replaced with clean caustic. This is a counter intuitive approach as the alumina industry spends significant funds in attempting to prevent the loss of caustic.

A significant portion of this thesis will focus on the continued development of this approach.

3 MATERIALS AND METHODS

During the progress of this thesis a variety of test methods and analytical procedures were utilised. Also many samples were collected and characterised. This chapter seeks to document those actions to allow standardisation as well as reproduction.

3.1 Materials

Specific by-product analyses are contained in the following research chapters. Some information is proprietary and is only available to the immediate research team. The Material Safety Data Sheet (MSDS) for supplied products and for manufactured by-products are supplied in Appendix 1. All photographs of samples were taken on a sheet of A4 paper at a distance of 15 cm.

3.1.1 Alkaloam®

Alkaloam (Figure 3-1) for these trials was sourced from the Kwinana refinery's (Figure 3-2) carbonation plant product lines, either as fresh slurry or as dried bed deposit.



Figure 3-1. Alkaloam^(R).

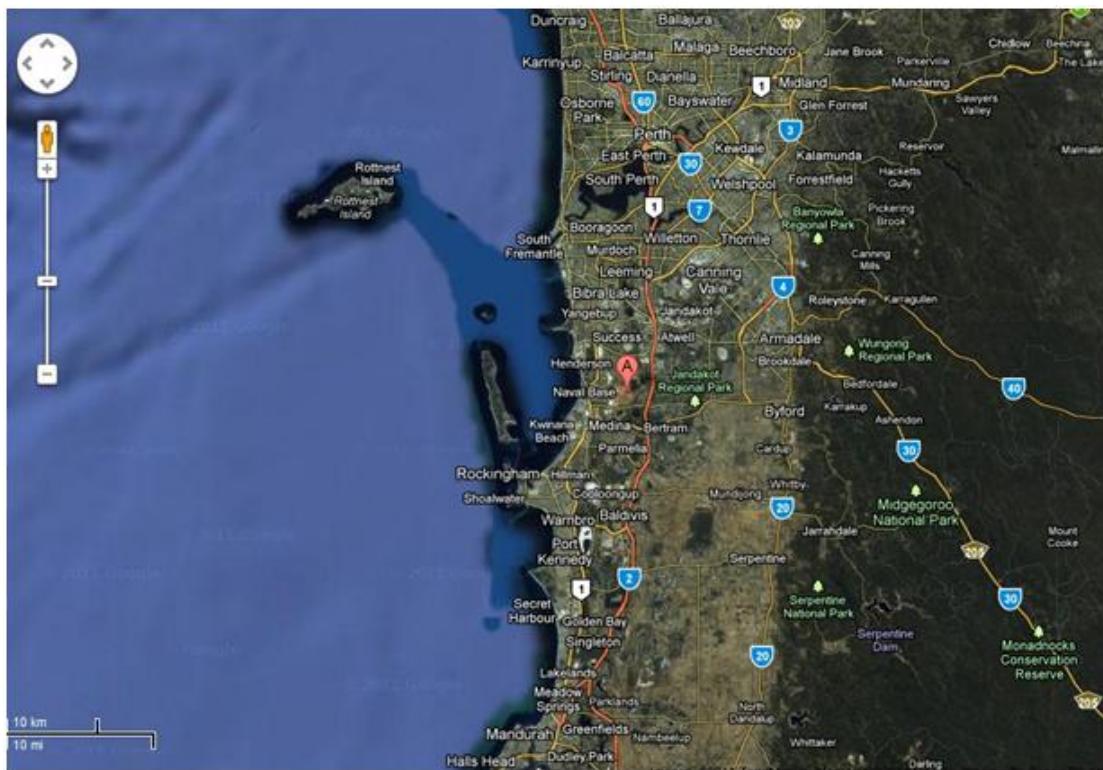


Figure 3-2. Kwinana, Perth Western Australia. (Google maps, 2011).

3.1.2 Sand

Sand utilised in road construction (Figure 3-3), for turf top-dressing and as fine fill in the production of Bayer geopolymers, was sourced from the sand pilot plant located at Wagerup refinery (Figure 3-4).



Figure 3-3. Red Sand^(TM) from Wagerup refinery.

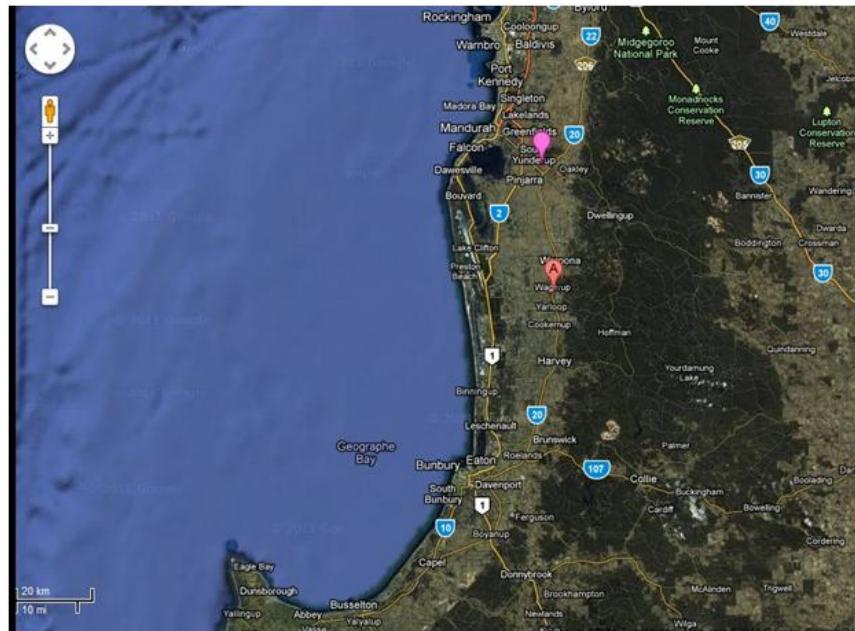


Figure 3-4. Wagerup Refinery, Western Australia. (Google maps, 2011).

3.1.3 Lime residue

Lime residue (Figure 3-5) or causticiser product was sourced from the lime pilot plant located at Kwinana refinery. The pilot plant is described in Chapter 4.4.



Figure 3-5. Red Lime^(TM).

3.1.4 Geopolymer

Geopolymer paste is made up from a soluble silica source (in this case silica fume and fly ash), a soluble aluminate source (fly ash and sodium aluminate solution) and a source of caustic soda (Bayer liquor concentrate) as described below.

3.1.4.1 Fly Ash

Fly ash (Figure 3-6) samples were utilised from various sites at Muja, Kwinana and Collie power stations (Figure 3-7). Trials were conducted utilising Collie fly ash Class C packed into bulk bags in July 2009 unless otherwise stated.



Figure 3-6. Fly ash.

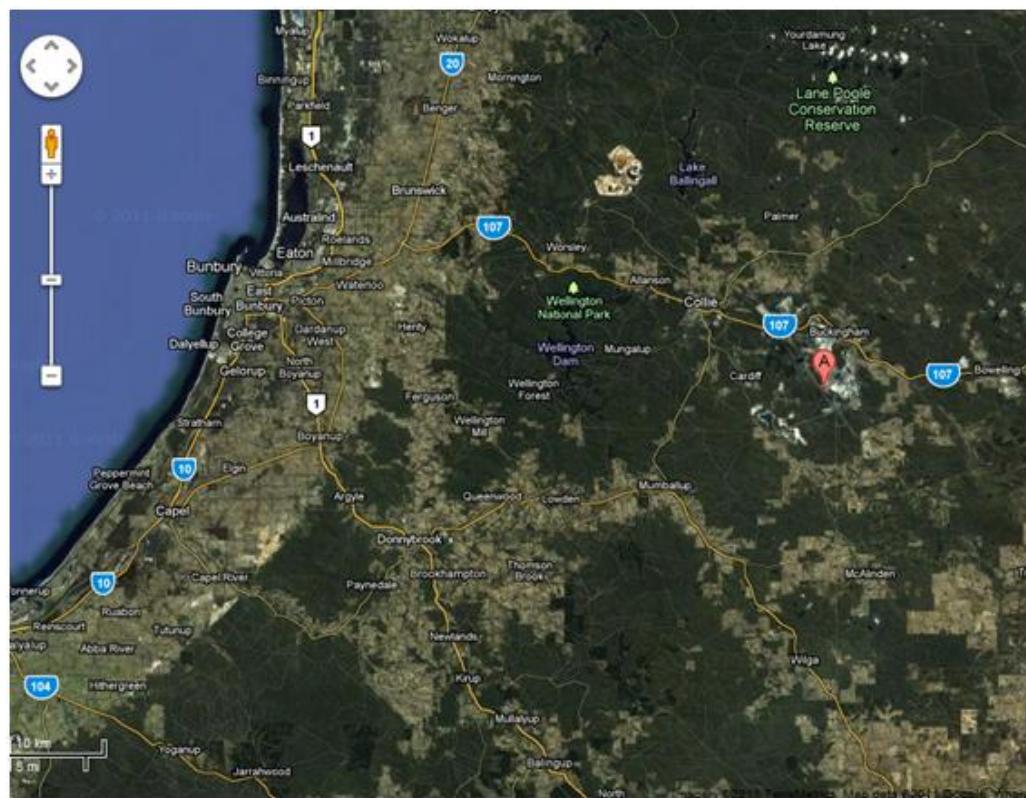


Figure 3-7. Muja power station. (Google maps, 2011).

3.1.4.2 Bayer liquor

Samples of Bayer liquor (Figure 3-8) were utilised from various sites at Wagerup, Kwinana and Pinjarra refineries, to take advantage of differing alumina to soda ratios. Liquor was concentrated to reach suitable caustic soda concentrations. Field trials were conducted utilising super-concentrator product from Wagerup refinery.



Figure 3-8. Bayer liquor concentrate.

3.1.4.3 Silica fume

Two sources of silica fume (Figure 3-9) were utilised during the experimental and field trials. The first was the white product by Australian Fused Materials AFM SF 98. The second product was black in colour because of the considerable level of carbon present. That product was BASF Rheomac SF 100.



Figure 3-9. Black and white silica fume.

3.1.4.4 Lime (HyLime)

Commercial calcium oxide was purchased as produced by Cockburn Cement using the product name HyLime (Figure 3-10).



Figure 3-10. HyLime.

3.1.4.5 Sand

Local construction sand (Figure 3-11) was used for mortar and concrete was procured.



Figure 3-11. Yellow “brickies” sand.

3.1.4.6 The market

Technically, the market is not a material, nor a method, but it is an essential element in this project. It is worthy to note that the geographical location of the ash, liquor and silica (ports) surround the urban growth corridor that extends from Rockingham to Bunbury (Annotations added in yellow for Figure 3-12). Construction products of aggregate, mortar and concrete will be in high volume and high value demand in this region for several decades. Traditional products are disadvantaged by having to travel significantly further on average.

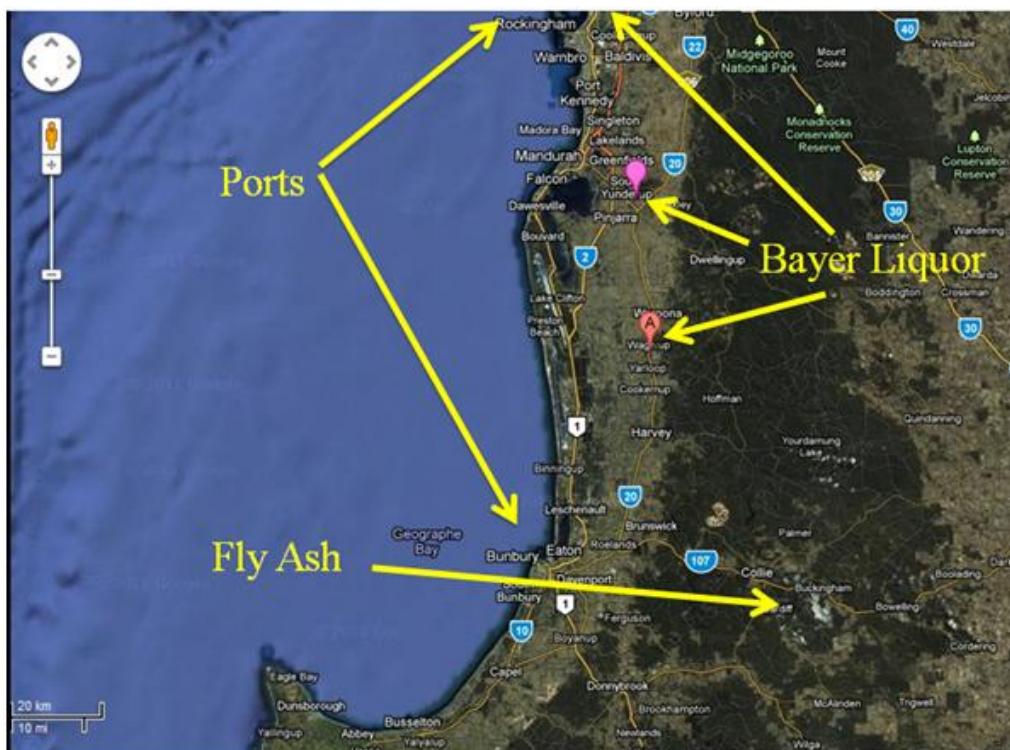


Figure 3-12. Location of Fly ash, liquor and ports in WA. (Google maps, 2011).

3.2 Methods

3.2.1 Acid Neutralisation Capacity (ANC)

Acid Neutralisation Capacity was determined by Genalysis Laboratory Services (now Intertek Laboratories) utilising a hydrochloric acid digest and back titration.

Lime Solids Analysis was also performed using Alcoa method 67533: Digestion of Residue Solids for Lime Solids Analysis (WAO).

3.2.2 ALiAn (Alcoa Liquor Analyser)

Liquor analysis is an automated titration (Figure 3-13), based on the method published by Watts & Utley (1956). This has lead to the name “ALiAn”. Liquor analysis is usually provided in the “industry terminology” of Al, FC, TA, TC, and TS. These are described below.

Al: Alumina concentration expressed in g/l Al_2O_3 .

FC: Free Caustic; the concentration of hydroxide expressed in terms of g/l sodium carbonate.

TC: Total Caustic; is the total sodium hydroxide concentration (i.e. Free Caustic plus Alumina concentration) expressed in terms of g/l sodium carbonate.

TA: Total Alkalinity; is the Total Caustic plus the carbonate concentration expressed in terms of g/l sodium carbonate.

TS: Total Solubility; is the Total Alkalinity plus concentrations of chloride, sulphate, and other impurities, expressed in terms of g/l sodium carbonate.



Figure 3-13. ALiAn auto-titration unit.

3.2.3 Australian Standard Leaching Protocol (ASLP)

Samples were assessed according to the Australian Standard Leaching Protocol (ASLP) to Australian Standard AS 4439.3 (1997). The pH points normally targeted were pH 2.9, pH 5 and the natural pH when leached with water. pH was recorded at start and completion of the leach assessment. Samples were held for 18 hours at ambient temperature at a liquid to solid ratio of 20 L/kg. Leach solutions were then analysed for metals by Genalysis Laboratory Services. Detection limits were set to allow for assessment of elements against the various regulatory standards.

3.2.4 California Bearing Ratio (CBR)

The CBR (Figure 3-14) was determined utilising the Australian Standard AS 1289.1.1 by Main Roads Western Australia and by WML consultants.



Figure 3-14. California Bearing Ratio (CBR) unit (Photos MRWA).

3.2.5 Composition analysis

Samples were analysed for elemental analysis by Ultratrace Laboratories (now Bureau Veritas). Pulverised samples were dissolved utilising either a mixed acid or aqua regia digest, or sodium peroxide fusion. Solutions were then analysed by ICP OES (Inductively Coupled Plasma Optical Emission Spectroscopy) or ICP MS (Inductively Coupled Plasma Mass Spectroscopy).

3.2.6 Compressive strength

Compressive strength on 30 mL laboratory samples was assessed according to ASTM C39 using a Lloyds EZ50 instrument with a 50 kN load cell. This procedure is the principle benchmark test for strength within the construction industry. The standard deviation between batch samples (normally 3-5 samples) was used for error evaluation. On occasion single samples are reported due to sample damage. A large average error of 10% is assumed to reflect the single sample nature.



Figure 3-15. Compressive strength crusher.

The compressive strength of 1.5 litre cylinders was conducted at Boral Laboratories, Maddington (Figure 3-15). Samples were prepared and analysed in accordance with Australian Standard AS 1012.

3.2.7 Density

Density is a loose term and needs to be defined. Here the following densities are recorded and measured.

Sample density: (Relative Density) measured by displacement of water.

Loose density: measured by filling a known volume with loose aggregate.

Tap density: as above but with some vibration to encourage packing of the sample.

Liquid density: measured as a weight of a specified volume at specified temperature.

Specific Gravity (SG) was conducted in accordance with Alcoa Method 1949.

Mass per unit volume of freshly mixed concrete was conducted at Boral laboratories, Maddington Western Australia as per Australian Standard AS 1012.

3.2.8 Faling Weight Deflectometer (FWD)

The FWD (Figure 3-16) impacts a load onto the road surface to simulate traffic. Typically this involves dropping a large known weight onto the road surface and measuring the deformation. The dynamic load is typically 566 kPa over 300 mm ID plate with deformation measured by geophones at distances of 0, 200, 300, 450, 600, 900 and 1500 mm (GSA, 2012; Austroads AG: AM/T006).



Figure 3-16. Falling weight deflection test in operation (pavementanalysis.com).

3.2.9 Geopolymer formation and terminology

The experimental procedure for geopolymer formation has been standardised by the Materials Research Facility at Curtin University and is adapted below. Further adaptions were made during the developmental procedures and are recorded where appropriate. This procedure is for use in the Kenwood food processor utilising stainless steel utensils as described below.

1. Place water, fly ash and HyLime into the mixer bowl and mix on lowest setting until powders appear well mixed after 1 minute. Use foil shroud to prevent dust escape.
2. Add about 1/4 of the Bayer liquor to the mixture. Mix with the Kenwood on setting 1 for 30 seconds.
3. Add about 1/4 of the silica fume and mix with the Kenwood on setting 1 for approximately 30 seconds.
4. Repeat steps 2 and 3 until all fume and liquor has been added. The sides of the bowel may need scraping to ensure complete mixing.
5. Mix on setting 2 for about 1 minute then on setting 3 for a further 9 minutes.

Modification for manufacture of mortar and concrete is to add the admixtures, sand and aggregate as required after the last minute of step 5, with the total ingredients being mixed for the last 9 minutes.

Geopolymer formation usually occurs within a set of reactive elemental ratios such as Si/Al of 1 - 4, Na/Al of 0.4 – 2 and H/Si of 3 - 5. However, when working with Bayer liquor, the ratios and the terminology are misleading.

For example, those in the Bayer industry use the terms “free caustic” “total caustic” and “total alkali” to represent different forms and combinations of caustic species. But which one reflects the actual amount of hydroxide available to catalyse the reaction? Here we use the total caustic (TC). Yet in the standard ratios, the term for caustic is represented by the chemical symbol of sodium, an element that plays very little part in the geopolymserisation process (apart from charge neutralisation). However, in Bayer liquor, there is a much higher sodium (Na) concentration in the liquor than free caustic (OH^-). As such, it is intended to replace the Na symbol with the more accurate OH^- to avoid confusion between the two industries.

Similarly, the term H (for Hydrogen) is utilised to provide an indication of the water content (H_2O). Yet in Bayer liquor, there are lots of compounds (particularly organics) containing significant hydrogen content that would have no relation to water content. Similarly the geopolymer industry would calculate the water content of Bayer liquor by simply subtracting the free caustic and the alumina. Yet the Bayer liquor contains many g/l sulphate (Na_2SO_4), Chloride (NaCl), organics, etc. These need to be accounted for. Hence to minimise confusion between the industries, the actual water content is calculated for each experiment and is expressed as a percentage H_2O .

3.2.10 Linear shrink

Linear shrink was conducted by Boral laboratories, Stonyfell Laboratories, South Australia, in accordance with Australian Standard AS 1012.

3.2.11 Microscopy

Samples were prepared and viewed on a Leica MZ75 optical microscope (Figure 3-17) fitted with a Leica DFC420 camera, utilising Alcoa Method 79297.



Figure 3-17. Optical microscope with camera.

3.2.12 Moisture content

Moisture content was determined utilising Alcoa Method 2008.

Alternatively moisture content was determined at Boral Laboratories using Australian Standard AS 1289 and particle size by Australian Standard AS 1141.

3.2.13 Particle Size Distribution (PSD)

The Particle Size Distribution (PSD) was determined utilising various screen sizes in accordance with Alcoa Method 38216 (Figure 3-18).

Alternatively, PSD were determined at Boral Laboratories Paddington using Australian Standard AS 1141.



Figure 3-18. Screens and shaker for dry PSD analysis.

3.2.14 Penetrometer

The Penetrometer is used to determine the setting time for hydraulic cement using a Vicat needle method as outlined in the standard ASTM C191 (Figure 3-19).

Vicat setting time test procedure

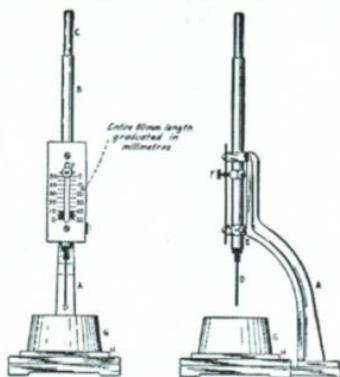


Figure 3-19. Diagram of Vicat needle penetrometer (Vicat).

3.2.15 pH dependent leach test

The pH dependent leach tests were conducted in accordance with European standard method CEN/TS 14429 (CEN, 2005). Samples are leached over a pH range from 4 to 12 at a liquid to solid ratio of 10 L/kg for 48 hours at 20°C.

This method has been adapted for use with soils, clays and highly alkaline materials by Attiwell (2013). Analysis of soil and by-products, have been conducted utilising this modified procedure.

3.2.16 Phosphorus Retention Index (PRI)

The Phosphorus Retention Index (PRI) is measured utilising the method reported by Allen & Jeffery (1990), where a soil sample is allowed to absorb a standard solution of phosphate for a period of time. The PRI is expressed as the ratio of phosphorus adsorbed by soil against the concentration of phosphorus in solution. Analysis was conducted by the Chemistry Centre, WA.

3.2.17 QEMSCAN

Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN) is a technique for the assessment of elemental and mineral distribution within a sample. QEMSCAN uses Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray Spectroscopy (EDS) in combination with Back-Scattered Electron brightness (BSE) and X-ray count to identify and locate mineral phases in the sample. Analysis was conducted by SGS (Johannesburg).

3.2.18 Reactive alumina and silica

The reactive alumina and silica can also be called the amorphous or the caustic soluble alumina and silica. Here the term means the amount of alumina and silica that is available for geopolymserisation. It has been determined by the method reported by Williams and Van Riessen (2010).

3.2.19 Scanning Electron Microscopy (SEM)

Samples for SEM were prepared utilising Alcoa Method 4218 and conducted on a FEI QUANTA 400F Scanning Electron Microscope (Figure 3-20).



Figure 3-20. FEI QUANTA 400F Scanning Electron Microscope.

3.2.20 Schmidt hammer hardness

The Schmidt hammer is an impact device that measures the rebound from striking concrete. As such it is a non-destructive method of assessment. The amount of rebound “r” depends upon the concrete strength, the sample size and shape, the angle of incidence and direction of application. The averaged rebound from a series of impacts is then compared against a series of charts to determine the compressive strength of the test specimen. Concrete samples need to be aged between 14 and 56 days to prevent surface carbonation impacting upon accuracy.

3.2.21 Soil incubation test

About 1.57 g of lime reagent (can be individual size fractions) was mixed with 1 kg of a sandy loam soil of pH ~4 and stored in sealed plastic bags (Figure 3-21). The moisture content was about 15 wt%. A blank sample was monitored as well as a control sample where analytical grade finely ground calcium carbonate was added. This sample was considered to be fully reacted. 5.85 g samples were taken and mixed with 29.25 mL of 0.01 Molar CaCl₂ for one hour. The pH was then recorded. Sampling can take place over 2 years and longer.



Figure 3.21. Soil incubation trial pots (Photo, Chemistry Centre WA).

3.2.22 Triaxial compaction

The permanent deformation and the resilient modulus were determined using standard methods Austroads APRG 00/33 (2000) and Austroads AG:PT/T053 (2007) respectively (Figure 3-22).



Figure 3-22. Sample in Triaxial load test instrument.

3.2.23 X-Ray Diffraction (XRD)

Samples were prepared for analyses using Alcoa Method 4083 and 4079. XRD was conducted on the “Scan” setting of a PANalytical (Philips) X’Pert Pro MPD X-Ray Diffractometer and mineralogical analysis was determined using “Traces” software (Figure 3-23).



Figure 3-23. PANalytical (Philips) X'Pert Pro MPD X-Ray Diffractometer.

3.2.24 X-Ray Fluorescence (XRF)

Samples were prepared on a XRF Scientific VFD 6000 automatic fluxer. Samples were analysed utilising the “Bauxite Program” (Alcoa Method 83379, modified for particle size and mineralogy) on a Philips model PW2400 XRF (Figure 3-24).



Figure 3-24. Automated XRF bead preparation.

3.3 Safety

Many of the reagents and much some of the equipment required to conduct this project requires proper training in handling and use.

Many of the samples and trials were conducted at alumina refineries that required Mine Site safety, company and site specific safety inductions. All were complied with, as required.

In addition safety equipment is often standard such as laboratory glasses or goggles, dust mask (P2 rated), hearing protection (as required), helmet (where required), covered foot-ware or steel capped boots, long sleeve shirt or laboratory coat, long trousers etc. (Figure 3-25). A can of DIPHOTERINE® solution (a first response buffer spray to treat chemical burns) was always present.



Figure 3-25. Author utilising safety equipment while measuring silica fume.

4 FROM WASTE TO RESOURCE

The aim of this thesis is to report on the development and utilisation of Bayer by-products. Part of that aim is to highlight the transition from laboratory to demonstration and utilisation trials. The following pilot plants were constructed prior to commencement of this thesis, however, the product evaluation trials are included. This author's involvement in the pilot plants is described as:

- Technical assistant for the carbonation of red mud plant at Kwinana,
- Program and project manager for the Red Sand™ pilot plant at Wagerup,
- Project manager for the Red Lime™ pilot plant at Kwinana,
- Technical assistant to the non-Bayer geopolymers field demonstrations.

4.1 From the laboratory to the field

The transition from laboratory and bench scale research projects into pilot and plant trial development projects is often called the “valley of death” because the void is so rarely crossed. Primarily this is because pilot and plant trials are typically orders of magnitude higher in cost compared to laboratory based research. In addition, there is often a change in personnel from chemistry to engineering-based disciplines and the inclusion of more “process” success criteria. All projects reported in this chapter have proceeded by utilising a stage gate process assessing the four categories of technical, environmental, stakeholder and market.

4.2 Red mud carbonation plant

In 2004, Alcoa of Australia's Kwinana refinery commissioned a red mud carbonation plant after many years of research and development. The driving need was practical, environmental and economic. Carbonation provided a material that was easier to handle (no longer a hazardous material) and was easier to develop into a series of by-products.

Traditional dry stacking storage of bauxite residue involves depositing a 0.5 m layer of slurry to allow atmospheric drying before another layer is added. During this process, the red mud is still highly alkaline and natural surface carbonation will result in a crust of sodium carbonate that can form a potential dust issue, as well as slowing the drying process. In addition sprinklers are frequently employed to wet the surface to prevent dust movement, also retarding the drying process. This is shown below in Figure 4-1.



Figure 4-1. A sprinkler riser protruding from a red mud "dry stacking" storage area.

Note the white surface is migrated caustic reacting with atmospheric carbon dioxide to form sodium aluminium carbonate, aluminium hydroxide and sodium carbonate ($\text{NaAl(OH)}_2 \cdot \text{CO}_3\text{Al(OH)}_3$ and Na_2CO_3) respectively.

To encourage drying and to prevent dust events, specially designed machines Amphirols, (Figure 4-2) are used to drag themselves across the residue area using Archimedes screws as propulsion. This breaks the crust surface allowing faster drying and ploughs any dust material into the soft interior as seen below.



Figure 4-2. An Amphirol mechanically breaking the carbonate crust.

As a method for prevention of dusting, forced residue carbonation was investigated. After several small scale development trials, full implementation was conducted at Kwinana refinery to process a flow of up to 250 kL/hr of thickened red mud slurry of up to 50 wt% solids. The feed slurry pH is above 13 and the reactor output is below pH 8. The concept is simple with carbon dioxide pumped under pressure into reactors where the target pH is maintained for a period of time to ensure longer term pH reversion does not elevate the pH above 10.5. A schematic is provided in Figure 4-3.

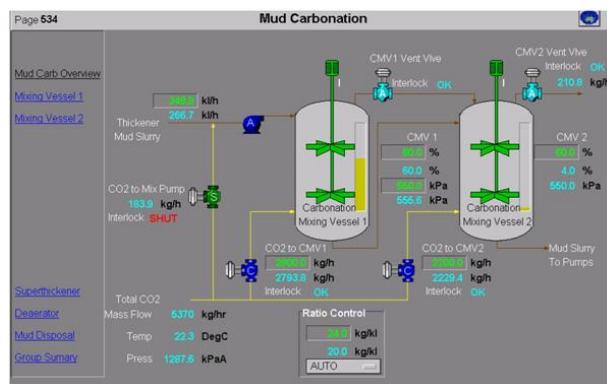


Figure 4-3. Red mud carbonation process control schematic.

Carbon dioxide was originally supplied in liquid form and requires an evaporation system (Figure 4-4) to enable constant supply. These were replaced by a direct CO₂ gas pipeline supplied from a local fertiliser manufacturer.



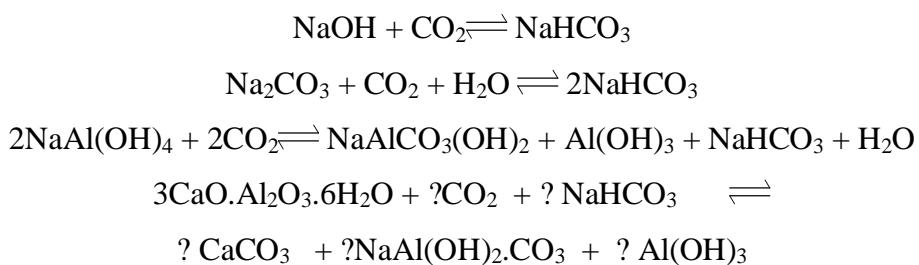
Figure 4-4. Liquid carbon dioxide evaporation unit.

An emergency CO₂ supply can be connected through a series of gas bottles shown in Figure 4-5. Two reaction vessels enable a longer hold time for conversion of solid alkalinity.



Figure 4-5. Carbonation reaction vessels and emergency CO₂ supply.

The chemistry behind the carbonation process involves the reaction of various alkaline species and solids (equation 4-1). The alkaline solids are slow to react and as the duration in the carbonation chamber is short, the entrained sodium bicarbonate solution buffers the slow reacting solid phases (eg Tricalcium aluminate -TCA6). This slow reaction is called reversion and if the solids do not sufficiently react, then washing of new mud will see fresh caustic produced and an elevated pH. Hence by-product development opportunities should concentrate on aged residue stockpiles and not end of pipe slurries.



Equation 4-1. The reaction of tricalcium aluminate (TCA6) is incomplete with a variety of mixed amorphous products (Cooling, 2005a; 2005b).

The benefits of carbonation are wide ranging and are listed below.

- Provides a long term carbon sink;
- Carbonated red mud is not a dangerous good;
- Reduced pH enables biological activity for soil health;

- Transport is easier without need of dangerous good carrier;
- By-product utilisation opportunities are more attractive with no dangerous good classification;
- Dust potential is reduced with no carbonate surface products formed;
- Sprinkler use and water consumption decrease;
- Drying time is decreased significantly;
- Reduced impurity return to refinery in reclaimed water;
- Reduced need for labour-intensive amphirol;
- Faster turnaround in residue management;
- Reduced long-term liability for drying area closure.

Due to the significantly increased drying rate, there is also a rapid rise in the structural integrity. Note footprints on bottom LHS of Figure 4-6.



Figure 4-6. Drying carbonated bauxite residue.

4.3 Sand pilot plant

It has been demonstrated that Red Sand^(TM) can be extracted from bauxite residue and utilised in a variety of markets (Jamieson *et al.* 2005; Jamieson *et al.* 2006). In 2007, construction commenced on a 10 t/hr Red SandTM extraction pilot plant. This was designed to produce 5000 tonne of sand suitable for road construction trials. The construction of the pilot plant was part of the Centre for Sustainable Resource Processing (CSRP) project 3B4.

Numerous laboratory trials provided a rough plant diagram for sand processing (Figure 4-7, Figure 4-8). Trials were conducted on various items of plant to determine if they were suitable for operation.



Figure 4-7. Demonstration of operation of flat bottom classifier.



Figure 4-8. Concept demonstration of carbonation of sand slurry.

A plant and flow diagram (Figure 4-9) was drawn and equipment ordered. Items were sourced to provide a production rate of 10 tonne per hour product.

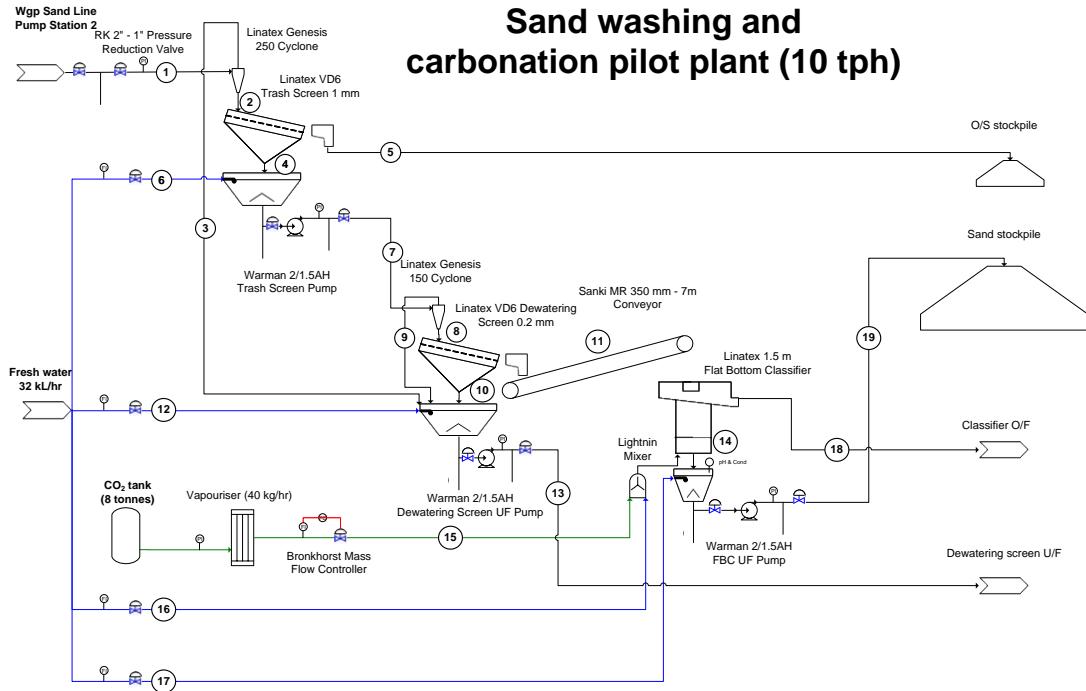


Figure 4-9. Flow and equipment diagram for the red sand pilot plant.

A product specification was based upon market acceptance and equipment performance. The Final pH of the product was not to exceed 10.5, the salt content was not to exceed 5 g/kg and there was to be minimal retained ultra-fines. While these requirements were difficult to meet, they would allow the product to be utilised in the widest range of applications. Further testing during operations determined that the particle size distribution was in fact too coarse, adversely impacting the California Bearing Ratio. Hence washing performance was scaled back and PSD was added to the performance criteria. Washing efficiency was still within acceptable limits. Construction of the pilot plant is shown in Figures 4-10 to 4-13.



Figure 4-10. Vibrating screen lowered into place.



Figure 4-11. Sand conveyor about to be lowered into place.



Figure 4-12. Flat bottom classifier being lifted from truck



Figure 4-13. Author showing CSRP management the operational sand pilot plant.

The process was relatively simple in concept, but decidedly more difficult in application. Sand from the refinery was mixed with water and pumped to the residue area. The pressure and flow rate were high to keep the sand in suspension, hence pressure management and abrasion needed to be managed.

A side-stream of sand was passed through a primary cyclone. This cyclone removed a significant volume of ultrafine particles, but its main function was to allow a pressure drop prior to the sand slurry hitting the first oversize filter.

The sump sand from the oversize screen was mixed with water and passed through the second cyclone. Here the ultra-fines were fully removed allowing for a clean product. (Note the presence of ultra-fines in the product resulted in their bleeding during subsequent applications. Being bright red, the effect was to be avoided.)

The second cyclone underflow was fed onto the second vibration screen (Figure 4-14). The transport water was allowed to drain free then wash water applied. Operation of the screen, the wash water and the feed cyclone were critical to quality control and PSD of the product. If the cyclone provided too little transport water, then there was a loss of recovery and frequent loss of stable bed. Too much and the transport water contaminated the process resulting in high CO₂ consumption and pH variation. Similarly if the wash water was too slow, then washing efficiency suffered; too fast and the wash water carried off too many fines. The ideal operation conditions resulted in about 5 cm of sand cake free falling onto the sand transport conveyor (Figure 4-15).



Figure 4-14. Sand slurry fed onto the vibration screen.



Figure 4-15. Sand from wash screen.

The sand was transported up a conveyor system to feed the flat bottom classifier (Figure 4-16). The classifier used water up-flow mixed with CO₂ to achieve a fluidised bed of sand. The gentle up-flow of water and gas also removed the final traces of ultrafine material. The CO₂ neutralised the transport solution and aided the reaction of solid phase alkalinity in the sand. Once the sand bed reached a specified height (based on retention times to allow reaction of solid phase alkalinity) a valve would discharge from the bottom.

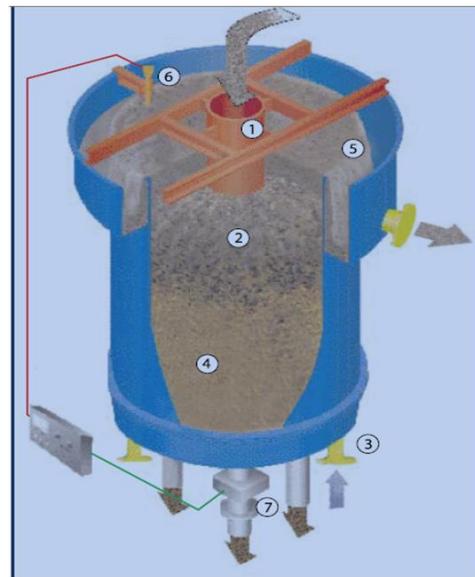


Figure 4-16. Schematic of flat bottom classifier. (Linotex, Weir Minerals.)

The classifier shown in Figure 4-16 is explained with the following key.

1. *Sand slurry feed.*
2. *Free fall zone (unhindered settling allowing maximum contact with neutralisation solution).*
3. *Wash water and CO₂ injection.*
4. *Fluidised sand bed.*
5. *Classifier overflow.*
6. *Sand bed height probe linked to control of underflow.*
7. *Underflow gate valve controlled by bed height.*

During operation of the flat bottom classifier, the CO₂ supply (Figure 4-17) was modified to maintain enough driving force for neutralisation.



Figure 4-17. CO₂ bubbling up through sand slurry in the flat bottom classifier.

The discharged sand had a high solids load, so required further dilution for transport to the stockpile. Free draining of the stockpile allowed remaining carbonate solution to continue its reactions with the solid-phase alkalinity, though complete reaction may be impossible to achieve in the short time scale. The product was immediately capable of being walked upon as shown in Figure 4-18. This material was then transported to temporary holding sites (Figure 4-19).



Figure 4-18. Author showing free draining of freshly deposited sand (Garside images).

The sand was then deposited in storage to prevent its accidental utilisation.

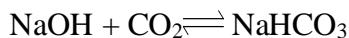


Figure 4-19. Some of the 5,000 tonne of Red Sand^(TM) in storage.

Sand from the pilot plant was utilised in a variety of demonstration projects and the results for these trials are reported in Chapter 6.

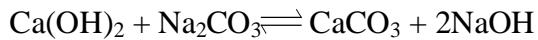
4.4 Lime pilot plant

During the Bayer process for alumina production, the recirculating liquor is continuously contaminated with CO₂ from a variety of sources including oxidation of organic species. This carbon dioxide reacts with the caustic in liquor to form carbonate as per Equation 4-2.



Equation 4-2. Carbon dioxide reaction.

The loss of caustic results in a less efficient alumina extraction, so the carbonate is reacted with lime in a process called causticisation. This process releases the caustic back into the liquor, but forms a series of solid phase alkaline reaction products shown in Equation 4-3. These reaction products can be separated and have been called Red LimeTM.



Equation 4-3. The formation of solid phases of calcium carbonate, tri-calcium aluminate (TCA₆) and tri-calcium aluminate monocarbonate (Monocarbonate), respectively.

Separation of this material in laboratory trials has shown Red LimeTM to be a valued by-product in need of further development. To prove the concept of Red LimeTM separation as well as to provide suitable volumes of material for demonstration trials, a pilot extraction plant was designed (Figure 4-20) and constructed at Alcoa's Kwinana refinery.

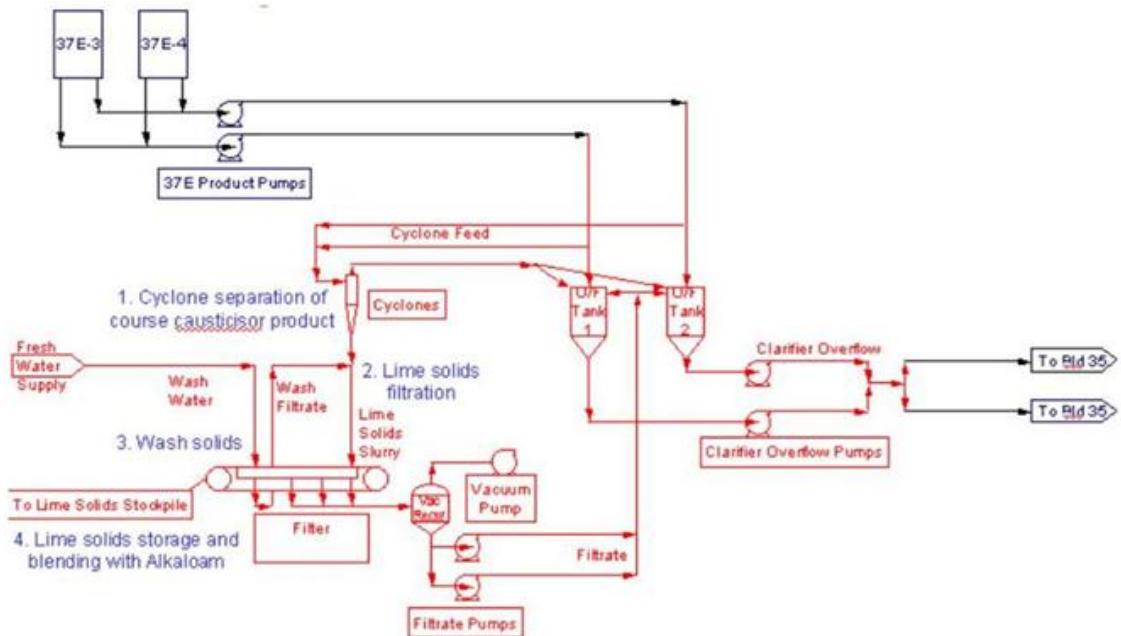


Figure 4-20. The equipment and flow diagram for extraction of Red Lime^(TM).

A side stream of causticiser product was taken off and fed into a cyclone (Figure 4-21). The fine fraction in the overflow was returned to the process. The coarse cyclone underflow dropped into a thickener, where the thickened solids fed an elutriation column (Figure 4-22). Both the thickener and elutriation column overflow were also fed back to the refinery.

The fines are valued for further reaction within the refinery, where the coarse material is ineffective. In addition the fines tend to block the belt filter shown in Figure 4-23.



Figure 4-21. Cyclone perched above thickener.

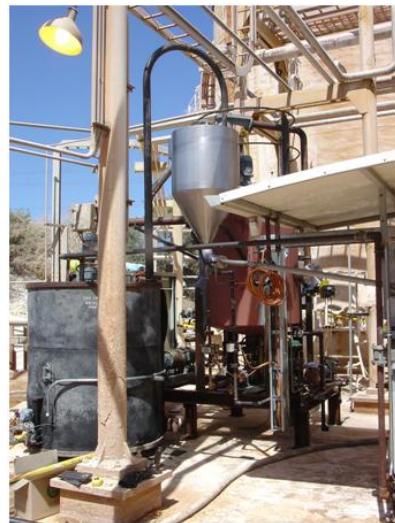


Figure 4-22. Elutriation column attached to side of thickener.



Figure 4-23. Operator in front of belt filter.

The solids were filtered and washed on a belt filter, then transported on a conveyor to holding bins for storage. Material from this plant was utilised in the CSRP project 4A4, evaluating the impact of industrial liming agents used in agricultural applications. Results and discussion are reported in Chapter 7.

4.5 Geopolymer pilot plant (Non –Bayer)

The initial geopolymer production demonstrations utilised known fly ash and sodium silicate solutions. This demonstration path was constructed at Curtin University linking the radio station to the basketball courts. The development of Bayer-derived geopolymer and subsequent demonstration trials are described in Chapter 8.

The production of fly ash – sodium silicate geopolymer does not require significant modification to existing concrete batching plants. Concrete plants already hold fly ash in hoppers, along with sand and various sized aggregate. An additional hopper for blast furnace slag (if required) and tank with pump for sodium silicate would allow for conversion to geopolymer production. For this trial, blast furnace slag was added via a bag dump hopper with fly ash and caustic sodium silicate solution. The mixture was mixed in a high shear mixing bowl (truck mounted) and transported to site. Just prior to application, lime was added and mixed to allow ambient cure. The process followed similar application as if the product were ordinary concrete and is shown in Figures 4-24 to 4-29. The only precautions were the insistence on a higher level of personal protective equipment and the vicinity of Diphoterine®.



Figure 4-24. Ground work preparation.



Figure 4-25. Steel reinforcing in place.



Figure 4-26. Site delivery.



Figure 4-27. Silicate derived geopolymer pour.



Figure 4-28. First section complete prior to a brush finish.



Figure 4-29. 48 hours after pour and the product looks like concrete.

5 CARBONATED RED MUD AND ALKALOAM®

The global demand for alumina and aluminium results in approximately 120 million tonnes of residue produced each year (CSIRO, 2011). To put that into perspective, if that residue were to be transported past your window in ten-tonne dump trucks, at least 22 trucks would be passing every second of every hour of every day. That figure is growing. For many, this is an unavoidable consequence of the need to fulfil society's consumption demands and the residue simply must be managed appropriately. To this author, it is an unacceptable wastage of a highly processed material that could be utilised to further benefit all the community. This is a vision shared by Alcoa.

Around 75 wt% of Alcoa's bauxite residue is fine bauxite residue called red mud. The fine residue can be carbonated to reduce the pH (carbonated red mud) and in Australia, this product is trademark registered as Alkaloam® for use as a soil ameliorant. This author has had significant input into the development of alternative applications for carbonated red mud, however, for this thesis, only product assessment and product demonstrations are included.

5.1 Carbonated Red Mud / Alkaloam® characterisation

A large sample of Kwinana refinery carbonated red mud was collected early in 2004 and utilised for student projects reported in Chapter 2.4 and as Alkaloam® for soil amelioration field trials. It has been re-analysed using the latest techniques and reported here.

5.1.1 XRD

The XRD analysis (Figure 5-1) identifies the major components as quartz, hematite, goethite, gibbsite with traces levels of calcite.

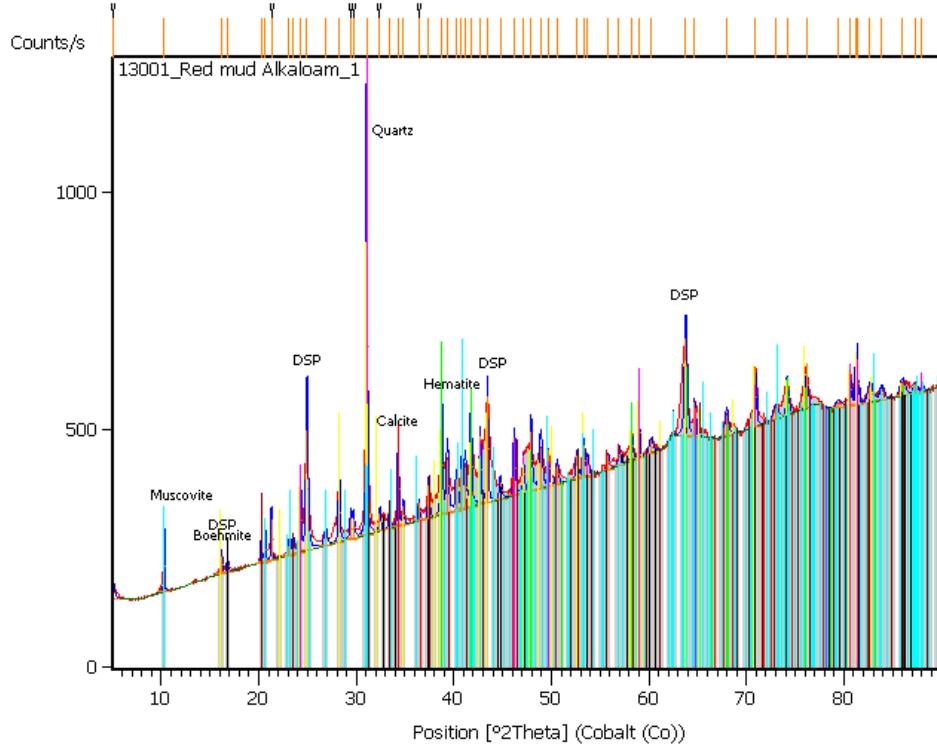


Figure 5-1. XRD spectra of Alkaloam® sample.

5.1.2 XRF

The XRF analysis for Alkaloam® is provided in Table 5-1. The remaining materials are water, organics, salts and trace metal oxides.

Table 5-1. XRF composition of Alkaloam®.

% w/w	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	Na ₂ O
Alkaloam®	22.1	28	27	4.4	2.6

5.1.3 Phosphate Retention Index (PRI)

The PRI of Alkaloam® has been determined to be 38 mL/g indicating that it has a high capacity to retain phosphate. By comparison, Bassendean sand has a low phosphate retention capacity with a PRI of 2 mL/g.

5.1.4 Particle Size Distribution (PSD) and Neutralisation Value (NV)

When evaluating the neutralising capacity of any potential liming agent, it is very important to couple the neutralising value with the PSD as shown in Table 5-2 as this is used to determine the Effective Neutralising Value (ENV) (See Chapter 7.1.3).

Table 5-2. Particle size distribution and neutralisation values for Alkaloam®.

Sieve Range	% Weight in each Range	Neutralising Value
0.000 - 0.125mm	20.1	15.4
0.125 - 0.250mm	6.6	15.6
0.250 - 0.500mm	8.8	15.7
0.500 - 1.000mm	11.7	14.7
+1.000mm	52.7	14.2
Weighted Average	%	14.7
Bulk Analysis	%	14.5

The ENV for Alkaloam® is calculated to be a low 8 wt% based upon all the particles reacting. The ENV is too low for commercial soil pH remediation, but is a bonus when used as part of a soil ameliorant.

5.1.5 Environmental performance

By-products and soil ameliorants must meet both performance standards as well as any environmental guidelines. In Western Australia there were no direct guidelines for environmental assessment of a soil ameliorant, hence comparison was made against the only guidelines available; waste regulations.

5.1.5.1 Waste landfill assessment - Composition analysis

The composition analysis of Alkaloam® was performed by Bureau Veritas and is provided in Table 5-3. An internal standard bauxite sample (KH09) was included for assessment of batch results as well as for comparison to Alkaloam®. KH09 is a natural bauxite sample mined from the Darling Range in Western Australia.

Table 5-3. Metals composition of Alkaloam® and bauxite standard KH09.

Sample	UNITS	Alkaloam® (KH09)	Sample	UNITS	Alkaloam® (KH09)
Ag	ppm	-0.5	Na	%	5.11
Al	%	9.66	Nb	ppm	34
As	ppm	45	Nd	ppm	9.15
B	ppm	-20	Ni	ppm	14
Ba	ppm	305	Pb	ppm	600
Be	ppm	0.6	Pr	ppm	29
Bi	ppm	0.2	Rb	ppm	2.68
Ca	%	2.5	S	ppm	31.2
Cd	ppm	-0.5	Re	ppm	-0.1
Ce	ppm	55	Sb	ppm	3500
Co	ppm	10	Sc	ppm	1150
Cr	ppm	350	Se	ppm	0.4
Cs	ppm	0.7	Si	%	0.2
Cu	ppm	18	Sm	ppm	20
Dy	ppm	1.35	Sn	ppm	13
Er	ppm	0.75	Sr	ppm	-5
Eu	ppm	0.35	Ta	ppm	1.8
F	%	0.12	Tb	ppm	0.8
Fe	%	19.2	Te	ppm	7
Ga	ppm	104	Th	ppm	8
Gd	ppm	1.4	Ti	%	188
Ge	ppm	-20	Tl	ppm	42
Hf	ppm	21.4	Tm	ppm	1.6
Hg	ppb	40	U	ppm	2.3
Ho	ppm	0.26	V	ppm	0.24
In	ppm	0.26	W	ppm	0.1
K	%	0.65	Y	ppm	-0.2
La	ppm	16.2	Yb	ppm	-0.2
Li	ppm	11	Zn	ppm	177
Lu	ppm	0.14	Zr	ppm	160
Mg	%	0.25			
Mn	ppm	166			
Mo	ppm	27			
		10			

The compositional data for Alkaloam® was compared against the 1996 Department of Environment, Landfill Waste Classification and Waste Definition Guidelines (DOE, 1996) as shown in Table 5-4. These guidelines were used as there were no valid assessment criteria for by-products or soil ameliorants.

Table 5-4. Composition of Alkaloam® against Landfill Waste Classification 1996.

Assessment against DoE Landfill Waste Classification and Waste Definitions 1996 Guidelines						
By Total composition						
All results in ppm	Landfill Waste classification by composition (mg/kg)				1 ppm = 0.0001%	10 ppm = 0.001%
Element	Class I Inert Landfill	Class II Putrescible landfill	Class III Putrescible landfill	Class IV Secure Landfill	Alkaloam®	KH09
					ppm	ppm
Arsenic	14	14	140	1400	45	22
Beryllium	2	2	20	200	0.6	0.4
Cadmium	0.4	0.4	4	40	-0.5	-0.5
total Chromium	-	-	-	-	350	150
Chromium (VI)	10	10	100	1000		
Lead	2	2	20	200	29	15
Mercury	0.2	0.2	2	20	0.04	0.1
Molybdenum	10	10	100	1000	27	10
Nickel	4	4	40	4000	14	8
Selenium	2	2	20	200	10	-5
Silver	20	20	200	2000	-0.5	-0.5
Fluoride	300	300	3000	30000	0.12	0.05
Aluminium					9.66	18.7
Barium					305	158
Boron						
Cobalt					10	10
Copper					18	10
Manganese					166	92
Vanadium					520	335
Zinc					24	14

For this analysis, total chromium was analysed and not chromium (VI) due to cost.

For assessment, the total chromium is assessed as if it were chromium (VI).

Assessment of the compositional data against the DoE Landfill Waste Classification 1996 indicates that Alkaloam®, if considered a waste, would exceed the requirements for inert disposal and would require secure storage. As a result, a second assessment is required based on leaching of the material. This finding is in line with that found for the CSRP by Harris & Howard (2009).

5.1.5.2 Waste landfill assessment - ASLP leach analysis

An ASLP leach assessment was conducted at natural pH by Genalysis Laboratory Services. Due to an oversight, beryllium was missed from this and other ASLP analyses (analysed as a single batch). This was not considered a significant issue as the beryllium concentration in the Alkaloam® composition meets the criteria for inert fill as shown in Table 5-4. Beryllium leaching from Alkaloam® has previously

been reported to be within Inert Landfill classification by Harris and Howard (2009) and Attiwell (2013). Results are shown in Table 5-5.

Table 5-5. ASLP leaching of Alkaloam® against Landfill Waste Classification 1996.

Note “x” means below detection limit which was below inert classification.

By Leachable concentration					Alkaloam®
Element	Landfill Waste classification by leachable conc (mg/L)				Alkaloam®
All results in ppm	Class I Inert Landfill	Class II Putrescible landfill	Class III Putrescible landfill	Class IV Secure Landfill	Natural
Final pH					10.2
Arsenic	0.5	0.5	0.7	7	0.000
Beryllium	0.1	0.1	1	10	
Cadmium	0.1	0.1	0.2	2	x
Total Chromium	-	-	-	-	x
Chromium (VI)	0.5	0.5	5	50	
Lead	0.5	0.5	1	10	x
Mercury	0.01	0.01	0.1	1	x
Molybdenum	0.5	0.5	5	50	x
Nickel	0.2	0.2	2	20	x
Selenium	0.5	0.5	1	10	0.001
Silver	1	1	10	100	0.000
Fluoride	15	15	150	1500	x

In conclusion, Alkaloam® is classed as “Inert Landfill” based upon leachability. It is noted that samples of carbonated red mud from different sites have been classified as “Putrescuble Landfill” by Harris and Howard (2009). Both classifications demonstrate that the Alkaloam® does not require secure impoundment.

Further comprehensive assessment of Alkaloam® and its interaction with soils has been reported by Attiwell (2013) under this author’s supervision. This included method development for determination of nitrate leaching and evaluation of soils containing clay. Collaborative work is published independently (see publications). Attiwell (2013) reported Alkaloam® was an environmentally safe material with beneficial properties when utilised as a soil ameliorant.

5.1.5.3 Radiological assessment

The Earth’s crust contains Naturally Occurring Radioactive Materials (NORMs) and bauxite ores and residue are no exception. Hence it is important to assess Bayer process by-products for radionuclides to ensure that the concentrations of NORMs

present in these materials are considered safe. The radiological activity of Alkaloam® is compared below against State and National standards. For this assessment, the Specific Activity and the Total Activity were calculated from the compositional analysis of the radionuclides uranium, thorium and potassium as shown in Table 5-6.

Table 5-6. Composition and Specific Activity of radionuclides in Alkaloam® and bauxite standard KH09.

Specific Activity	U	Th	K	Th	U	K
	ppm	ppm	%	Bq/g	Bq/g	Bq/g
Alkaloam®	15.8	177	0.65	0.72	0.20	0.20
KH09	13.2	160	0.37	0.65	0.16	0.11

The ARPANSA National Directory for Radiation Protection (2011) states that a material can be exempt from radiological legislative control if the specific activity of the head-of-chain radionuclides (that is Th-232 and U-238) do not exceed 1 Bq/g and for K-40 do not exceed 100 Bq/g. As can be seen, the samples were well below these criteria and hence do not need to be controlled.

In addition, the Western Australia Radiation Safety Act regulations Western Australian Radiation Safety Act (1975 – 1979) and the Western Australia Radiation Safety (General) Regulations (1983 – 2003), state that a natural radioactive substance is exempt from radiological control if the activity of all progeny for a parent radionuclide (i.e. U 238 series and Th 232 series) does not exceed 30 Bq/g. Table 5-7 highlights that neither Alkaloam® nor the bauxite standard exceeded this criteria.

Table 5-7. Total Activity of Alkaloam® and bauxite samples.

Total Activity	Th	U	K	Total activity
	Bq/g	Bq/g	Bq/g	Bq/g
Alkaloam®	7.17	2.74	0.20	10.11
KH09	6.48	2.29	0.11	8.88

Alkaloam® did not exceed the state or national radiological criteria, hence it is concluded that Alkaloam® is exempt from radiological control.

5.1.5.4 Dangerous goods assessment

According to the Australian Code for the Transport of Dangerous Goods by Road and Rail (NTC, 2011), *Class 8 substances (corrosive substances) are substances which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport.*

The method of determination of severe damage is by exposure testing. *In the absence of human experience the grouping must be based on data obtained from experiments in accordance with OECD Guideline 404. (OECD Guidelines for testing of chemicals No. 404 “Acute Dermal Irritation/Corrosion” 1992).* (NTC, 2011).

For this thesis, these trials were not conducted. It is thought that Alkaloam® is unlikely to be classified as a dangerous good as it is a solid and the pH is kept below 10.5.

Testing is recommended prior to any possible commercialisation.

5.1.5.5 Controlled waste assessment

The Department of Environment and Conservation (DEC, 2004) defined controlled waste as any waste that cannot be disposed of as a Class I, II or III landfill site, as described by the DOE (1996) Landfill Waste Classifications. Alkaloam® was classified as Class I, hence is not a controlled waste.

5.1.5.6 Hazardous substance assessment

Work-safe Australia Standards (NOHSC:1008, 2004) defines a hazardous material as containing more than 0.5 wt% NaOH or a pH greater than 11.5. Alkaloam® has a pH less than 10.5 hence is not a hazardous substance.

5.1.5.7 Contaminated sites assessment

Guidelines for contaminated sites are provided by the Department of Environment and Conservation (DEC, 2010). Compositional assessment is made against Health Investigation Levels (HIL) and classification codes are listed below.

A: Standard residential with garden/accessible soil (home grown produce contributing less than 10 wt% of vegetable and fruit intake; no poultry); this category includes children's day-care centres, kindergartens, pre-schools and primary schools.

D: Residential with minimal opportunities for soil access; includes dwellings with fully or permanently paved yard space such as high rise apartments and flats.

E: Parks, recreational open space and playing fields, includes secondary schools.

F: Commercial/Industrial, includes premises such as shops and offices as well as factories and industrial sites.

Under this assessment criteria, Alkaloam® is classified HIL code D, while natural bauxite samples are classified as D and F (Table 5-8). However, when Alkaloam® is amended into soil at a rate of 20 t/ha, the HIL classification is reduced to class A.

Table 5-8. Health Investigation Level assessment of Alkaloam®.

Element	Health Investigation Levels (ppm)						
	A	D	E	F	Alkaloam®	Bauxite KH09	Bauxite KH10
Antimony	31	-	-	820	0.4	0.2	11.2
Arsenic	100	400	200	500	45	22	15
Barium	15000	-	-	190000	305	158	111
Beryllium	20	80	40	100	0.6	0.4	0.3
Boron	3000	12000	6000	15000	-20	-20	20
Cadmium	20	80	40	100	-0.5	-0.5	-0.5
Chromium III	120000	480000	240000	600000	350	150	150
Chromium VI	100	400	200	500	-	-	-
Cobalt	100	400	200	500	10	10	15
Copper	1000	4000	2000	5000	18	10	14
Lead	300	1200	600	1500	29	15	23
Manganese	1500	6000	3000	7500	166	92	100
Methyl Mercury	10	40	20	50	-	-	-
Mercury	15	60	30	75	40	100	70
Molybdenum	390	-	-	5100	27	10	7
Nickel	600	2400	600	3000	14	8	10
Tin	47000	-	-	610000	7	8	5
Vanadium	550	-	-	7200	520	335	275
Zinc	7000	28000	14000	35000	24	14	8

Ecological Investigation Levels (EIL) shown in Table 5-9 indicate that Alkaloam® and the standard bauxite samples have triggered the EILs. However, once ameliorated into soil, the values for Alkaloam® would be significantly lower and would not trigger the EIL's.

Table 5-9. Ecological Investigation Level assessment of Alkaloam®.

Ecological Investigation Levels (ppm)				
Element		Alkaloam®	Bauxite KH09	Bauxite KH10
Antimony	20	0.4	0.2	11.2
Arsenic	20	45	22	15
Barium	300	305	158	111
Cadmium	3	-0.5	-0.5	-0.5
Chromium III	400	350	150	150
Chromium VI	1	-	-	-
Cobalt	50	10	10	15
Copper	100	18	10	14
Lead	600	29	15	23
Manganese	500	166	92	100
Mercury	1	40	100	70
Molybdenum	40	27	10	7
Nickel	60	14	8	10
Tin	50	7	8	5
Vanadium	50	520	335	275
Zinc	200	24	14	8
Sulphur	600	3500	1150	700
Sulphate	2000	-		

5.1.5.8 Comparison of Alkaloam® against West Australian legislation

A quick review of some of the regulations and guidelines that could be applied to Alkaloam® is provided in Table 5-10, however, none of the regulations adequately provide a representative assessment for the use of by-products.

Table 5-10. Review of Alkaloam® against various regulations.

Regulation	Classification
WA Landfill Waste Classification	Landfill Classification I, Inert Landfill.
Radiological assessment	Does not require radionuclide control
Dangerous Good	Not likely
Controlled Waste	No (Not a liquid and landfill Class I)
Hazardous Substance	No (pH < 11.5.)
Contaminated sites HIL	Class D
Contaminated sites EIL	Triggers EIL

It is clear that Alkaloam® met various criteria for different regulations in agreement with the assessment made by Attiwell (2013). The biggest hurdle for Alkaloam® to be utilised as a genuine product, is that there are no formal criteria for assessment as a product, as reported by Harris (2007). Many fertilisers and other common household items fail these criteria, but are viewed as products and not a waste. Until Alkaloam® is recognised as a manufactured product derived from bauxite, it is unlikely to become a commercial commodity.

5.2 Carbonated red mud for iron production

The utilisation of fine bauxite residue for the production of iron and other metals has been described in chapter 2.2.1 and evaluated more recently within chapter 2.4.2. Both these investigations clearly demonstrated that enrichment of iron oxide in red mud would not achieve 50 wt% (i.e. 33 wt% as metal). Commercial grades of iron ore require a minimum of 50 wt% as iron metal indicating the economic gap that remains. During times of extreme shortage of iron ore supply, the grade may be lowered but not low enough or for long enough to encourage a long term capital investment.

Feedstock to iron ore furnaces typically require lump ore and grade control can be critical. Fine bauxite residue and even residue sand will require significant capital in order to allow even a 5 wt% bleed rate into the iron furnaces. This is a significant impediment to the business case.

In addition the impurities associated with red mud such as aluminium are significant penalty elements for iron production and cause downstream issues and product quality issues.

It is for these reasons that the author believes beneficiation of fine bauxite residue for iron production will probably never be achieved.

5.3 Carbonated red mud for Acid Sulphate Soil (ASS) remediation

Carbonated red mud has been shown to have a neutralisation capacity in addition to a soil amelioration potential (i.e. Alkaloom®). The neutralisation has been measured at 14.5% but a higher neutralisation can be achieved if the acid is very low in pH and the mineralogy of the residue is allowed to break down. The inducement for this application appears to be the large volume of red mud, its technical effectiveness and the equally large areas of ASS requiring remediation (E.g. Paradis *et al.* 2006).

There are advantages in using carbonated red mud for ASS remediation. The neutralisation media has many species such as sodium hydroxide, sodium carbonate, calcium carbonate, calcium oxide and tri-calcium aluminate. All these species exhibit buffering capacity and are likely to react at different rates.

In addition, the significant abundance of iron and aluminium oxides present surface active sites highly conducive to encouraging amorphous precipitated materials to transform into more ordered minerals with time. This would ensure that any mobile metal species within the ASS would be effectively bound and incorporated into a more geologically stable mineral. The converse is also true. Should the precipitated matrix be re-acidified within a short time (1-2 years), then there is significant likelihood that not only would the precipitated and captured species be dissolved, but that the core elements of the carbonated red mud may also be attacked releasing a variety of metals, predominately iron and aluminium.

While there are significant benefits in treating ASS with carbonated red mud, it is the low neutralising capacity that causes the greatest issue. The significant costs associated with transport will ensure that this product option cannot compete with agricultural lime agents of significantly higher neutralising capacity (>70%). The price of the product is often smaller than the transport cost to application sites. A similar analysis has been performed by Tuazon & Corder (2008) evaluating the life cycle of seawater neutralised red mud. While the neutralisation capacity is of lower energy and CO₂ output than lime, the transport impacts can be up to 24 times greater.

5.4 Alkaloam® for soil amelioration

The Centre for Sustainable Resource Processing (CSRP) under the Bauxite Residue Program established a project to evaluate soil amelioration and lime effect (Project 4A4 Alternative Lime Source Trial). The CSRP contracted the combined resources of the Department of Agriculture and Food Western Australia (DAFWA), the Centre for Eco-hydrology and the Chemistry Centre of Western Australia as the research providers. This author was the program manager and project sponsor. The five year project commenced prior to this thesis. A confidential report was issued by Clarendon *et al.* (2010) with some data reported by Attiwell (2013). This chapter summarises relevant data, discloses additional evidence and draws conclusions.

The study assessed lime agent performance on soil and plants of alternative materials such as Alkaloam® and Red Lime™. Three locations were assessed: Busselton (clover production of high rainfall with a sandy soil and a clay / loam soil), Merredin and Newdegate (both for crop production of low rainfall on sandy soil). During the trial period, the South West of Western Australia was impacted by drought and trial results were supplemented with glass house pot plant trials. The key findings were:

At the highest rate of application, Alkaloam® and Alcoa Lime Residue both worked as well or better, than crushed limestone and lime sand, in raising soil pH. The effect of liming was not seen until the second year after application and started to diminish by the third year for all tested ameliorants.

Metal analysis of pot trial plant tissue samples indicated that there were no deleterious effects on the plants from using lime residue or Alkaloam®. As with previous trials undertaken using Alkaloam®, there was an increase in total aluminium in the soil but no associated increase in exchangeable aluminium. Exchangeable aluminium levels were, in fact, reduced by all treatments.

*Soil sodium levels from Alkaloam® application remained in the soil profile for the three years of data at the Merredin location due to the very low rainfall over the trial period. Elsewhere, sodium quickly leached through the soil profile (Clarendon *et al.* 2010).*

This author has no further comment to be drawn from the data other than to note that anecdotally the Alkaloam® and Red Lime™ did out-perform other lime agents for plant growth response in the first year of the Busselton sandy field trial (Figures 5-2 and 5-3). This was observed with late rains causing a late boost in clover growth, after official harvesting had occurred. Unfortunately this impact was not statistically confirmed with subsequent glass house pot plant trials by DAFWA, highlighting the variability that can be observed in field applications. Clover and wheat crops are shown in Figures 5-4 and 5-5. Glass house conditions were performed with idealised rainfall resulting in all lime agents having significant opportunity to impact pH. In fact the ideal conditions even caused the nil or blank sample to grow very well, potentially masking any impacts.



Figure 5-2. Anecdotal evidence showing post-harvest growth of clover with significant seed set for Alkaloam® on sand soil site.



Figure 5-3. Site showing significant growth after first harvest for standard lime application. Note how growth has invaded the sampling site.



Figure 5-4. Second season clover on Busselton sandy and loam soils (DAFWA).



Figure 5-5. Second season wheat in Merredin and Newdegate soils (DAFWA)

These field trials successfully demonstrated that Alkaloam® is an alternative agricultural lime agent and allowed quantitative assessment of the pH elevating capacity. This, in addition to phosphate retention, improved soil wetting and water holding capacity highlight that Alkaloam® is a significant soil ameliorant, particularly for sandy soils.

At no point has Alkaloam® amendment been demonstrated to have negative impacts upon crop or clover production; it has been shown that the mild lime impact is as reactive as other agricultural agents. It is apparent that the use of Alkaloam® as a soil ameliorant is highly desirable. The proximity of Alkaloam® to degraded farmland soils of the Peel Harvey region should be seen as a remarkable opportunity.

Further progress in this area is unlikely to come from scientific endeavour. However, it is recommended that the embodied energy of Alkaloam® be calculated and compared to other ameliorants; to highlight the growing social benefit for its use.

5.5 Carbonated red mud in reactive barriers

The aim of this demonstration trial was to show that carbonated red mud could be used as the active core of a reactive barrier in a wet land environment. The aim of the reactive core was the removal of phosphate and other contaminants. The barrier was designed to allow slow flowing waters to pass through and be stripped of phosphate and heavy metals. Monitoring was to assess performance and to ensure minimal impact upon the local environment.

This project was initiated as part of the Centre for Sustainable Resource Processing (CSRP) under the Bauxite Residue Program, for which this author was the Program Manager. The project has run for several years but will wind up by December 2013. The Department of Agriculture and Food Western Australia (DAFWA) were contracted to monitor the reactive barrier performance (note some photographs provided by DAFWA). The Wallis Group Pty Ltd were contracted to design and construct the reactive barrier. The project was a collaborative effort between those listed below.

- SRP INTELLECTUAL PROPERTY LTD (SRPIPL)
- SRP MANAGEMENT LTD (SRPML)
- DEPARTMENT OF AGRICULTURE AND FOOD WA (DAFWA)
- ALCOA OF AUSTRALIA LIMITED (ALCOA)
- MAIN ROADS WESTERN AUSTRALIA (MRWA)
- SOUTHERN GATEWAY ALLIANCE(SGA)
- WALLIS GROUP PTY LTD
- PEEL HARVEY CATCHMENT COUNCIL (PHCC)
- CONSERVATION COUNCIL OF WESTERN AUSTRALIA (CCWA)

5.5.1 Barrier design

MRWA provided the constructed wetland at Mayfield in the road reserve site of the Perth to Bunbury Highway (Figures 5-6 and 5-7). Southern Gateway Alliance (SGA) were contracted to conduct the civil works including the wetland and an oil trap.



Figure 5-6. Wetland under construction; centre, shape of 8. (Google Earth)

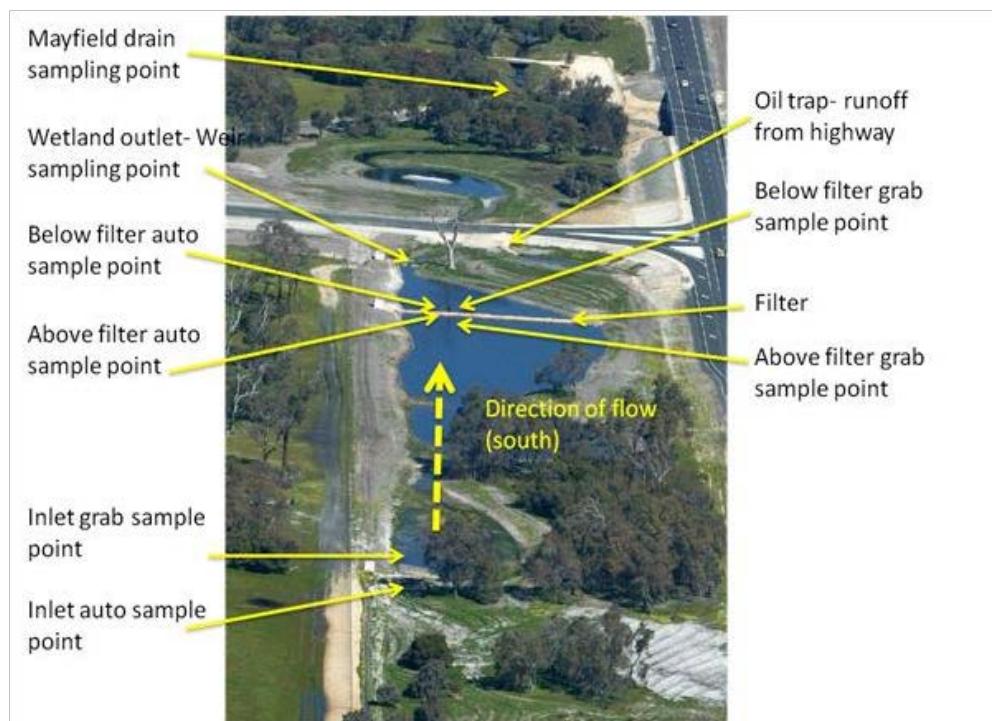


Figure 5-7. Overview of completed site and main structural elements (DAFWA).

5.5.2 Construction

Wallis Water Group were contracted to provide and install a Storm-max filter using red mud gypsum mixed with local sand. The construction progress was captured in Figures 5-8 to 5-10.



Figure 5-8. Construction of the Reactive barrier with cages in place (DAFWA).



Figure 5-9. Construction of the Reactive barrier with rock armour (DAFWA).



Figure 5-10. Construction of the Reactive barrier complete (DAFWA).

DAFWA were required to install and maintain a V-notch weir for level control (Figure 5-11), deployment of the sampling equipment, sampling and reporting on performance.



Figure 5-11. V notch weir used for control of water flow and level (DAFWA).

5.5.3 Field performance

A comprehensive water quality monitoring program was established based upon expected site flow directions according to Figure 5-12.

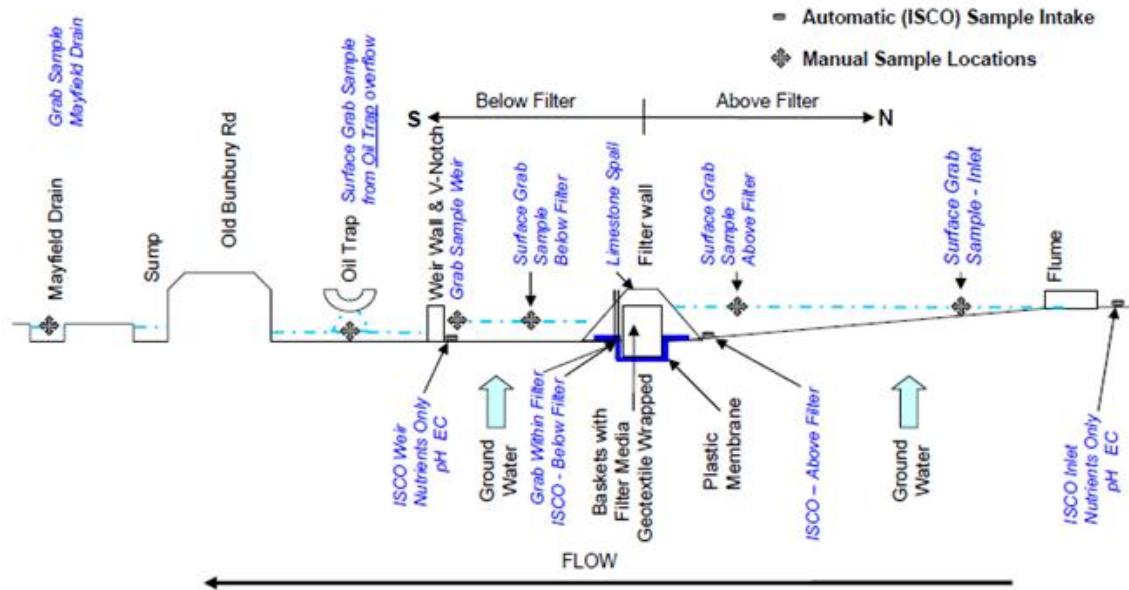


Figure 5-12. Site sampling cross section of reactive barrier (DAFWA).

Sampling of the site was conducted by DAFWA with the key assessments listed in Table 5-11. The Conservation Council of WA assisted with the coordination of project implementation and performance assessment.

Table 5-11. List of the required water assessments.

pH	Fluoride
EC	Iron
Total P, FRP	Lead
Total N, Nitrate	Manganese
Suspended solids	Mercury
TOC (Total Organic Carbon)	Molybdenum
Aluminium	Nickel
Arsenic	Selenium
Beryllium	Silver
Boron	Thorium
Cadmium	Tin
Chromium (total)	Uranium
Chromium (VI)	Vanadium
Cobalt	Zinc
Copper	

The project confidentiality agreement prevents results being published until the project is complete, however, approval has been received for these interim findings:

- The initial flush of water from the reactive barrier contained a slight elevation of some parameters including heavy metals, some attributed to the gypsum and others to the carbonated red mud. This occurred at the beginning of each wet season but concentrations decreased with each passing year.
- No release was at a level that would damage the local environment.
- The effectiveness of the barrier is masked by several field complications
 - The water flow through the barrier was lower than expected.
 - The freshly exposed sands of the artificial wet land were more reactive than expected.
 - A severe weather event inundated the wetland with mulch from the roadside.
 - Ground water ingress to both sides of the barrier made data evaluation difficult.

- Results from within the reactive barrier suggest the process is meeting requirements but a different implementation is recommended for further trials.
- Anaerobic conditions need to be avoided if possible as they can contribute to re-dissolution of some elements such as aluminium and phosphorus although relatively minor in effect.
- The reactive barrier did not appear to be clogged with iron oxyhydroxide precipitates suggesting the mixing of Alkaloam® with sand has improved long term permeability in line with observations reported by Lapointe *et al.* (2006).

A cross section of the reactive barrier under idealised performance is shown in Figure 5-13, while Figures 5-14 and 5-15 show the issues associated with significant ground water flow and nutrient bypass.

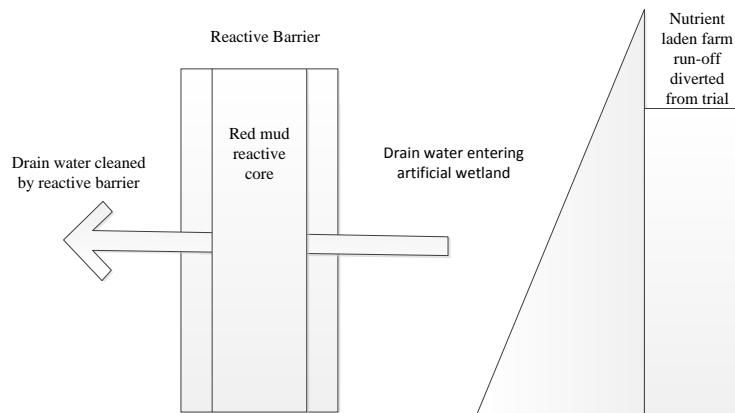


Figure 5-13. Representation of the expected key water flows.



Figure 5-14. Farm run-off diverted into the catchment (DAFWA).

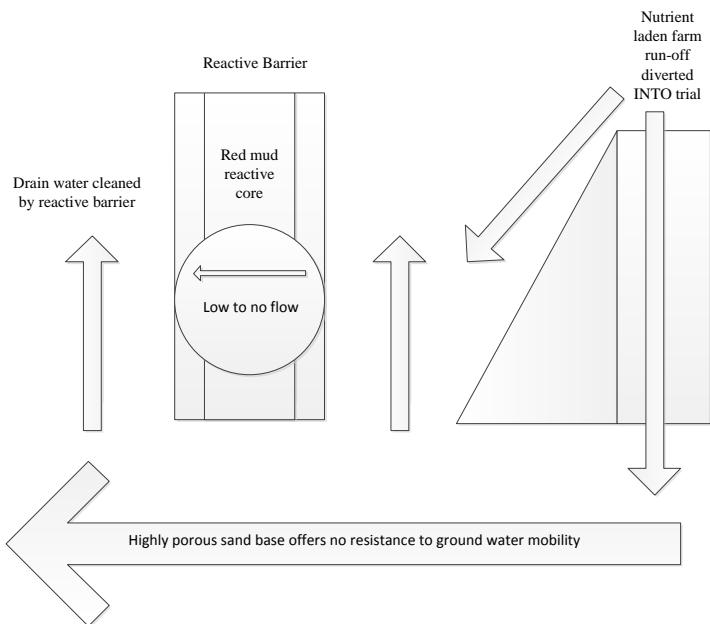


Figure 5-15. Representation of the actual water flows.

In conclusion the reactive barrier appeared to perform its task but design modifications are required for future trials (designed higher head pressure and modification to prevent ground water site contamination). In addition the reactivity of the freshly created wetland was high, resulting in the reactive barrier not being able to demonstrate the effective phosphate control. One option is to place the reactive barrier at the inflow to the new wetland allowing it to react with the high phosphate water. However, the more desirable outcome is to add carbonated red mud directly to the soil of the wetland during creation. This would ensure the reactivity of the wetland is not a temporary event and that ground water ingress would also be treated. This method of treatment would also significantly reduce the initial capital cost.

5.6 Conclusions on carbonated red mud /Alkaloam®

Over several decades, Alkaloam® has been independently demonstrated to be an effective safe product for a number of applications. It has the potential to be used to ameliorate poor quality or degraded soils, elevate pH and reduce phosphate leaching.

In summary,

- Alkaloam® is safe to use as a soil ameliorant. It is particularly beneficial when applied to sandy soils used for agriculture,
- Carbonated red mud appears to meet the requirements for reactive barriers of having a high phosphate retention index and the ability to remove metal contaminants from solution,
- Carbonated red mud/Alkaloam® does not exceed the state or national radiological criteria hence is exempt from radiological control,
- Carbonated red mud/Alkaloam® is not a controlled waste,
- There are potential markets for Alkaloam® as a soil ameliorant
- There are potential markets for carbonated red mud for remediation applications.

6 SAND

Coarse bauxite residue, or Red Sand™, is a significant by-product of the alumina industry.

By volume: Sand typically only represents 5 wt% of residue at most alumina refineries but those in Western Australia utilising Darling Range bauxite can have between 40-50 wt%. This is a result of the high quartz content of the ore body and the difficulty to grind all feedstock finely. Hence for Western Australia's refineries, sand is a significant volume representing up to 20,000 tones per day.

By Process: Sand is relatively easier to neutralise and wash, compared to red mud. It represents a lower level of technical challenge and will have a much lower Capex (Capital expenditure) and Opex (Operational expenditure).

By Market: Sand is a highly marketable commodity utilised frequently in construction and in significant volumes. It can also be stored indefinitely without degrading, providing a buffer from supply and demand cycles.

Following significant laboratory and bench scale evaluations (some of which are outlined in Chapter 2.6), a pilot plant was constructed at Alcoa's Wagerup refinery, as has been reported in Chapter 4.

6.1 Red Sand™ characterisation

This chapter presents a characterisation of the Wagerup pilot plant sand. The author was project manager and it is his interpretation of data. Data was collected from Alcoa Technology Group and external contract services.

6.1.1 XRD

The XRD pattern for Wagerup sand is shown in Figure 6-1 while Table 6-1 shows that quartz, hematite, gibbsite and goethite are the main mineral fractions for sand from each of Alcoa's three West Australian refineries.

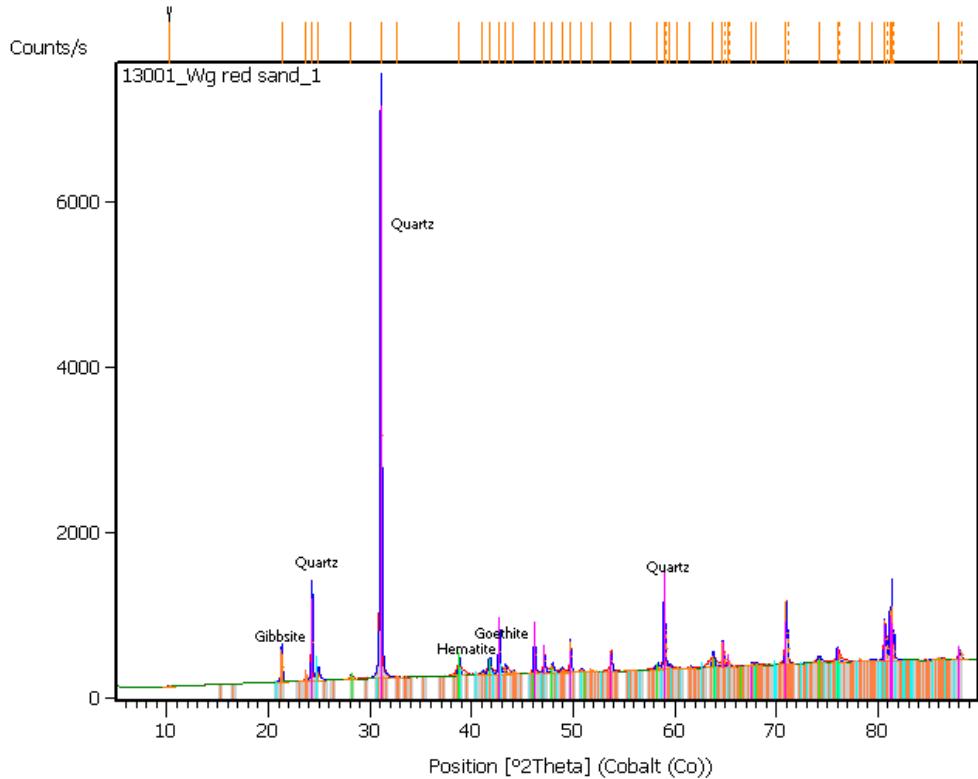


Figure 6-1. XRD of Red SandTM from the Wagerup pilot plant.

Table 6-1. Mineral components of Red SandTM from three refineries.

Red Sand ^(TM) from three Alcoa refineries			
Refinery	Major	Minor	Trace
Kwinana	Quartz	Gibbsite, Haematite, Goethite	Muscovite, Calcite, Gibbsite
Pinjarra	Quartz	Gibbsite, Haematite, Goethite	Muscovite, Gibbsite
Wagerup	Quartz	Gibbsite, Haematite, Goethite	Muscovite, Gibbsite

6.1.2 XRF

The XRF of Red SandTM (Table 6-2) is consistent with XRD with the predominant minerals being silicon, iron and aluminium oxides.

Table 6-2. XRF analysis of Carbonated Wagerup Red SandTM.

Oxides	
Al ₂ O ₃	10.60%
Fe ₂ O ₃	21.70%
Na ₂ O	0.35%
SiO ₂	59.00%
CaO	0.10%
TiO ₂	0.80%
Ga ₂ O ₃	0.01%
K ₂ O	0.04%
P ₂ O ₅	0.02%
SO ₃	0.06%
Total	92.68%

6.1.3 Microscopy

It is relatively easy to identify the mineral components of sand shown in Figure 6-2. Dark red particles are hematite, yellow are goethite, clear are quartz and white are calcite. These images are consistent with the mineralogy identified by XRD. The image also shows the angular nature of manufactured Red SandTM as was reported by Wahyuni *et al.* (2006) and Jones (2011).

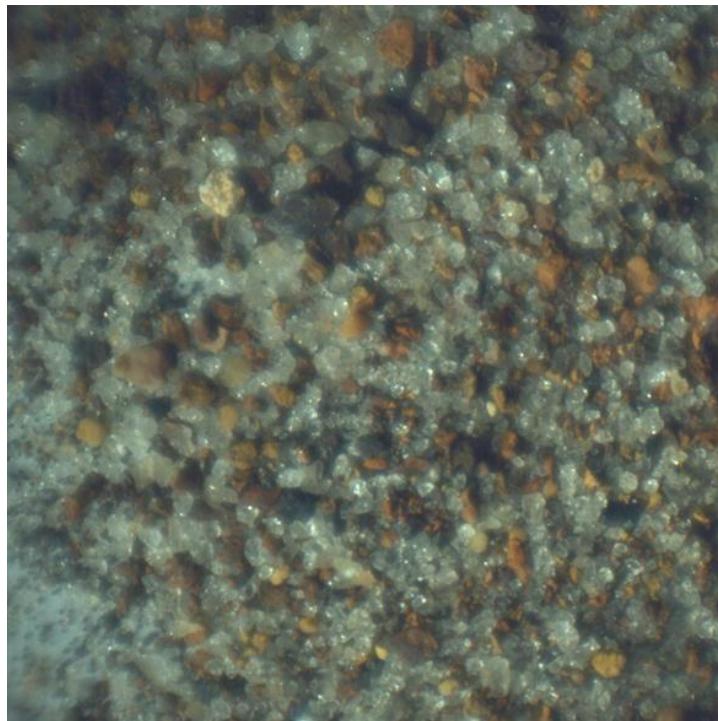


Figure 6-2. Microscope image of Wagerup pilot plant Red SandTM (Large particles are 1mm in diameter).

6.1.4 Residual Caustic and pH

The Red Sand™ from the Wagerup pilot plant has been assessed for residual caustic and the results listed below.

The Total Alkalinity was recorded at 0.14 g/L but this was carbonate and bicarbonate. No hydroxide was present. The sand pH was recorded at 10.2, but this was reduced to 8.9 when the sand was ameliorated with 0.25 wt% gypsum.

The conductivity was low at 0.34 mS/mL.

6.1.5 Phosphate Retention Index (PRI)

The PRI was recorded at a high 20 mL/g which is classed as “good”.

This is a relative term but is a significantly high result, making the sand well suited for phosphate retention and probably significant adsorption of other cations.

6.1.6 Particle Size Distribution (PSD)

The particle size distribution of Red Sand™ from three Alcoa of Australia refineries is shown in Figure 6-3.

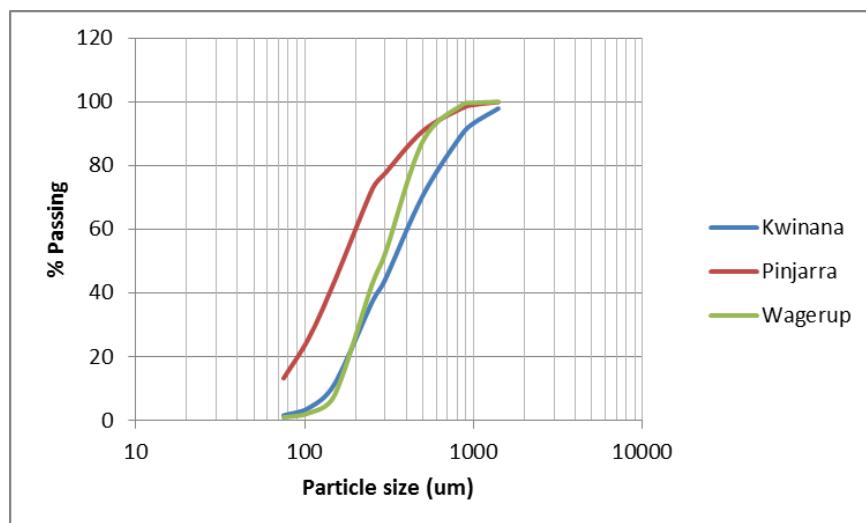


Figure 6-3. PSD of Red Sand™ from three Alcoa refineries.

6.1.7 Moisture content and density

The water holding capacity of soaked sand was between 5 and 7 wt%.

The free draining moisture content of the sand was 25 wt%, indicating a well-drained material.

The loose dry density was 1.4 g/cm³.

Tapping pack density was 1.5 g/cm³.

Optimal Dry Density (ODD) was 1.7 g/cm³ at optimal moisture content of 17.9 wt%.

The water displacement density was calculated to be 2.8 g/cm³.

The Helium Pycnometer density was 3.3 g/cm³.

6.1.8 California Bearing Ratio (CBR)

The CBR was determined on soaked and un-soaked samples by Main Roads Department Western Australian and also by WML consultants. A range of CBR results were recorded from 50 to 90%, expressed as a percentage of a standard crushed rock specimen. The low CBR was consistent with the results obtained by Jitsangiam (2007) and Jitsangiam & Nikraz (2013). However, through manipulation of sampling, sizing and washing, a different particle size distribution has been consistently obtained, having a CBR above 60%; the minimum standard for road base limestone is the South West Region of WA (Soaked CBR at 95% MMDD). From the chart shown in Figure 6-4, a thickness of 200 mm would ensure a long service life for any road made form a material of this CBR rating.

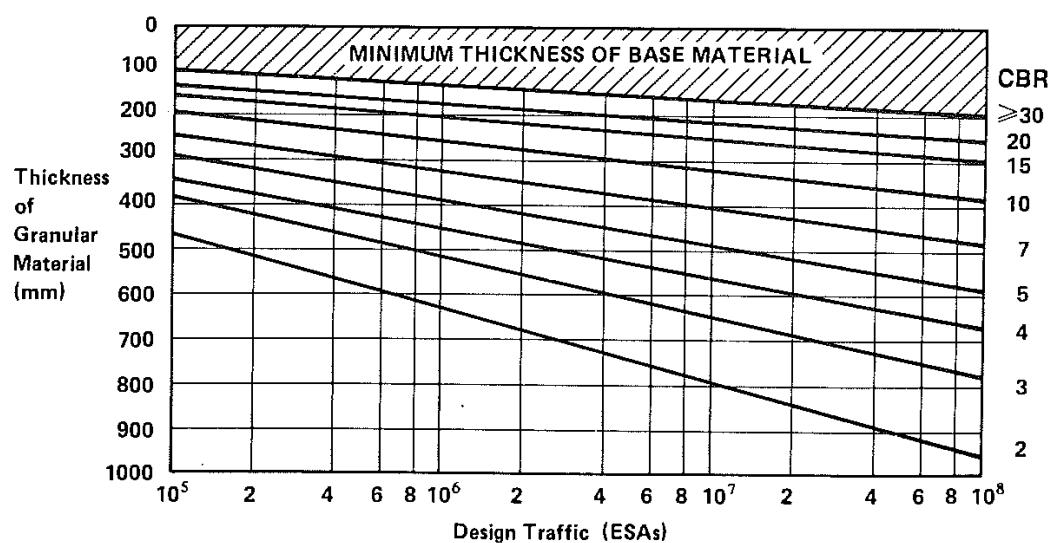


Figure 6-4. The Estimated Standard Axels (ESA) is a measure of the road use. The chart generally provides a 90% confidence of achieving a 25 year life (Hubner & Jameson, 2008).

6.1.9 Environmental performance

All proposed products need to meet both the performance standards as well as any environmental guidelines. In Western Australia there are no direct guidelines for by-products environmental assessment, hence comparison is made against the only guidelines available, waste classification.

6.1.9.1 Waste landfill assessment - Composition analysis

A compositional analysis of Red Sand™ is shown in Table 6-3. This was assessed against landfill waste guidelines.

Table 6-3. Composition analysis of Red Sand™ against Landfill Waste Classification.

Assessment against DoE Landfill Waste Classification and Waste Definitions 1996 Guidelines					
By Total composition					
All results in ppm	Landfill Waste classification by composition (mg/kg)				
Element	Class I Inert Landfill	Class II Putrescible landfill	Class III Putrescible landfill	Class IV Secure Landfill	Red Sand™ ppm
Arsenic	14	14	140	1400	6
Beryllium	2	2	20	200	1.1
Cadmium	0.4	0.4	4	40	-0.5
total Chromium	-	-	-	-	100
Chromium (VI)	10	10	100	1000	
Lead	2	2	20	200	18
Mercury	0.2	0.2	2	20	0.04
Molybdenum	10	10	100	1000	6.5
Nickel	4	4	40	4000	18
Selenium	2	2	20	200	-5
Silver	20	20	200	2000	-0.5
Fluoride	300	300	3000	30000	0.02
Aluminium					5.66
Barium					329
Boron					
Cobalt					
Copper					
Manganese					
Vanadium					
Zinc					

The compositional testing suggests that Red Sand™ does not require secure storage.

6.1.9.2 Waste landfill assessment ASLP leach analysis

Results for leach testing using ASLP are shown in Table 6-4. From this assessment all the trigger elements were shown to be within the Inert Landfill classification.

Table 6-4. Leach analysis of Red Sand™ against Landfill Waste Classification

By Leachable concentration					
Element	Landfill Waste classification by leachable conc (mg/L)				Red Sand™
All results in ppm	Class I Inert Landfill	Class II Putrescible landfill	Class III Putrescible landfill	Class IV Secure Landfill	Natural
Final pH					10.8
Arsenic	0.5	0.5	0.7	7	0.003
Beryllium	0.1	0.1	1	10	
Cadmium	0.1	0.1	0.2	2	X
Total Chromium	-	-	-	-	0.020
Chromium (VI)	0.5	0.5	5	50	
Lead	0.5	0.5	1	10	0.001
Mercury	0.01	0.01	0.1	1	X
Molybdenum	0.5	0.5	5	50	0.008
Nickel	0.2	0.2	2	20	X
Selenium	0.5	0.5	1	10	0.009
Silver	1	1	10	100	0.003
Fluoride	15	15	150	1500	2.100

Note that total chromium was analysed and not chromium (VI) due to cost, but was assessed as if all were chromium (VI). Also note that due to an oversight, beryllium leaching was not analysed. This is not a concern as beryllium did not require secure impoundment when assessed for total composition.

From this assessment it is concluded that Red Sand™ has passed the criteria for Inert Landfill Class I.

6.1.9.3 Radiological assessment

The ARPANSA National Directory for Radiation Protection (2011) states that a material can be exempt from radiological legislative control if the Specific Activity concentration of the head-of-chain radionuclides Th-232 and U-238 do not exceed 1 Bq/g and for K-40, do not exceed 100 Bq/g. The Specific Activity reported in Table 6-5 shows that Red Sand™ is below the criteria requiring control.

Table 6-5. Specific Activity of Red Sand™.

Specific Activity	U	Th	K	Th	U	K
	ppm	ppm	%	Bq/g	Bq/g	Bq/g
Red Sand™	9.4	112	0.26	0.45	0.12	0.08

The Western Australian Radiation Safety Act (1975 – 1979) and the Western Australian Radiation Safety (General) Regulations (1983 – 2003), are based upon the Total Activity. This is stated such that a natural radioactive substance is exempt from radiological control if the activity of all progeny for a parent radionuclide (i.e. U 238 series and Th 232 series) does not exceed 30Bq/g. Results for Total Activity shown in Table 6-6 demonstrate that Red SandTM is below criteria and does not need control.

Table 6-6. Total Activity of Red SandTM.

Total Activity	Th	U	K	Total activity
	Bq/g	Bq/g	Bq/g	Bq/g
Red Sand TM	4.54	1.63	0.08	6.25

6.1.9.4 Dangerous goods assessment

According to the Australian Code for the Transport of Dangerous Goods by Road and Rail (NTC, 2011), *Class 8 substances (corrosive substances) are substances which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport.*

The method of determination of severe damage is by exposure testing. *In the absence of human experience the grouping must be based on data obtained from experiments in accordance with OECD Guideline 404. (OECD Guidelines for testing of chemicals No. 404 “Acute Dermal Irritation/Corrosion” 1992).* (NTC, 2011).

For this thesis, these trials were not conducted. It is thought that Red SandTM is unlikely to be classified as a dangerous good as it is a solid and the pH is kept below 10.5 (pilot plant).

Testing is recommended prior to any possible commercialisation.

6.1.9.5 Controlled waste assessment

The Department of Environment and Conservation (DEC, 2004) defined controlled waste is as any waste that cannot be disposed of at a Class I, II or III landfill site, as described by the DOE (1996) Landfill Waste Classifications. Red Sand™ has been classified as Class I hence is not a controlled waste.

6.1.9.6 Hazardous substance assessment

Worksafe Australia Standards (NOHSC:1008, 2004) defines a hazardous a material as containing more than 0.5 wt % NaOH or a pH greater than 11.5. Red Sand™ has a pH of less than 11.5 hence is not a hazardous substance.

6.1.9.7 Contaminated sites assessment

Guidelines for contaminated sites are provided by the Department of Environment and Conservation (DEC, 2010); now called the Department of Environmental Regulation (DER). A compositional assessment is made against Health Investigation Levels in Table 6-7, where Red Sand™ was shown to be classed as level D, suitable for... *Residential with minimal opportunities for soil access; includes dwellings with fully or permanently paved yard space such as high rise apartments and flats* (DEC, 2010).

Table 6-7. Health Investigation Level assessment of Red Sand™.

Element	Health Investigation Levels (ppm)				Red Sand™
	A	D	E	F	
Antimony	31	-	-	820	-0.2
Arsenic	100	400	200	500	6
Barium	15000	-	-	190000	329
Beryllium	20	80	40	100	1.1
Boron	3000	12000	6000	15000	-0.5
Cadmium	20	80	40	100	-20
Chromium III	120000	480000	240000	600000	100
Chromium VI	100	400	200	500	-
Cobalt	100	400	200	500	15
Copper	1000	4000	2000	5000	8
Lead	300	1200	600	1500	18
Manganese	1500	6000	3000	7500	172
Methyl Mercury	10	40	20	50	-
Mercury	15	60	30	75	40
Molybdenum	390	-	-	5100	6.5
Nickel	600	2400	600	3000	18
Tin	47000	-	-	610000	3
Vanadium	550	-	-	7200	195
Zinc	7000	28000	14000	35000	30

From Table 6-8 it can be seen that Red Sand™ does trigger composition based Ecological Investigation Level. This means that further investigation is required.

Table 6-8. Ecological Investigation Level assessment of Red Sand™.

Ecological Investigation Levels (ppm)		
Element		Red Sand™
Antimony	20	-0.2
Arsenic	20	6
Barium	300	329
Cadmium	3	-0.5
Chromium III	400	100
Chromium VI	1	-
Cobalt	50	15
Copper	100	8
Lead	600	18
Manganese	500	172
Mercury	1	40
Molybdenum	40	6.5
Nickel	60	18
Tin	50	3
Vanadium	50	195
Zinc	200	30
Sulphur	600	450
Sulphate	2000	-

6.1.9.8 Comparison of Red Sand™ against West Australian legislation

Red Sand™ has had to be assessed against waste regulations as there are no directly applicable regulations in Western Australia to assess by-products for environmental impact. Table 6-9 is an assessment summary of those regulations and classifications.

Table 6-9. Evaluation of Red Sand™ against various regulations.

Regulation	Classification
WA Landfill Waste Classification	Landfill Classification I, Inert Landfill.
Radiological assessment	Does not require radionuclide control
Dangerous Good	Not likely
Controlled Waste	No (Not a liquid and landfill Class I)
Hazardous Substance	No ($\text{pH} < 11.5$)
Contaminated sites HIL	Classed as level D
Contaminated sites EIL	Triggers EILs

Red Sand™ would appear to be an inert material that has a high potential for applications as a construction material.

6.2 Red Sand™ in concrete.

An assessment of Wagerup pilot plant Red Sand™ was made for the application as fine aggregate in concrete. Wahyuni *et al.* (2006) has reported that manufactured sand (coarse bauxite residue) will cause rheological issues with concrete slump (a measure of wet concrete rheology). This is a common issue for recycled aggregates, as is bleeding rate and surface finish, but can be overcome by use of admixtures and blending with natural sand (CCAA, 2008; CCAA T60, 2008; CCAA, 2010). To counter the rheology problem, an investigation was made into the application of admixtures to modify the slurry rheology. In addition, sand blending and methods of sand “smoothing” were investigated. Parsons Brinckerhoff (PB) was commissioned to look at admixture use (subcontracted to BASF Technical Services Laboratory) and sand smoothing techniques (subcontracted to Amdel).

6.2.1 Admixtures and sand dilution

Three admixtures were investigated to cover the range of chemistry types. Polyheed 819, Pozzolith 370C and Rheomac VMA 362 were utilised at different dose rates to modify the impact of the angularity of Red Sand™. The results (not shown) indicated

that the high angular nature of the Red Sand™ caused issues with rheology and water bleed consistent with the results published Wahyuni *et al.* (2006). These issues were not able to be fully compensated for by using admixtures.

Red Sand™ was mixed with well-rounded local sand at rates of 20, 40, 60 and 80 wt%. A sand flow test was conducted (time to flow through a conical funnel) and the results shown in Table 6-10 clearly show the impact of Red Sand™.

Table 6-10. Assessment of sand blending.

Sand Mix	Average flow time (s)	Bulk Density Kg/m ³	% void
100% Virgin sand	20.2	1537	40.8
80% Virgin sand, 20% Red Sand™	20.7	1500	42.3
60% Virgin sand, 40% Red Sand™	21.2	1463	43.7
40% Virgin sand, 60% Red Sand™	21.7	1427	45.1
20% Virgin sand, 80% Red Sand™	22.5	1388	46.6
100% Red Sand™	23.1	1350	48.1

The bulk density was consistent with earlier work. The level of voids may be reduced with a wider particle size distribution, but this would not improve the friction.

It was concluded that Red Sand™ will not be able to replace fine aggregate in concrete without significant use of admixtures and the results would still be inferior for handling concrete compared to using virgin sand.

6.2.2 Red Sand™ modification

Attrition tests and angularity measurement were conducted by Amdel as service providers to the Parsons Brinckerhoff contract. Photographs and graphs were provided by Amdel.

Microscopy of Red Sand™ and natural sand highlight the differences in angularity and immediately explains why Red Sand™ has friction issues in Figure 6-5.

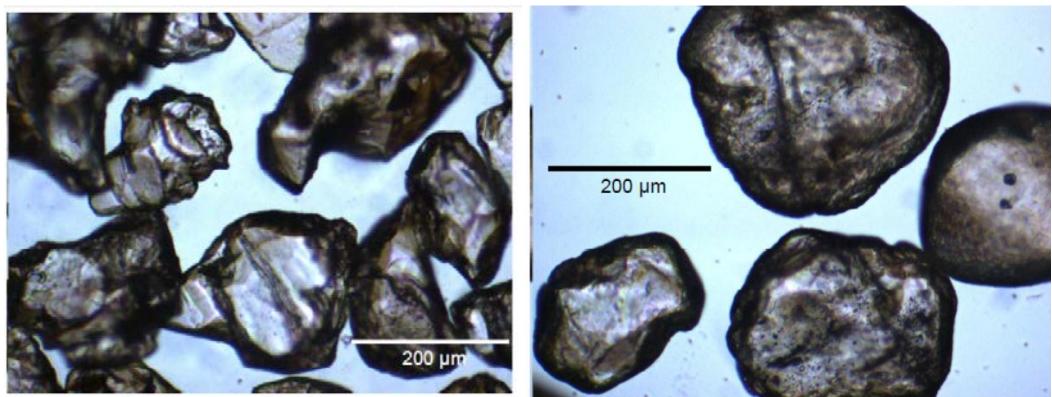


Figure 6-5. microscopy image of Red SandTM and normal sand (Amdel).

The Red SandTM was classified into three ratings of angular, semi-angular and round. A percentage was assigned, based upon microscopy and particle counting methods as shown in Figure 6-6.

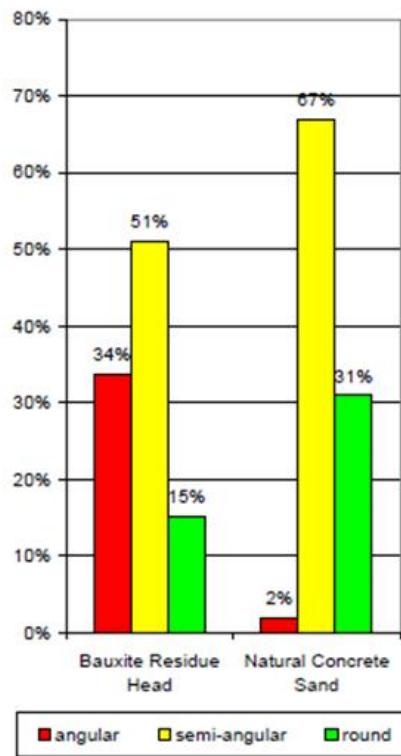


Figure 6-6. Angularity of Red SandTM and normal sand (Amdel).

Various attrition methods were then assessed to determine if the Red SandTM could be morphologically changed.

Red Sand™ was conditioned in a Denver attritioner at 50 wt% solids with two opposing propellers rotating at 1400 rpm over periods from 1, 5, 10 and 30 minutes. Results are shown Figure 6-7.

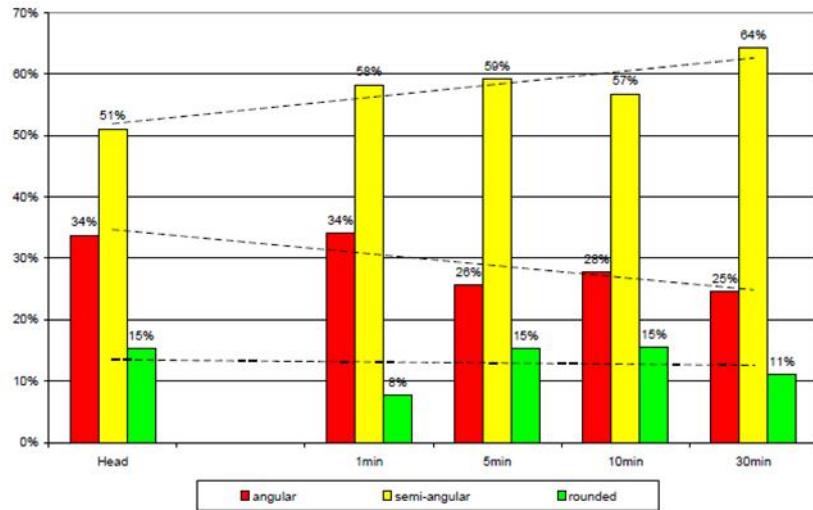


Figure 6-7. Attrition test results (Amdel).

Figure 6-7 shows that the attrition of Red Sand™ failed to increase the level of rounded material, but did slightly abrade the angular down to semi-angular.

Samples were subjected to a tumble mill at 70 rpm, with the mill operated at different solids loading, total revolutions and added media. Results are shown in Figures 6-8 and 6-9.

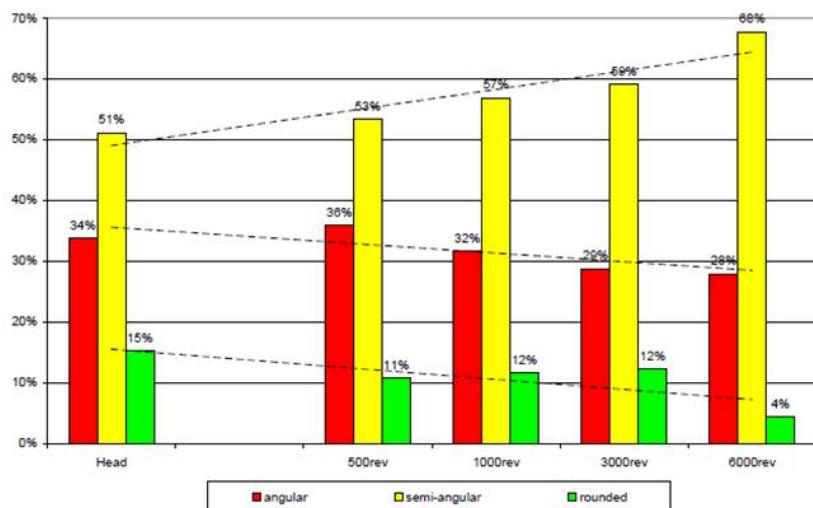


Figure 6-8. Tumble test without media results (Amdel).

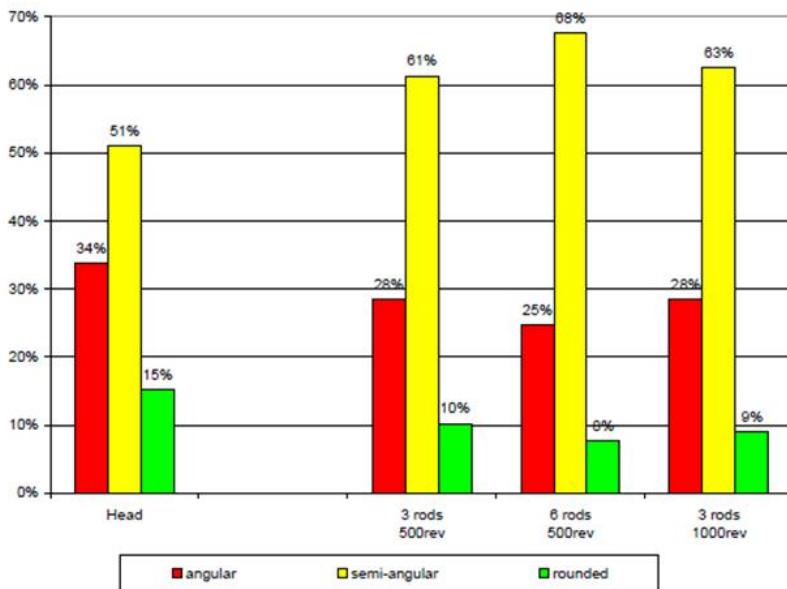


Figure 6-9. Tumble test with media (Amdel).

In both cases, with and without media, the tumble tests actually lowered the level of round particles but had some success at decreasing the percentage of angular particles.

Samples of Red Sand™ were subjected to a baffled bottle roll test and a drum scrubber test with opposing filters. The baffled bottle test was conducted at 50 wt% solids for 6000 total revolutions. The batch scrubber test used 55 wt% solids and the scrubber rotated at 24 rpm for 8 hours. Results are shown in Figure 6-10.

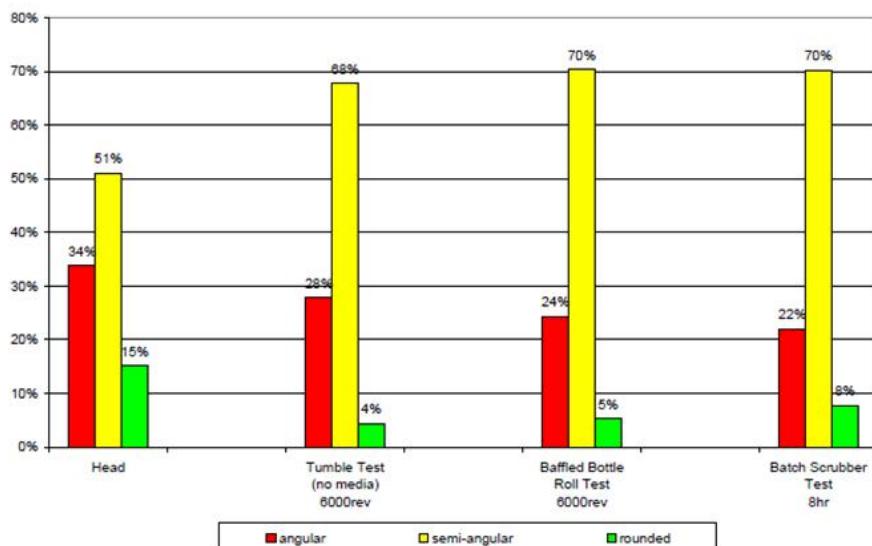


Figure 6-10. Tumble test, baffled bottle and batch scrubber test (Amdel).

These tests show that neither the baffled bottle test nor the scrubber testing successfully increased the level of rounded particles but did reduce the levels of angular sand.

Given the significant energy required to operate any of these particle shape modifiers and the marginal results achieved, it is unlikely that they would be employed to modify the character of Red Sand™.

Most telling are the results of the earlier experiments where even 20 wt% Red Sand™ added to rounded natural sand, still caused issues with concrete bleed and friction.

It is therefore concluded that Red Sand™ will probably not be utilised as fine aggregate in concrete manufacture while supplies of virgin sand remain plentiful.

6.3 Red Sand™ for top dressing – the Fairbridge oval assessment

This demonstration trial sought to show Red Sand could be used as clean fill (in this case top dressing) of the Fairbridge oval. The author was project manager. This project was commenced prior to this thesis but will continue even when the thesis is complete. Data supplied by contractors is quoted from source and interpretation is by this author. Dust monitoring and wind direction and speed were supplied by Ecotech under contract. The impact monitoring and assessment was contracted to MBS Environmental.

A large market for sand is the use as top dressing of lawn and turf. Red Sand™ has several qualities that make it highly desirable for top dressing of soil for turf growth.

- The sand has a high Phosphate Retention Index making it a suitable Phosphate retaining material. By absorbing soluble phosphate, the nutrients are prevented from rapid leaching and polluting of downstream environments. The Phosphate is also available for subsequent plant growth.

- The sand has a high angular nature allowing it to be compacted and not displaced preventing rut formation.
- The local environment contains high levels of gravel and the Red Sand™ provides better aesthetics.
- The sand being course in nature allows for rapid water mobility, allowing the field to drain freely.
- The sand is weed free.

Fairbridge Village is a historical site located 90 km South West of Perth in Western Australia. The village and oval are utilised for community events and the village management hoped to hold cricket matches on the oval. Unfortunately the oval was subject to drainage issues, was uneven and the cricket pitch was elevated with respect to the field. The field needed to be top dressed with a suitable material and Red Sand™ was proposed.

6.3.1 Top dressing site test

To ensure that the Red Sand™ was compatible with the existing turf (being a weed infested natural couch), trial areas were covered with sand at the appropriate depth. The sand was provided from the Wagerup sand pilot plant having a pH of less than 10.5 and a salt content of less than 0.2 g/L. As can be seen in Figures 6-11 to 6-15, the grass grew through the sand test site rapidly over a period of six weeks.



Figure 6-11. Red Sand™ trial application day.



Figure 6-12. Red Sand™ having been washed into grass after 2 weeks.



Figure 6-13. Red Sand™ after 3 weeks.



Figure 6-14. Red Sand™ after 5 weeks.



Figure 6-15. Red Sand™ after 6 weeks.

With no negative impacts observed, the trial was approved for full implementation. One recommendation was made that the sodicity (impact of sodium cations on soil structure) be improved by the addition of gypsum, which would also serve to lower the pH. This recommendation was incorporated into the trial.

6.3.2 Application

A weed eradication program was employed prior to sand application. Red Sand™ was spread over Fairbridge Oval to a depth of between 1 and 5 cm. The sand had been treated with gypsum and all-round fertiliser was applied to aid growth. Watering was employed during the summer periods. A total of about 1700 tonne of Red Sand™ was applied to Fairbridge oval as shown in Figures 6-16 to 6-19.



Figure 6-16. Red Sand™ collected from stockpile.



Figure 6-17. Red Sand™ delivered to site.



Figure 6-18. Red Sand™ being spread.



Figure 6-19. Red Sand™ being smoothed.

6.3.3 Performance

The assessment of this demonstration trial was centred upon the physical performance of the sand and the grass recovery, the dust impact and an environmental assessment.

6.3.3.1 Grass recovery

Grass recovery at Fairbridge Oval is shown in Figures 6-20 to 6-26.



Figure 6-20. Finished product with field now level with central cricket pitch.



Figure 6-21. Grass regrowth after 1 month.



Figure 6-22. Grass regrowth after 3 months.



Figure 6-23. Grass regrowth after 5 months.



Figure 6-24. Deep holes did not regrow after 5 months. Lawn seeding was recommended.



Figure 6-25. Grass regrowth after 12 months.



Figure 6-26. Grass regrowth after 18 months.

After 42 months, Fairbridge oval was in full use as a sports field. It was noted that the lawn showed signs of high wear and slow winter growth (Figure 6-27).



Figure 6-27. Grass regrowth after 42 months.

Clearly now the grass is in need of fertiliser for spring. It is very important to note the heavy wear areas are part of a baseball diamond but the sand has not moved and there is no rut formation. This is a significant benefit for Red Sand™ and can be attributed to the higher inter particle friction. This is the same property that made Red Sand™ not attractive for use in concrete, but is beneficial in this application.

A core sample shows good root development (Figure 6-28) into red, yellow and black sand, indicating no issue with the sand media



Figure 6-28. Grass root penetration.

Drainage issues were noted to have improved and this can be directly attributed to the high drainage rate of Red Sand™.

It is concluded that the use of Red Sand™ for levelling of the oval playing field was successful. As with all sporting venues, continued care with weed eradication and grass fertiliser application is required. The grass appeared to recover well from the

covering and root growth does not appear to be negatively impacted. Furthermore the sand appears to hold in place well with very heavy traffic. As such this trial was considered a technical success.

6.3.3.2 Dust generation

Dust generation was monitored by two Electronic Beta Attenuation Monitors (EBAM) supplied by Ecotech under contract (Figure 6-29). Wind direction and speed was also monitored as the area is prone to strong “gully” winds from the nearby escarpment. The wind is normally E-W and vise-versa hence the monitors were placed on the eastern and western boundaries of the oval.



Figure 6-29. EBAM air quality monitor.

The EBAM units measured the Total Suspended Particulates (TSP) and results are shown in Figure 6-30.

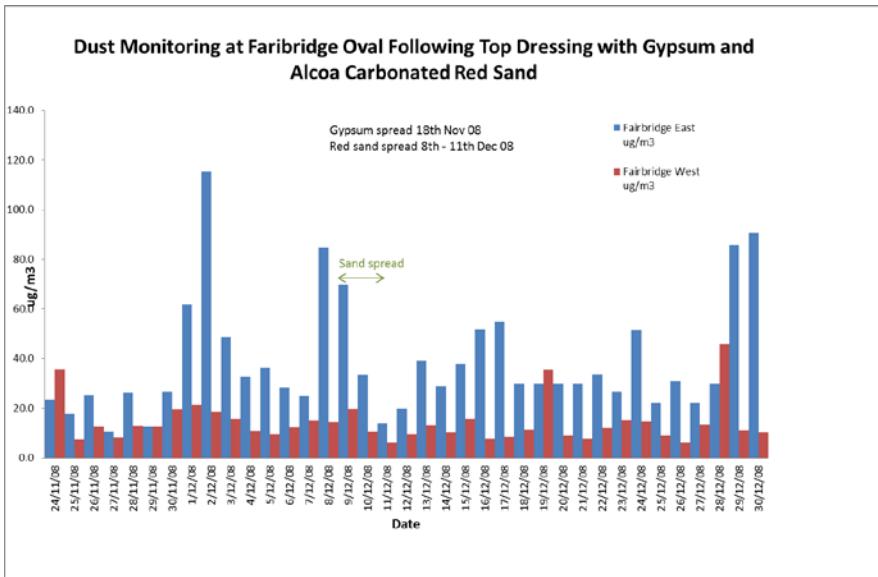


Figure 6-30. EBAM air quality monitor results (1 day TSP averages).

There are no national regulations for TSP, however, the Kwinana Industris Council (KIC) has a recommendation for TSP to be lower than $120\mu\text{g}/\text{m}^3$ while the Kwinana refinery licence has an operational limit of $90\mu\text{g}/\text{m}^3$. As can be seen the TSP did not exceed either of these guidelines. In fact the high dust events were shown to occur on days of very strong easterly winds with the first monitoring station (east) recording the dust blowing onto the site across open sand and gravel roads. On these occasions, the west side showed a reduction in the air borne dust, as it had settled onto the cricket field.

6.3.3.3 Environmental impact

Part of the trial was to confirm that there were no negative impacts upon the environment through the use of Red Sand™. MBS Environmental were contracted to monitor soil, turf and water quality during the trial.

A series of water quality, turf tissue and soil quality tests were conducted with the objectives of:

- Assess surface and drainage water for any impact;
- Assess any changes to the quality of the soil;
- Identify any turf deficiencies or toxicities resulting from the application.

This work was conducted over the first year following application and key sample points are shown in Figures 6-31 and 6-32.

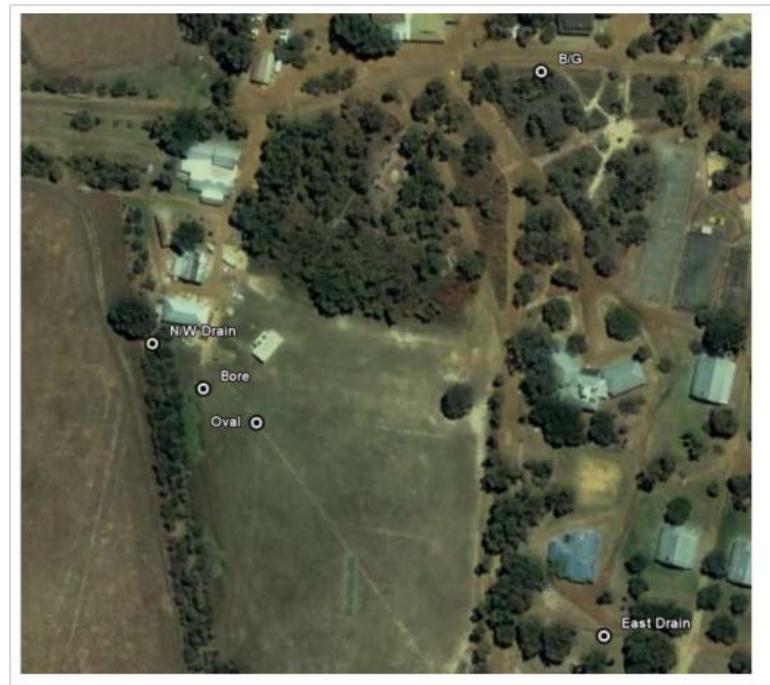


Figure 6-31. Photograph indicating water sampling sites (MBS).



Figure 6-32. Photograph indicating soil sampling sites (MBS).

The MBS Environmental report has been summarised and is reported below.

- Monitoring indicated no evidence of reduced run off water quality.
- Monitoring indicated no evidence of reduced sub-soil water quality.
- Aluminium in water did trigger 95% protection level for fresh water ecosystem, but the value was lower than the ambient site background.
- Copper and zinc in water also trigger 95% protection level for fresh water ecosystem, but were attributed to turf fertilizer.
- Insoluble chromium in soil triggered the Ecological Investigation Level (EIL) but was considered to be minimal environmental risk as it was not in the sub soil water. It is noted that the values found by MBS were higher than the Red Sand™ compositional analysis.
- Turf did not appear to suffer any adverse impact but required a modified fertiliser practice for sporting activities.

It is concluded that the application of Red Sand™ is well suited for turf management and clean fill.

The market for clean construction fill in the immediate vicinity of Kwinana refinery is in the range of 40 million tonnes. Bossilkov and Lund (2008) list the following potential construction projects in this area.

- *James Point Port, Stage 1 – 0.3 Mt fill and 3. Mt materials;*
- *Kwinana Quay Project – depending on the option to be chosen, 7-22.4 Mt fill and 3.6 – 4 Mt materials;*
- *Kerralup –0-10 Mt fill and 1 Mt road materials;*
- *Wungong Urban Water - 16.5 Mt fill and 0.4 Mt road materials;*
- *Latitude 32 and many other projects with unknown quantities for imported fill and construction materials.*

With limited supply sites in the area, the opportunity to supply these infrastructure markets is considerable.

6.4 Red Sand™ as iron ore

Bauxite residue sand, like residue mud, has high iron content in the range of 20 to 30 wt% as Fe₂O₃. This is much lower than low grade iron ore which is rated at about 50 wt% as Fe. However, residue sand has the option of being magnetically beneficiated. Evaluations of Low Intensity Magnetic Separation (LIMS) and Wet High Intensity Magnetic Separation (WHIMS) using residue sand have been reported by Davies *et al.* (2005) and Jamieson *et al.* (2006). While significant beneficiation was found, there are still significant hurdles for this technology.

One issue is the associated trace metals in bauxite residue would cause significant purity problems to blast furnace reduction of iron metal. Of particular concern would be the high residual alumina content as reported by Jones (2011).

Assessment of mineralogy within the sand grains has now been assessed by Quantitative Evaluation of Minerals by SCANning electron microscopy (QEMSCAN) and shown in Figure 6-33.

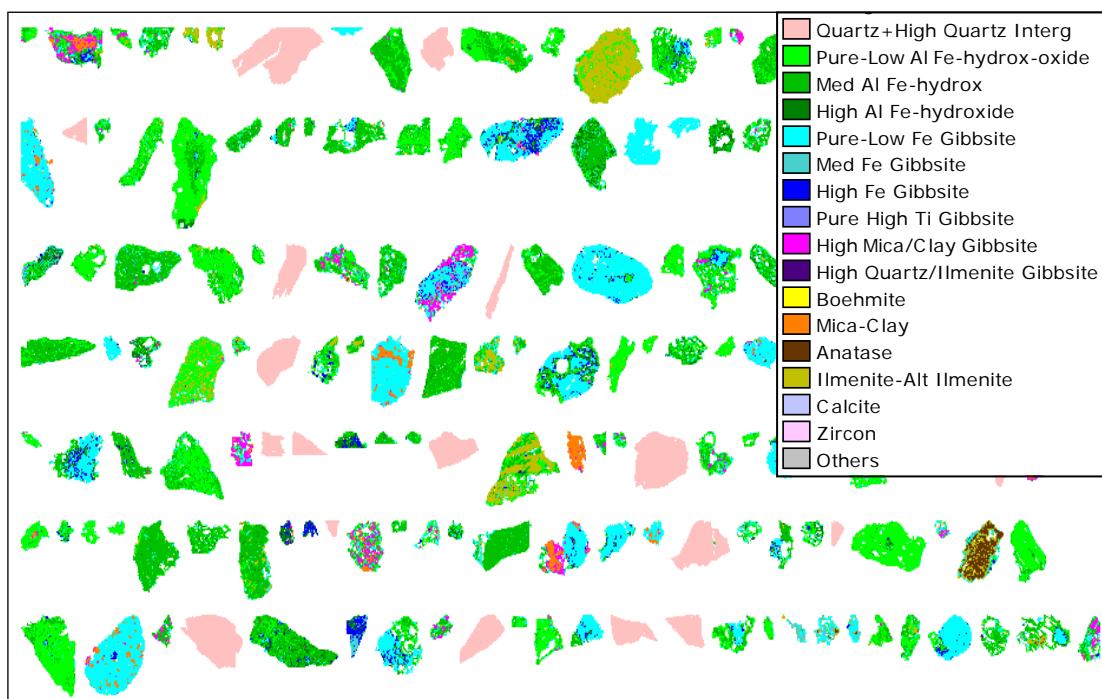


Figure 6-33. Mineral map of Kwinana Red Sand™ by QEMSCAN PSD 150-250µm.

This image highlights that iron oxides are not separate minerals within the bauxite residue and even though they can be beneficiated, there will always be a significant level of contaminant minerals that will be a problem for iron quality.

In conclusion, the beneficiation of Red Sand™ is possible using standard techniques and can produce a product close to low grade iron ore (63 wt% as Fe₂O₃ as reported by Jamieson *et al.* 2006). However, the loading of penalty elements such as aluminium is very high. There is also a need for capital equipment to bleed the fine ores into furnace feed (as described in the Alkaloam® review). This will result in the economics of processing Red Sand™ becoming uncompetitive in comparison to other low grade iron ores.

6.5 Red Sand™ in road construction trials.

Road construction uses volumes of sand as fill for road sub-base, sub-grade and embankments (note sub-grade is a road construction term and is not to be considered the same as inferior). To determine if Red Sand™ could be utilised in these areas, a project was set up within the CSRP, where this author was Program and Project Manager. Though the project started prior to the commencement of this thesis, results are reported and interpreted here for the first time and monitoring continues.

The project was to demonstrate the use of 2000 m³ of Red Sand™ in road construction as sub-grade. Several Stage Gate reviews were conducted within Alcoa and a risk assessment was contracted to GHD (2009). With these being successfully completed, a trial was proposed with Main Roads Department Western Australia (MRDWA) to use Red Sand™ as sub-grade material in the construction of a section of Greenlands Road, South of Pinjarra in Western Australia. Following successful application of the first trial a second trial utilising Red Sand™ as sub-base was proposed and constructed on the same carriageway.

Road construction was conducted by MRDWA utilising the services of Southern Road Services (SRS). The road performance was monitored by MRDWA through the service providers WML. The environmental performance was monitored by the Department of Agriculture and Food, Western Australia (DAFWA).

6.5.1 Road construction requirements.

Road construction is an expensive activity but can become more so if not conducted correctly. In Figure 6-34, the base, sub-base or sub-grade layers have displaced laterally allowing for plastic deformation and the resulting breakdown of the asphalt seal. With the next water inundation, surface adhesion and suction to tyres will rapidly degrade the surface and a pothole results. One predictive measure of road performance is the Californian Bearing Ratio (CBR) of the underlying base materials. The CBR has been utilised to predict the life expectancy of roads and has been developed into formation charts.



Figure 6-34. Road deformation and rutting.

6.5.2 Trial design

The planned trial was to utilise 2000 m³ of Red Sand™ as ‘sub-grade course’ in a section of Greenlands Road, South of Pinjarra. The road was to be widened and a trial section 670 metres in length, 6 metres in width and a thickness ranging from 200 to 400 mm was to utilise Red Sand™. Trial one utilised Red Sand™ as 200 mm of Sub Grade material. The second trial repeated trial one, but also utilised Red Sand™ for the Sub Base layer as shown in Figure 6-35.

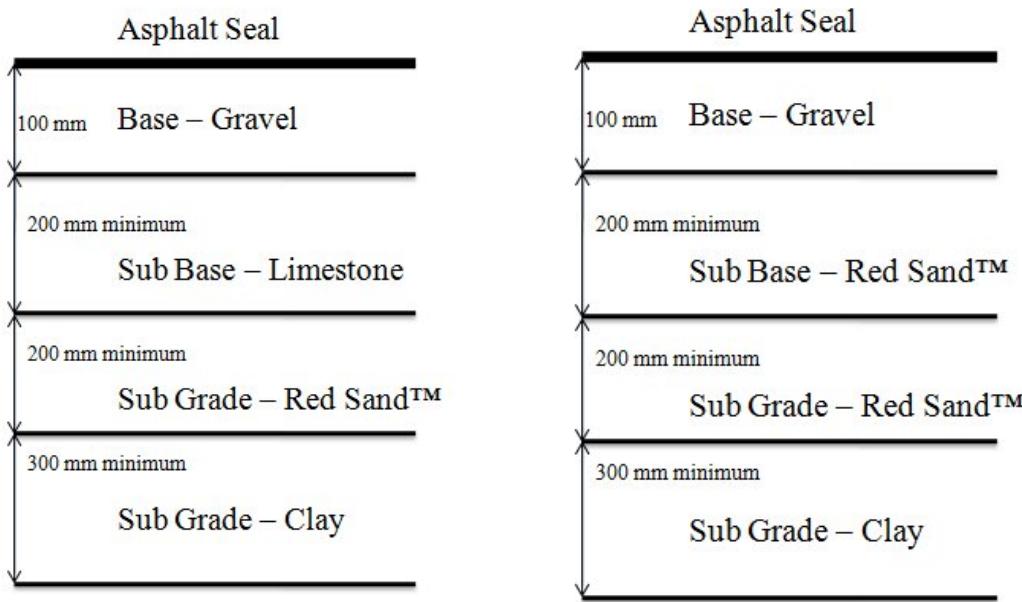


Figure 6-35. Road profile indicating use of Red SandTM in each of the two trials.

During construction, feedback from the construction crew supplied by Southern Road Services was very positive and included:

- Drainage of Red SandTM was very good. Wetting for compaction was both even and fast.
- Red SandTM required less preparation to allow heavy construction vehicle access. In some instances, a mere grading of the sand allowed truck access.
- Rolling and grading produced a smooth surface with a high degree of “polish”.
- Compacted sand did not deform under load.
- Compaction of red sand appears superior to traditional materials allowing a wider range of uses. Red SandTM can potentially be used in place of more expensive materials in the road profile.

It was this last point that allowed a second trial to be constructed close to the first where the Red SandTM was utilised as ‘sub-base’. The locations of the field trials are shown in Figure 6-36.



Figure 6-36. View of Greenlands Road showing proposed locations for trial 1 and trial 2 (MRDWA).

6.5.3 Application

The application of Red Sand™ to road construction is shown in Figures 6-37 to 6-40.



Figure 6-37. TDG Pilot Plant producing Red Sand™ for trials.



Figure 6-38. Delivery of Red Sand™ to Greenlands Road.



Figure 6-39. Demonstration of length of road and depth of Red Sand™.



Figure 6-40. Grading of Red SandTM.

Sub-grade materials are required to achieve 90% of their characteristic density, during compaction. Red SandTM achieved 96% compaction after 4 passes of a 12 tonne smooth drum roller which used low vibration cycle waves and a further 6 on high vibration cycle waves. Moisture content was measured at 80% of the saturation level.

Heavy vehicles are able to drive on Red SandTM with very little compaction compared to normal sand. Note in Figure 6-41 how quickly the water drained away behind the water tanker.



Figure 6-41. Soaking of Red SandTM.

A thin layer of yellow sand was used to cover the Red SandTM on advice by GHD to prevent any dusting (no dust was observed) and to remove any visible impact (Figure

6-42). Once covered with base-course gravel and bitumen, no sand would be visible. Hence this step is considered unnecessary.



Figure 6-42. On site with veneer of yellow sand covering Red Sand™.

The Department of Water WA stated that the road side drain was not a pristine receiving environment (Figure 6-43). This is an important consideration for environmental monitoring. One of the DAFWA trucks can be seen preparing to drill a monitoring bore in Figure 6-44, next to the field trial.



Figure 6-43. Road-side drains are the “receiving environment” for any leachate.



Figure 6-44. DAFWA drilling rig preparing to sink monitoring bore.

The second field trial required a thicker layer of Red Sand™ application and is shown in Figure 6-45.



Figure 6-45. Delivery of Red Sand™ on top of standard sub-base.

6.5.4 Road performance - compaction

WML Consultants and Southern Road Services provided the final density testing of the road trials, indicating that the Red Sand™ achieved a Modified Maximum Dry Density (MMDD) of 97%, which exceeds the minimum requirement of 94%.

Limestone used within the trial had a MMDD of 101% while the minimum requirement was 94%. These results show that the Red Sand™ could indeed replace the limestone in sub-base application.

The relative ease of compaction, the non-“bogging” nature and the ability to replace expensive limestone, make Red Sand™ very useful commodity for road construction. In addition, if Red Sand™ could be used in place of several layers, the road construction would become faster and costs would be reduced.

Determination of the particle size of supplied Red Sand™ was also compared to other sand products previously used for road construction. Figure 6-46 demonstrates that all the used sand sources fall within the black standard lines.

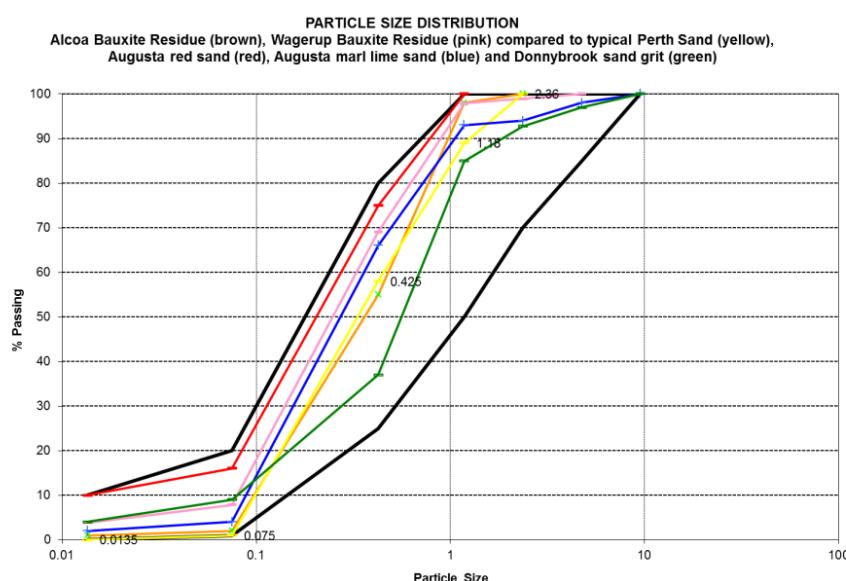


Figure 6-46. Particle size distribution for Red Sand™ and other sand sources that have been successfully used for road construction (WML consultants).

6.5.5 Road performance - pH dependence test

Samples of Red Sand™ were prepared for pH dependence leach testing in duplicate and the final pH accepted if the difference between 44 and 48 hours was less than 0.3 pH units (Table 6-11). Samples of the leach solutions were analysed (Table 6-12) and pH profiles constructed (Figure 6-47).

Table 6-11. Determination of final pH for Red Sand™ leach assessment.

Sample	Desired pH	pH					
		30 min	2 hrs	3.0 hrs	44 hrs	48 hrs centrifuged	Diff 48 to 44
1	12.0	13.06	12.35	12.87	13.10	13.25	0.16
2	12.0	13.00	12.45	12.95	13.07	13.17	0.10
3	10.0	11.32	10.72	11.16	10.98	11.09	0.11
4	10.0	11.32	10.79	11.19	11.07	11.12	0.05
5	9.0	11.06	10.56	10.16	10.07	10.09	0.01
6	9.0	11.13	10.67	10.22	10.10	10.12	0.03
7	8.0	10.84	10.28	8.73	9.79	9.76	-0.03
8	8.0	10.83	10.49	8.44	9.71	9.72	0.01
9	6.0	10.06	8.48	6.75	8.99	8.93	-0.06
10	6.0	9.97	8.58	6.63	8.85	8.87	0.02
11	4.0	6.83	5.52	4.31	6.60	6.46	-0.14
12	4.0	6.96	5.61	4.35	6.48	6.56	0.08
13	2.0	3.08	2.59	2.24	2.84	2.85	0.01
14	2.0	3.60	2.68	2.28	2.96	2.99	0.03
15	0.5	1.01	1.17	1.27	1.01	1.00	-0.01
16	0.5	0.85	1.09	0.89	0.90	0.96	0.06

Table 6-12. leach data at specific pH.

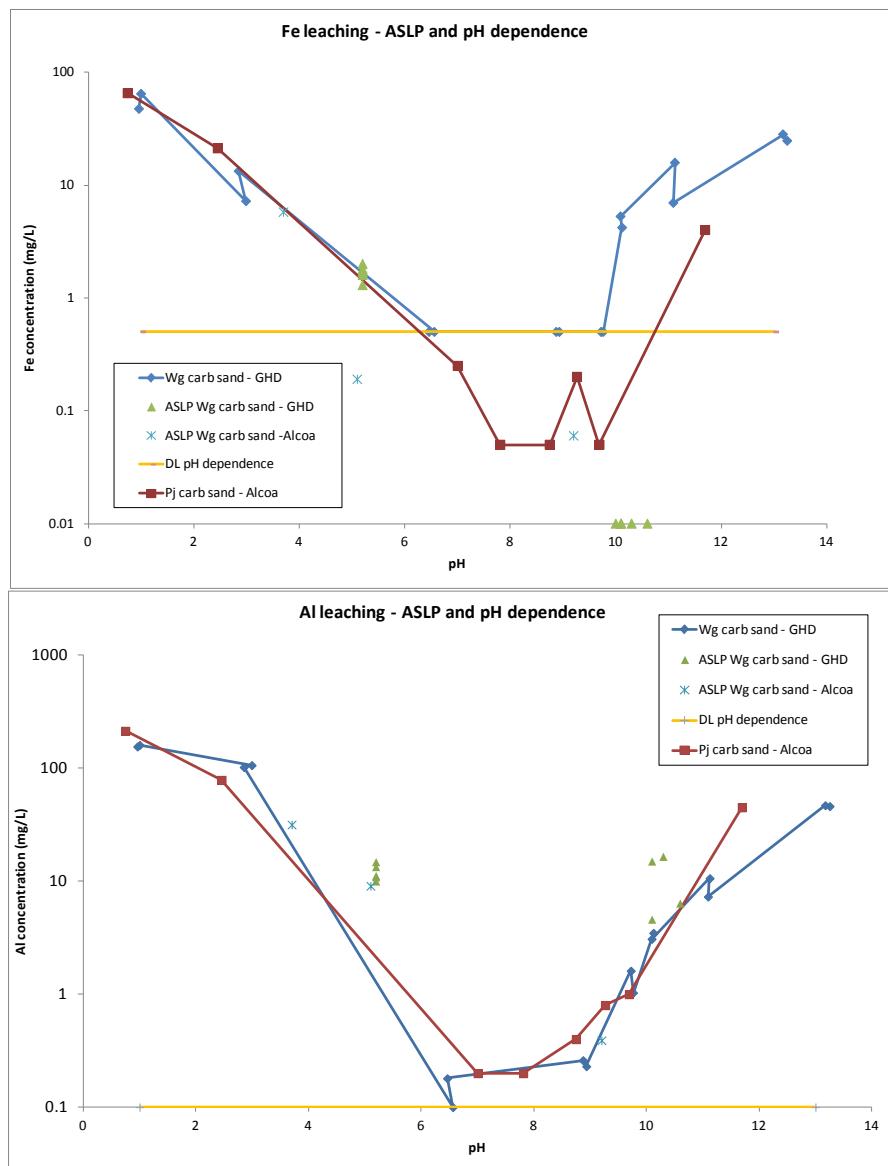


Figure 6-47. pH profile for the leaching of iron and aluminium from Red Sand™. The dark blue line is pilot plant sample pH profile, the orange line is the detection limit and the blue dots are pilot plant production samples.

Knowing the dissolution pH dependence curve is critical for application acceptance. For aluminium leaching, it is expected that there be a high dissolution at low pH (acid dissolution) as well as at high pH (basis of the Bayer extraction process). Hence controlling the pH of the product to below 10.5 not only removes the product from a hazardous rating, but also limits the level of leaching. If Red Sand™ were to encounter very low pH, then the aluminium would again begin to leach, however, it would be only one of many sources (most minerals and soils have an appreciable alumina content).

The pH dependence testing compares well with the ASLP leach assessment of Red Sand™ reported earlier. This indicates that the metals are at the concentration associated with the controlling mineralogy and the associated pH. While an expected outcome, it does ensure there will be a very low probability of anomalous results. Hence the production of Red Sand™ is likely to be a consistent product with standard quality assurance and quality control.

6.5.6 Road performance in situ – non destructive testing

WML Consultants were contracted to monitor the two Red Sand™ trials over a period of up to 5 years using techniques such as the Falling Weight Deflectometer (FWD). Initial results for Deflection and Curvature are described here and monitoring is expected to continue. The Deflection is the elastic deformation caused by standard vehicles at the point of contact. A high deflection would indicate a weak subgrade in the road and the likelihood of rutting increases. The Curvature is the difference in the deflection between the point of contact and a point 200 mm away. If this value is high, then the likelihood of rutting is also high because the load is not being distributed.

Greenlands Road was required by the Main Roads Department of West Australia to have a 40 year design life which can be expressed as a maximum Deflection and Curvature requirements as listed in Table 6-13.

Table 6-13. Falling Weight Deflection measurements on Greenland Road by WML
 (Location markers 2.18 to 2.78 SKL).

Greenlands Road 2.18 to 2.78 SLK Red Sand Trial Section - Year 1				
	95th percentile Deflection (mm)	Deflection Requirements	Mean Curvature (mm)	Curvature Requirements
Red sand shoulder	1.01	1.10	0.26	0.18
Red sand outer wheel path	0.84	1.10	0.21	0.18
Limestone shoulder	0.65	1.10	0.17	0.18
Limestone outer wheel path	0.59	1.10	0.16	0.18

Greenlands Road 2.18 to 2.78 SLK Red Sand Trial Section - Year 2				
	95th percentile Deflection (mm)	Deflection Requirements	Mean Curvature (mm)	Curvature Requirements
Red sand shoulder	0.94	1.10	0.26	0.18
Red sand outer wheel path	0.85	1.10	0.21	0.18
Limestone shoulder	0.65	1.10	0.18	0.18
Limestone outer wheel path	0.54	1.10	0.15	0.18

Greenlands Road 2.18 to 2.78 SLK Red Sand Trial Section - Year 3				
	95th percentile Deflection (mm)	Deflection Requirements	Mean Curvature (mm)	Curvature Requirements
Red sand shoulder	0.847	1.10	0.263	0.18
Red sand outer wheel path	0.806	1.10	0.238	0.18
Limestone shoulder	0.689	1.10	0.200	0.18
Limestone outer wheel path	0.660	1.10	0.167	0.18

Table 6-13 shows that Red Sand™ used for sub-base meets the requirements for Deflection, but not for Curvature. Limestone sub-base with Red Sand™ sub-grade meets both requirements.

While the results are of concern for failing to meet the curvature requirements, WML Consultants point out that similar roads constructed in Western Australia have actually had a poor correlation between the curvature and the roughness deterioration (road performance). Their experience has led them to suggest that Red Sand™ will still be shown to meet the performance criteria in situ, though only continued monitoring will confirm this.

It is concluded that Red Sand™ meets all criteria for embankment fill as well as for sub-grade in road construction. It is expected that the Red Sand™ will also be proven as a suitable sub-base material and that only a minimum design thickness of base course material is required in construction.

It is therefore recommended that Falling Weight Deflectometer be continued to be monitored at Greenlands Road for a period of 5 years or longer to determine if the Red Sand™ does in fact withstand load bearing as expected and that the Curvature is not a reliable indicator of roughness deterioration for this type of material.

6.5.7 Road performance in situ - environmental performance

The Department of Agriculture and Food Western Australia (DAFWA) was contracted to assess run off water quality from the Red Sand™ treated area and compare it to the run off from the normal road construction site (untreated). Bore sites for ground water and surface sites for surface water are indicated in Figure 6-48, provided by DAFWA.



Figure 6-48. Photograph showing the Red Sand™ was applied to the Southern side of the road and shoulder. Water flow direction is also indicated (DAFWA).

The key findings from Keipert and Summers (2009) (DAFWA) are below.

- *The only element that showed significantly ($P<0.05$) greater concentration in the runoff from the Red Sand™ treated road relative to the undisturbed control road was F which would be expected from a material derived from bauxite.*

- *The concentration of Co, Ni, Cr (total), B, Th, Pb, Cd, V, Al, Sn, Fe, Zn, Cu and Mn were all significantly ($P<0.05$) higher in the runoff from the untreated, undisturbed section of road. The concentrations of these elements were alarmingly high and in most cases above ANZECC levels. ...The origin of these toxic elements may be derived from the burning of fossil fuels (previously containing added lead) and from the abrasion of car tyres.*

Sampling and analysis has continued since this report but as results have made no impact upon findings, a new report has not been issued.

These findings indicate that Red Sand™ did incur a wash out of elevated (against background) pH and also of salts. However, the elevation of salts was below a statistical significance confidence level of $P<0.05$. The only exception was fluoride, where a modest elevation above background was found.

This is in contrast to the run off waters from the Northern half of the road construction site. This section of roadwork utilised virgin materials yet showed a significant level of metal leaching. The metals were assumed to come from car exhaust emissions that have settled on the central section of the road. Run off water would have passed through both shoulder road expansion sites. That is, the metals would also have flowed through the Red Sand™ extension as well as the normal sand extension. However, virgin sand has very little iron or aluminium oxides to bind metal species, whereas Red Sand™ contains a significant percentage of each (totalling about 30 wt%). This resulted in Red Sand™ scrubbing the runoff water clean, in accord with laboratory data.

It is concluded that Red Sand™ does not pose an environmental hazard in its use and actually acts as an in situ environmental filter system.

6.5.8 Conclusions for Red Sand™ in road construction

The use of recycled concrete and other building materials for road base has been investigated with increased vigour due to the shortage of natural materials and the

desire to achieve use of wasted products (Bowman and Associates 2009). It is within this environment that Red Sand™ has now been shown to meet the technical criteria for use as embankment fill and for use as sub-grade in road construction. Continued assessments will determine if it will also meet the requirements for use as sub-base in road construction.

Red Sand™ was well suited to this construction project and performed superiorly to virgin sand.

Composition and leach testing was confirmed by environmental field monitoring, that Red Sand™ had minimal impact upon the receiving environment and may have reduced runoff pollution.

During construction of the road trials, the potential for radical alteration of road construction became apparent. During normal construction, each layer of sub grade, sub base, base, etc, is layered sequentially and requires multiple passes of compaction and grading. However, the Red Sand™ could alter this process. If one sand could be utilised for all these grades, then the degree of layering and compaction is radically altered. Especially as the Red Sand™ appears to compact rapidly and can be driven on even after only minimal grading. The opportunity to reduce the cost of materials is large and the ability to increase construction speed is high.

Clearly there is a significant potential market that can benefit all parties and the environment at the same time.

6.6 Ecological footprint from use of Red Sand™

Red Sand™ was assessed for its sustainability through a contract placed with the CSRP utilising resources at the University of Queensland and the Sustainable Minerals Institute. The contract was to compare and contrast the sustainability measures for the use of Red Sand™ with the use of virgin quarry sand, for the production of road base material.

Two comparisons were made having a range of energy consumption values for the production of Red Sand™ and for virgin quarry material. For this thesis, only the more conservative comparison is reported. The report concluded that each tonne of Red Sand™ replacing virgin quarry sand for road construction as base would result in:

- *energy usage being reduced by up to 50%,*
- *greenhouse gas emissions being reduced in the range of 35 - 40%,*
- *residue volume being reduced by nearly 40%,*
- *land usage for quarrying/sand extraction being reduced by 0.5 – 1.0 m² per tonne of Red Sand™* (McLellan & Corder, 2010).

The report specifically left out the transport of the product to the final destinations because that would be different for each and every case. As such, a series of topographical envelopes could be drawn on location maps indicating areas of potential energy saving, greenhouse gas reduction and ultimately financial benefit.

With the introduction of a carbon tax, an argument could be made to simplify the concentric envelopes to just financial. That is, if the product can be delivered to site at a cheaper cost than virgin quarry sand, then it is likely that there will be an energy consumption reduction and a lower greenhouse gas emission. In addition there would be a reduction in residue storage volume and also a corresponding reduction in virgin quarry sand extraction. A summary assessment is shown in Figure 6-49.

A quick look at Figure 3-4 would indicate that the supply sites of Red Sand™ are ideally situated along the southern population growth corridor, in close proximity to proposed major infrastructure projects. In this same area, traditional sand quarries are rapidly diminishing and supply is relying upon increased haulage from distant sites (CCI, 2007).

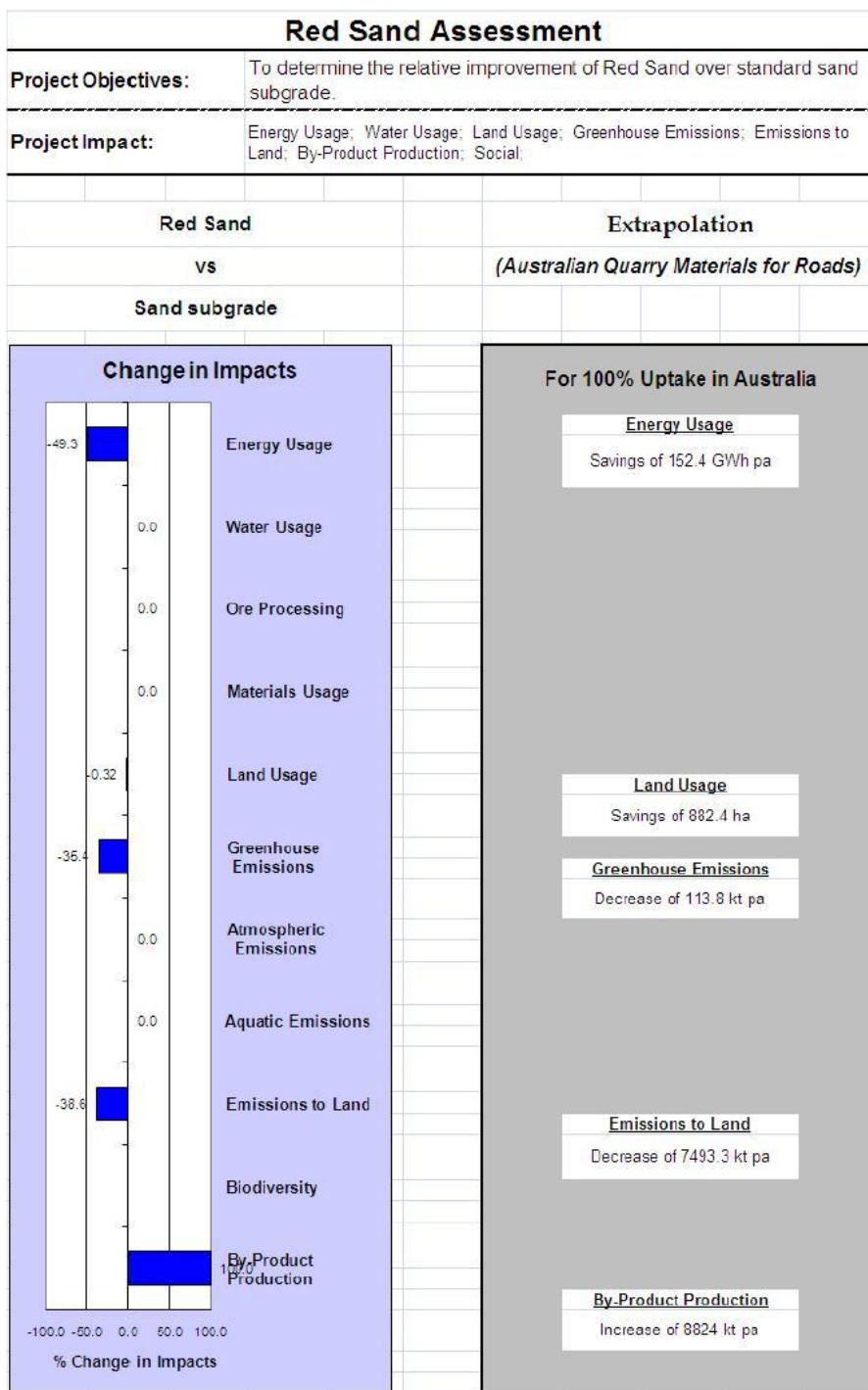


Figure 6-49. Sustainability impact assessment from McLellan & Corder (2010).

It is concluded that the use of Red Sand™ has many environmental benefits in addition to the product performance.

7.0 RED LIME™

Approximately 3-5 wt% of the 120 million tonnes of bauxite residue produced globally each year is fine lime residue. If this material were extracted and processed to approved specifications, then 3 to 6 million tonnes of lime products would become available to the commodities market that would have otherwise have been lost. In Western Australia alone, that figure could be close to 1 million tonnes annually.

7.1 Red Lime™ characterisation

A sample of Red Lime™ (Causticiser Product) was collected from Kwinana refinery for analysis. The following analysis shows the major components are calcium and aluminium as would be predicted through the causticisation process described in Chapter 4.4 using Equation 4.3.

7.1.1 XRD

XRD analysis of Red Lime™ shown in Figure 7-1, indicates that the major component was calcite, minor components were quartz and TCA6 (katoite), with a trace component of TCA monocarbonate. This is consistent with Equation 4.3 outlined in Chapter 4.4.

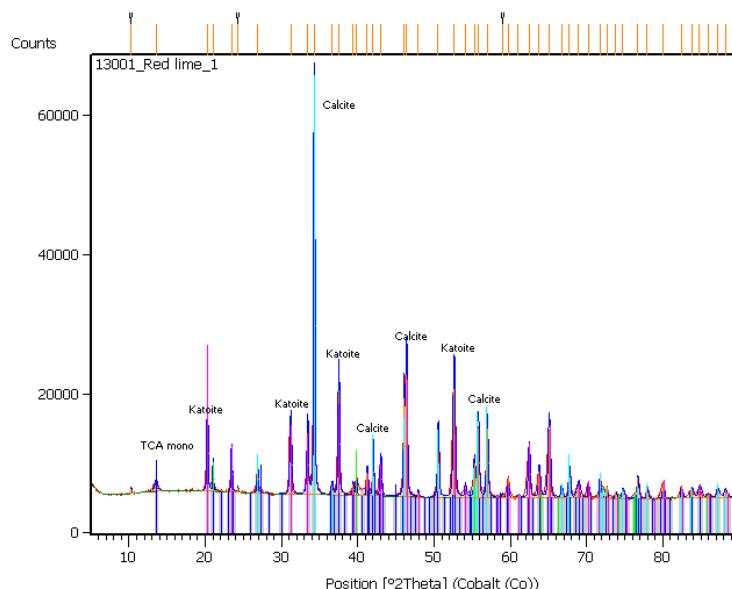


Figure 7-1. XRD analysis of Red Lime™ field sample.

7.1.2 XRF

The XRF analysis of Red Lime is listed in Table 7-1. The remaining material will include moisture, some organics and various anions associated with salts.

Table 7-1. XRF analysis of Red LimeTM field sample.

Red Lime TM	
Element	%
Al ₂ O ₃	14.7
Na ₂ O	1.5
SiO ₂	8.4
Fe ₂ O ₃	0.4
CaO	41.3
TiO ₂	0.0
K ₂ O	0.2
MgO	2.8
P ₂ O ₅	0.5
SO ₃	0.4
SrO	0.3
ZrO ₂	0.0
Total	70.6

7.1.3 Particle Size Distribution (PSD) and Neutralisation Value (NV)

A particle size distribution (PSD) is provided in Table 7-2 along with an evaluation of the neutralising value for field trial Red LimeTM. The high neutralising value and the fine PSD combine to make this a reactive material for pH control.

Table 7-2. Neutralisation value with particle size for Red LimeTM

Sieve Range	% Weight in each Range	Neutralising Value
0.000 - 0.125mm	26.0	76.6
0.125 - 0.250mm	38.7	69.5
0.250 - 0.500mm	19.0	72.7
0.500 - 1.000mm	7.2	72.8
+1.000mm	9.0	75.0
Weighted Average	%	72.6
Bulk Analysis	%	73.6

Using the PSD and the neutralisation values, the Effective Neutralisation Value (ENV) can be calculated using the Aglime of Australia web based calculator; utilising the methods approved by the Department of Agriculture and Food Western Australia. <http://www.aglime.com.au/liming-onlinelimecalculator.htm>. The ENV was determined to be a respectable 64%, given 20 wt% of the cake is still water (See TGA analysis).

7.1.4 Thermo-Gravimetric Analysis (TGA)

Thermo-gravimetric analysis shown in Table 7-3 is consistent with the formation reactions for Red Lime™. There is more TCA6 present by this analysis compared to XRD, but the XRD was not run for quantitative analysis.

Table 7-3. Thermo-Gravimetric Analysis (TGA) of field trial Red Lime™.

TCA monocarbonate	TCA6	CaCO ₃	Moisture
10%	35%	21%	20%

Each of these compounds (moisture excluded) is an effective neutralising agent providing the right environments. They also react at different rates creating a buffering effect.

7.1.5 Environmental assessment

Products need to meet both the performance standards as well as any environmental guidelines. In Western Australia there are no direct guidelines for by-products hence comparison was made against waste regulations.

7.1.5.1 Landfill waste assessment - Composition analysis

Composition analysis was performed by Bureau Veritas – Ultra Trace Pty Ltd and is shown below in Table 7.4. This data was used for comparison to the 1996 Department of Environment, Landfill Waste Classification and Waste Definition Guidelines (DOE, 1996) shown in Table 7-5.

Table 7-4. Composition of Red Lime™.

Sample	UNITS	Red Lime™	Sample	UNITS	Red Lime™
Ag	ppm	-0.5	Na	%	0.99
Al	%	7.38	Nb	ppm	5
As	ppm	151	Nd	ppm	14.9
B	ppm	-20	Ni	ppm	112
Ba	ppm	314	P	ppm	2250
Be	ppm	1.2	Pb	ppm	8
Bi	ppm	0.1	Pr	ppm	4.12
Ca	%	26.7	Rb	ppm	10.2
Cd	ppm	-0.5	Re	ppm	-0.1
Ce	ppm	35	S	ppm	1600
Co	ppm	10	Sb	ppm	-0.2
Cr	ppm	100	Sc	ppm	3
Cs	ppm	0.3	Se	ppm	5
Cu	ppm	6	Si	%	5.95
Dy	ppm	2.3	Sm	ppm	2.95
Er	ppm	1.3	Sn	ppm	23
Eu	ppm	0.6	Sr	ppm	2050
F	%	0.59	Ta	ppm	0.2
Fe	%	1.44	Tb	ppm	0.38
Ga	ppm	20.4	Te	ppm	-0.2
Gd	ppm	2.4	Th	ppm	13.6
Ge	ppm	-20	Ti	%	0.12
Hf	ppm	3.6	Tl	ppm	2.8
Hg	ppb	40	Tm	ppm	0.2
Ho	ppm	0.48	U	ppm	9.9
In	ppm	0.02	V	ppm	1460
K	%	0.17	W	ppm	13
La	ppm	18.3	Y	ppm	15.8
Li	ppm	4.5	Yb	ppm	1.9
Lu	ppm	0.18	Zn	ppm	40
Mg	%	1.53	Zr	ppm	292
Mn	ppm	80			
Mo	ppm	9			

Table 7-5. Composition of Red Lime against WADOE (1996).

Assessment against DoE Landfill Waste Classification and Waste Definitions 1996 Guidelines					
By Total composition					
All results in ppm	Landfill Waste classification by composition (mg/kg)				Red Lime™ ppm
	Inert Landfill	Putrescible landfill	Putrescible landfill	Secure Landfill	
Arsenic	14	14	140	1400	151
Beryllium	2	2	20	200	1.2
Cadmium	0.4	0.4	4	40	-0.5
total Chromium	-	-	-	-	100
Chromium (VI)	10	10	100	1000	
Lead	2	2	20	200	8
Mercury	0.2	0.2	2	20	0.04
Molybdenum	10	10	100	1000	9
Nickel	4	4	40	4000	112
Selenium	2	2	20	200	5
Silver	20	20	200	2000	-0.5
Fluoride	300	300	3000	30000	0.59
Aluminium					7.38
Barium					314
Boron					
Cobalt	5% by weight	5% by weight	10% by weight	20% by weight	10
Copper					6
Manganese					80
Vanadium					1460
Zinc					40

The compositional analysis indicates that arsenic, nickel and fluoride exceed the requirements for landfill and needs secure storage. These results are similar to the field trial sample of Red Lime™ utilised for soil remediation, where arsenic lead and fluoride were in excess of guidelines. Because the sample failed the compositional requirements, leach assessment was required.

7.1.5.2 Landfill waste assessment - Leach analysis

ASLP leach analysis was conducted at the material's natural pH by Genalysis Laboratory Services. A fresh sample of Red Lime™ was assessed and compared to the sample used for the field trials. This leach data was used for comparison to the Landfill Waste Classification Guidelines in Table 7-6.

Table7-6. Leach comparison of Red Lime™ against (DOE, 1996). (Natural pH).

By Leachable concentration					Red Lime™
Element	Landfill Waste classification by leachable conc (mg/L)				Natural pH
	Class I Inert Landfill	Class II Putrescible landfill	Class III Putrescible landfill	Class IV Secure Landfill	ppm
Final pH					12.5
Arsenic	0.5	0.5	0.7	7	0.226
Beryllium	0.1	0.1	1	10	
Cadmium	0.1	0.1	0.2	2	0.000
Total Chromium	-	-	-	-	0.010
Chromium (VI)	0.5	0.5	5	50	
Lead	0.5	0.5	1	10	x
Mercury	0.01	0.01	0.1	1	x
Molybdenum	0.5	0.5	5	50	1.264
Nickel	0.2	0.2	2	20	x
Selenium	0.5	0.5	1	10	0.760
Silver	1	1	10	100	0.226
Fluoride	15	15	150	1500	3.800

This data indicates that the Red Lime™ product meets the putrescible standard and does not need secure storage. In comparison, the field trial sample of Red Lime™ produced by the pilot plant and used for soil amelioration, met inert landfill criteria. This sample and the comparison are shown in Table 7-7.

Table 7-7. Field trial lime leaching against leach classifications (DOE, 1996).

element (mg/L)	WA ASLP Criteria - Upper Limits (mg/L)				Natural pH	(pH2.9)	(pH 5)
	Class I	Class II	Class III	Class IV	(mg/L)	(mg/L)	(mg/L)
	Inert Landfill	Putrescible landfill	Putrescible landfill	Secure Landfill	Inert Landfill	Inert Landfill	Inert Landfill
Final pH					12.4	10.1	12
Arsenic	0.5	0.5	0.7	7	0.018	0.005	0.006
Beryllium	0.1	0.1	1	10	<0.001	<0.001	<0.001
Cadmium	0.1	0.1	0.2	2	<0.0002	<0.0002	<0.0002
Chromium (VI)	0.5	0.5	5	50	<0.01	<0.01	<0.01
Lead	0.5	0.5	1	10	0.009	<0.005	<0.005
Mercury	0.01	0.01	0.1	1	<0.001	<0.001	<0.001
Molybdenum	0.5	0.5	5	50	0.0636	0.0604	0.0356
Nickel	0.2	0.2	2	20	0.03	<0.01	<0.01
Selenium	0.5	0.5	1	10	0.147	0.049	0.056
Silver	1	1	10	100	<0.0001	<0.0001	<0.0001
Fluoride	15	15	150	1500	3.6	0.5	0.8

The primary difference between the recent sample and the field trial material is the method of preparation. The field trial sample was manufactured and processed on a pilot plant that ensured good washing through an elutriation column. The laboratory prepared samples may have retained more selenium and molybdenum. Another explanation is that there has been an elevation of these elements in the lime utilised within the refinery. While the levels are higher than “Inert Landfill” status, they still fall well short of requiring secure storage. It should be noted that the Red Lime™ will be used in small doses over a large area, similar to a fertiliser application. It does however, emphasise the need for Quality Assurance (QA) and Quality Control (QC) and that by-products need to be made fit to purpose.

7.1.5.3 Radiological assessment

ARPANSA National Directory for Radiation Protection (2011) states that a material can be exempt from radiological legislative control if the Specific Activity concentration of the head-of-chain radionuclides Th-232 and U-238 do not exceed 1 Bq/g and K-40 does not exceed 100 Bq/g. As can be seen from the Table 7-8, Red Lime™ meets the criteria hence is exempt from radiological control.

Table 7-8. The Specific Activity for Red Lime™.

Specific Activity	U	Th	K	Th	U	K
	ppm	ppm	%	Bq/g	Bq/g	Bq/g
Red Lime™	9.9	13.6	0.17	0.06	0.12	0.05

The Western Australian Radiation Safety Act (1975 – 1979) and the Western Australian Radiation Safety (General) Regulations (1983 – 2003) state that a natural radioactive substance is exempt from radiological control if the activity of all progeny for a parent radionuclide (i.e. U 238 series and Th 232 series) does not exceed 30Bq/g. Results for Total Activity are shown in Table 7-9 and indicate that Red LimeTM meets the criteria for exemption.

Table 7-9. Total Activity of Red LimeTM

Total Activity	Th	U	K	Total activity
	Bq/g	Bq/g	Bq/g	Bq/g
Red Lime TM	0.55	1.72	0.05	2.32

7.1.5.4 Dangerous good assessment

According to the Australian Code for the Transport of Dangerous Goods by Road and Rail (NTC, 2011), *Class 8 substances (corrosive substances) are substances which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport.*

The method of determination of severe damage is by exposure testing. *In the absence of human experience the grouping must be based on data obtained from experiments in accordance with OECD Guideline 404. (OECD Guidelines for testing of chemicals No. 404 “Acute Dermal Irritation/Corrosion” 1992).* (NTC, 2011).

For this thesis, these trials were not conducted. Red LimeTM has a NaOH content of 1.57 wt% and the pH is 12.4 (Pilot plant) to 12.5 (laboratory grab sample). This suggests that Red LimeTM may be close to being classified as a dangerous good. Testing is recommended prior to any possible commercialisation.

7.1.5.5 Controlled waste assessment

The Department of Environment and Conservation (DEC, 2004) defined controlled waste is as any waste that cannot be disposed of as a Class I, II or III landfill site, as described by the DOE (1996) Landfill Waste Classifications. Red Lime™ has been classified as Class I (Pilot plant and field trial sample) or class III (laboratory grab sample). Hence Red Lime™ is not classified as a controlled waste.

7.1.5.6 Hazardous substance assessment

Worksafe Australia Standards ((NOHSC:1008, 2004) defines a hazardous a material as containing more than 0.5 wt% NaOH or a pH greater than 11.5. Red Lime™ contains 1.57 wt% NaOH, and has a pH higher than 11.5 hence is a hazardous substance under this criteria.

7.1.5.7 Contaminated sites assessment

Guidelines for contaminated sites are provided by the Department of Environment and Conservation (DEC, 2010). Compositional assessment is made against Health Investigation Levels (HIL) shown in Table 7-10, where the Red Lime™ is shown to be within class D, suitable for... *Residential with minimal opportunities for soil access; includes dwellings with fully or permanently paved yard space such as high rise apartments and flats* (DEC, 2010).

Table 7-10. Health Investigation Level assessment of Red Lime™.

Element	Health Investigation Levels (ppm)				Red Lime™
	A	D	E	F	
Antimony	31	-	-	820	-0.2
Arsenic	100	400	200	500	151
Barium	15000	-	-	190000	314
Beryllium	20	80	40	100	1.2
Boron	3000	12000	6000	15000	-20
Cadmium	20	80	40	100	-0.5
Chromium III	120000	480000	240000	600000	100
Chromium VI	100	400	200	500	
Cobalt	100	400	200	500	10
Copper	1000	4000	2000	5000	6
Lead	300	1200	600	1500	8
Manganese	1500	6000	3000	7500	80
Methyl Mercury	10	40	20	50	-
Mercury	15	60	30	75	0.04
Molybdenum	390	-	-	5100	9
Nickel	600	2400	600	3000	112
Tin	47000	-	-	610000	23
Vanadium	550	-	-	7200	1460
Zinc	7000	28000	14000	35000	292

The compositional data is also assessed against the Ecological Investigation Levels (EILs) as shown in Table 7-11. There it can be seen that Red Lime triggers EILs.

Table 7-11. Ecological Investigation Level assessment of Red Lime™.

Ecological Investigation Levels (ppm)		
Element		Red Lime™
Antimony	20	-0.2
Arsenic	20	151
Barium	300	314
Cadmium	3	-0.5
Chromium III	400	100
Chromium VI	1	-
Cobalt	50	10
Copper	100	6
Lead	600	8
Manganese	500	80
Mercury	1	0.04
Molybdenum	40	9
Nickel	60	112
Tin	50	23
Vanadium	50	1460
Zinc	200	292
Sulphur	600	1600
Sulphate	2000	-

It should be pointed out that these assessments are on the pure product and not on the product application. That is, once applied as a soil pH amendment, the level of various elements would diminish below EILs. This is the same effect as any agricultural fertiliser.

7.1.5.7 Comparison of Red LimeTM against West Australian legislation

The characterisation of Red LimeTM suggests it to be a commodity product of intrinsic value for the modification of pH. There is scope for manufacture of the by-product to ensure it meets all environmental criteria and can also be excluded from dangerous goods classification depending on preparation processes (Table 7-12).

Table 7-12. Regulatory evaluation of Red LimeTM.

Regulation	Classification
WA Landfill Waste Classification	Landfill Class I or III, but does not require secure landfill
Radiological assessment	Does not require radionuclide control
Dangerous Good	Possible
Controlled Waste	No (Not a liquid and landfill Class I- III)
Hazardous Substance	Yes (pH > 11.5.)
Contaminated sites HIL	Class D
Contaminated sites EIL	Red Lime triggers EILs

7.2 Red LimeTM in cement manufacture

The manufacture of Ordinary Portland Cement (OPC) requires the high temperature calcination of a variety of products to provide a specific combination of metal oxide species that react with water to form a binding agent. Typically the required ingredients are calcium, aluminium and some iron. This would seem to make Red LimeTM an ideal feedstock and could replace the current consumption of bauxite.

This desk top evaluation involved the comparison of commercially sensitive data. However, it is sufficient to state that Red LimeTM met all criteria except for two elements. They were sodium and arsenic.

In an effort to reduce the sodium content, a series of experiments were conducted on various filtration and washing techniques. It was found that any filtration method

with a wash cycle would lower the sodium to a suitable level. Alternatively a pressure filtration system could also achieve the desired requirements.

Arsenic has been shown above in Table 5.2 to pass environmental leach assessment criteria. It is the very fact that the arsenic is unavailable to leaching that prevents any product washing from removing it. Hence it is unable to be lowered for use in OPC manufacture. Nevertheless, the levels of arsenic are not excessive and careful feedstock selection could still allow Red LimeTM to be utilised.

A desk top assessment of Red LimeTM has shown that with some additional processing, it could be part of the production feedstock for OPC manufacture. However, the market economics are tight for OPC and a new feedstock would require additional holding bins and a drying circuit. The additional capital and operational expense make Red LimeTM uncompetitive at this time. As other feedstocks become more expensive, it is possible that Red LimeTM would become more competitive; however, it is likely other higher value options for the lime would also be available.

7.3 Red LimeTM for soil amelioration

Red LimeTM has potential to become a commercial product for treatment of acid sulphate soils and for soil remediation. The Centre for Sustainable Resource Processing (CSRP) conducted a five-year field trial into the use of Red LimeTM as a soil ameliorant. The project was designated “4A4 -Alternative Lime Source Trial” and was conducted using the combined research providers of the Department of Agriculture and Food Western Australia, the Centre for Eco-hydrology and the Chemistry Centre of Western Australia. These trials were conducted in several locations within Western Australia on sandy and clay soils, used for animal grazing or for cereal crops (Figure 7-2). This author was program and project manager. This five-year project was commenced prior to this study, but the relevant results are discussed here with anecdotal insights and conclusions drawn.



Figure 7-2. Red Lime™ and Alkaloam® at trial site in Newdegate (DAFWA).

The trials assessed the impact of the lime agent on the soil and crops for a fiveyear period. Red Lime™ and Alkaloam® were both assessed along with two of the current agricultural lime agents known for their rapid response (Figures 7-3 and 7-4). The trials were significantly impacted by drought and results were supplemented with glass house pot plant trials. The key findings are reproduced below.

At the highest rate of application, Alkaloam® and Alcoa Lime Residue both worked as well or better than crushed limestone and lime sand in raising soil pH. The effect of liming was not seen until the second year after application and started to diminish by the third year for all tested ameliorants (Clarendon et al. 2010).



Figure 7-3. Spreading of Red Lime™ and Alkaloam® at trial site in Busselton.



Figure 7-4. Clover growth with Red Lime™ and Alkaloam® at sandy site, Busselton, Western Australia.

There was anecdotal evidence that the initial application of Red Lime™ may be too high a pH without the washing impact of a fresh rain event. Plant design proposals now allowed for ambient product drying and partial atmospheric carbonation. Other options allow for forced carbonation. Both options remove the potential for any initial localised high pH impact.

The CSRP report by Clarendon *et al.* (2010) is definitive in showing the positive impact for the use of Red Lime™ as a soil ameliorant. The absence of negative impacts on plant and soil is reassuring. This product will become a highly valued commodity product but will require constant quality assurance and quality control based upon recent results.

7.4 Red Lime™ for Acid Sulphate Soil (ASS) remediation

The scope of ASS and potential ASS in Western Australia is widespread with significant damage possible to infrastructure and the environment (DOE, 2003; DOE, 2006; EPHC, 2011). The Department of Environment and Conservation (DEC) in Western Australia has produced ASS risk maps, provided assessment methodologies and links to technical reports via their web site (DEC, 2012). Of particular issue are the low lying estuarine regions that include Swan coastal plain and the Peel – Harvey region of Western Australia (Figures 7-6 to Figure 7-9), where some results have been as high as 0.5 wt% sulphur (DEC, 2012). Even regions below the considered risk level of 0.03 wt% sulphur can have acid risk because of their low buffering

capacity. Such soils are usually also very sandy (e.g. Bassendean sand) and as such, disturbance and elevation of the soil above the water table will result in rapid drainage, oxidation and the release of acid and metallic impurities. This can be seen as the blood red stain of iron oxyhydroxides below.



Figure 7-5. Author recording a pH of 1.8 in a dredge spoils pond in Mandurah.



Figure 7-6. Acid leaking from dredge spoils pond walls into Mandurah estuary.



Figure 7-7. Red iron acid drainage leaking from canal dredge spoils in Mandurah.



Figure 7-8. Yellow Jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$) in soils with red iron floc are a sign of acidification of surface drains in the Mandurah Region Western Australia.



Figure 7-9. Iron (red) and alumina (white) floc in surface drains of the Mandurah and Peel – Harvey region of Western Australia.

While the risk of ASS is continuing to gain public awareness, the issues of surface drainage, disturbance of ASS and the use of dredge spoils (sub water Table soil) is continuing to cause issues. The remediation of ASS is currently managed by the application of a neutralisation agent at a rate of 1.5 times the acid generating potential (DEC, 2013). While the calculation also takes into account the rate of neutralisation capacity through the Effective Neutralisation Value (ENV), in practice, the rapid release of acid is only partially negated by the incorporated limestone and red and white iron and aluminium flocs are often seen seeping from canal development walls, precipitating upon the lime based retaining walls (Figure 7-10).



Figure 7-10. Mobile iron and aluminium floc staining retaining walls.

While red mud (Alkaloam®) is considered suitable for soil amelioration to control phosphorus, it is also known for its liming potential. Doye & Duchesne (2005) used column leach trials to show that red mud could control the pH and metal mobility of acid mine tailings. Douglas & Degens (2006) have proposed red mud as a potential material for treatment of acidic drainage waters from the Western Australian Wheatbelt region. While the application is possible, the low neutralising value of red mud (Alkaloam®) would make transport prohibitively expensive. This would not be the case for Red Lime™ which has a much higher neutralising value.

The fine particle size distribution and the variety of rapidly acting neutralising materials within Red Lime™ would appear to be well suited for such an application. The initial reaction would consume the fast reacting species and the more stable products would remain to ensure a significant buffering potential. These environmental conditions would allow for precipitated metals to be stabilised as indicated by pH dependence trials as reported by Attiwell (2013).

To assess the ability of Red Lime™ to modify ASS, soil incubation tests were conducted. The data used in Figure 7-11 was contracted to the Chemistry Centre WA prior to the commencement of this thesis. However, results are publicly reported here for the first time and the discussion and conclusion are by this author in the context of this thesis. A sample of Red Lime™ was screened into various particle size fractions and added to an acidic soil. These incubation trials are designed to observe real time soil pH amendment properties of ameliorants. Here the size fractions of Red Lime™ are compared to other known soil pH amendment products.

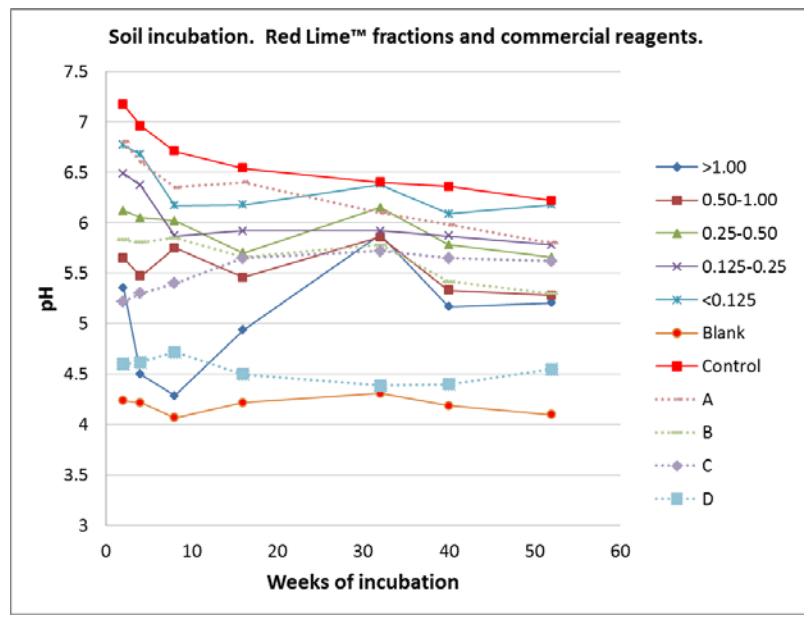


Figure 7-11. Soil incubation trials of Red Lime in comparison to commercial lime reagents commonly used to treat ASS.

As can be seen from the soil incubation trials, the fractions of Red Lime™ all react similarly to existing soil liming reagents. This indicates that the products all contain similar minerals (as confirmed by XRD). As a result, the product reactivity is a simple combination of the reactivity of the particle size fractions. As expected, the finest particle fraction has resulted in the greatest reactivity and the highest soil pH. As the PSD increased, the reactivity decreases and the soil pH is higher. All samples fall within the blank and control samples. The reactivity of the Red Lime™ size fractions overlaps with commercial lime sand and limestone products having similar neutralisation values. This indicates Red Lime™ is a suitable product for treatment of acid soils, in line with several other commercially available products.

In conclusion, the opportunity to use Red Lime™ for ASS remediation is significant. The multiple levels of reactivity of the lime would ensure containment of acid mobilised metals while allowing for a buffered stabilisation of the soil. The fine particle size would ensure rapid response to the rapid release of acid in the sandy soil environments. The location of three sites for the production of the by-product of Red Lime™ all reside within the Peel–Harvey region. The volumes of by-product are large enough to make a substantial impact upon this growing problem.

7.5 General Conclusions

The applications of Red Lime™ appear to be many and varied. The fine particle size and differing minerals provide a range of neutralisation efficiencies that would appear to be very suitable for the treatment of ASS and probably also acid mine tailings.

The development of this product would appear to be contingent upon economic considerations, something that is changing rapidly with the dwindling supply of natural lime sources.

8 BAYER-DERIVED GOPOLYMERS (BAYER STONE™)

Chapter 8 reports on the technical innovation of Bayer-derived geopolymers, the development into a suitable replacement for cement and the subsequent demonstration of geopolymers product trials.

The alumina industry has technological overlap with the production of geopolymers. Both industries involve dissolution of silicate and aluminate species in concentrated sodium hydroxide solutions. The amount of silicate and aluminate dissolved is manipulated depending on reaction conditions and starting materials. Both result in the precipitation of alumina silicates, being the primary product for geopolymer production but an impurity for alumina production. Both manipulate temperature to enhance reaction kinetics. Given their similarities, these two industries have potential for synergy. Some of the areas of synergy are highlighted below.

The alumina industry has traditionally underpinned the demand for caustic (50 wt% solution) hence it is a large market player with economies of scale. There are well-established trade routes, suppliers and existing caustic storage facilities.

The alumina industry has teams of skilled scientists, engineers and operators trained in the safe use of high concentration caustic and aluminate solutions. In particular there are already well established Quality Assurance/Quality Control (QA/QC) capabilities for alumina liquors.

The alumina industry has significant quantities of “low value” steam (i.e. atmospheric pressure and <100°C), which is suitable to steam cure geopolymer concrete.

The alumina industry is established with infrastructure such as road, rail and port hubs. Often alumina refineries are located in heavy industrial areas where other reagents may be available such as fly ash and blast furnace slag.

The alumina industry consumes large quantities of concrete providing the opportunity for plant scale demonstrations of geopolymers. Other alumina industry

by-products can also be utilised in the formulation of geopolymer concrete, such as fine residue for colour, coarse residue as a sand replacement and lime for product cure.

Another opportunity for synergy is highlighted in the patent developed by Jamieson (2008b). The export of Bayer liquor for the production of geopolymers results in an impurity bleed for the recirculating liquor contaminants. By using Bayer liquor as feedstock for geopolymer production, these contaminants are locked within the geopolymer structure forming a benign construction product.

8.1 Geopolymer identification and assessment techniques

The development of Bayer-derived geopolymers was conducted in association with Curtin University Department of Imaging and Applied Physics, under a series of contracts. Some of this work predates the commencement of the thesis and is labelled below as CSRP Project P132, but is reported publicly here for the first time with this author's interpretation. Much of the geopolymer preparation reported in this chapter was conducted by this author under contract at Curtin University. Interpretation is by this author.

Geopolymer development is an emerging technology so it is important to confirm that Bayer-derived polymer is truly geopolymer. This will allow the Bayer-derived products to utilise geopolymer standards and codes currently under development RILEM (2012). However, it is surprisingly difficult to prove the quality or otherwise of an amorphous polymeric aluminosilicate made from industrial by-products. The following analyses are indicators that point to the formation of geopolymer. It is only when taken collectively that geopolymer formation is assured.

Geopolymers are alkali-activated alumino-silicates. It is the caustic that activates the dissolution and condensation reactions. The silicate or aluminate species act to catalyse the reaction process. As such, the choice of aluminate or silicate should not heavily influence the product. Phair & Van Deventer (2002) were able to demonstrate that geopolymers can be made using aluminate activation solutions. Bayer liquor is essentially an alkali alumina solution hence would be expected to

make geopolymers. Therefore the theory for Bayer-derived geopolymers formation is sound.

Geopolymers demonstrate significant compressive strength beyond hardened clay indicating chemical bonding. By starting with an alkali silicate formulation and progressively replacing the silicate with aluminate, the impact upon strength and presumably product chemistry can be monitored. The combination products required much longer mix times utilising many more step additions to prevent formation of weak zeolites. Two sets of elemental ratios (Mix A – Red, Mix B – Blue), were utilised to observe any impact. Figure 8-1 shows that the compressive strength was maintained within experimental error for both formulations implying no impact upon product chemistry. The difference between the mixes is attributed to the chemical ratios. Compressive strength is one of the primary physical properties as it gives direct comparison to many construction products including concrete.

It is important to note that the experimental error of compressive strength is taken as one standard deviation of several measurements. The errors, recorded in Appendix 5, range from 5% for higher strength products to as much as 25% for weaker materials. With a large standard deviation, an argument can be made to use the median result rather than the mean results reported here. Another way to reduce the standard deviation is to remove extraneous results from the sample set, but this was only done if a significant deformity was observed such as large pores, etc.

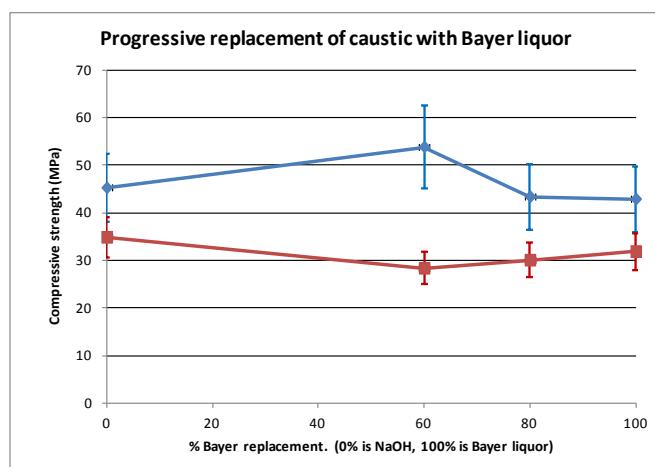


Figure 8-1. Progressive replacement of alkali silicate solution with alkali aluminate solution within geopolymers formulation (P132 Project).

The amorphous character actually relates to the X-ray amorphous nature of the product, and the XRD pattern shown in Figure 8-2 demonstrates the expected elevated background of amorphous material between 25 and 35° 2θ (copper radiation).

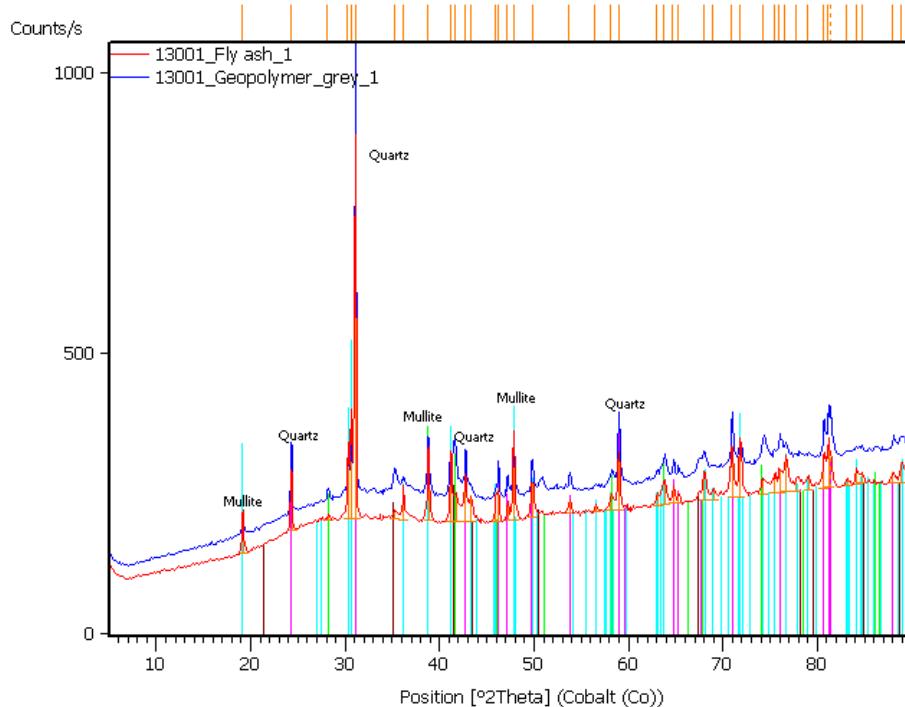
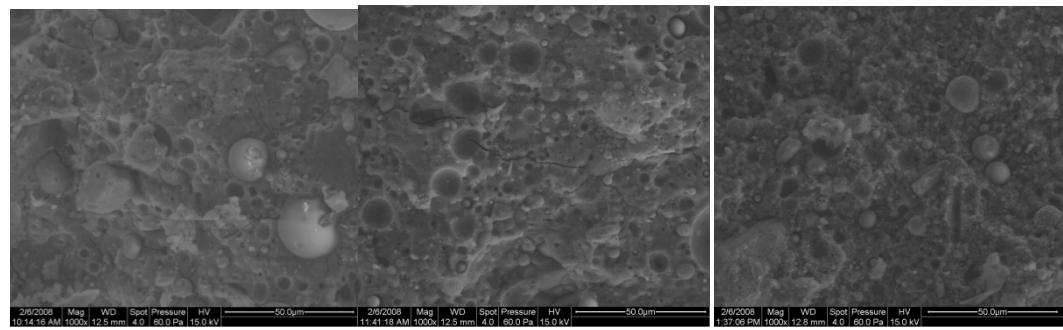


Figure 8-2. XRD pattern of fly ash and Bayer geopolymer.

A key indicator for permanent bonding within a geopolymer is the ability to hold together in cold or boiling water. This test will eliminate non-chemical-hardened products. The Bayer-activated material did not lose mass when submersed in cold water for in excess of 1 month or in boiling water for 4 hours, implying chemical bonding had occurred.

SEM evaluations shown in Figure 8-3 clearly show a few un-reacted fly ash spheres encased in a poly-condensed matrix for samples of different activator. Figure 8-4 is a high magnification of 100 wt% Bayer-derived geopolymer, with the matrix in clear evidence. This is another indicator of the formation of amorphous binding agent.



0 wt% Bayer activator 50 wt% Bayer activator 100 wt% Bayer activator

Figure 8-3. SEM images of Bayer activated product with 7 wt% lime (P132 Project).

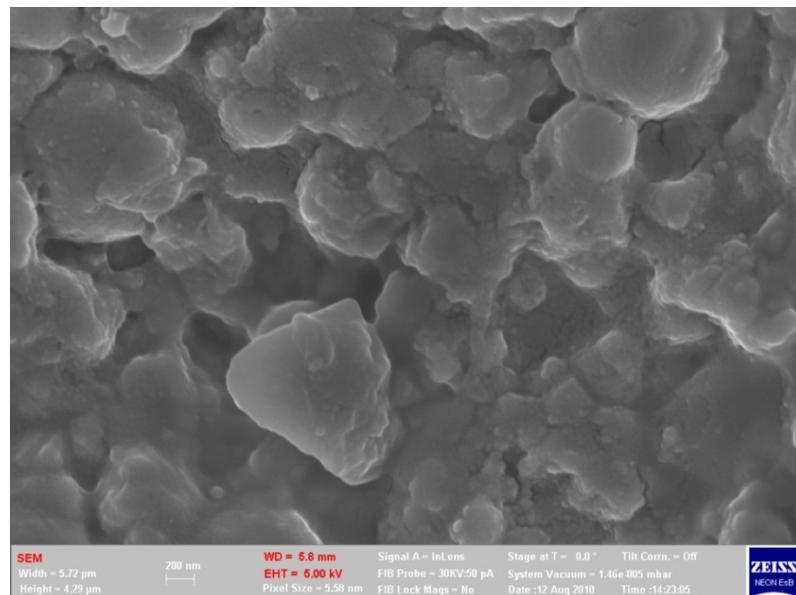


Figure 8-4. High magnification SEM image of 100 wt% Bayer activated product with 7 wt.% lime (P132 Project).

Finally the geopolymser formation conditions themselves are a reliable indicator. A generalisation of Loewenstein's aluminium avoidance principle (i.e. an Al-O-Si bond is preferred energetically over an Al-O-Al bond) suggests that the ratio of Si/Al should not drop below one (Loewenstein, 1954; Davidovits, 2008). Once the dissolved alumina exceeds the silicate, very little geopolymserisation takes place. This rule holds for the Bayer-derived product (note it is applied to the newly-formed product and not to the starting solutions). The impact of this principle can be seen in Figure 8-5 with the declining compressive strength of geopolymser as the ratio approaches one. In this experiment, progressively more sodium aluminate solution (Bayer activator) is added to the fly ash mixture. Hence the impact of increased

hydroxide (increasing strength) and water (decreasing strength) will also be present (formulation ratios are given in Appendix 5).

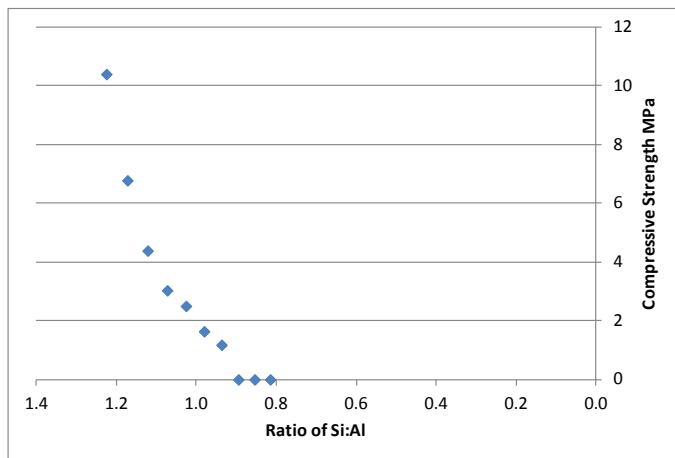


Figure 8-5. Si/Al ratio versus compressive strength after 7 day oven cure at 70°C.

Other ratios that are essential for geopolymer formation (such as the water to solids ratio and Na/Al ratio) also hold true for Bayer-derived product. That is, the Bayer-derived material will only cure under normal geopolymer formation conditions.

The culmination of the above results, indicate that Bayer liquor can be utilised for the manufacture of an amorphous polymeric aluminosilicate, also known as geopolymers.

8.2 Bayer-derived geopolymers formulation

One of the key failings of geopolymers research is the lack of investigation into the fundamentals of chemistry and the nature of the products used (Sagoe-Crentsil & Brown, 2007). For example, reproducibility of formulations from batch to batch can only be achieved having fully characterised the starting reagents and determining the reactive components. Such fundamental research has been reported for fly ash by Chen-Tan *et al.* (2009) and Rickard *et al.* (2011); and for metakaolin by Williams *et al.* (2011). These methods have been incorporated into all experimental formulations used within Chapter 8 of this thesis.

It was determined from the CSRP P132 project that the following formation characteristics should provide a geopolymers of significant compressive strength and

minimal efflorescence. The author believes these criteria are critical to commercial success as they are the hardest to simultaneously achieve, again based upon experience with the CSRP 132 project.

- A Si/Al ratio between 1 and 4.
- A Na/Al ratio between 0.5 and 1.5.
- A water content less than 15 wt% for paste.
- Cure temperature of 70°C.

It is noted that these ratios are guides with a level of flexibility. The high silicon to aluminium provides significant strength. The low sodium to aluminium provides enough caustic for dissolution without resulting in caustic efflorescence on the product. The water content is sufficient to make the product workable while maintaining the product strength.

Using these guides, knowledge of the reagents and their true reactivity (caustic solubility) will allow formulations to be devised. This is best achieved through the manual manipulation of first principles on a spread-sheet. This allows a grasp of the manipulation of ingredients to be developed; which cannot be replaced by automated systems. For example, the ratio for caustic concentration is usually referred to as Na/Al. However, Bayer liquor has a sufficiently high salt concentration to ensure that the sodium (Na) concentration has very little resemblance to the hydroxide (OH) concentration. Thus the Na/Al ratio is replaced with OH/Al for Bayer liquors. However, once the “art” is learnt, the automated system can be trusted with caution.

The automation utilised for this thesis was based upon a spread-sheet developed as part of the CSRP P132 project. This program was significantly modified during this thesis to reflect the changing requirements of industrial materials and the use of multiple ingredients.

One of the first things noted about Bayer geopolymer is that it is stickier than normal geopolymer and potentially more difficult to work. In an attempt to grade the geopolymer workability, classifications have been made as follows.

- **Very high:** Workability is very high and a slump can be recorded.
- **High:** The geopolymer can be worked with a little effort but there is no free slump.
- **Good:** The geopolymer can be worked with vibrational effort.
- **Poor:** Significant vibration is required to work the product.
- **Difficult:** The geopolymer is unresponsive to vibration and is difficult to manipulate by hand.

In an effort to grade the stickiness, five descriptors have also been used.

- **Very sticky:** Difficult to remove mixture even with shaking.
- **Sticky:** Majority of the mixture will be removed with shaking.
- **OK:** Majority of the mixture will drain or slump free under gravity.
- **Not sticky:** The mixture does not stick to the mixer or bowl.

While this is still a subjective assessment, it does help to clarify the measure. It is recommended that further assessment be conducted to compare these definitions with those used in the OPC industry. The stickiness of the Bayer geopolymer can be seen in Figure 8-6 where the paste remains on the mixer and walls without slumping off. When the mixer is removed, the majority of the paste will remain on the mixer and not fall off without shaking. That would represent a “Very sticky” classification and there is obviously no free slump.



Figure 8-6. Bayer geopolymer paste classified as “very sticky” and having no slump.

The increased stickiness of Bayer-derived geopolymers over silicate derived materials is likely to be caused by a combination of:

- Bayer geopolymers utilise a higher silica fume content which can increase viscosity;
- Bayer liquor has a lower water activity, as the water molecules are largely tied to ionic solvation (Bayer liquor is often called a solid solution because of the significant amount of dissolved species);
- It is suspected that the organic content of Bayer liquor (in excess of 20 g/L) carries many ionic active sites encouraging the organic species to act like soap. Such molecules are known to act as rheology modifiers.

The presence of the high concentration of ionic organic species in Bayer liquor raised a concern that they may impact upon the geopolymserisation process and could be detrimental to product strength. To evaluate this issue, a comparison was made with geopolymers manufactured from Bayer liquor supplied from a refinery of low organic content. A Si/Al of 2.3 and OH/Al of 0.8 was maintained for both sets of samples. The compressive strength was measured at 40 MPa which is comparable to 43 MPa for the standard Bayer liquor mixture. This indicates that the organics content does not appear to be detrimental to compressive strength. However, it is recommended that further research be conducted into this area as it may provide insight into geopolymser reaction mechanisms.

8.3 Product development for ambient setting

Ordinary Portland Cement (OPC) is a very versatile binding agent because it will cure at ambient temperature. Geopolymers require elevated temperature (60-100°C) to cure, but it is known that the addition of lime can promote ambient temperature curing. Research conducted as part of the P132 project has shown that lime, both in the form of calcium oxide and as part of blast furnace slag, will enhance room temperature curing. The products made from Muja IV fly ash, Wagerup Bayer liquor and AFM silica fume targeted a Si/Al ratio of 2.15 and a OH/Al ratio of 0.9. Results shown in Figure 8-7 indicate that the addition of calcium from blast furnace slag (expressed as wt% CaO) facilitated ambient cure and increased the compressive strength with increased dose rate. This is consistent with Duxton *et al.* (2007a) who reported in a review that the calcium reacts with silica and alumina to form hydrate phases which are the basis of OPC production. It is believed the calcium

concentration (and form) changes the reaction pathway impacting on cure time and temperature and upon the product physical properties.

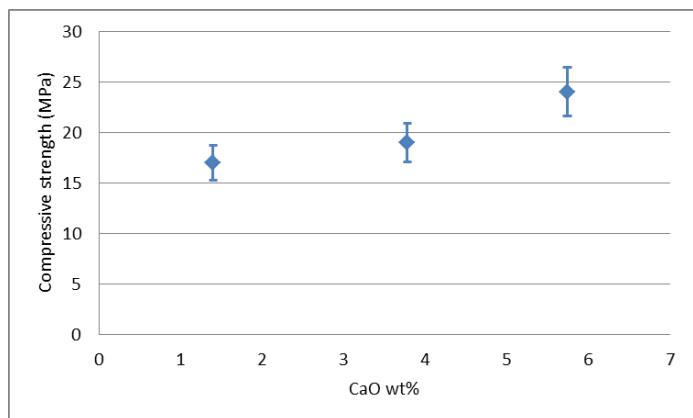


Figure 8-7. Seven-day compressive strength for Bayer geopolymer ambient cured with blast furnace slag (CSRP 132 Project).

While it is expected that the strength will increase with aging, the product utilising blast furnace slag is significantly lower in strength than previously seen for oven cured product.

The same experiments were conducted utilising HyLime as the source of calcium. Muja IV fly ash, Wagerup Bayer liquor and AFM silica fume were used to target a Si/Al ratio of 2.15 and an OH/Al ratio of 0.7. Results for 7-day ambient cure compressive strength are shown in Figure 8-8 and indicate both a higher strength per unit CaO, as well as a higher rate of strength response. This is consistent with the data reported by Duxson *et al.* (2007a) noting that form of the calcium can influence product properties and also create a higher hydroxide concentration (presumably localised around the CaO particle).

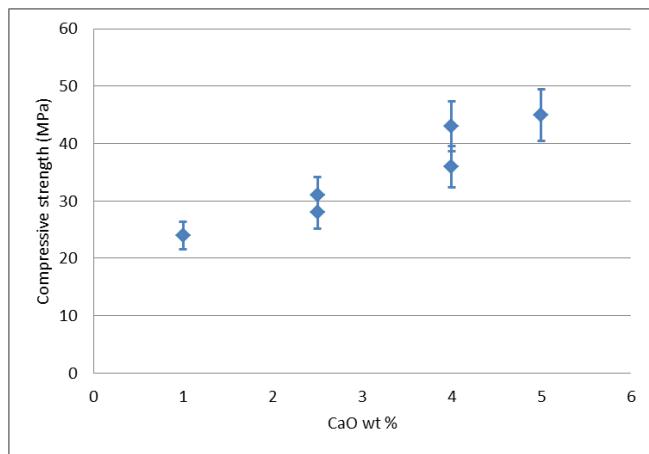


Figure 8-8. Seven day strength of Bayer geopolymer cured with lime (CSRP 132 Project).

These experiments determined that HyLime was a better choice of reagent because it improved the product compressive strength and was more readily available to local industry. While HyLime impacted both the geopolymer paste workability and the cure rate, these parameters were not recorded. To determine these parameters, a paste formulation was made with varying levels of lime (HyLime). The compressive strength, setting time and workability were all recorded and described in Table 8-1 and in Figure 8-9.

Table 8-1. Bayer geopolymer paste elemental ratios for HyLime addition.

Sample	0	1	2	3	4	5
Lime wt%	0.0	1.0	2.0	3.0	3.9	4.8
Si/Al	2.2	2.2	2.2	2.2	2.2	2.2
OH/Al	0.7	0.7	0.7	0.7	0.7	0.7
Water wt%	13.6	13.5	13.3	13.2	13.1	13.0
Stickiness	V sticky	V sticky	V sticky	Sticky	Sticky	Sticky
Workability	Good	Good	Good	Good	Poor	Poor
Estimated slump	nil	nil	nil	nil	nil	nil
Strength (MPa) 1 day 70C	22	25	24	21	30	33
Strength (MPa) 7 day Amb	5	5	8	11	12	12
Strength (MPa) 28 day Amb	21	23	25	23	27	28

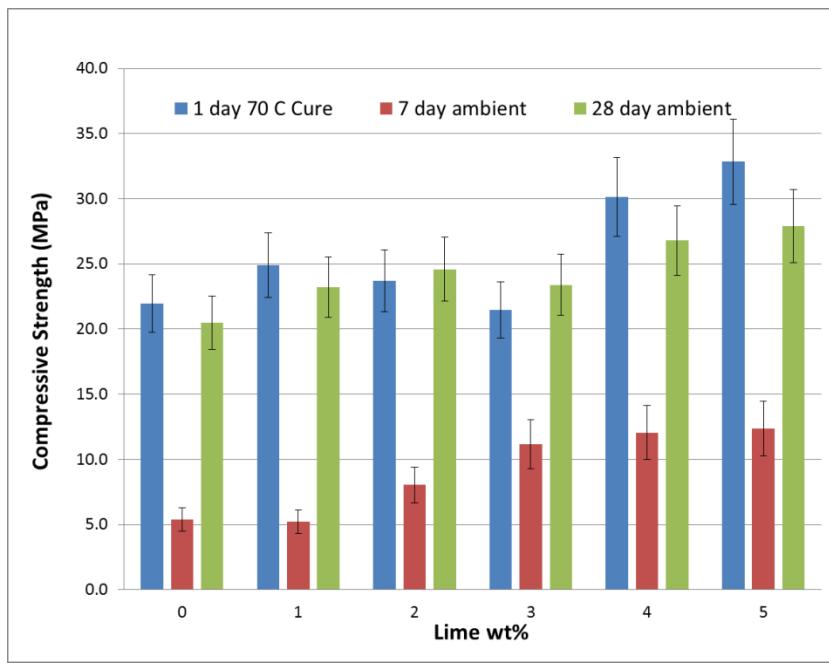


Figure 8-9. Compressive strength for Bayer geopolymer paste cured with HyLime.

The compressive strength in these lime addition experiments is lower than the CSRP 132 lime addition experiments and is most likely due to the different Si/Al and OH/Al ratios and the higher paste water content. These conditions were different as a different Bayer liquor concentrate source was utilised having different concentrations (See Appendix 5). The increase in lime content increased the compressive strength. Oven cured samples generally have a higher compressive strength than 7-day ambient cured samples, however, by day 28 these numbers are within experimental error. This is in line with Lloyd (2009) who reported that fly ash based geopolymers cured at ambient temperatures continued to strengthen after 6 months.

Information can also be gained from the compressive strength compaction curves. Figures 8-10 and 8-12 show compaction curves for Bayer-derived geopolymer after 7 and then 28 days ambient temperature cure. As can be seen the strength has clearly increased with duration of aging, however, the curve also indicates that the 7-day cured sample failed by crumbling of the sample indicating the long and multiple failures. The 28-day cured sample in Figure 8-11 has a clear sharp break, indicating it has achieved a higher cure and resulting fracture. This can also be seen in Figure 8-12 for the oven-cured sample.

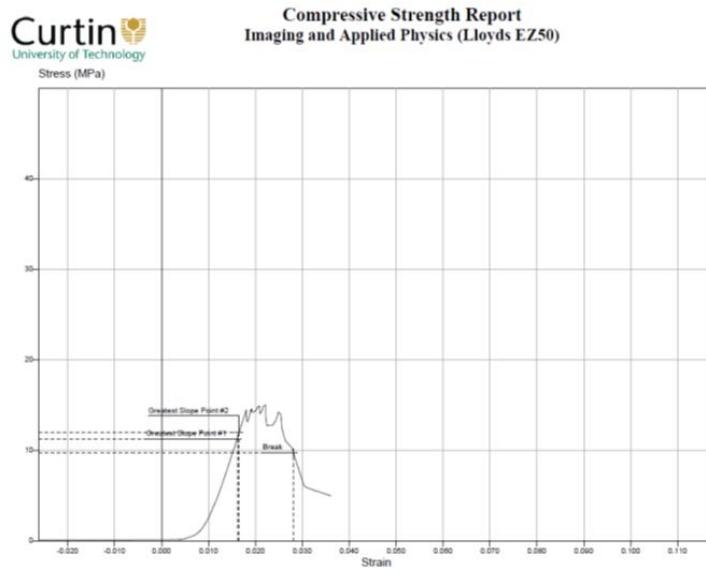


Figure 8-10. Stress-strain curve for a 5 wt% lime sample after 7 days ambient cure.

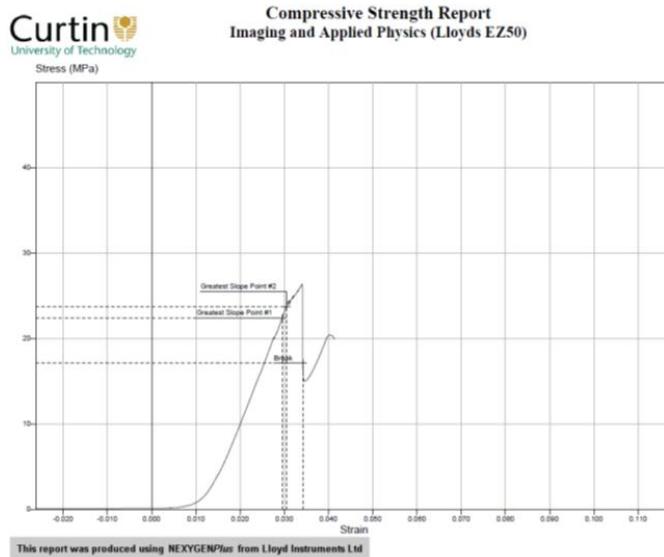


Figure 8-11. Stress-strain curve for a 5 wt% lime sample after 28 days ambient cure.

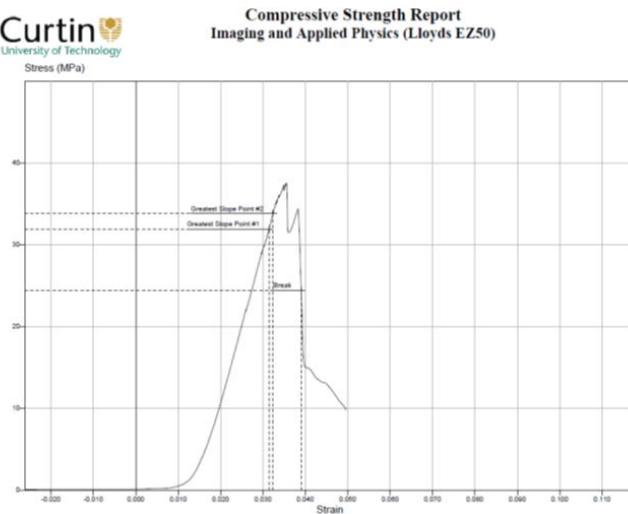


Figure 8-12. Stress-strain curve for a 5 wt% lime sample after 1 day at 70°C cure.

The workability of a sample is subjective to the observer and is not always obvious. Figure 8-13 shows a sample with very high stickiness and nil slump. However with a little vibration, the workability is good. Hence a more analytical approach was required.



Figure 8-13. Bayer geopolymers paste stuck to a mixer, indicating zero slump.

To determine a less subjective measure of paste workability, the Vicat Needle Penetrometer was utilised as per ASTM C191. This method is used to determine the Time of Setting of Hydraulic Cement, but also provides an indication of workability leading up to “first set”.

Vicat operation determines the penetration of the needle over 30 seconds, however, many of the paste samples reached full penetration during this time. For these samples, the time for full penetration was recorded to determine a measurable rate as shown in Figure 8-14.

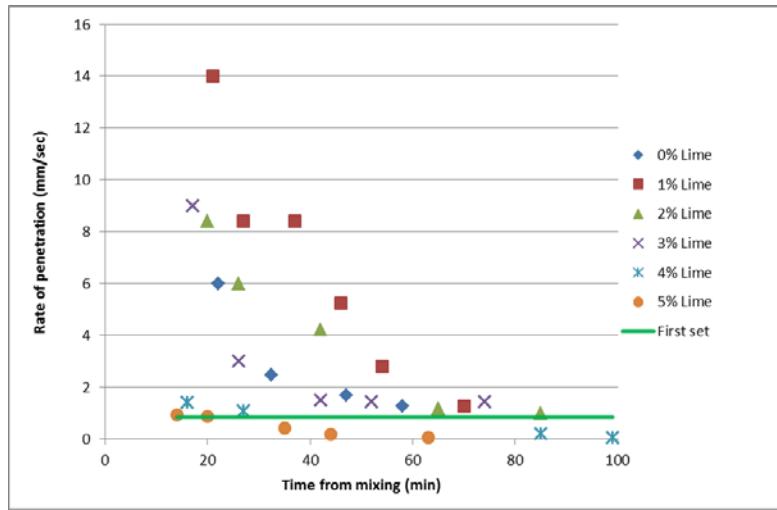


Figure 8-14. Rate of Vicat needle penetration into curing geopolymers samples.

Using this method, it can be seen that the samples all started to set after 1 hour, though they were observed to remain plastic for some hours with the exception of the 5 wt% lime sample.

The penetrometer results require more than a cursory glance. It appears that an admixture was supplied with the HyLime product to improve workability. This admixture may increase the initial workability of low percentage lime samples. However, as the percentage of lime increases above 2 wt%, the impact of the lime is shown to significantly encourage the onset of first set and limit working time. This will have significant impact upon formulation choice to match equipment maintenance and cleaning when exploring options for pilot and plant design. It also highlights that the right admixture can have significant effect.

From these observations it can be concluded that:

- The higher the lime content the higher the compressive strength,
- All samples were sticky and had nil slump,
- Workability is dramatically reduced after about 2 wt% lime,
- First set for 2 wt% lime is about 60 minutes,
- First set for 4-5 wt% lime is reduced to about 20 minutes,
- Additives appear to have an impact upon workability.

These observations are important for formulations but also for addition sequencing.

Addition of Red LimeTM:

Red LimeTM is a by-product from the alumina industry and is discussed in Chapter 7. Being a source of calcium, experiments were conducted using Red LimeTM similar to those reported in Table 8-1. Samples utilising Red LimeTM failed to cure at ambient temperature and crumbled on removing from the sample moulds. It appears that calcium alone does not improve the curing rate. It is reasonable to assume that the effect of CaO or Ca(OH)₂ may be to causticise the carbonates or simply produce highly localised caustic. This may have the effect of encouraging rapid cross linking of the polymeric chains resulting in a rapid cure and higher compressive strength, an effect noted by increasing caustic concentration as reported by Ariffin *et al.* (2011). This is different to the findings of Yip & Van Deventer (2002) who suggested that the ability of calcium to dissolve was the critical factor, something that may also play a role with the complex range of calcium products described as Red LimeTM. Juenger *et al.* (2011) in a review also reported that calcium ions played a role in the chain linking process creating different reaction pathways. The results of the Red LimeTM experiment suggest that simply adding a calcium compound is not enough. There is a need to ensure caustic solubility and possibly caustic generation. It is recommended that further experiments be conducted by adding calcium chloride to a geopolymers and observe cure rate. A direct comparison would be to add NaOH pellets (for localised pH changes) to see if this enhances cure rate.

8.4 Product development of geopolymers mortar

Mortar is created when sand is added to a binding agent such as OPC or geopolymers (Figure 8-15 and Figure 8-16). There are many factors involved including the level of sand, the water content and the order of mixing.



Figure 8-15. Bayer geopolymer mortar showing lack of slump.

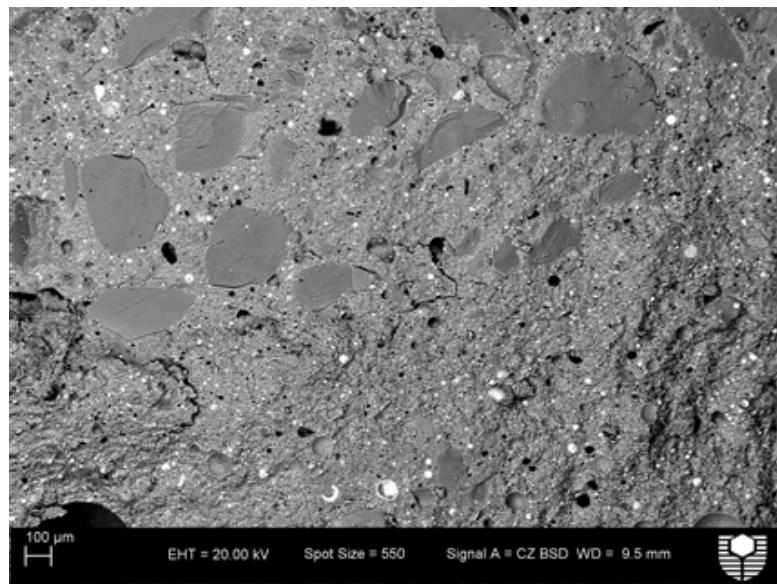


Figure 8-16. Sand encased in geopolymer paste.

While the product does not freely flow, it can be extruded and it will flow with applied vibration. This is very similar behaviour to non-Bayer geopolymer mortar.

8.4.1 Sand content

The first parameter requiring optimisation is the level of sand. Up to 50 wt% sand was added and the compressive strength measured (Table 8-2). Higher levels of sand proved too difficult for manual sample preparation.

Table 8-2. Mortar preparations utilising different sand ratios.

Sample	nil	20%	33%	43%	50%
Yellow Sand wt%	0	20	32	43	49
Lime wt% of paste	4.8	4.8	4.8	4.9	4.8
Si/Al	1.6	1.6	1.6	1.6	1.6
OH/Al	0.5	0.5	0.5	0.5	0.5
Water wt% of paste	14.3	14.3	14.3	14.6	14.3
Water wt% of total	14.3	11.4	9.7	8.3	7.3
Stickiness	Sticky	Sticky	OK	OK	OK
Workability	High	High	Good	Difficult	Difficult
Estimated slump	nil	nil	nil	nil	nil
Strength 1 Day 70C (MPa)	26	23	32	25	27
Strength 7 Day Amb (MPa)	25	24	23	26	22
Strength 28 Day Amb (MPa)	39	35	41	44	42

The table above shows that the sand content will impact the workability through friction, as well as the physical reduction in the water content. The compressive strengths of these samples are provided in Figure 8-17.

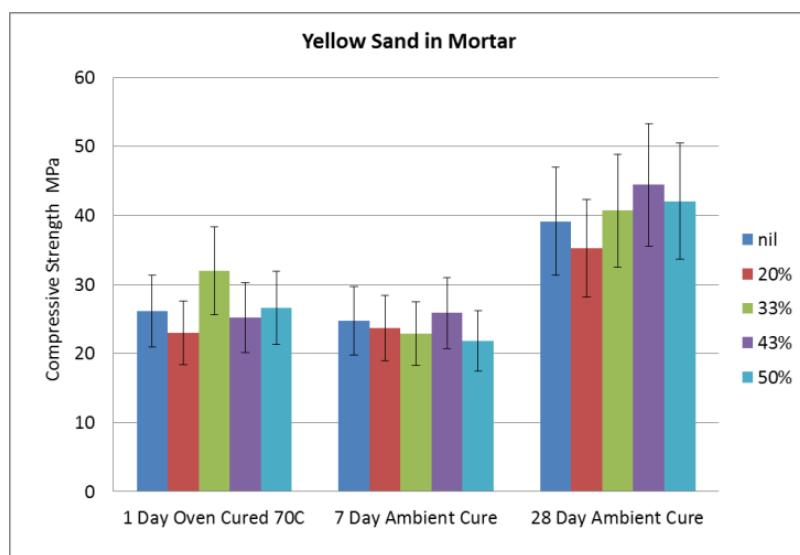


Figure 8-17. Impact of sand content upon mortar strength.

The addition of sand does not have any impact upon the compressive strength. However, samples having 50 wt% sand were very difficult to work.

The above experiment was repeated utilising a lower content of HyLime content at 2.5 wt%. Results (Table 8-3) indicate that the sand content made little impact upon mortar strength but workability was limited beyond about 40 wt% sand.

Table 8-3. Mortar preparations utilising different sand ratios with lower lime content.

Sample	nil	20%	33%	43%
Yellow Sand wt%	0	20	33	43
Lime wt% of paste	2.4	2.4	2.4	2.5
Si/Al	1.6	1.6	1.6	1.6
OH/Al	0.5	0.5	0.5	0.5
Water wt% of paste	14.6	14.6	14.6	14.9
Water wt% of total	14.6	11.6	9.8	8.4
Stickiness	Sticky	OK	OK	OK
Workability	High	High	Good	Difficult
Estimated slump	nil	nil	nil	nil
Strength 1 Day 70C (MPa)	22	23	23	18
Strength 7 Day Amb (MPa)	17	16	20	19
Strength 28 Day Amb (MPa)	25	28	32	31

Temuujin *et al.* (2010) observed a decrease in compressive strength when the sand content exceeded 50 wt% for silicate activated fly ash geopolymers mortar. Presumably the workability of the samples decreased to a point where the sand failed to achieve point to point bonding with geopolymers.

8.4.2 Addition of Red Sand™

Because of the ready accessibility of the by-product Red Sand™ to the source of Bayer liquor, it would be beneficial to utilise this resource in the manufacture of Bayer geopolymers mortar. The characterisation of Red Sand™ is described in Chapter 6, while the geopolymers results are listed in Table 8-4.

Table 8-4. Experimental ratios used for evaluation of Red Sand™.

Sample	Yellow Sand			Red Sand™		
	0.2	0.33	0.43	0.2	0.33	0.43
Sand wt%	20	33	43	20	33	43
Lime wt% of paste	2.4	2.4	2.5	2.4	2.4	2.5
Si/Al	1.6	1.6	1.6	1.6	1.6	1.6
OH/Al	0.5	0.5	0.5	0.5	0.5	0.5
Water wt% of paste	14.6	14.6	14.9	14.6	14.6	14.9
Water wt% of total	11.6	9.8	8.4	11.6	9.8	8.4
Stickiness	OK	OK	OK	OK	OK	OK
Workability	High	Good	Difficult	High	Good	Difficult
Estimated slump	nil	nil	nil	nil	nil	nil
Strength 1 Day 70C (MPa)	23	23	18	22	28	28
Strength 7 Day Amb (MPa)	16	20	19	15	19	22
Strength 28 Day Amb (MPa)	28	32	31	34	36	28

This data shows a slight increase in compressive strength for the utilisation of Red Sand™ in line with expectations from trials with OPC concrete (Wahyuni *et al.* 2006). Similarly, the workability of the geopolymers mortar was negatively impacted by the Red Sand™ and the higher level of paste to sand (50 wt%) was unable to be worked at all.

These observations support the belief that Red Sand™ will not be suitable for use in high slump Bayer geopolymers mortar or concrete. However, the use in aggregate formation is still an option depending on process design and equipment selection.

8.4.3 Colouring agents

Bayer-derived geopolymers mortar can be utilised for many applications such as brick binding, moulded products and even for the production of aggregates. Many applications require the use of colour agents, so to determine how well the Bayer-derived geopolymers accepted colour, a series of metal oxides were added to a standardised mortar mixture as shown in Figures 8-18 and 8-19. The impact upon compressive strength is shown in Table 8-5 and Figure 8-20. Note the agents needed different concentrations to achieve full colouration.



Figure 8-18. Manufacture of green aggregate by hand rolling.



Figure 8-19. part of the 24 kg of rolled aggregate.

Table 8-5. Experimental ratios for the addition of colour agents to mortar.

Sample	Green 1	Black 1	Red 1	Yellow 1
Sand wt%	30.9	32.0	32.0	31.4
Lime wt% of paste	4.5	4.7	4.7	4.6
Si/Al	1.6	1.6	1.6	1.6
OH/Al	0.5	0.5	0.5	0.5
Colour wt% of paste	4.8	1.3	1.3	2.4
Water wt% of paste	14.6	14.1	14.1	15.0
Water wt% of total	10.1	9.6	9.6	10.3
Stickiness	Sticky	V sticky	V sticky	V sticky
Workability	Poor	Good	Good	Good
Estimated slump	nil	nil	nil	nil
Strength (MPa)				
7 Day Ambient	22	22	22	24

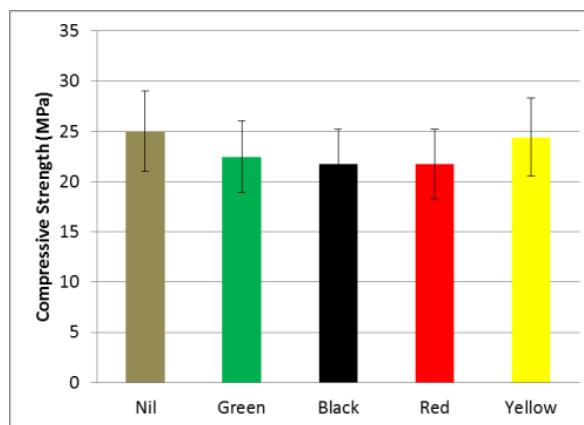


Figure 8-20. Impact on compressive strength of mortar by addition of colour agent.

It was concluded that Bayer geopolymer mortar could successfully take up a colouring agent without adverse impact upon the compressive strength.

8.4.4 Evaluation of alternative silica sources

The use of aluminate solutions for geopolymer activation requires highly reactive silica in the solid phase ingredients to keep the Si/Al ratio above one. In many cases, the reactive silica of fly ash needs to be supplemented with highly reactive silica fume or blast furnace slag. While silica fume was considered a waste product, application development has resulted in growing demand, and this can result in a relatively high cost depending on locality.

In Western Australia, various sources of silica fume are expensive due to low production volume and relatively high demand. Hence there is a need for alternatives to be investigated. In this investigation, ground glass, Muja power station ash, Kwinana power station ash, Edesa Power station ash and a source of silica fume imported from China (Rheomac) were investigated.

Ground glass and Muja power station fly ash were investigated as part of P132 Project. Kwinana fly ash, Edesa fly ash and Rheomac silica fume have been investigated during this thesis.

Micronized glass samples failed to provide any benefit when added to a Collie ash and Bayer activated geopolymer mixture. This was presumably because the powdered glass was still too coarse and failed to dissolve. It may also mean that “amorphous glass” as we know it, is not the same as “reactive silica” for geopolymers. Cyr *et al.* (2012) have demonstrated that glass cullet can be made into inorganic polymers but they utilised lower levels of dissolved alumina than Alcoa can provide.

Muja fly ash was determined to have a much higher reactive Si/Al ratio, favouring application with Bayer liquor feedstock. Little, if any, additional sources of silica were required. Muja ash also had a smaller particle size that may have allowed a greater proportion of the higher reactive silica to be utilised. The reactivity of alumina and silica for the different products is shown in Table 8-6.

Table 8-6. Amorphous Si and Al (wt % as oxides) for various silica sources.

	Reactivity	
	SiO2	Al2O3
Muja Flyash No1 (CSRP - P132)	22%	10%
Muja Flyash No2 (CSRP - P132)	27%	12%
Muja Flyash No4 (CSRP - P132)	27%	13%
Muja Flyash No5 (CSRP - P132)	25%	12%
Kwinana Flyash1	16%	20%
Kwinana Flyash 2	9%	13%
Kwinana Flyash 3	25%	19%
Kwinana Flyash 4	23%	20%
Collie Flyash	21%	15%
AFM SF98 Silica fume	94.10%	0%
Rheomac SF 100 Silica fume	86.34%	0%

Targeted ratios of Muja IV fly ash geopolymer, were Si/Al = 2.15 and OH/Al = 0.90. Compressive strength for Muja ash Bayer geopolymers was in excess of 40 MPa using 4-5 wt% HyLime. Experiments with Kwinana ash with no added silica fume achieved pavement strength of 10.4 MPa (Si/Al = 1.2 and OH/Al = 1.0). These results suggest that utilisation of different sources of fly ash can be a suitable mechanism to minimisation the need of expensive silica fume.

Silica fume imported from China (Rheomac SF100) was also evaluated as it is considerably cheaper than local source material. Rheomac SF100 was black indicating the presence of carbon. This was confirmed by XRD (Figure 8-21) and semi quantified by the LOI from the provided composition (Table 8-7).

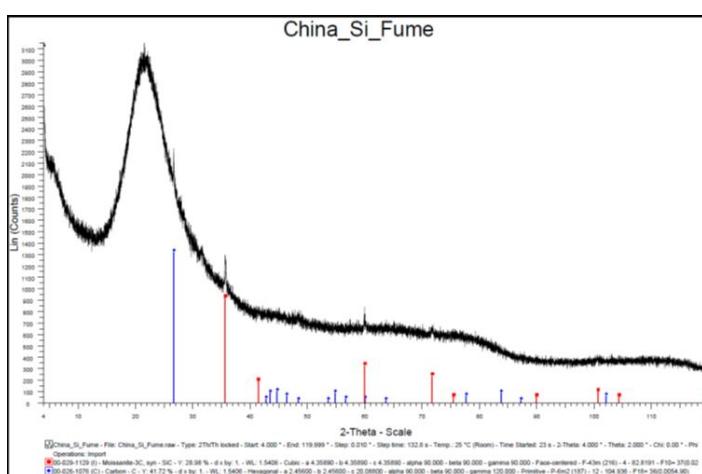


Figure 8-21. XRD pattern of Rheomac SF 100. Red peaks: Moissanite-3C (SiC).
 Blue peaks: Carbon (C).

Table 8-7. Manufacturer's composition (wt%) of Rheomac SF 100.

Item	Analysis	Requirement
% SiO ₂	86.34	85, Min.
% Cl	0.06	0.2, Max.
% Ca	0.24	N.A.
% Eq: Sol. Na ₂ O	1.45	2, Max.
% LOI	2.63	6, Max.
% Moisture	0.42	3, Max.
m ² /g Spec. Surface (BET)	18502	15000, Min.
% Retained over 45µm	2.7	10, Max.
Activity Index	110	105, Min.
g/m ³ Bulk Density	668	N.A.

An observation of the Rheomac fume was that it was almost granular and did not dust. This is a significant handling benefit from an Occupational Health and Safety (OHS) perspective. An SEM investigation determined that the particles were quite large as shown in Figure 8-22. Both factors are significant when planning pilot and plant demonstrations.

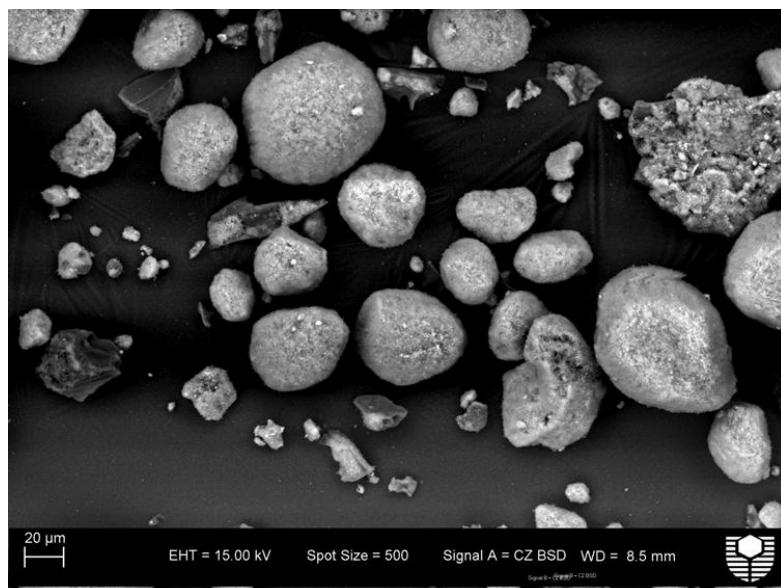


Figure 8-22. SEM of Rheomac SF 100.

A direct comparison between the two silica fume sources was made. Experimental details and results for AFM silica fume and Rheomac SF 100 fume are shown in Table 8-8. Both types of fume were added to formulations of Collie fly ash and Bayer liquor feedstock.

Table 8-8. Experimental formulation ratios and resulting compressive strength for AFM SF 98 and Rheomac SF 100 fume trials using a Collie ash.

Fume type	Rheomac SF 100			AFM SF 98		
Sample	Nil Sand	20 wt% Sand	33 wt% Sand	Nil Sand	20 wt% Sand	33 wt% Sand
Sand wt%	0.0	20.0	33.3	0.0	20.4	32.8
Lime wt% of paste	2.4	2.4	2.4	2.4	2.4	2.4
Si/Al	1.6	1.7	1.7	1.6	1.6	1.6
OH/Al	0.5	0.5	0.5	0.5	0.5	0.5
Water wt% of paste	14.6	11.5	12.7	14.6	14.6	14.6
Water wt% of total	14.6	11.7	9.8	14.6	11.6	9.8
Stickiness	V sticky	OK	OK	Sticky	OK	OK
Workability	Good	Good	Good	High	High	Good
Estimated slump	Nil	Nil	Nil	nil	nil	nil
Strength 7 Day Amb (MPa)	21	22	18	17	16	20
Strength 28 Day Amb (MPa)	25	31	23	25	28	32

During preparation, it was noted that the coarse Rheomac SF 100 fume created a dry crumbly cake. The mixture looked like a failure until, with time (2-5 minutes), the silica began to dissolve and a wet but sticky paste formed.

Results indicated that both sources of silica fume performed their task in geopolymer formation and the compressive strength results were within experimental error. This demonstrated that either silica source could be utilised. It is also concluded that understanding the fundamental reactivity of all reagents allows for formulation of ingredients while having a certainty of product outcome. Hence industry will be capable of implementing a quality assurance and quality control system.

The cured sample in Figure 8-23 still shows the adhesion pattern as the polymer was rolled between gloved hands. This suggests that achieving an acceptable surface finish could be problematic for any resulting concrete.



Figure 8-23. Bayer-derived geopolymers made utilising Rheomac SF 100fume.

8.4.5 Bench scale mortar trials

To demonstrate the production of mortar on a bench scale, five batches of 40 kg were made with a variety of sand and lime contents. Samples were made into 1.5 litre cylinders for commercial compressive strength testing. Mix 2 and particularly Mix 3 generated significant internal heat and set within 20 minutes. To overcome the rapid cure, the lime content was lowered. Laboratory samples were taken along with those for bench scale testing at Boral. With the move towards larger scale product demonstrations, a method of non-destructive strength measurement such as use of the Schmidt hammer, was also investigated. Results are shown in Table 8-9.

Table 8-9. Experimental ratios and results for the bench scale production of mortar.

Sample	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5
Sand wt%	20.0	32.4	32.4	32.9	43.4
Lime wt% of paste	4.8	4.8	4.8	2.5	2.6
Si/Al	1.6	1.6	1.6	1.6	1.6
OH/Al	0.5	0.5	0.5	0.5	0.5
Water wt% of paste	14.3	14.4	14.4	14.7	14.9
Water wt% of total	11.4	9.7	9.7	9.9	8.4
Stickiness	Sticky	Sticky	OK	OK	OK
Workability	High	High	Good	Difficult	Difficult
Estimated slump	low/nil	low/nil	nil	ok	ok
Schmidt Hammer (MPa)	33	29	26	31	30
Strength 28 Day Amb (MPa). BORAL Tested	42	38	30	36	40
Equivalent Laboratory mix Strength 28 Day Amb (MPa)	35	41	41	32	31

One of the findings from this work was the relative worth of the Schmidt hammer. The Schmidt hammer results follow the trend of commercial compressive strength testing, suggesting it to be an ideal rapid and non-destructive test method. The key highlight is the trend holds true for mix 3, where rod holes were suggested as the cause of poor relative strength in the cylinder compressive testing (Figure 8-24). The fact that the hammer results follow those of the commercial laboratory, suggests the rodding holes (holes left in the geopolymer from a compaction tool used for making a sample) were less of an impact than the fundamental geopolymer strength. As this batch suffered rapid set trapping the rod holes in place, it is highly likely that the geopolymer strength has been compromised.

It is recommended that this non-destructive test method should be investigated further for experimental laboratory applications. Aydin & Saribiyik (2010) found that the Schmidt hammer gave a higher strength than corresponding destructive testing for OPC concrete. The geopolymer samples were all understated, suggesting the hammer results need further investigation as to result scaling.



Figure 8-24. Evidence of cavity from compaction rods for batch 3.

As all samples achieved compressive strength in excess of 30 MPa, the batches were crushed and combined to make a 200 kg of aggregate for application testing. Samples were screened into various size fractions then the required weight of each fraction recombined to make the appropriate particle size distribution.

Finally, a sample of Mix 5 was utilised to make a 400 x 400 (mm) decorative wall slab (Figure 8-25). The mix was sticky, however, applied vibration caused the mix to flow and fill the mould.



Figure 8- 25. Bayer geopolymer mortar vibrated to make a decorative slab.

The surface finish of the dried product was good and has been on display for 18 months. This small scale demonstration indicates that Bayer-derived geopolymers may be suitable for moulded product formation.

8.5 Product development

While there are many similarities and opportunities for synergy between alumina refining and the production of geopolymers, there are some differences that need to be conceptualised to allow further development.

One fundamental hurdle between integration of these two industries is that alumina production is a 24-hour business and so requires a constant bleed of liquor for geopolymer production. However, construction concrete production is periodic with most demand early in the morning. The concept design shown in Figure 8-26 is an attempt to accommodate this difference by capturing a slow bleed into a process tank that could be utilised as a transport hub.

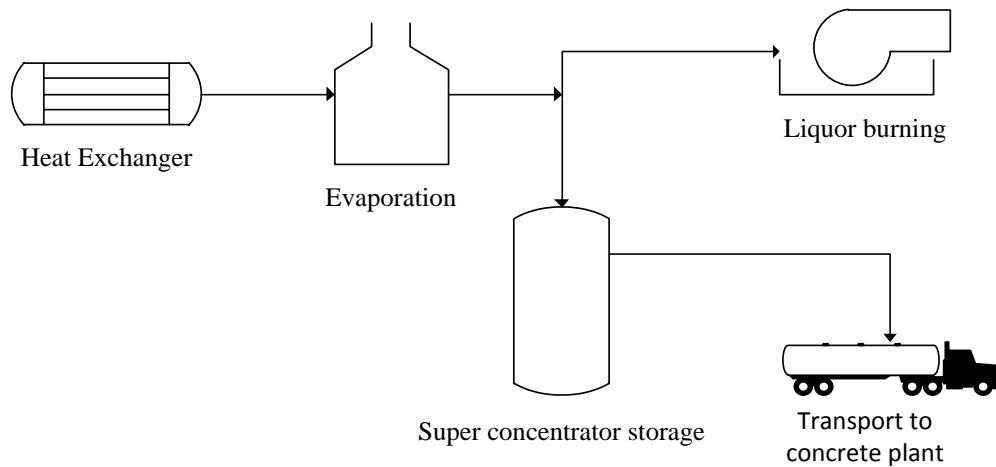


Figure 8-26. Flow diagram for ad-hoc production of Bayer-derived geopolymers.

This simplistic solution is made possible by the stability of the Bayer liquor feedstock. Samples for testing are frequently collected and cooled on one day and transported the next. Laboratory formulations would typically begin a day later. Anecdotally, the Bayer liquor feedstock remains active for many weeks or even months, although a thorough statistical investigation is recommended. The stability

of the highly evaporated aluminate solution is attributed to the very high caustic concentration and high Total Organic Carbon (TOC) levels.

Another hurdle is the sheer capacity of the alumina process. This is described further below while outlining the need for multiple product development and the need for large and varied markets.

8.6 Alternative products

To date, the geopolymers industry is gradually creating a niche market highlighting its green credentials (Rocla, 2012), as well as specific properties (Halcrow 2012). Market penetration will grow with time as the products become accepted within the general construction industry. However, the Bayer geopolymers market does not have the luxury of slow growth and development. Typically the supply of Bayer liquor feedstock will be governed by the need for impurity removal and the forward price of 50 wt% caustic solution. This will likely require a minimum base load production, with regular fluctuations depending upon circumstance. This base load could be in the range of 1 to 10 kL per hour of feedstock, producing up to 400 tonnes of concrete per hour. Alcoa has three sites in Western Australia in the South Western development corridor and if full production is met, it would be close to the yearly Western Australian consumption of OPC concrete. Clearly such complete market penetration is impossible hence alternative products need to be found.

OPC can be utilised for the manufacture of many different products and the use of geopolymers as a binder creates even more opportunities. However, each utilisation requires specialised knowledge. OPC has been used for many years and research is still being conducted into applications. It is therefore logical to conclude that it will take time to similarly develop geopolymers application technology. Some of the applications will be easy to implement while others will require the development of specialty chemicals to assist. Some applications are evaluated and discussed below.

8.6.1 High slump concrete

High slump concrete is the largest market for concrete and is the product most commonly seen. It is utilised for construction of paths, curbs, driveways, house pads, etc. High slump concrete is a competitive market, but also a potentially lucrative one. However, experimentation has shown that Bayer-derived geopolymers paste has effectively no slump. Making the geopolymers concrete with the heavy aggregate will improve the slump, but probably not to the level of 80 +/- 20 mm using method ASTM C143 / C143M - 12. To evaluate this concern, a Bayer-derived geopolymers concrete was formulated with the following parameters in a high-shear pan mixer. The paste Si/Al ratio was 1.6. The OH/ Al ratio was 1.5, and the paste water content was 13.6 wt%. The concrete had 12 wt% dry sand, 30 wt% dry 10 mm aggregate and 28 wt% dry 14 mm aggregate. A lime content of 5 wt% was utilised to ensure high strength. No slump measurements were conducted as the mixture was too stiff to slump as can be seen in Figure 8-27.



Figure 8-27. Bayer geopolymers concrete in wheelbarrow.

The following investigation was conducted into mechanisms to improve the slump of Bayer-derived geopolymers.

8.6.1.1 Water addition

The standard operation for OPC concrete is to add water and water minimisers to improve concrete rheology. Control of the water content is important for curing of OPC concrete but it is critical for geopolymers. It may be a limiting factor in the development of geopolymer industries. The water content must be maintained during the curing of geopolymer. Too little water and the mobility of chemical reaction products will cease. Too much water and reagent dissolution will stop. Thus water addition for rheology modification is not possible.

This is a fundamental change to the operation of high slump concrete utilisation. Moisture content and maintenance are critical and must become the stable factor, while additives and formulations must change to modify the resulting rheology.

Water also represents a method of killing the reaction. Should a truck break down or fail to deliver its product on time, a kill mechanism is required to stop the concrete curing in the back of the truck. For OPC concrete, sugar is added to stop the reaction. For geopolymers, water will have the same effect.

8.6.1.2 Addition of super-plasticiser

Because of the need to maintain the water content of geopolymers, water minimisers, admixtures and super-plasticisers are essential to modify the mixture rheology.

Current market admixtures are designed for OPC concrete but there are significant differences in chemistry and surface charge compared to geopolymer concrete. In fact, the majority of super-plasticisers have been reported as ineffective with the exception of naphthalene based products (Palacios & Puertas, 2005; Joseph & Mathew, 2012). Hardjito & Rangan (2005) also successfully applied a naphthalene sulphonate super plasticiser (Rheobuild 100) to their geopolymer concrete.

To determine whether other available reagents are effective, a range of admixtures were incorporated at the start of the mixing process. It is important to make this clarification because the starting caustic concentrations in geopolymer formulations

are much higher than for OPC concrete. However, as the geopolymer reaction takes place, the level of free caustic drops rapidly. Thus admixtures that do not work at the start of the reaction may work once the dissolution reaction is complete. Samples were tested at a standard dose rate of 15 mL/kg of binder. Results for compressive strength and workability are reported in Table 8-10 and Figure 8-28. However, it was noted that none of the reagents made a significant change to the stickiness of the mortar mixture and one even promoted the first set.

Table 8-10. Experimental ratios and results for the comparison of commercially available admixtures applied to Bayer geopolymer mortar containing 33 wt% sand.

Sample	nil	Sika LC 02	Sika LC 02	Rheobuild 1000	Sikament NN	Tamol NH3703
Reagent g/kg	0.0	13.1	13.3	13.1	13.1	13.1
Si/Al	2.3	2.3	2.3	2.3	2.3	2.4
OH/Al	0.7	0.7	0.7	0.7	0.7	0.7
Lime wt% in paste	2.4	2.4	0.0	2.4	2.4	2.4
Water wt%	13.3	13.0	13.3	13.0	13.0	12.7
Stickiness	Sticky	Sticky	Sticky	Sticky	Sticky	Sticky
Workability	Good	Good	Good	Difficult	Good	Good
Estimated slump	nil	nil	nil	nil	nil	nil
Strength (Mpa)						
7 Day Amb	15	15	19	19	13	19
Strength (Mpa)						
28 Day Amb	33	29	22	33	29	ND

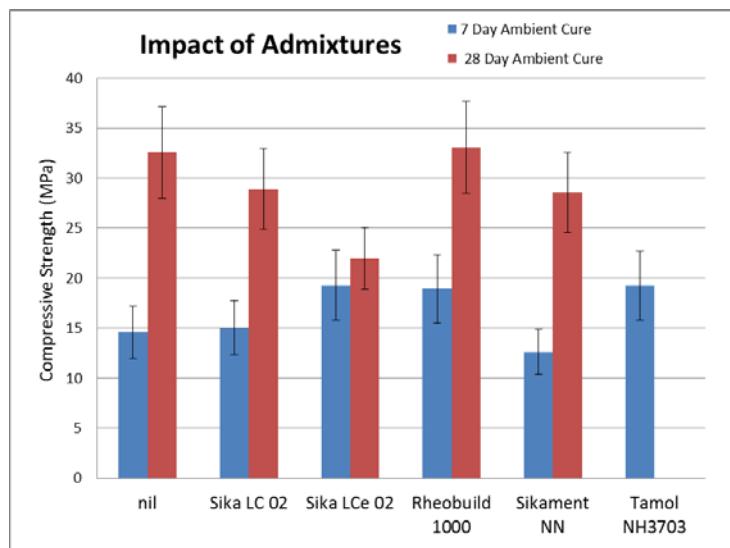


Figure 8-28. Compressive strength of geopolymer with various super-plasticisers.

The blank sample was low for this batch and may reflect that the Bayer liquor was aging. However, the data is still suitable for comparison. There is little statistically

significant difference in the compressive strength between the samples, with the exception of Sika LCe 02 which also had higher air entrainment. The entrainment was visibly assessed and is a stated side effect from some to the reagents. Vicat needle penetration trials were conducted but the samples all set relatively rapidly (averaged 30 minutes to first set) (Figure 8-29). This is possibly a result of the Bayer liquor activator aging as suspected above but may also be an interaction with the super-plasticisers. As the results are in doubt, they have not been reported further, however, further investigations are recommended.



Figure 8-29. Bayer mortar with Sika LCe 02 plasticiser showing Vicat needle marks.

It was concluded that the admixtures did not make a significant difference to the mortar paste handling characteristics at the concentrations used. This could also have been a result of the timing for reagent addition in the mixing process. However, these results mirror those of Criado *et al.* (2009) suggesting the very chemistry is too different from that of OPC.

Testing was conducted on concrete samples to ensure the impact of the heavy coarse aggregate is not missed in creating slump. Two mixes were made with the attempt to achieve a slump of 80 mm from the cone initial height of 300 mm (Table 8-11). To achieve this slump, significant water was added as well as excessive levels of super-plasticiser. In achieving the slump (in the absence of lime and with higher binder to aggregate ratio) the strength was considerably reduced.

Table 8-11. High slump geopolymers concrete formulation ratio and results.

Sample	Boral Mix 1	Boral Mix 2
Lime wt%	0	0
Si/Al	2.4	2.4
OH/Al	0.6	0.6
Water wt% Paste	20.8	20.7
wt% sand of concrete	27.8	27.8
wt% 10 mm aggregate of concrete	42.7	42.7
Mass of Sika NN	30	90
Stickiness	OK	OK
Workability	Good	Good
Slump (Aim 80 mm)	ND	80
Strength (MPa) 1 Day 70C Boral tested	7	6

Similar results were achieved at Boral laboratories where extra water was added to increase the slump (Table 8-12). No admixtures were utilised. The high water content and no lime explain the poor ambient cure compressive strength.

Table 8-12. High slump geopolymers concrete formulation ratio and results.

Sample	Boral Mix 2 at Boral	Boral Mix 2 at Boral
Lime wt%	0	0
Si/Al	2.4	2.4
OH/Al	0.7	0.7
Water wt% Paste	21	26
"Saturated surface-dry" estimate water wt% total	11	16
wt% sand	17	16
wt% aggregate	53	50
Stickiness	OK	OK
Workability	Good	Good
Slump (Aim 80 mm)	40	85
1 day oven 70C (MPa)	10	3.5
28 day ambient cure (MPa) (No Lime)	2.3	1.1

It is clear that without admixtures specialised for the aluminate solutions, the prospect of high slump concrete will face technical difficulties.

It is recommended that general rheology modifiers designed for high pH be assessed. Also, suppliers of chemical admixtures should be encouraged to specifically design reagents for Bayer-derived geopolymers.

8.6.2 Low slump concrete

Low slump concrete is utilised for pre-formed products such as pipes, culverts, columns etc. It is a high value product. This market is relatively small compared to that of high slump concrete (~10% by volume in Western Australia based upon data from ABS, 2012). However, it is better suited to geopolymer use. Pre-formed products are usually produced in a controlled environment and this would suit geopolymers. Several companies in Australia already produce pre-formed geopolymer products such as pipes, crypts, railway sleepers and tunnel lining. Bridge spans and columns are currently being performance tested (Wagner, 2012). For this market to consume a significant volume of Bayer liquor, the market would need to be expanded to include paving, bricks, slabs, noise barricades and wall retainers. Due to the need for moulds, applied vibration, etc, this market is relatively capital intensive compared to the high slump market. The products however, have a higher profit margin. A low slump concrete mixture was made and tested at Boral laboratories. The results are shown in Table 8-13 and in Figure 8-30.

Table 8-13. Low slump geopolymer concrete formulation ratio and results.

Sample	Low slump
Lime wt%	0
Si/Al	2.4
OH/Al	0.7
Water wt% Paste	16.9
Water wt% total	4.7
wt% Sand	28.4
wt% 10 mm Aggregate	43.6
Stickiness	OK
Workability	Good
Slump	nil
Strength (MPa) 1 day 70 C Boral	12

While the strength was low for this sample, the concept for low slump geopolymer concrete utilising virgin aggregates has been demonstrated. There may be a temptation to draw a comparison between geopolymer binder with geopolymer aggregate later described in chapter 8.6.5.2, but the composition ratios are too different and the number of samples too small. This sample was noted to have small bubbles present which would have also impacted upon the strength. This issue was subsequently rectified with application of vibration, a normal process for low slump concrete.

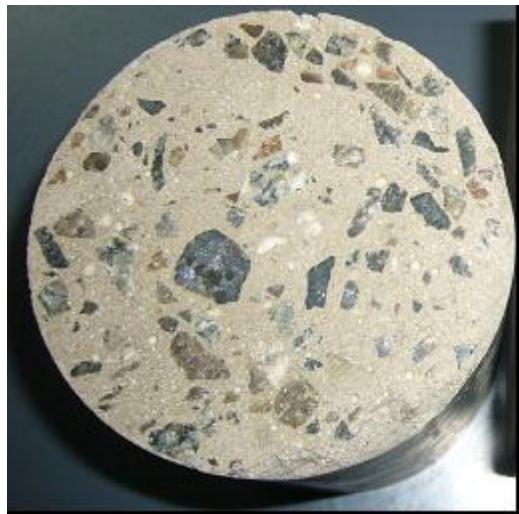


Figure 8-30. Low slump, Bayer-derived geopolymers concrete (10 cm diameter).

8.6.3 Shot-crete

Shot-crete is a term used for OPC products that are thrown or sprayed against a wall to hold loose material in place as well as to strengthen the structure. Shot-crete is a very expensive product that requires significant quantities of admixtures to OPC to achieve the desired product specifications. Bayer-derived geopolymers is however, naturally very sticky as shown in Figure 8-31 and so appears highly suited for shot-crete application (Table 8-14). The market volume is small and little work has been conducted on this product. However, it may be a lucrative side market that can be expanded with time and research.



Figure 8-31. Natural stickiness and shape holding of Bayer geopolymer.

Table 8-14. Elemental ratios used for geopolymer paste only formulation, that may be suitable as a shot-crete like material.

Sample	Paste
Yellow Sand wt%	0
Lime wt% of paste	4.8
Si/Al	1.6
OH/Al	0.5
Water wt% of paste	14.3
Water wt% of total	14.3
Stickiness	Sticky
Workability	High
Estimated slump	nil
Strength 1 Day 70C (MPa)	26
Strength 7 Day Amb (MPa)	25
Strength 28 Day Amb (MPa)	39

Similar results have been published by Temuujin *et al.* (2012) who were able to spray coat geopolymer on to surfaces for thermal protection.

8.6.4 High thermal performance products

The thermal performance of geopolymers is known to be significantly superior to OPC and is the reason why geopolymers are being investigated for tunnel lining. Some geopolymers have been able to retain their strength to over 1000°C, though it was originally believed that the Bayer geopolymer was unlikely to achieve this. The Bayer feedstock has a high organic content in excess of 40 g/L. In addition there are significant levels of carbonates in the liquor up to 140 g/L. The fly ash can have up to 2 wt% as carbon and the Rheomac silica fume can have up to 6 wt% LOI. It was believed that these impurities would cause structural degradation. Samples of Bayer-derived geopolymer were prepared for thermal stability testing. Eight different batches from other experiments (Table 8-15) were dried for 24 hours at 70°C then taken up to 250, 350, 550, 750, 950 and 1150°C. The heat up rate was 300°C per hour and the samples were held at temperature for 3 hours, before being removed from the furnace to air cool.

Table 8-15. Experimental ratios and performance of samples used for thermal testing.

Sample	nil	Sika LC 02	Sika LC 02	Rheobuild 1000	Sikament NN	Tamol NH3703	Rheomac fume 20 wt% sand	Rheomac fume 33 wt% sand
Reagent g/kg	0.0	13.1	13.3	13.1	13.1	13.1	0.0	0.0
Si/Al	2.3	2.3	2.3	2.3	2.3	2.4	1.7	1.7
OH/Al	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Lime wt% in paste	2.4	2.4	0.0	2.4	2.4	2.4	2.4	2.4
Water wt%	13.3	13.0	13.3	13.0	13.0	12.7	11.5	12.7
Stickiness	Sticky	Sticky	Sticky	Sticky	Sticky	Sticky	Sticky	Sticky
Workability	Good	Good	Good	Difficult	Good	Good	Good	Good
Estimated slump	nil	nil	nil	nil	nil	nil	nil	nil
7 Day Compressive Strength MPa	15	15	19	19	13	19	22	18
28 Day Compressive Strength MPa	33	29	22	33	29	ND	31	23
After 1150°C MPa								27

As can be seen from Figure 8-32, all samples appear unaffected by temperatures up to 950°C for a period of 3 hours. This is in contrast to Subear (2004) who found substantial shrinkage and cracking in fly ash geopolymers treated to this temperature.

Sample batch 8 (Rheomac fume and 33 wt% sand) appears to have withstood 1150°C for 3 hours without significant weight loss or shape change (Figure 8-32). This sample was tested for compressive strength post thermal treatment at 1150°C and was shown to have increased the compressive strength, presumably through partial melting (Table 8-15). The potential use of this product for fire protection is large and should be considered a candidate for further research and development.

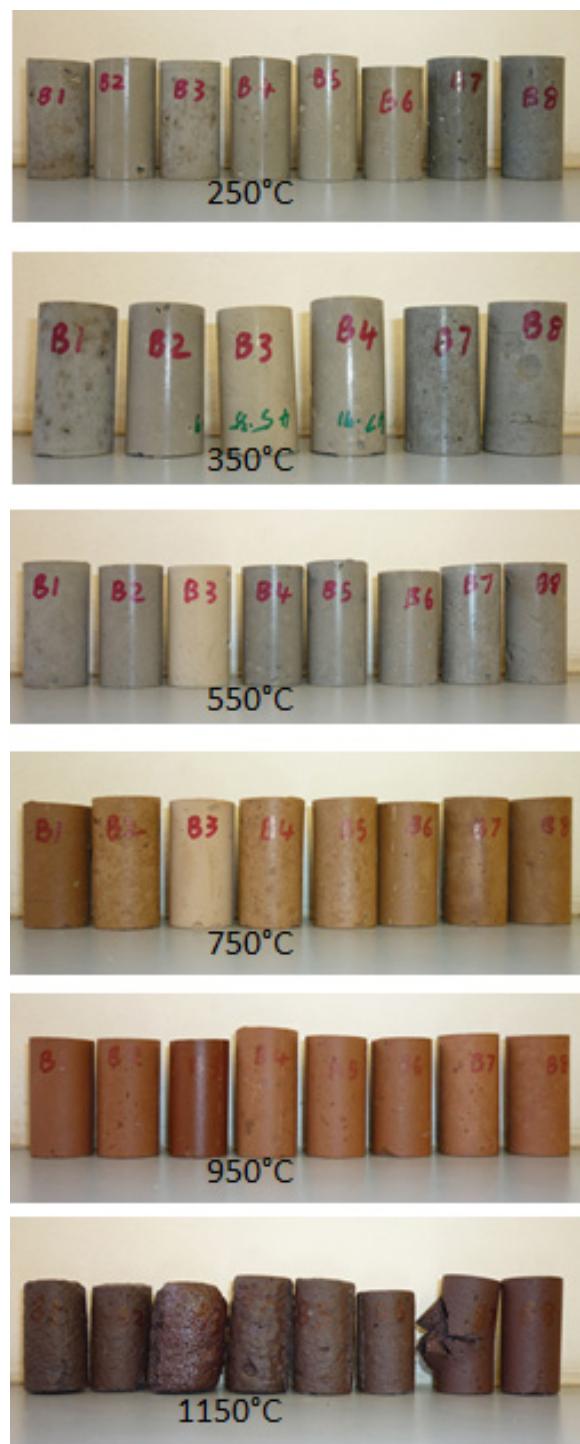


Figure 8-32. Bayer geopolymer samples subjected to high temperatures.

The process of vitrification or transformation appears to taken place with all samples at 1150°C. Though the majority of samples softened, mix 8 appeared to be completely unaffected by the thermal test. Final mass loss across the sample range appeared to be less than 6% and most samples experienced less than 3 % change in height (Figure 8-33 and Figure 8-34).

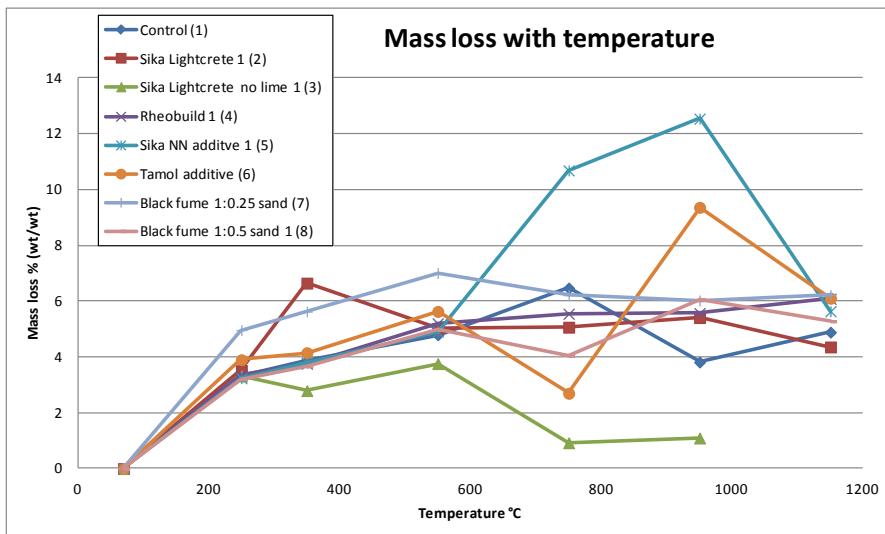


Figure 8-33. Graph of mass change with thermal treatment.

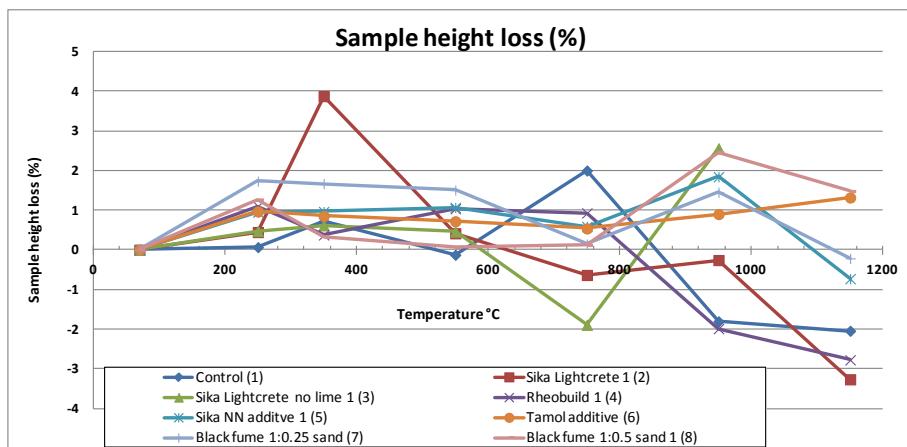


Figure 8-34. Graph of height change with thermal treatment.

The largest differences in performance were mixture 8 which effectively improved in strength, and mixture 3 which foamed and melted. An optical and SEM investigation of sample 8 (Figure 8-35) shows the beginnings of an amorphous glass phase melt, while an XRD (Figure 8-36) shows the sample retains the absence of crystallisation. This supports the view that the thermal changes are akin to melting and glass formation, exactly the same as brick formation. The compressive strength curve (Figure 8-37) shows the distinct breakage of a more rigid structure.

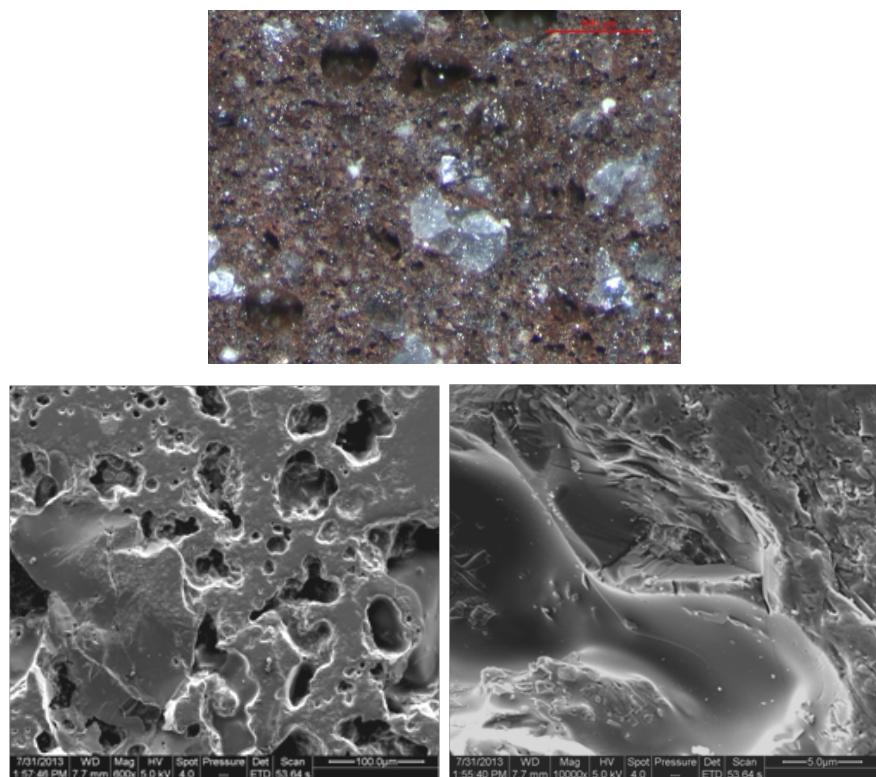


Figure 8-35. Microscopy and SEM images of Sample 8 after treatment at 1150°C.

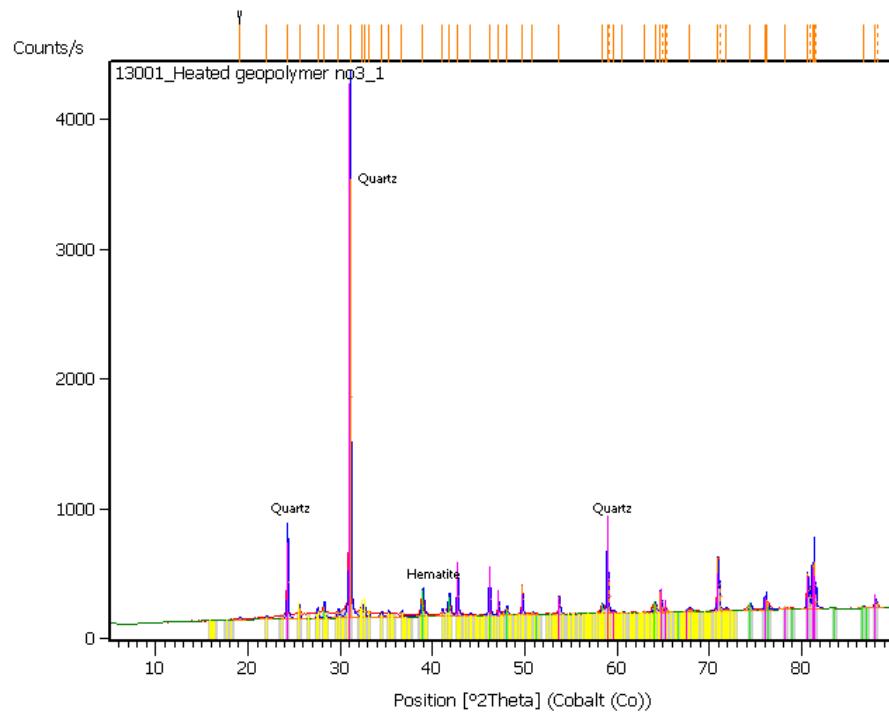


Figure 8-36. XRD of sample 8 showing lack of new crystallisation.

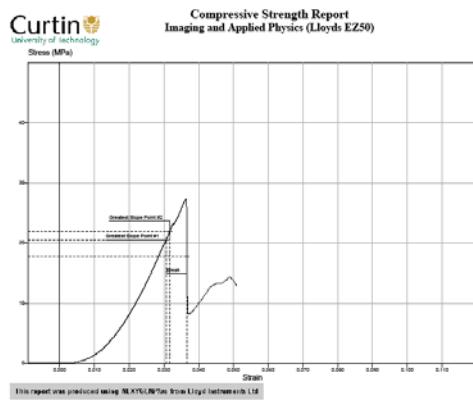


Figure 8-37. Stress - strain curve for sample 8 (Rheomac fume and 33 wt% sand) after heating to 1150°C.

Mixture 3 foamed considerably (Figure 8-38), while mixture 2 was relatively unaffected. How the absence of 2.4 wt% lime could make such a difference in the product performance at 1150°C is not known. The presence of lime could be expected to possibly outgas at high temperature, or to lower the melting temperature by acting as a flux but the opposite has occurred. Clearly this relates to the reaction mechanism during the cure process and the ability of calcium to allow different phases to form. Further research is recommended into identifying the possible reaction pathways.

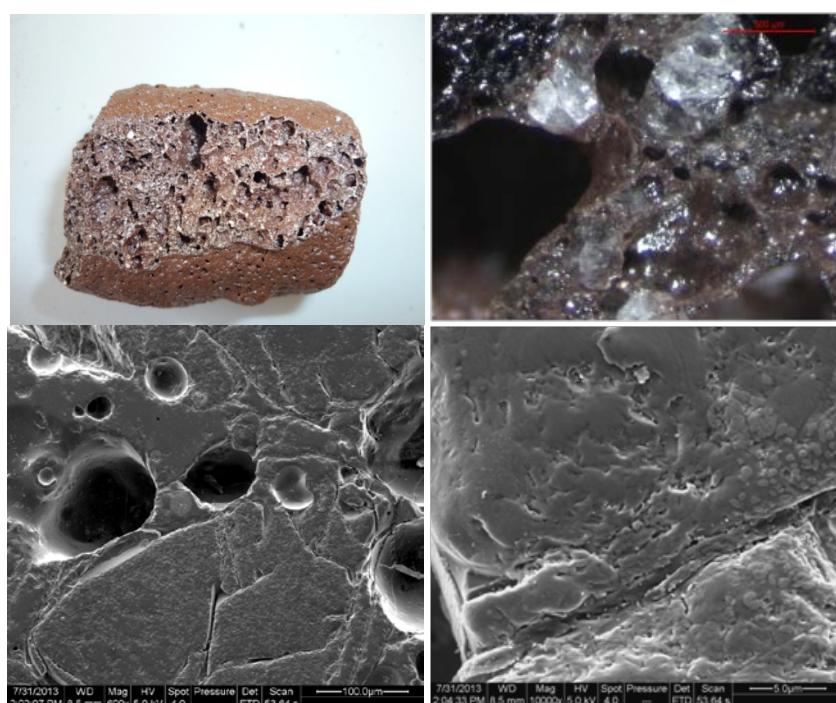


Figure 8-38. Microscopy and SEM images of sample 3 after 3 hours at 1150°C

The other mixes with the exception of 7 and 8, also slumped or foamed but not to such an extent. The foamed sample mix 3 was surprisingly strong and has a similar appearance to pumice. Further research is recommended to determine if the foamed product can be utilised as kiln refractory.

Mixture 7 was perhaps the most perplexing of all the samples (Figure 8-39). All three specimens appeared to be untouched on the outside but had nucleated a phase transformation internally that ruptured the sample in an “Aliens” like fashion.



Figure 8-39. Sample mixture 7 having appeared to nucleate a ceramic material within the sample core at 1150°C.

Further research is recommended into this mixture (7) to determine if a ceramic has formed and what are its properties. Mixture 8 only had slightly more sand present than mix 7. It is possible that this extra quartz stabilised the product and prevented melting, or physically prevented melt from flowing. A full chemical analysis of samples specifically evaluating the iron content would be valuable for comparison to the work of Rickard *et al.* (2011) who found that the iron content of fly ash was a key factor in the thermal performance of geopolymers. In this case the additional sand may be reducing the iron content through dilution. Rickard *et al.* (2011) provided data to support the iron content impact but there also appeared to be a correlation between the initial geopolymer density and its ability to develop strength through temperature exposure. This would be another avenue to investigate.

One obvious implication of the thermal resistance of Bayer geopolymers is their ability to be used in structural environments where fire is a significant danger. For example, Wagner (2012) is utilising the thermal stability properties of geopolymers to make tunnel liners to protect traffic tunnels from the danger of automobile fires. Other defence applications for Bayer-derived geopolymers are highly likely, particularly coupled with the high compressive strength.

8.6.5 Production of aggregates

Artificial aggregate may seem like a strange choice for application of a significant new binding system. However, the attractiveness lies in the very large size of the market. Aggregates are a highly competitive market with many sources and the commodity is relatively cheap. However, this cheapness is also a benefit. There are many sites that need aggregate in large quantity but the source is at a considerable distance (often in excess of 100 km). Transport is now a large proportion of costs, so being able to produce aggregate in an area of low natural abundance is a significant advantage. This is the case for Alcoa's three Western Australian refineries and others globally such as Suriname, where both sand and aggregate are scarce commodities.

For a Bayer geopolymer project to be implemented, the volumes would be significant and would require multiple, large and varied markets. Aggregates fit these criteria as a base load production. Any excess production can be indefinitely stored awaiting demand. Alternatively the formulation of the aggregates can be modified to utilise more Bayer feedstock if required.

Production of aggregates can take a continuous minimum bleed stream (24 hours/day), while allowing higher value products to be manufactured according to demand on an ad hoc basis as shown in concept in Figure 8-40.

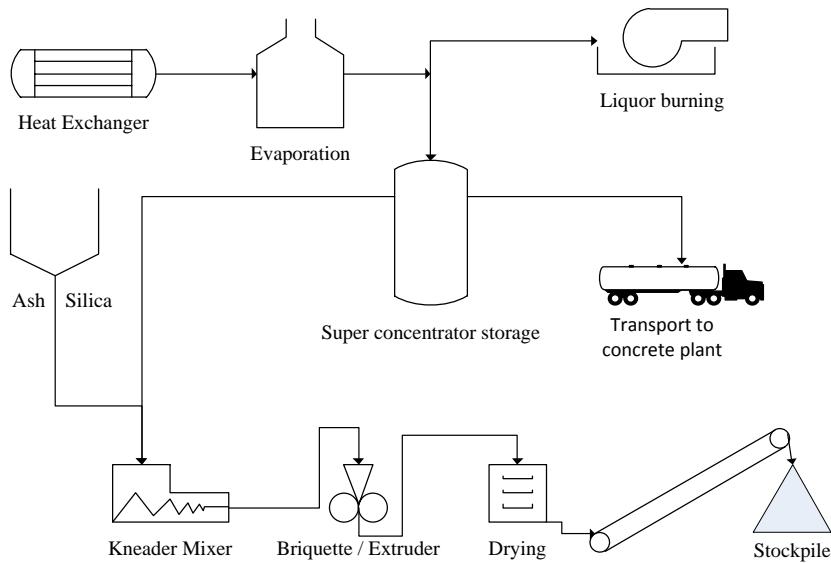


Figure 8-40. Flow diagram for collection of Bayer concentrate for continuous geopolymer aggregate production and ad-hoc manufacture of concrete.

8.6.5.1 Aggregate formation methods

Samples of Bayer-derived geopolymers have been made into a mortar to improve handling characteristics. The mortar has then been made into aggregates of different shapes using a variety of different methods. The desire is to produce products that can be assessed in different applications as well as for demonstration purposes.

The first method assessed was to utilise a rotating drum for the creation of artificial pisolites shown in Figure 8-41, Table 8-16 and Figure 8-42.



Figure 8-41. Bayer geopolymer mortar tumble rolled to form aggregate.

The tumbled material is easy to handle but the formation can be an issue. Due to the stickiness of the product, a surface coating of fly ash or other agent such as alcohol is added to allow free tumbling. The use of these products complicates the production process and significantly adds to occupational health and safety issues. This will increase capital and operational costs. In addition, many applications prefer a non-rounded product.

Table 8-16. Bayer geopolymers mortar for aggregate production using heat cure.

Sample	nil
Yellow Sand wt%	50
Lime % of paste	0.0
Si/Al	2.3
OH/Al	0.7
Water wt% of paste	13.6
Water wt% of total	6.8
Stickiness	OK
Workability	Good
Estimated slump	nil
1 Day 70C Strength (Mpa)	39



Figure 8-42. Bayer geopolymers mortar tumble rolled aggregate of different sizes.

Though not a serious evaluation, a series of hand moulded samples were made to highlight the possibilities as shown in Figure 8-43



Figure 8-43. Hand moulded aggregates.

A second method for the formation of aggregates was to extrude the product then mechanically cut it into any desired aggregate size distribution (Figure 8-44).



Figure 8-44. Bayer geopolymer mortar hand rolled or mechanically extruded then cut into 1 cm segments.

Mechanical extrusion and cutting was favoured by Penna (2012). He applied sand to the extruded surface as a method of preventing binding during the curing process.

An alternative method is to allow the mechanically extruded product to achieve first set, then break or crumble the product into an aggregate (Figure 8-45). This removed the requirement for sand coating as the extruded product was no longer sticky.



Figure 8-45. Bayer geopolymer mortar allowed to reach first set then crumbled.

The final aggregate production method evaluated was to allow the mechanically extruded product to completely cure then crush the geopolymer to the desired PSD (Figure 8-46). This method most closely reflects the production of aggregate from virgin granite.



Figure 8-46. Bayer geopolymer mortar allowed to cure then crushed and screened

8.6.5.2 Application of artificial aggregate in geopolymers concrete

Samples of the Bayer-derived geopolymers mortar have previously been made into coloured balled aggregate (Chapter 8.4.3). This aggregate was utilised with a Bayer-derived geopolymers mortar to make a geopolymers concrete. The coloured aggregate, the sand and the geopolymers binder were all about 20 MPa compressive strength. The formation ratios and results are shown in Table 8-17.

Table 8-17. Bayer-derived geopolymer concrete, formulation and results.

Sample	Bayer geopolymer concrete with Bayer geopolymer aggregate
Sand wt%	21.2
Aggregate wt%	43.2
Si/Al	2.3
OH/Al	0.7
Lime wt% of paste	0.0
Water wt% of total	9.5
Stickiness	Ok
Workability	Good
Estimated slump	Nil
28 Day Boral Compressive Strength (MPa)	19

A slice of the Bayer-derived concrete is shown in Figure 8-47. The coloured aggregate provides an idea as to how a polished pavement slab may look. It also allows for easier detection of the aggregate and binder interface.



Figure 8-47. Coloured geopolymer aggregate in geopolymer concrete (D= 10 cm).

With a non-optimised compressive strength of 19 MPa, this demonstration product nearly meets “Normal” class concrete at 20 MPa (AS 1379, 2007). Not only does it demonstrate the potential for Bayer geopolymer concrete to be formulated for high volume applications (as part of Normal class concrete) but it also highlights the fact that Bayer geopolymer can be recycled and used as aggregate in subsequent construction. In Figure 8-47, Bayer geopolymer has also been crushed and used as the fine aggregate. It can be identified as the light red irregular sharp shapes within the paste background.

The interaction of Bayer aggregate with Bayer geopolymer binder was investigated to determine the interfacial bond. The micrographs in Figures 8-48, 8-49 and 8-50 show that the paste has reacted with the aggregate surfaces creating a chemical bond.

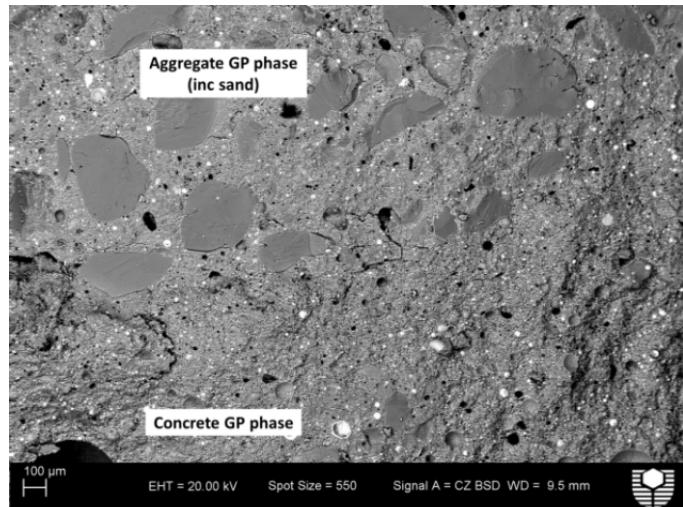


Figure 8-48. Micrograph showing geopolymer aggregate in geopolymer mortar.

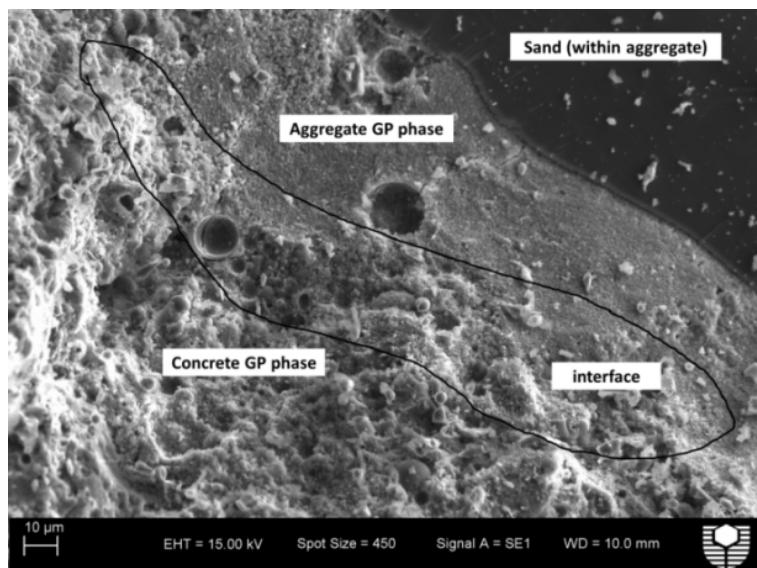


Figure 8-49. Micrograph of aggregate binder interaction indicating a reactive bond.

Note also above the very clear bond between the aggregate geopolymer phase and the sand within the aggregate. Lee & Van Deventer (2004) noted that geopolymers did not form as good a bond if silicate were not present in the activating solution. The evidence above would indicate that aluminate in solution also creates a strong chemical bond.

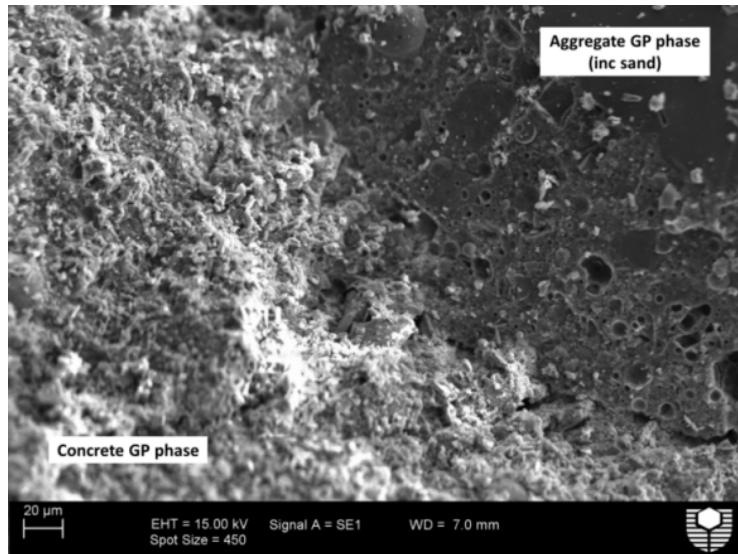


Figure 8-50. Micrograph of aggregate and binder delamination in lower RHS.

The delamination surrounding some particles could be due to the moisture absorption by the dry polymer aggregate creating localised cavitation. It is recommended that aggregate be allowed to be “saturated surface-dry”, a term used in the concrete industry to denote the aggregate is internally saturated but effectively surface dry (AS 1379, 2007). As a result it will not add or remove moisture from the binding mixture. Re-evaluation using saturated surface dry conditions should determine if this was the cause of any delamination, or if there is a simple surface-wetting effect. Improved vibration would remove this problem.



Figure 8-51. Crushed sample of Bayer aggregate in Bayer concrete displaying the breakage through the binder (diameter = 10 cm).

Note in Figure 8-51 that the fracture pattern cleanly breaks some aggregate but mostly follows lines of the binder. In this case, the aggregate is stronger than the binder. Also note that there is very little evidence of surface cleavage.

In conclusion it is apparent that artificial aggregates are well suited to binding with geopolymers paste to make concrete. Use of saturated surface-dry aggregate is recommended in future to prevent any localised moisture loss issues. It would also allow a dryer paste to be made of higher strength.

It is recommended that Bayer-derived geopolymers concrete be assessed for linear cure shrinkage as outlined in AS 1012.13. OPC concrete will average between 500 and 800 micro-strain though less than 1000 can be accepted in general use. By comparison, silicate-activated geopolymers concrete has been reported to have less than 400 micro-strain shrinkage after one year (Sagoe-Crentsil *et al.* 2011).

8.6.5.3 Artificial aggregate use in road base

Bayer-derived geopolymers aggregate was made by crushing of geopolymers mortar. The mortar was a combination of samples made for the evaluation of sand content. The total batch size was 200 kg and required multiple passes through a 19 mm jaw crusher, followed by screening out material above 19 mm.

The final recombined PSD is shown in Table 8-18 as part of a material test report provided by Boral. Wet strength was 99 kN and dry strength was 150 kN as determined in accordance with AS1141.22 (AS 1141, 1999). The weighted average particle density was determined in accordance of AS 1141.5. The dry density was 2020 kg/m³ (granite is 2700 kg/m³) and the saturated surface-dry density was 2170 kg/m³. Water absorption was determined to be 7.7 wt%.

Table 8-18. PSD of Bayer-derived geopolymers aggregate.

Sieve Size	% Passing
19.0mm	100
13.2mm	77
9.5mm	52
6.7mm	35
4.75mm	24
2.36mm	14
1.18mm	9
600µm	6
300µm	4
150µm	2
75µm	1

Compaction tests were conducted in accordance with test method MRWA 133.1 (2012). Samples were dried at 70°C and water added progressively. The compaction curve (Figure 8-52) was then used to determine the aggregate optimum water content (15 wt%) and maximum dry density (1760 kg/m^3). This water content is high but is expected to be lower with plant-produced aggregate (less air entrapment).

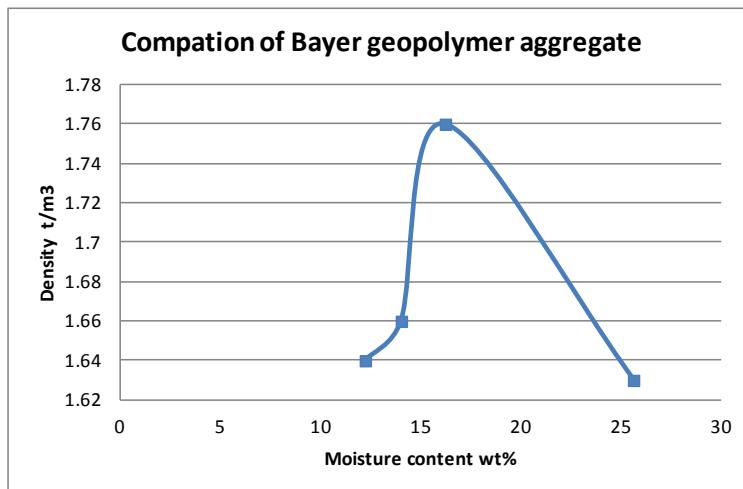


Figure 8-52. Density and moisture content optimisation.

The California Bearing Ratio was assessed in line with method MRWA 141.1 (2012). The Force-displacement curve is shown in Figure 8-53. The CBR measured at 5 mm penetration was determined to be 100%. This equates to being equal to crushed rock, the standard for base course in road construction. Note the descending force curve was not captured.

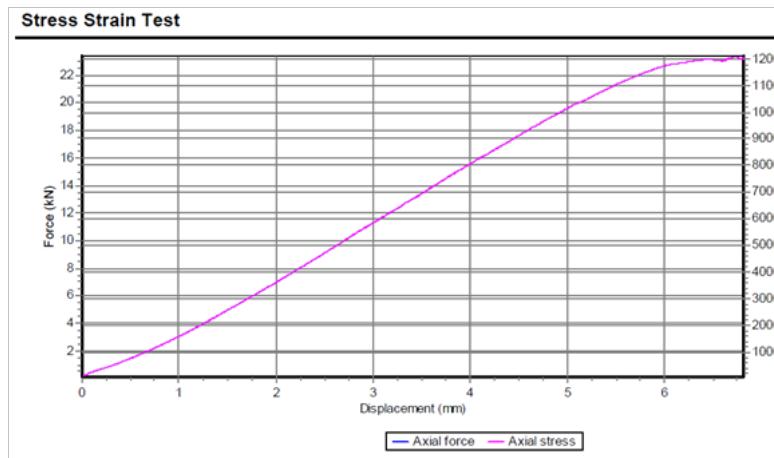
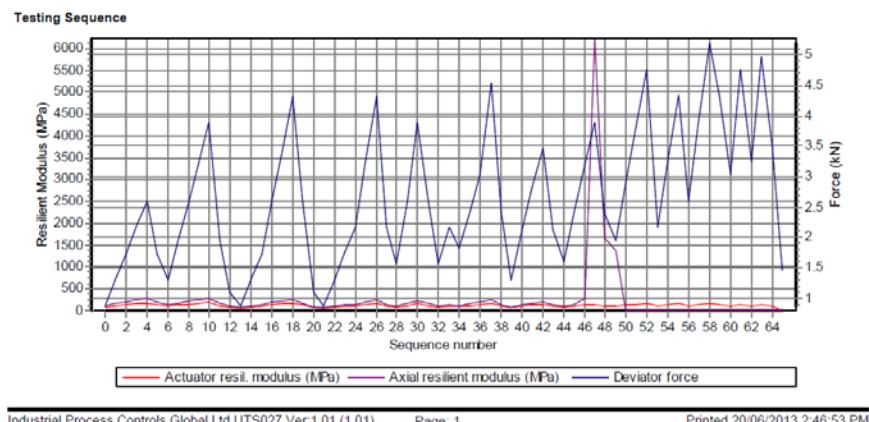


Figure 8-53. Force-displacement curve for Bayer geopolymer aggregate.

The permanent deformation and the resilient modulus were determined using standard methods Austroads APRG 00/33 (2000) and Austroads AG:PT/T053 (2007) respectively. Results are shown in Figure 8-54.



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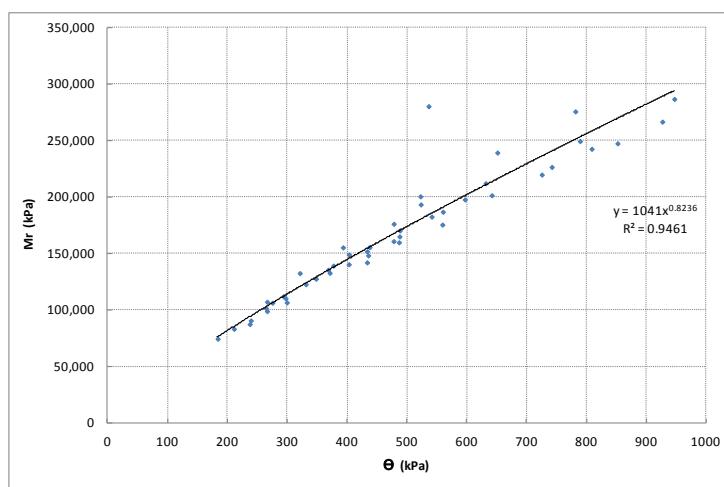


Figure 8-54 Resilient Modulus (Mr) curves for Bayer geopolymer aggregate.

Model	Equation	The regression coefficients			Symbols
		K_1	K_2	K_3	
K -Theta ($K - \theta$)	$M_r = k_1\theta^{k_2}$ (Hicks and Monismith 1971)	6.317	0.628	—	M_r = Resilient modulus, MPa θ = Bulk stress = $(\sigma_1 + \sigma_2 + \sigma_3)$ k_1, k_2 = Regression coefficients

Equation 8-1. Determination of the Resilient Modulus (Mr).

From the data provided in Figure 8-54 and using Equation 8-1, various Mr can be calculated to range between 150 and 250 MPa. This is lower than expected but may be a result of the high porosity of the aggregate and associated water (Chummuneerat et al 2012). It is also a single indicator test. More testing is recommended on product derived with applied vacuum.

In conclusion, the initial assessments of Bayer-derived geopolymers mortar aggregate is promising and suggests that further testing be conducted on pilot plant derived material.

8.6.5.4 Artificial aggregate use in OPC concrete

Normal OPC concrete contains 70 - 85 wt% aggregate, usually granite of high density (2700 kg/m^3). The combined concrete typically ranges in density from 2300 to 2600 kg/m^3 . Bayer geopolymers paste has a density of between 1800 and 2000 kg/m^3 . With the addition of sand and aggregate, the density of geopolymers concrete is similar to that of OPC concrete. However, if the granite aggregate were replaced with Bayer geopolymers aggregate, then the finished concrete density would drop considerably. Weight savings of 10 to 30% could be formulated. With a reduction in weight comes a reduction in transport costs, etc.

The same argument holds for the use of Bayer geopolymers aggregate within OPC concrete. This would offer a significant saving on weight as well as open options for new production sites. It is also the lowest perceived risk option for implementation, where the Bayer geopolymers was encapsulated in OPC. This would allow confidence to grow and for technical certainty surrounding Bayer geopolymers concrete applications to be robustly demonstrated.

A 40 kg batch of OPC concrete was made at Boral Laboratories utilising the same bulk aggregate mix utilised for road base testing in Chapter 8.6.5.3. The mix design is given in Appendix 5. The goal was to make a light weight OPC concrete with compressive strength of 45 MPa and to meet minimum slump characteristics.

The batch slump test was shown to be 65 mm, just within the criteria of $80 \text{ mm} \pm 20 \text{ mm}$. It was noted that the slump is not only dependent on rheology, but also on the density of the aggregate. As the geopolymer aggregate was significantly lighter than granite, the slump would naturally be smaller.

A sample of wet concrete was taken and shown to have a wet (plastic) density of 2080 kg/m^3 . The 7-day hardened density was 2125 kg/m^3 , significantly lighter than a standard 45 MPa concrete of about 2400 kg/m^3 . The Bayer geopolymer mortar contained 33wt% sand and the OPC concrete used sand for fine aggregate, which has a density of 2650 kg/m^3 . As Bayer aggregate is only 2020 kg/m^3 , replacing the sand with geopolymer sand would lower the density of the resulting concrete further.

Compressive strength was conducted after 7 days curing with some interesting results. The artificial aggregate OPC concrete achieved a compressive strength of 50MPa after 7 days cure. The aim was for 45 MPa after 56 Days. At day 27 the compressive strength had increased to 57 MPa and continued to climb to 69MPa (Figure 8-55).

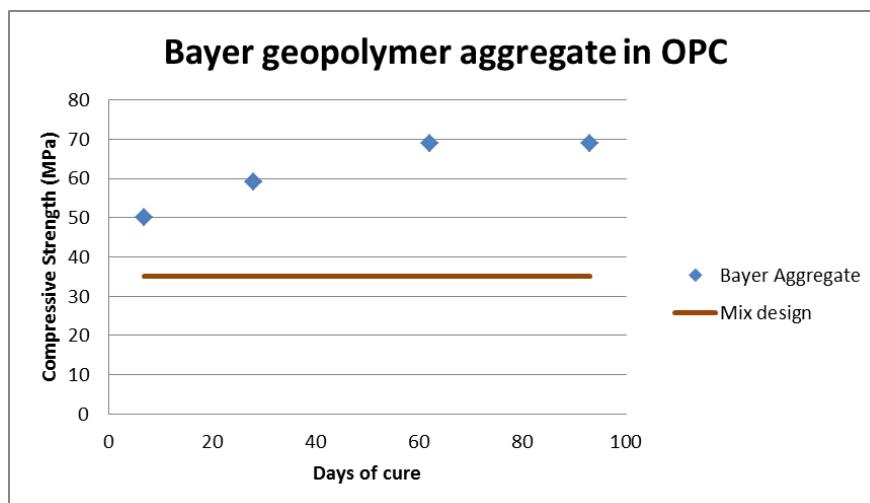


Figure 8-55. Compressive strength for OPC concrete using geopolymer aggregate.

It is concluded that the Bayer geopolymer aggregate has increased the concrete compressive strength while decreasing the product density.



Figure 8-56. OPC concrete using Bayer geopolymer aggregate (diameter = 10 cm).

Figure 8-56 gives the first clues as to why the artificial aggregate in OPC concrete was so much stronger than expected. Looking at a crushed sample indicates that the aggregate was sheared in preference to either OPC or surface adhesion sites. By this, it is surmised that the aggregate was the weakest point, having a compressive strength about 40 MPa. Normal granite aggregate can have a compressive strength of 200 MPa so it is seldom the weak link. However, it is widely acknowledged that the surface bonding between OPC and granite is poor (Shi et al. 2006) and crushing will normally follow the surface contact sites. It appears that the geopolymer aggregate has bonded very well at the surface (Figure 8-57) and hence the actual aggregate is the weakest link. This has resulted in a significant improvement in compressive strength. Shi et al. (2012) also noted an increase in compressive strength using geopolymer and OPC binder/aggregate combination, believing this to reflect an intimacy of surface contact.

Another factor at play can also be that the aggregate and the binder are closer in mechanical properties than the binder (OPC) and natural aggregate (granite). Husem (2003) proposed a scenario where by a large difference in mechanical properties between the binder and aggregate would accelerate the development and spread of

micro-cracks. With OPC and geopolymer being close in mechanical properties, the composite concrete is actually stronger in performance.

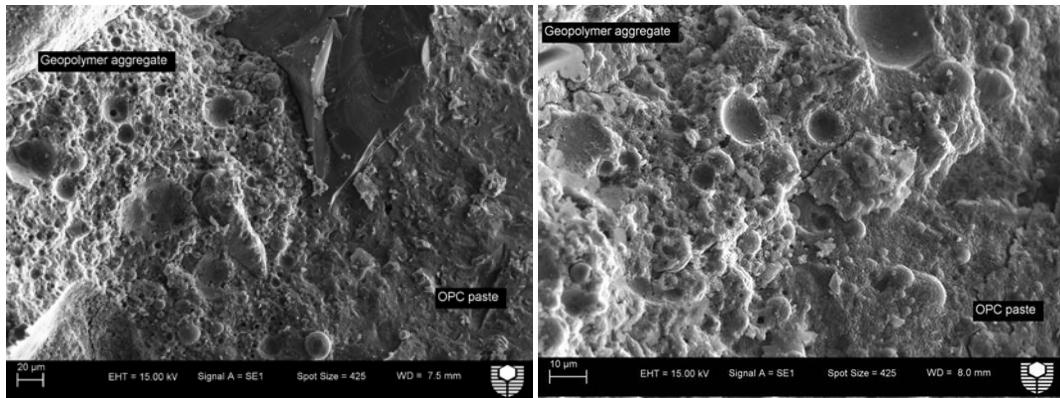


Figure 8-57. SEM of aggregate and OPC showing strong surface interaction.

Other parameters of interest in the experiment were the dry or cure shrinkage as shown in the Figure 8-58. In this case the aggregate has not impacted upon the shrinkage of the concrete cylinder and results are within normal levels as communicated by Boral laboratories.

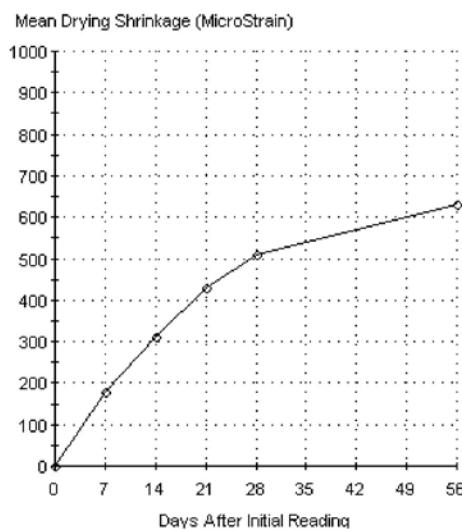


Figure 8-58. Cure shrinkage for OPC concrete using Bayer geopolymer aggregate.

There are several implications from this work that should be mentioned at this point. By lowering the concrete density, the transport cost, vehicle wear and road deformation will be reduced. In a state like Western Australia, many pre-cast products can be transported over 1000 km, hence lighter concrete is rated a premium product.

In addition, as the compressive strength is increased, it is probable that the OPC content could be lowered to return the mixture to the original design specification and reduce the cost of the concrete. As a side effect, there would also be a decrease in the concrete embodied energy and a lowering of the green-house gas emissions. Alternatively, the thickness of the concrete can be reduced to meet the minimum standards, therefore reducing the weight of the cast significantly.

It is concluded that geopolymer aggregate can be utilised in geopolymer concrete.

Finally the success of this trial demonstration has some wider implications. Galvin & Lloyd (2011) and Pacheco-Torgal *et al.* (2012) have proposed that OPC recycled aggregate may be utilised within geopolymer concrete, once geopolymers have become the dominant binding agent. This is an important proposal as the European Union has decreed that by 2020 70% of construction and demolition waste must be recycled (European Waste Framework Directive, 2008/98/EC). While it has been demonstrated here that bonding between OPC and geopolymers may be superior to virgin aggregate, Galvin & Lloyd (2011) suggest a maximum of 30% recycled OPC concrete presumably because the aggregate may not be as strong as the binder.

8.6.5.5 Conclusions on aggregate

Bayer-derived geopolymer mortar aggregate has the best chances of early implementation for the following reasons:

- Least operational risk as aggregate can be made to different grades as expertise is developed.
- Aggregate production is a continuous process.
- Aggregate can be stored indefinitely while benefits occur immediately for alumina refineries.
- Aggregates have the largest market volume though are of low value.
- Aggregate can be used internally to the alumina refineries for dust suppression on residue, replacing a purchased product.

- Aggregate can be manufactured utilising other residue products such as sand.
- Aggregate production can utilise off the shelf equipment.
- Aggregate production is low technological risk with wide standards.
- Bayer-derived geopolymers aggregate may be superior to virgin granite aggregate in some applications, including light weight concrete.

Aggregate production offers the chance to commence utilisation while minimising operational risk. Artificial aggregate production also potentially allows for very good QA/QC control of aggregates made and graded for specific use, a trend reported by Frisk (2007).

8.6.6 Foam block

The potential for Bayer geopolymers to make light weight foam concrete is significant and is investigated below. It has already been demonstrated that some admixes induce foam which the geopolymer and possibly the dissolved organic help to stabilise. Consequently, one additive was applied at a high dose rate to induce the foam. No optimisation has been made and results are presented in Table 8-19.

Table 8-19. Formulation ratios and results for foamed geopolymer.

Sample	XS Sikament NN
Regent g/kg	82.4
Si/Al	0.8
OH/Al	0.7
Lime wt% in paste	0.0
Water wt%	11.0
Stickiness	Sticky
Flow	Good
Estimated slump	nil
Strength (MPa) 1 day 70C	14
Strength (MPa) 7 day	
Ambient	5
Strength (MPa) 28 day	
Ambient	13
Strength (MPa) 56 day	
Ambient	16

Such a low initial strength is unusual for geopolymers where high early strength is normal. However, it has been observed by Chong *et al.* (2011) and is probably a result of having low to no lime within the mixture.



Figure 8-59. Bayer mortar foam, ambient cure.

As shown in Figure 8-59, the foamed product takes the moulded form with nice finish while achieving a density of 1600 kg/m^3 . This product had compressive strength of 5 MPa after 7 days of ambient curing. This is not strong but will still support human traffic (not stilettos!). After 28 days of ambient cure, the strength had risen to 13 MPa and had achieved 15.8 MPa by day 56 (Figure 8-60). These are significant results given the high level of foam and resulting low density. With formulation optimisation, this product could be suitable for some structural applications (as well as non-load bearing applications).

The density is significantly higher than that reported by Bui *et al.* (2012) who made aggregates from alkali-activated blast furnace slag to achieve densities between 770 and 1060 kg/m^3 . The reported compressive strength ranged from 6 - 16 MPa and water absorption between 8 and 20 wt%. It is recommended that foamed Bayer geopolymers be made without sand and compared to the results of Bui *et al.* (2012).

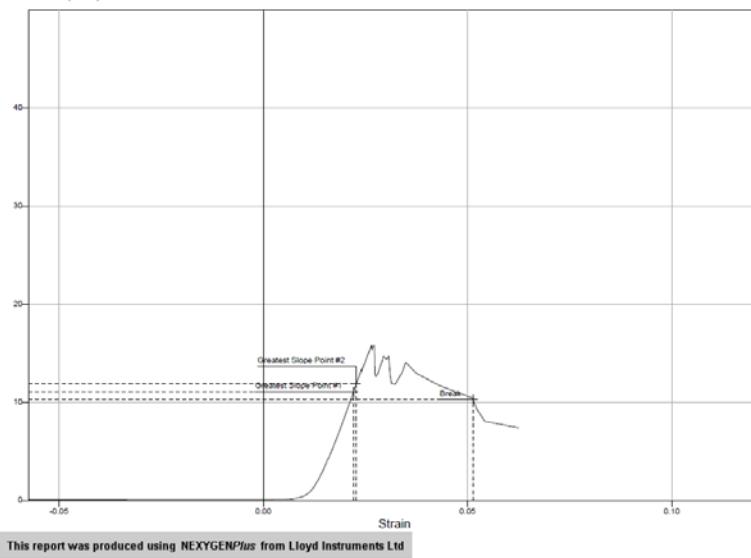


Figure 8-60. Compression curve for foam cured for 56 days at ambient temperature.



Figure 8-61. Bayer mortar foam, 70°C cure.

The same foam mixture was also cured at a temperature of 70°C. As seen in Figure 8-61, the product took the moulded form with a nice finish while maintaining a density of 1500 kg/m³. This product had compressive strength of 14 MPa which exceeds the requirements for standard non-load bearing mortar of 5.2 MPa and load bearing mortar of 12.4 MPa, but not structural lightweight concrete, which needs to exceed 17 MPa. A significant complication was that the sample cracked during the curing process. This is believed to be a result of the rate of temperature elevation and also a loss of moisture, so the cracking may be preventable.

It is concluded that this light weight mortar has the potential to make ultra-light weight concrete ($< 1440 \text{ kg/m}^3$) and is an area recommended for further study.

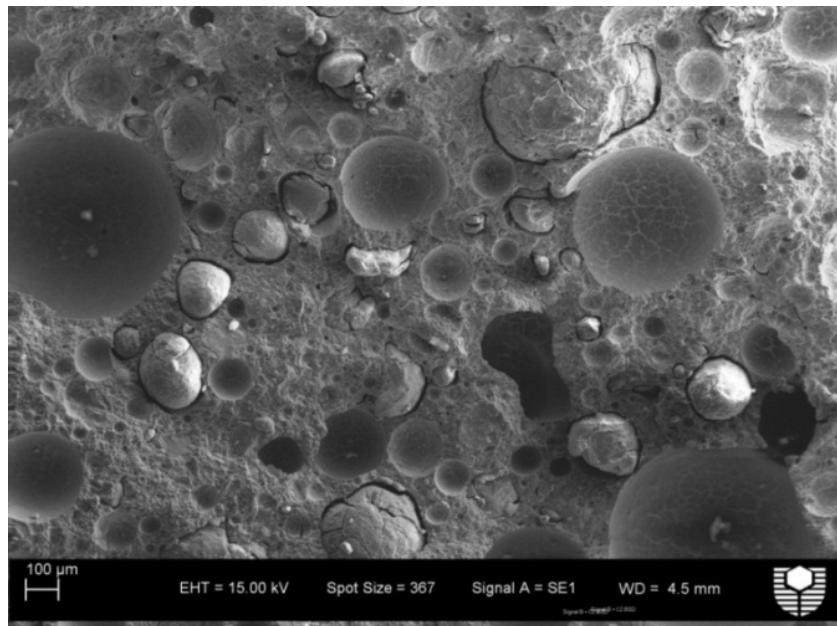


Figure 8- 62. SEM micrograph of foam geopolymers.

Figure 8-62 shows the sand grains and the inclusion of bubbles of 50 – 1000 μm . To make the material of lower density, the removal of the higher density sand would be the next step and should not be difficult to achieve.

These results are different from those of Pham & Le (2010) who utilised hydrogen peroxide to generate foam with bubbles 500 - 3000 μm in diameter. The density was considerably lower at 200 – 800 kg/m^3 , but so was the strength at 2 MPa or less. Their results are similar in pore size to those of Rickard (2012) which were generated with the use of aluminium. It appears that the Bayer-derived geopolymers may be situated within a niche market utilising micro-bubbles but retaining structural properties. The bubbles are much easier to create than those using peroxide or aluminium powder, so production should be cheaper too.

This preliminary investigation has shown that research is warranted into this field. The limited number of samples has prevented more definitive conclusions and it is believed that further investigations will improve the understanding as well as enabling formulation optimisation.

8.6.7 Geopolymer environmental performance

One of the proposed applications for geopolymer is the entombment of toxic metals including nuclear waste. Hence it is reasonable to expect that geopolymers will have minimal environmental impact in use. While toxic metal entombment is not envisioned for Bayer-derived geopolymers, it is necessary to ensure that any metal impurities in the Bayer liquor are immobilised. Therefore all proposed products need to meet both the performance standards as well as any environmental guidelines. In Western Australia there are no direct guidelines for by-products hence comparison is made against the only guidelines available: waste regulations.

8.6.7.1 Waste landfill assessment - Composition analysis

The elemental composition of various geopolymer samples are compared to the 1996 Department of Environment, Landfill Waste Classification and Waste Definition Guidelines (DOE, 1996). Compositional analysis was performed by Bureau Veritas – Ultra Trace Pty Ltd. Results are recorded in Tables 8-20 to 8-23. The samples represent 23 formulations that can be used for different applications and can contain various additives. These different formulations also provide a higher level of confidence in the results. Comparison is also made against OPC concrete.

Table 8-20. Composition analysis of Bayer Geopolymer formulations against DoE Landfill Waste Classification 1996.

Assessment against DoE Landfill Waste Classification and Waste Definitions 1996 Guidelines By Total composition								1 ppm = 0.0001%
Element	Landfill Waste classification by composition (mg/kg)				All results in ppm		1000 ppm = 0.1%	
	Class I	Class II	Class III	Class IV	Mix 24 full lime No sand	Mix 24 half lime yellow sand 1:0.5	Mix 24 half lime red sand 1:0.5	Mix 24 half lime yellow sand black silica 1:0.5
	Inert Landfill	Putrescible landfill	Putrescible landfill	Secure Landfill				
Arsenic	14	14	140	1400	18	10	11	9
Beryllium	2	2	20	200	10.9	6.8	8	7.4
Cadmium	0.4	0.4	4	40	0.5	0.5	0.5	0.5
total Chromium	-	-	-	-	100	200	100	150
Chromium (VI)	10	10	100	1000				
Lead	2	2	20	200	64	44	51	43
Mercury	0.2	0.2	2	20	0.05	0.05	0.06	0.04
Molybdenum	10	10	100	1000	46.5	31.5	35	33
Nickel	4	4	40	4000	144	86	112	102
Selenium	2	2	20	200	10	5	5	10
Silver	20	20	200	2000	0.5	-0.5	-0.5	-0.5
Fluoride	300	300	3000	30000	0.01	-0.01	0.01	0.01
Aluminium	5% by weight	5% by weight	10% by weight	20% by weight	10.1	6.92	9.06	7.06
Barium					2630	1760	1820	1760
Boron					70	45	50	50
Cobalt					56	40	42	38
Copper					528	350	408	340
Manganese					145	90	170	85
Vanadium					272	170	188	200
Zinc								

Table 8-21. Bayer geopolymer composition against Landfill Waste Classification.

Element	Lime 0%	Lime 1%	Lime 2%	Lime 3%	Lime 4%	Lime 5%
All results in ppm						
Arsenic	12	9	10	9	9	9
Beryllium	9.7	10.1	9.4	9.9	9.4	9.3
Cadmium	0.5	0.5	0.5	0.5	0.5	0.5
total Chromium	100	100	150	100	150	100
Chromium (VI)						
Lead	68	71	66	70	67	66
Mercury	0.07	0.08	0.08	0.07	0.07	0.07
Molybdenum	55	54.5	52.5	54.5	54	53.5
Nickel	130	136	122	118	116	128
Selenium	10	10	10	10	10	5
Silver	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5
Fluoride	0.01	0.01	0.01	0.01	0.01	0.01
Aluminium	9.65	9.13	8.72	8.98	8.96	8.8
Barium	2280	2320	2220	2270	2390	2340
Boron						
Cobalt	60	55	65	60	65	65
Copper	50	52	48	48	48	48
Manganese	450	444	430	444	428	432
Vanadium	125	95	85	90	85	90
Zinc	242	236	230	224	224	224

Table 8-22. Bayer geopolymers composition against Landfill Waste Classification.

Element	Light weight mix (density 1.40)	Sand 1:1	Sand 1: 0.25	Sand 1: 0.75	OPC Concrete	Black Additive	Red additive	Mix 24 no lime with red sand coating
All results in ppm								
Arsenic	10	12	15	12	2	8	7	6
Beryllium	10	5.5	9.2	6.2	2	7.4	7.2	4.9
Cadmium	0.5	-0.5	0.5	-0.5	-0.5	0.5	0.5	-0.5
total Chromium	150	100	200	50	100	50	100	50
Chromium (VI)								
Lead	69	37	55	40	26	48	61	38
Mercury	0.16	0.05	0.06	0.05	0.02	0.05	0.07	0.04
Molybdenum	51	25.5	42.5	28.5	2	29.5	44	27.5
Nickel	134	80	112	84	16	94	92	60
Selenium	10	-5	10	5	-5	5	5	-5
Silver	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5
Fluoride	0.01	-0.01	0.01	0.01	0.02	0.01	0.02	-0.01
Aluminium	9.32	5.67	8.33	6.26	6.43	7.03	8.51	5.3
Barium	2540	1360	2190	1510	403	1820	1850	1220
Boron								
Cobalt	60	35	55	35	20	45	50	30
Copper	50	34	42	32	16	40	46	28
Manganese	434	268	408	304	448	440	462	240
Vanadium	95	75	110	90	60	75	85	65
Zinc	234	136	228	160	60	262	212	140

Table 8-23. Bayer geopolymers composition against Landfill Waste Classification.

Element	Aggregate mix B 1	Aggregate mix B 4	Aggregate mix B 5	Aggregate mix B 5-2	Low aggregate mix 1 Jul2012	Mix 24 full lime with yellow sand 1:0.5
All results in ppm						
Arsenic	17	17	17	18	6	15
Beryllium	12	10.7	14.2	14.1	3.4	7.2
Cadmium	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5
total Chromium	100	100	150	100	-50	150
Chromium (VI)						
Lead	50	41	58	61	30	49
Mercury	0.04	0.03	0.03	0.04	0.04	0.07
Molybdenum	31	30	38	37.5	13.5	32.5
Nickel	132	120	144	146	52	90
Selenium	10	5	5	5	-5	5
Silver	-0.5	-0.5	-0.5	-0.5	0.5	-0.5
Fluoride	0.02	0.01	0.02	0.02	0.04	0.01
Aluminium	7.58	6.95	8.79	8.74	6.24	7
Barium	1420	1190	1570	1570	1480	1690
Boron						
Cobalt	65	50	65	65	25	45
Copper	44	38	52	50	38	44
Manganese	142	118	142	140	546	324
Vanadium	125	125	135	130	115	100
Zinc	186	180	230	236	104	172

The colour coding within the tables highlights that several elements are elevated. Compositional assessment indicates that chromium, lead, and nickel, exceed the first stage of compositional classification and would require secure storage. It is noted that the chromium level was measured as total chromium but assessed as if it were all hexavalent chromium. This is a cost-related analytical issue and chromium (VI) would only be analysed if the total chromium failed the next stage of leach assessment. By way of comparison, OPC concrete was tested and also exceeded composition limits for similar elements. It would also require ASLP testing.

8.6.7.2 Waste landfill assessment - ASLP leach analysis

Since the composition assessment levels were exceeded, leach analysis is required to determine whether the elements are mobile. Genalysis Laboratory Services conducted ASLP leach analysis at the material's natural pH. Data is provided below in Tables 8-24 to 8-27.

Table 8-24. Bayer geopolymers leaching against Landfill Waste Classification.

By Leachable concentration		Landfill Waste classification by leachable conc (mg/L)							
Element	Landfill Waste classification by leachable conc (mg/L)				Mix 24 full lime No sand	Mix 24 half lime yellow sand 1:0.5	Mix 24 half lime red sand 1:0.5	Mix 24 half lime yellow sand black silica 1:0.5	
All results in ppm	Class I Inert Landfill	Class II Putrescible landfill	Class III Putrescible landfill	Class IV Secure Landfill	Natural	Natural	Natural	Natural	
Final pH					11.8	11.5	11.5	11.5	
Arsenic	0.5	0.5	0.7	7	0.280	0.358	0.255	0.310	
Beryllium	0.1	0.1	1	10					
Cadmium	0.1	0.1	0.2	2	0.000	0.000	0.000	0.000	
Total Chromium	-	-	-	-	X	X	0.010	X	
Chromium (VI)	0.5	0.5	5	50					
Lead	0.5	0.5	1	10	0.005	0.006	0.005	0.005	
Mercury	0.01	0.01	0.1	1	X	0.000	X	X	
Molybdenum	0.5	0.5	5	50	1.778	1.322	1.302	1.447	
Nickel	0.2	0.2	2	20	0.030	0.060	0.030	0.060	
Selenium	0.5	0.5	1	10	0.328	0.294	0.292	0.339	
Silver	1	1	10	100	0.280	0.358	0.255	0.310	
Fluoride	15	15	150	1500	X	0.400	0.400	1.100	

Table 8-25. Bayer geopolymers leaching against Landfill Waste Classification.

Element	Lime 0%	Lime 1%	Lime 2%	Lime 3%	Lime 4%	Lime 5%
	Natural	Natural	Natural	Natural	Natural	Natural
All results in ppm						
Final pH	10.8	11.1	11.5	11.7	11.9	12
Arsenic	0.487	0.522	0.446	0.401	0.379	0.344
Beryllium						
Cadmium	0.000	0.000	0.000	0.000	X	0.000
Total Chromium	0.010	0.010	0.010	0.010	0.010	0.010
Chromium (VI)						
Lead	0.010	0.010	0.007	0.008	0.007	0.006
Mercury	0.000	X	0.000	0.000	0.000	X
Molybdenum	2.628	2.698	2.452	2.394	2.397	2.269
Nickel	0.030	0.070	0.100	0.100	0.090	0.070
Selenium	0.382	0.638	0.562	0.547	0.547	0.536
Silver	0.487	0.522	0.446	0.401	0.379	0.344
Fluoride	1.900	2.300	2.200	2.000	2.200	1.200

Table 8-26. Bayer geopolymers leaching against Landfill Waste Classification.

Element	Light weight mix (density 1.40)	Sand 1:1	Sand 1: 0.25	Sand 1: 0.75	OPC Concrete	Black Additive	Red additive	Mix 24 no lime with red sand coating
	Natural	Natural	Natural	Natural	Natural	Natural	Natural	Natural
All results in ppm								
Final pH	10.7	11.1	10.9	11.1	11.9	11.8	11	10.4
Arsenic	0.417	0.233	0.328	0.309	0.011	0.162	0.450	0.234
Beryllium								
Cadmium	X	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total Chromium	X	X	0.020	0.010	X	X	X	0.020
Chromium (VI)								
Lead	0.005	0.005	0.009	0.005	0.001	0.005	0.007	0.005
Mercury	0.000	X	0.000	X	X	X	X	X
Molybdenum	2.713	0.972	1.611	1.102	0.035	1.275	2.569	1.219
Nickel	0.020	0.020	0.050	0.020	X	0.020	0.040	0.030
Selenium	0.482	0.213	0.260	0.248	0.014	0.256	0.618	0.217
Silver	0.417	0.233	0.328	0.309	0.011	0.162	0.450	0.234
Fluoride	1.000	X	X	X	0.100	X	1.800	1.200

It is noted that total chromium was analysed and not chromium (VI) but the colour coding was assessed as if were chromium (VI). Note also, that due to an oversight, beryllium leaching was not analysed. This is not a concern as beryllium did not require secure impoundment when assessed for total composition, hence did not need to be analysed. Nevertheless, it is recommended that an assessment be conducted to ensure completeness. Also note that the pH of some of the crushed products exceeds 11.5 (including OPC). To avoid a “hazardous material” rating, QC/QA needs to ensure pH is less than 11.5.

Table 8-27. Leach assessment against DoE Landfill Waste Classification 1996

Element	Aggregate mix B 1	Aggregate mix B 4	Aggregate mix B 5	Aggregate mix B 5-2	Low aggregate mix 1 Jul2012	Mix 24 full lime with yellow sand 1:0.5
	Natural	Natural	Natural	Natural	Natural	Natural
All results in ppm						
Final pH	11.2	11.4	11.6	10.3	11.7	10.2
Arsenic	0.602	0.530	0.270	0.233	0.248	0.001
Beryllium						
Cadmium	0.000	0.000	X	0.000	0.000	X
Total Chromium	0.010	X	X	X	X	0.010
Chromium (VI)						
Lead	0.005	0.006	0.006	0.007	0.005	0.005
Mercury	X	X	X	X	X	X
Molybdenum	1.367	1.264	1.577	0.667	1.172	0.000
Nickel	0.070	0.070	0.020	X	0.020	X
Selenium	0.312	0.264	0.270	0.166	0.243	0.002
Silver	0.602	0.530	0.270	0.233	0.248	0.001
Fluoride	1.800	0.700	0.100	0.600	X	0.100

From the tables above it is apparent that only molybdenum and occasionally selenium and arsenic exceed the lowest classification of inert landfill. This is in agreement with the findings of Izquierdo *et al.* (2009) who reported that the oxy-anionic elements may be solubilised by the high pH, but could be controlled through careful geopolymer formulation. None of the elements are classified as requiring secure storage. Note that OPC concrete, Red Sand™ and Alkaloam® all met the lowest criteria. It is concluded from the leach testing that all of the products tested do not require secure impoundment if treated as waste.

The next step is to conduct a pH dependence test as per Van der Sloot *et al.* (2001) and Van der Sloot & Dijkstra (2004). This should be coupled with a mineralogical assessment. Understanding the solubility of the specific mineralogy is critical to environmental control and this is a key recommendation.

Given that most geopolymer applications are monolithic in nature and the testing was on finely crushed material, it is likely that actual receivable environments will experience much lower levels than even those reported above. Hence pH dependence testing of monoliths is also recommended as per Van der Sloot & Dijkstra (2004).

8.6.7.3 Radiological assessment

Bayer-derived geopolymer binder, mortar and concrete samples were assessed for their radiological content. State and National standards require the Specific Activity and the Total Activity of the radionuclides thorium, uranium and potassium be determined. These are calculated from the compositional analysis using a proprietary Alcoa method developed by Brian O'Conner (Attiwell, 2013).

The ARPANSA National Directory for Radiation Protection (2011) states that a material can be exempt from radiological legislative control if the Specific Activity concentration of the head-of-chain radionuclides Th-232 and U-238 do not exceed 1 Bq/g and K-40 does not exceed 100 Bq/g. The Specific Activity is shown in Table 8-28. All geopolymer samples meet the criteria hence are exempt from radiological control.

Table 8-28. Specific Activity of Bayer geopolymers against ARPANSA directory.

Specific Activity	U	Th	K	Th	U	K
	ppm	ppm	%	Bq/g	Bq/g	Bq/g
Mix 24 full lime No sand	17	36.1	0.32	0.15	0.21	0.10
Mix 24 half lime yellow sand 1:0.5	11	24.6	0.34	0.10	0.14	0.11
Mix 24 half lime red sand 1:0.5	14.9	73.8	0.24	0.30	0.18	0.07
Mix 24 half lime yellow sand black silica 1:0.5	6.3	23.9	0.43	0.10	0.08	0.13
Lime 0%	21.7	44.8	0.29	0.18	0.27	0.09
Lime 1%	23.6	33.7	0.27	0.14	0.29	0.08
Lime 2%	19.9	31.6	0.32	0.13	0.25	0.10
Lime 3%	23.2	32.7	0.27	0.13	0.29	0.08
Lime 4%	23.3	31	0.28	0.13	0.29	0.09
Lime 5%	22.8	30.8	0.28	0.12	0.28	0.09
Light weight mix (density 1.40)	24.1	32.1	0.29	0.13	0.30	0.09
Sand 1:1	8.9	18.4	0.42	0.07	0.11	0.13
Sand 1:0.25	14	30.1	0.33	0.12	0.17	0.10
Sand 1:0.75	10.3	21.4	0.43	0.09	0.13	0.13
OPC Concrete	5.4	15.9	2.61	0.06	0.07	0.81
Black Additive	12.1	25.1	0.36	0.10	0.15	0.11
Red additive	19.6	28.9	0.91	0.12	0.24	0.28
Salt cake liquor plus NaOH	29.8	31.8	0.28	0.13	0.37	0.09
Mix 24 no lime with red sand coating	12	20.5	0.3	0.08	0.15	0.09
Aggregate mix B1	12.7	26.8	0.42	0.11	0.16	0.13
Aggregate mix B4	11	22.8	0.42	0.09	0.14	0.13
Aggregate mix B5	14.8	30	0.36	0.12	0.18	0.11
Aggregate mix B5(2)	14.5	30	0.36	0.12	0.18	0.11
B concrete with low aggregate mix 1 Jul2012	7.3	18.7	1.33	0.08	0.09	0.41
Mix 24 full lime with yellow sand 1:0.5	11.6	24	0.4	0.10	0.14	0.12

The WA Radiation Safety Act regulations Western Australian Radiation Safety Act (1975 – 1979) and the Western Australian Radiation Safety (General) Regulations (1983 – 2003) state that a natural radioactive substance is exempt from radiological control if the activity of all progeny for a parent radionuclide (i.e. U 238 series and Th 232 series) does not exceed 30 Bq/g. Results are shown in Table 8-29.

Table 8-29. Total activity of Bayer geopolymers products against WA regulations.

	Th Bq/g	U Bq/g	K Bq/g	Total activity Bq/g
Mix 24 full lime No sand	1.46	2.95	0.10	4.51
Mix 24 half lime yellow sand 1:0.5	1.00	1.91	0.11	3.01
Mix 24 half lime red sand 1:0.5	2.99	2.58	0.07	5.65
Mix 24 half lime yellow sand black silica 1:0.5	0.97	1.09	0.13	2.19
Lime 0%	1.81	3.76	0.09	5.67
Lime 1%	1.36	4.09	0.08	5.54
Lime 2%	1.28	3.45	0.10	4.83
Lime 3%	1.32	4.02	0.08	5.43
Lime 4%	1.26	4.04	0.09	5.38
Lime 5%	1.25	3.95	0.09	5.29
Light weight mix (density 1.40)	1.30	4.18	0.09	5.57
Sand 1:1	0.75	1.54	0.13	2.42
Sand 1:0.25	1.22	2.43	0.10	3.75
Sand 1:0.75	0.87	1.79	0.13	2.79
OPC Concrete	0.64	0.94	0.81	2.39
Black Additive	1.02	2.10	0.11	3.23
Red additive	1.17	3.40	0.28	4.85
Salt cake liquor plus NaOH	1.29	5.16	0.09	6.54
Mix 24 no lime with red sand coating	0.83	2.08	0.09	3.00
Aggregate mix B1	1.09	2.20	0.13	3.42
Aggregate mix B4	0.92	1.91	0.13	2.96
Aggregate mix B5	1.22	2.57	0.11	3.89
Aggregate mix B5(2)	1.22	2.51	0.11	3.84
B concrete with low aggregate mix 1 Jul2012	0.76	1.27	0.41	2.44
Mix 24 full lime with yellow sand 1:0.5	0.97	2.01	0.12	3.11

All the Bayer-derived geopolymers products meet the criteria and are therefore exempt from control.

It is concluded that the Bayer geopolymers products are exempt from radiological control as assessed against ARPANSA National Directory for Radiation Protection (2011) and the WA Radiation Safety Act regulations Western Australian Radiation Safety Act (1975 – 1979) and Regulations (1983 – 2003).

8.6.7.4 Dangerous goods assessment

According to the Australian Code for the Transport of Dangerous Goods by Road and Rail (NTC, 2011), *Class 8 substances (corrosive substances) are substances which, by chemical action, will cause severe damage when in contact with living tissue, or, in the case of leakage, will materially damage, or even destroy, other goods or the means of transport.*

The method of determination of severe damage is by exposure testing. *In the absence of human experience the grouping must be based on data obtained from experiments in accordance with OECD Guideline 404. (OECD Guidelines for testing of chemicals No. 404 “Acute Dermal Irritation/Corrosion” 1992).* (NTC, 2011)

These trials were not conducted for this thesis. It is thought that geopolymers are unlikely to be classified as a dangerous good as they are solid materials. However, some samples have had a high pH from ASLP testing hence dangerous goods assessment is recommended prior to any possible commercialisation.

8.6.7.5 Controlled waste assessment

The Department of Environment and Conservation (DEC, 2004) defined controlled waste as any waste that cannot be disposed of at a Class I, II or III landfill site, as described by the DOE (1996) Landfill Waste Classifications. Finely crushed Bayer-derived geopolymers have been classified as Class III, hence are not controlled wastes.

8.6.7.6 Hazardous substance assessment

Worksafe Australia Standards (NOHSC:1008, 2004) defines a hazardous material as containing more than 0.5 wt% NaOH or a pH greater than 11.5. Finely crushed laboratory produced Bayer-derived geopolymers can have a pH higher than 11.5 but not all of them. Hence it is important to ensure that production processes ensure the pH is less than 11.5. It is also important to evaluate monolith assessment.

8.6.7.7 Contaminated sites assessment

Guidelines for contaminated sites are provided by the Department of Environment and Conservation (DEC, 2010). Compositional assessment is made against Health Investigation Levels (HIL) and Ecological Investigation Levels (EIL).

It is apparent that crushed Bayer-derived geopolymers meet Class A from the HIL assessment shown in Tables 8-30 to 8-33.

Table 8-30. Health Investigation Level assessment of Bayer-derived geopolymer

Element	Health Investigation Levels (ppm)				Mix 24 full lime No sand	Mix 24 half lime yellow sand 1:0.5	Mix 24 half lime red sand 1:0.5	Mix 24 half lime yellow sand black silica 1:0.5
	A	D	E	F				
Antimony	31	-	-	820	0.2	-0.2	0.2	0.6
Arsenic	100	400	200	500	18	10	11	9
Barium	15000	-	-	190000	2630	1760	1820	1760
Beryllium	20	80	40	100	10.9	6.8	8	7.4
Boron	3000	12000	6000	15000	-20	-20	80	-20
Cadmium	20	80	40	100	0.5	0.5	0.5	0.5
Chromium III	120000	480000	240000	600000	100	200	100	150
Chromium VI	100	400	200	500	-	-	-	-
Cobalt	100	400	200	500	70	45	50	50
Copper	1000	4000	2000	5000	56	40	42	38
Lead	300	1200	600	1500	64	44	51	43
Manganese	1500	6000	3000	7500	528	350	408	340
Methyl Mercury	10	40	20	50	-	-	-	-
Mercury	15	60	30	75	0.05	0.05	0.06	0.04
Molybdenum	390	-	-	5100	46.5	31.5	35	33
Nickel	600	2400	600	3000	144	86	112	102
Tin	47000	-	-	610000	-1	-1	2	3
Vanadium	550	-	-	7200	145	90	170	85
Zinc	7000	28000	14000	35000	202	74	580	132

Table 8-31. Health Investigation Level assessment of Bayer-derived geopolymer

Element	Health Investigation Levels (ppm)				Lime 0%	Lime 1%	Lime 2%	Lime 3%	Lime 4%	Lime 5%
	A	D	E	F						
Antimony	31	-	-	820	0.2	0.2	0.2	0.2	-0.2	-0.2
Arsenic	100	400	200	500	12	9	10	9	9	9
Barium	15000	-	-	190000	2280	2320	2220	2270	2390	2340
Beryllium	20	80	40	100	9.7	10.1	9.4	9.9	9.4	9.3
Boron	3000	12000	6000	15000	-20	-20	-20	-20	20	-20
Cadmium	20	80	40	100	0.5	0.5	0.5	0.5	0.5	0.5
Chromium III	120000	480000	240000	600000	100	100	150	100	150	100
Chromium VI	100	400	200	500	-	-	-	-	-	-
Cobalt	100	400	200	500	60	55	65	60	65	65
Copper	1000	4000	2000	5000	50	52	48	48	48	48
Lead	300	1200	600	1500	68	71	66	70	67	66
Manganese	1500	6000	3000	7500	450	444	430	444	428	432
Methyl Mercury	10	40	20	50	-	-	-	-	-	-
Mercury	15	60	30	75	0.07	0.08	0.08	0.06	0.05	0.07
Molybdenum	390	-	-	5100	55	54.5	52.5	54.5	54	53.5
Nickel	600	2400	600	3000	130	136	122	118	116	128
Tin	47000	-	-	610000	1	2	-1	2	-1	-1
Vanadium	550	-	-	7200	125	95	85	90	85	90
Zinc	7000	28000	14000	35000	880	2010	746	1810	664	692

Table 8-32. Health Investigation Level assessment of Bayer-derived geopolymers

	Health Investigation Levels (ppm)				Light weight mix (density 1.40)	Sand 1:1	Sand 1: 0.25	Sand 1: 0.75	OPC Concrete	Black Additive	Red additive	Salt cake liquor plus NaOH	Mix 24 no lime with red sand coating
Element	A	D	E	F									
Antimony	31	-	-	820	0.2	-0.2	0.2	-0.2	-0.2	0.2	0.2	-0.2	
Arsenic	100	400	200	500	10	12	15	12	2	8	7	8	6
Barium	15000	-	-	190000	2540	1360	2190	1510	403	1820	1850	2340	1220
Beryllium	20	80	40	100	10	5.5	9.2	6.2	2	7.4	7.2	9.3	4.9
Boron	3000	12000	6000	15000	20	20	-20	20	140	-20	40	-20	20
Cadmium	20	80	40	100	0.5	-0.5	0.5	-0.5	-0.5	0.5	0.5	0.5	-0.5
Chromium III	120000	480000	240000	600000	150	100	200	50	100	50	100	100	50
Chromium VI	100	400	200	500	-	-	-	-	-	-	-	-	-
Cobalt	100	400	200	500	60	35	55	35	20	45	50	55	30
Copper	1000	4000	2000	5000	50	34	42	32	16	40	46	48	28
Lead	300	1200	600	1500	69	37	55	40	26	48	61	79	38
Manganese	1500	6000	3000	7500	434	268	408	304	448	440	462	446	240
Methyl Mercury	10	40	20	50	-	-	-	-	-	-	-	-	-
Mercury	15	60	30	75	0.16	0.05	0.06	0.05	0.02	0.05	0.07	0.05	0.04
Molybdenum	390	-	-	5100	51	25.5	42.5	28.5	2	29.5	44	21.5	27.5
Nickel	600	2400	600	3000	134	80	112	84	16	94	92	116	60
Tin	47000	-	-	610000	1	-1	1	-1	2	-1	-1	-1	-1
Vanadium	550	-	-	7200	95	75	110	90	60	75	85	95	65
Zinc	7000	28000	14000	35000	1310	85	432	68	161	192	1190	568	121

Table 8-33. Health Investigation Level assessment of Bayer-derived geopolymers

	Health Investigation Levels (ppm)				Aggregate mix B1	Aggregate mix B 4	Aggregate mix B 5	Aggregate mix B 5(2)	B concrete with low aggregate	Mix 24 full lime with yellow sand 1:0.5
Element	A	D	E	F						
Antimony	31	-	-	820	0.2	0.2	0.4	0.4	-0.2	-0.2
Arsenic	100	400	200	500	17	17	17	18	6	15
Barium	15000	-	-	190000	1420	1190	1570	1570	1480	1690
Beryllium	20	80	40	100	12	10.7	14.2	14.1	3.4	7.2
Boron	3000	12000	6000	15000	20	40	-20	20	-20	20
Cadmium	20	80	40	100	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5
Chromium III	120000	480000	240000	600000	100	100	150	100	-50	150
Chromium VI	100	400	200	500	-	-	-	-	-	-
Cobalt	100	400	200	500	65	50	65	65	25	45
Copper	1000	4000	2000	5000	44	38	52	50	38	44
Lead	300	1200	600	1500	50	41	58	61	30	49
Manganese	1500	6000	3000	7500	142	118	142	140	546	324
Methyl Mercury	10	40	20	50	-	-	-	-	-	-
Mercury	15	60	30	75	0.04	0.03	0.03	0.04	0.04	0.07
Molybdenum	390	-	-	5100	31	30	38	37.5	13.5	32.5
Nickel	600	2400	600	3000	132	120	144	146	52	90
Tin	47000	-	-	610000	-1	-1	2	2	-1	-1
Vanadium	550	-	-	7200	125	125	135	130	115	100
Zinc	7000	28000	14000	35000	189	337	794	834	201	120

Ecological Investigation Levels are shown below in Tables 8-34 to 8-37. From this assessment, finely crushed Bayer-derived geopolymers trigger EILs, as does Ordinary Portland Cement.

Table 8-34. Ecological Investigation Level assessment of Bayer-derived geopolymers

	Ecological Investigation Levels (EIL) (mg/kg)	Mix 24 full lime No sand	Mix 24 half lime yellow sand 1:0.5	Mix 24 half lime red sand 1:0.5	Mix 24 half lime yellow sand black silica 1:0.5
Element					
Antimony	20	0.2	-0.2	0.2	0.6
Arsenic	20	18	10	11	9
Barium	300	2630	1760	1820	1760
Cadmium	3	0.5	0.5	0.5	0.5
Chromium III	400	100	200	100	150
Chromium VI	1	-	-	-	-
Cobalt	50	70	45	50	50
Copper	100	56	40	42	38
Lead	600	64	44	51	43
Manganese	500	528	350	408	340
Mercury	1	0.05	0.05	0.06	0.04
Molybdenum	40	46.5	31.5	35	33
Nickel	60	144	86	112	102
Tin	50	-1	-1	2	3
Vanadium	50	145	90	170	85
Zinc	200	202	74	580	132
Sulphur	600	900	550	650	950
Sulphate	2000	-	-	-	-

Table 8-35. Ecological Investigation Level assessment of Bayer-derived geopolymers

	Ecological Investigation Levels (EIL) (mg/kg)	Lime 0%	Lime 1%	Lime 2%	Lime 3%	Lime 4%	Lime 5%
Element							
Antimony	20	0.2	0.2	0.2	0.2	-0.2	-0.2
Arsenic	20	12	9	10	9	9	9
Barium	300	2280	2320	2220	2270	2390	2340
Cadmium	3	0.5	0.5	0.5	0.5	0.5	0.5
Chromium III	400	100	100	150	100	150	100
Chromium VI	1	-	-	-	-	-	-
Cobalt	50	60	55	65	60	65	65
Copper	100	50	52	48	48	48	48
Lead	600	68	71	66	70	67	66
Manganese	500	450	444	430	444	428	432
Mercury	1	0.07	0.08	0.08	0.06	0.05	0.07
Molybdenum	40	55	54.5	52.5	54.5	54	53.5
Nickel	60	130	136	122	118	116	128
Tin	50	1	2	-1	2	-1	-1
Vanadium	50	125	95	85	90	85	90
Zinc	200	880	2010	746	1810	664	692
Sulphur	600	500	550	600	550	650	650
Sulphate	2000	-	-	-	-	-	-

Table 8-36. Ecological Investigation Level assessment of Bayer-derived geopolymers

	Ecological Investigation Levels (EIL) (mg/kg)	Light weight mix (density 1.40)	Sand 1:1	Sand 1: 0.25	Sand 1: 0.75	OPC Concrete	Black Additive	Red additive	Salt cake liquor plus NaOH	Mix 24 no lime with red sand coating
Element										
Antimony	20	0.2	-0.2	0.2	-0.2	-0.2	-0.2	0.2	0.2	-0.2
Arsenic	20	10	12	15	12	2	8	7	8	6
Barium	300	2540	1360	2190	1510	403	1820	1850	2340	1220
Cadmium	3	0.5	-0.5	0.5	-0.5	-0.5	0.5	0.5	0.5	-0.5
Chromium III	400	150	100	200	50	100	50	100	100	50
Chromium VI	1	-	-	-	-	-	-	-	-	-
Cobalt	50	60	35	55	35	20	45	50	55	30
Copper	100	50	34	42	32	16	40	46	48	28
Lead	600	69	37	55	40	26	48	61	79	38
Manganese	500	434	268	408	304	448	440	462	446	240
Mercury	1	0.16	0.05	0.06	0.05	0.02	0.05	0.07	0.05	0.04
Molybdenum	40	51	25.5	42.5	28.5	2	29.5	44	21.5	27.5
Nickel	60	134	80	112	84	16	94	92	116	60
Tin	50	1	-1	1	-1	2	-1	-1	-1	-1
Vanadium	50	95	75	110	90	60	75	85	95	65
Zinc	200	1310	85	432	68	161	192	1190	568	121
Sulphur	600	1000	550	700	550	1100	600	500	1000	300
Sulphate	2000	-	-	-	-	-	-	-	-	-

Table 8-37. Ecological Investigation Level assessment of Bayer-derived geopolymers

	Ecological Investigation Levels (EIL) (mg/kg)	Aggregate mix B1	Aggregate mix B4	Aggregate mix B5	Aggregate mix B5 (2)	B concrete with low aggregate	Mix 24 full lime with yellow sand 1:0.5
Element							
Antimony	20	0.2	0.2	0.4	0.4	-0.2	-0.2
Arsenic	20	17	17	17	18	6	15
Barium	300	1420	1190	1570	1570	1480	1690
Cadmium	3	-0.5	-0.5	-0.5	-0.5	-0.5	-0.5
Chromium III	400	100	100	150	100	-50	150
Chromium VI	1	-	-	-	-	-	-
Cobalt	50	65	50	65	65	25	45
Copper	100	44	38	52	50	38	44
Lead	600	50	41	58	61	30	49
Manganese	500	142	118	142	140	546	324
Mercury	1	0.04	0.03	0.03	0.04	0.04	0.07
Molybdenum	40	31	30	38	37.5	13.5	32.5
Nickel	60	132	120	144	146	52	90
Tin	50	-1	-1	2	2	-1	-1
Vanadium	50	125	125	135	130	115	100
Zinc	200	189	337	794	834	201	120
Sulphur	600	900	500	900	850	1000	650
Sulphate	2000	-	-	-	-	-	-

8.6.7.8 Comparison against West Australian legislation

Bayer-derived geopolymers have been assessed against a range of Western Australian regulations and the findings are summarised in Table 8-38. It is noted that the fine crushed material can have a pH above the limit of 11.5. However, this is a

result of incomplete geopolymserisation and will be prevented by a quality control and quality assurance system.

Table 8-38. Comparison of Bayer geopolymers against regulations.

Regulation	Classification
WA Landfill Waste Classification	Crushed material is landfill Class III, but does not require secure landfill
Radiological assessment	Does not require radionuclide control
Dangerous Good	Not likely
Controlled Waste	No (Not a liquid and landfill Class III)
Hazardous Substance	Possible. Need QA/QC to keep pH < 11.5
Contaminated sites HIL	Crushed material is Class A
Contaminated sites EIL	Crushed material triggers EIL.

8.7 Pilot plant design

A pilot plant is a demonstration of concept design. For Bayer-derived geopolymers, the key items that need to be demonstrated on a pilot plant scale are:

- Mixing of the dry and wet ingredients,
- Mechanical feeding of equipment
- Production of a solid suitable for handling,
- Curing the product,
- Assessing the product.

Only after these criteria are met can the secondary manipulation of formulations and assessing of products begin. That is, a pilot plant designed for any particular geopolymer formulation will be of similar value for many other applications.

For this pilot plant trial, the primary aim was to demonstrate the concept of liquor solidification at the Kwinana alumina refinery. Liquor solidification is the use of geopolymer formation as an impurity removal process for the refinery, by consuming and encapsulating the liquor into a non-mobile matrix (geopolymer). The low

strength material may be subsequently utilised for dust prevention or embankment stabilisation within the bauxite residue impoundment area.

The criteria called for the maximisation of Bayer liquor and the minimisation of costs, as there will be no products for sale. The geopolymers matrix will be stored as part of the bauxite residue impoundment. Alcoa's Kwinana refinery was chosen because of its central location and because the source of fly ash is conveniently located on the Kwinana Industrial Strip. The geopolymers needed sufficient strength to allow handling and to prevent breakdown and release of Bayer liquor impurities. To achieve this result, a minimum compressive strength of 3 MPa was required, as determined experimentally and shown below. The elemental ratios that best suited the starting mix are given in Table 8-39.

Table 8-39. Elemental ratios and results for Kwinana liquor and Kwinana power station ash. Mix "C" was selected as having the best properties.

Sample	A	B	C	D	E	F	G	H	J	K
Si/Al	1.2	1.2	1.1	1.1	1.0	1.0	0.9	0.9	0.9	0.8
OH/Al	1.0	1.0	1.1	1.1	1.2	1.2	1.3	1.3	1.3	1.4
Water wt%	20.3	21.6	22.9	24.1	25.4	26.6	27.7	28.9	30.0	31.1
Stickiness	OK	OK	OK	OK	OK	OK	sticky	sticky	sticky	sticky
Workability	V Low	V Low	low	ok	ok	Good	Good	Good	Good	Good
Estimated slump	nil	nil	nil	nil	nil	nil	nil			
Compressive Strength (MPa)	10.4	6.8	4.4	3.0	2.5	1.6	1.2	0	0	0
Efflorescence	No	No	No	No	Yes	Yes	Yes	Yes	Yes	Yes

Two possible plant designs have been described below. Both have advantages and disadvantages.

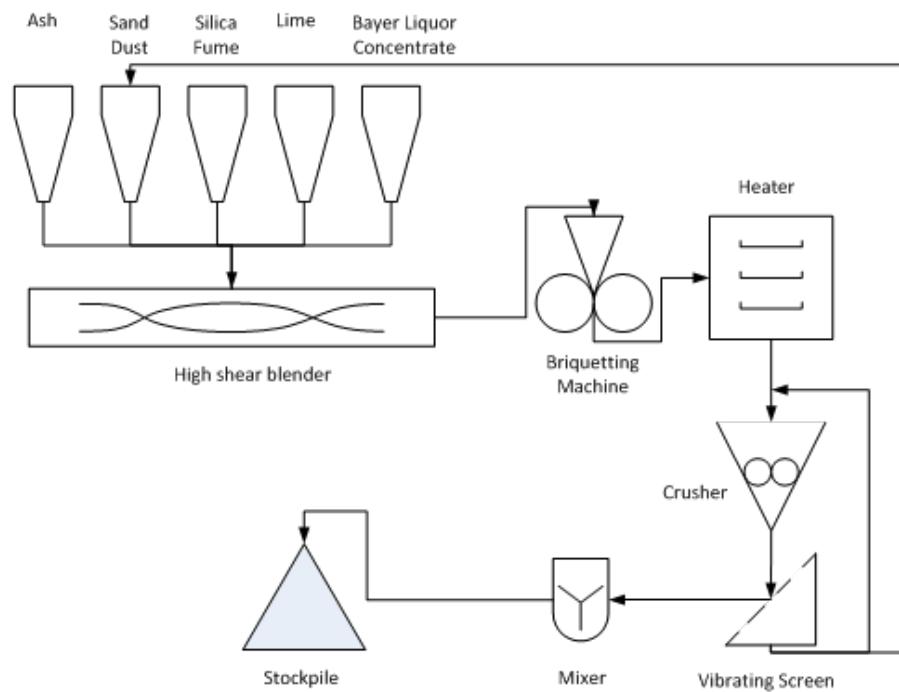


Figure 8-63. Process flow sheet for thermal cure of aggregate with options to recombine aggregates for specific applications.

The pilot plant shown in Figure 8-63 utilises a series of vibrational feed systems to add various ingredients to a shear mixer, normally used for breaking and blending clay. The mixture is fed into a briquetting machine to make a compressed product suitable for handling and heating in a high humidity heater. The role of the heater is not to dry the geopolymer but to elevate the temperature to about 90°C for about 1 hour. This ensures the geopolymer will cure into the hardened structure, without the need to add lime and without the hazard of “flash set” occurring.

Once cured, the briquettes can be used or stored in their current form. Later experiments with stronger formulations can be crushed and graded to make an ideal particle size distribution for aggregates, to be used in road base or concrete formation. This section of the pilot plant is not required for initial testing but can be added to either design for subsequent product development.

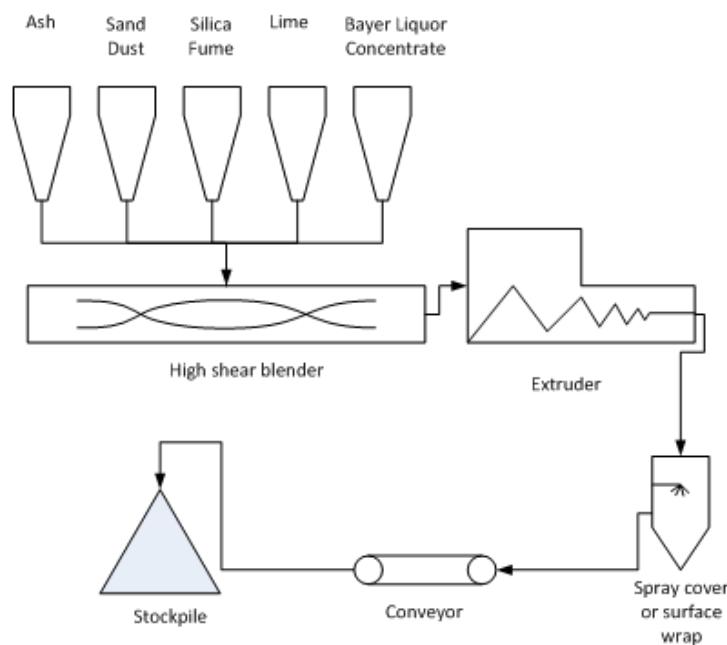


Figure 8-64. Process flow design for bulk geopolymer with CaO.

This pilot plant design shown in Figure 8-64 uses the same ingredients and mixing system as the one shown in Figure 8-63, however, the mixer output is fed into a dual-screw pug mixer self-feeding extruder. Additional liquor can be added to the pug mixer allowing for supercharging of the liquor composition as per the first stage of design specifications. It is important to limit the interaction of liquor in the blender with lime present to prevent “flash set”, though the current design specifications for low strength product would make this unlikely. The use of lime allows for ambient curing without the need for a steam heater. However, this creates issues with breakdown and maintenance where the equipment must be cleaned or it will cure in-situ. The extruder will also have a vacuum system to de-air the geopolymer mix.

In order to allow the geopolymer to form at ambient temperature with lime, the water content of the product must be maintained for several days as the strength develops. This creates the need for the product to be wrapped, bagged or spray coated to prevent moisture loss. This is not an ideal situation, but is the only alternative to the use of elevated temperature with moisture control.

Whichever of these two possible pilot plants are constructed, it is clear that the construction of full scale Bayer-derived geopolymer production facilities will not be capital intensive. It is rare to find published specific details because of “commercial

in confidence” issues, however, Sonafrank, (2010) reported that a geopolymmer production plant would be similar in design to a standard concrete batching plant and as such would be up to three orders of magnitude cheaper to construct than a full OPC production facility. This is in line with this author’s expectations and is reflected in the uncomplicated process design and the ability to utilise standard design production equipment.

8.8 Evaluation of carbon footprint

One of the often quoted claims of geopolymers is that the binder has a much smaller environmental footprint than Ordinary Portland Cement (OPC). However, there are many different ways to calculate this comparison and each method is reliant on different assumptions and circumstances.

The carbon footprint of geopolymers has been compared with OPC concrete by many. Most claimed that the formation of geopolymers has significantly lower greenhouse gas emissions than OPC concrete. Mix design and material selection also impact the carbon footprint (Yang *et al.* 2013).

The geopolymers concrete manufacturer E-Crete has the following claim (see also Figure 8-65).

With the support of the Resource Smart Business Program of Sustainability Victoria through the Department of Sustainability and Environment, Zeobond commissioned Netbalance to complete a Life Cycle Analysis of E-Crete™, our low-carbon concrete. The result – using E-Crete™ reduces the CO₂ footprint of cement by 80%! Zeobond (2013).

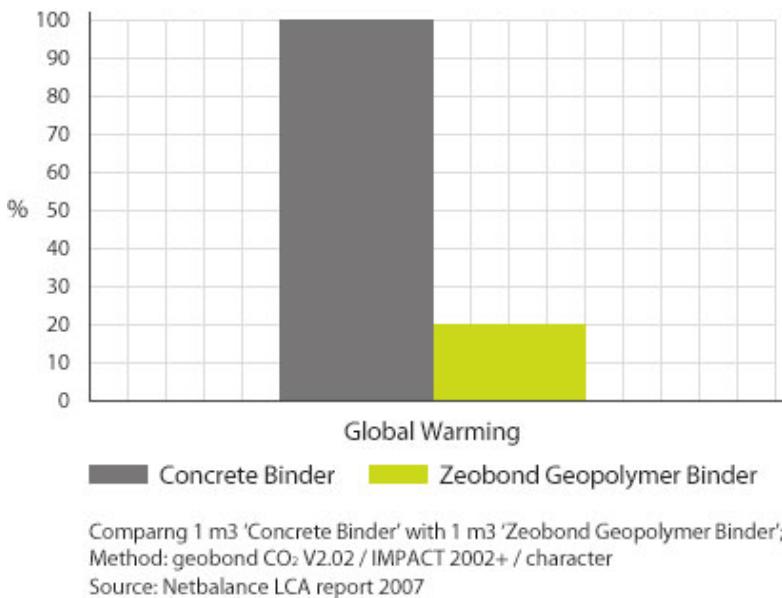


Figure 8-65. Geopolymer footprint (with permission, Zeobond, 2013).

While this comparison is made for binder, concrete is only 15 – 30 wt% binder. The rest being aggregates of very low carbon emission. In addition, the carbon footprint of OPC can be lowered significantly through blending materials and the use of green energy (CCAA, 2010). Hence OPC concrete is not necessarily the environmental menace that it is sometimes portrayed as. It is, however, still a significant source of carbon dioxide and utilisation of alternative binders such as geopolymers will make a reduction to the carbon footprint.

There are many different ways to calculate the environmental impact of the binding agent, with each method being reliant on different assumptions and circumstances (McGuire *et al.* 2011). It is therefore very important to identify and report those assumptions.

For example:

Many different materials can be used for geopolymer manufacture and each has different assumptions. The approach outlined below will be based on an “ex-gate” process. That is, the reagents for both geopolymer and OPC concretes will be assumed to be on location. This is not true in reality but both concrete manufacturers will require delivery of sand, aggregate, etc. Unless there is a specific case study to evaluate distances, then the preferable method is to say both will be similar on average and to negate them.

Both concrete formulations will normally utilise admixtures to enhance performance. While these materials are complex chemicals, because of their very small volume they can be negated in most comparisons (Stengel *et al.* 2009; Habert *et al.* 2010). Van den Heede and De Beile (2012) noted that the carbon dioxide foot print of admixtures is only slightly lower than OPC and their relative small volume made their contribution negligible. Hence the removal of admixtures from assessment is considered a valid assumption.

Table 8-40 shows a list of embodied energies that have been published. Values not listed need to be derived with explanation. It is from these embodied energies and related assumptions that a comparison of binders can be made.

Table 8-40. Embodied energy of various feedstock materials.

Material	Included stages	Embodied energy (GJ/t)		Reference <u>Underlined</u> is assigned value.
		Value assigned	Range	
Primary materials				
Clay	Mining	0.1	0.1 0.07	<u>McLellan et al., 2012</u> Alcorn, 2001
Limestone	Mining	0.1	0.1 0.03-0.06 0.124	<u>McLellan et al., 2012</u> Alcorn, 2001 Goggins et al. 2010
Sand	Mining, Separation	0.1	0 0.1 0.022-0.5	Reddy & Jagadish 2003 Alcorn, 2001 Langer, 2009
Coarse aggregate	Mining, Crushing, Separation	0.1	0.03-0.06 0.022-0.5 0.0124 0.124 0.2 0.1 0.25 (Recycled aggregate) 1.0 Stone 0.4 (Recycled stone) 0.3 Gravel	Alcorn, 2001 Langer, 2009 Calculated from Reddy & Jagadish 2003 Goggins et al. 2010 Jiao et al. 2012 <u>Hammond & Jones 2011</u> Hammond & Jones 2011 Hammond & Jones 2011 Hammond & Jones 2011 Hammond & Jones 2008a
Fly ash	Capture, Separation	0.05	0.05 0.1 (Mined) 0.09	<u>McLellan et al., 2011</u> McLellan et al. 2012 Hammond & Jones 2011
Si fume	Capture, Separation	0.05	0.05 0.1 (Mined)	<u>McLellan et al., 2011</u> McLellan et al. 2012
NaOH	Electrolysis of brine	5.7	4.7-5.7 5.3-6.4	European Commission, 2001 EE allocated 50/50 EE allocated by mass
Bauxite	Mining	0.07	0.0549 0.07 0.1 0.04	Norgate & Haque 2010 <u>IAI, 2007</u> McLellan, 2012 Smith et al. 2007
Secondary (derived) materials				
Bayer liquor Feedstock		Not reported		
Lime (CaO)	Calcining, Milling	4.5 (fuel) + 0.4 (electricity)	4.9 5.63	<u>IEA 2007</u> Reddy & Jagadish 2003
OPC	Blending, Calcining, Milling	4.5 (fuel) + 0.4 (electricity)	4.9 Clinker 3.1-3.7 Clinker 3.2-3.7 6.0-8.2 5.6 4.2-7.5 6.15 5.8-6.5 4.6±0.2 5.5 (94% clinker)	<u>IEA 2007</u> Van den Heede & De Belie 2012 Valderrama et al. 2012 Van Deventer et al. 2012 Milne & Reardon 2010 quoting 1996 data Reddy & Jagadish 2003 Goggins et al. 2010 Alcorn, 2001 Hammond & Jones 2008b Hammond & Jones 2011
Onsite operations				
Concrete processing		0.1		(Estimate)

There is no embodied energy evaluated for Bayer liquor feedstock. That is, the free caustic and aluminate species. In addition, the preparation of Bayer feedstock has an energy requirement of its own.

Bayer feedstock active agent consists of:

- 230 g/L alumina (Al_2O_3) though likely to be in the form of $\text{Al}(\text{OH})_4^-$.
- 220 g/L caustic soda (as NaOH) in the form of OH^- .
- 180 g/L caustic soda (as NaOH) in the form of $\text{Al}(\text{OH})_4^-$.

Bayer liquor is made of a 50% solution of sodium hydroxide from the Chlor-alkali process with an embodied energy of 5.7 GJ/t (European Commission, 2001). The contribution of sodium hydroxide to the embodied energy of the Bayer liquor feedstock is calculated to be 2.4 GJ/m³. As the density of the feedstock is 1.6 t/m³, the embodied energy of Bayer feedstock from sodium hydroxide is 1.5 GJ/t.

Calculating the embodied energy of dissolved alumina from the Bayer process is more problematic. Some estimates are given below.

- 1) A Commonwealth Government of Australia (CGA, 2000) report on the energy efficiency of the alumina industry claimed the embodied energy of alumina was 11 GJ/t. However, alumina is a precipitated, filtered, washed, dried and calcined version of the alumina in Bayer liquor. Using an energy figure for calcination of 3.9 GJ/t (Smith *et al.* 2007), an embodied energy for alumina in Bayer liquor can be estimated to be 7.1 GJ/t.
- 2) Smith *et al.* (2007) reported an alternative embodied energy for calcined alumina as 12.3 GJ/t. Subtracting the energy for calcination (3.9 GJ/t) the embodied energy for alumina in Bayer liquor would be 8.4 GJ/t.
- 3) The International Aluminium Institute (IAI, 2012b) has collected the embodied energy for the production of “hydrate” (the product before calcination) over recent years; this is published here for the first time as being 8.9 GJ/t. This figure is a maximum as the embodied energy of solution hydrate does not include the steps of precipitation, filtration, washing and drying.

Given that the IAI figure is based on data from 57% of world production, this would be considered to be the most reliable. The figure does not include a mining component which has been reported by Smith *et al.* (2007) to be 0.04 GJ/t of bauxite. It takes 2-3 tonnes of bauxite to produce a tonne of alumina, so a figure of 0.1 GJ/t will be added to the IAI number. Thus we will use 9.0 GJ/t as a maximum (conservative) estimate of the embodied energy for dissolved alumina in Bayer liquor. The contribution of dissolved alumina to the embodied energy of Bayer liquor feedstock is calculated to be 2.1 GJ/m³, or 1.3 GJ/t (feedstock density 1.6 t/m³).

Thus the active components of Bayer liquor feedstock combine to be 2.1 GJ/t of indirect embodied energy (i.e. caustic + alumina = 1.5 + 1.3 = 2.8 GJ/t). Furthermore, the Bayer liquor feedstock is processed from Bayer spent liquor with a direct energy cost of 0.8 GJ/t (Moore, 2012). Thus the embodied energy for Bayer liquor feedstock of 3.6 GJ/t. For comparison, sodium silicate solution used for activation of geopolymers has an embodied energy of 5.4 GJ/t (Turner & Collins, 2011 quoting Fawer *et al.* 1999).

This evaluation for the embodied energy of Bayer liquor feedstock can now be applied to specific geopolymer formulations. A standard concrete mix for OPC and Bayer-derived geopolymer is provided in Table 8-41. The comparison of embodied energy is shown in Table 8-42.

Table 8-41. Bayer-derived geopolymer and OPC concrete formulation (dry wt%).

Concrete type	Bayer liquor	Fly ash	Lime	Silica fume	OPC	Sand	Coarse aggregate
Bayer Geopolymer	3.9	9.3	0.2	3.6	0	33	50
OPC	0	0	0	0	17	33	50

Table 8-42. Embodied energy calculated for Bayer geopolymer and OPC concrete.

CONCRETE		Binder							
Composition	Cement (t)				Sand (t)	Aggregate (t)	Mixing (t)	Concrete (t)	
Ratio	0.17				0.33	0.5	1	1	
Embodied Energy	4.9				0.1	0.1	0.1		
EE contribution (GJ)	0.833				0.033	0.05	0.1	1.016	
Embodied Energy per tonne OPC concrete (GJ/t)								GJ/t	1.0
GEOPOLYMER		Binder	Binder	Binder	Binder				
Composition	Bayer Liquor (t)	Flyash (t)	Lime	si fume	Sand (t)	Aggregate (t)	Mixing (t)	Concrete (t)	
Ratio	0.039	0.093	0.002	0.036	0.33	0.5	1	1	
Embodied Energy	3.57	0.05	4.9	0.05	0.1	0.1	0.1		
EE contribution (GJ)	0.14	0.00	0.01	0.00	0.03	0.05	0.10		0.34
Embodied Energy per tonne Bayer derived geopolymer concrete(GJ/t)								GJ/t	0.34

The comparison in Table 8-42 shows that the Bayer-derived geopolymer concrete embodied energy is 34% that of the OPC concrete. The geopolymer mixture is stiffer

than the OPC concrete but has not been optimised with rheology modifiers. The geopolymers concrete does flow well with applied vibration.

The comparative advantage of Bayer-derived geopolymers concrete can be manipulated in a number of ways depending upon application and specific formulations. For example if we add a significant transport cost to the sand and aggregate components, the comparative advantage is reduced (McLellan *et al.* 2011). Similar impacts can be made if the OPC concrete utilised high levels of fly ash and green energy.

A simplified method of comparison is to look at embodied energy of the binders alone. OPC has a range of reported embodied energy but the one used here is 4.9 GJ/t as quoted by IEA (2007). The embodied energy of Bayer geopolymers binder can be calculated as shown in Table 8-43, to have an embodied energy of 0.91 GJ/t.

Table 8-43. A spread sheet snapshot of the embodied energy calculated for Bayer geopolymers binder compared to OPC.

Ordinary Portland Cement (GJ/t)	4.9			
<u>GEOPOLYMER</u>	Binder	Binder	Binder	Binder
Composition	Bayer Liquor	Flyash	Lime	si fume
Ratio %	23	55	1	21
Embodied Energy (GJ/t)	3.57	0.05	4.9	0.05
EE contribution (GJ)	0.82	0.03	0.06	0.01
EE Bayer geopolymers binder (GJ/t)	0.91			

This value is 19% of that of the embodied energy of OPC. This is in line with figures quoted by Davidovits (1994b; 2005) and Zeobond (2013).

This value is significant and defendable, but the argument can be carried further. The export of Bayer liquor from the Bayer process is an impurity removal system (Jamieson, 2008b) and as such the caustic aluminate will be a waste product with an ascribed embodied energy of zero. That is because all of the energy involved in producing that exported liquor is accounted for in the manufacture of alumina. Hence the embodied energy of the Bayer liquor feedstock should only include the direct

processing cost to bring the product up to minimum criteria. These assumptions are used in a comparison as shown in Table 8-44.

Table 8-44. A spread-sheet snapshot of the embodied energy calculated for Bayer geopolymers binder, utilising Bayer liquor as a wasted product, compared to OPC.

Embodied Energy of Binders				
Ordinary Portland Cement (GJ/t)	4.9			
GEOPOLYMER	Binder	Binder	Binder	Binder
Composition	Bayer Liquor	Flyash	Lime	si fume
Ratio %	23	55	1	21
Embodied Energy (GJ/t)	0.78	0.05	4.9	0.05
EE contribution (GJ)	0.18	0.03	0.06	0.01
EE Bayer geopolymers binder (GJ/t)	0.27			

The embodied energy for one tonne of Bayer-derived geopolymers binder is only 0.27 GJ/t, and is a mere 6% of the embodied energy of OPC. For the first time, we can now discuss binding agents within the same embodied energy range as manufactured sand (Langer, 2009) gravel (Hammond & Jones, 2008a) and recycled stone (Hammond & Jones, 2011).

Further implications can now be drawn. For Bayer geopolymers to be a commercial reality, a high utilisation of Bayer feedstock is required. Hence as discussed previously, it is important to make artificial aggregates as a method of utilising significant volumes of Bayer-derived geopolymers. Now it is possible that Bayer-derived geopolymers aggregate can be manufactured containing 50 wt% sand (probably Red Sand™) which has an embodied energy assumed in the range of 0.1 GJ/t. Adding a similar value for processing, then it is reasonable to assume that the manufactured aggregate would have an embodied energy of 0.23 GJ/t. This evaluation of embodied energy of manufactured Bayer geopolymers aggregate could be considered equal to that of virgin or recycled aggregated currently utilised (Hammond & Jones, 2011). Thus the manufacture of Bayer-derived geopolymers aggregate would not represent an increase in the energy impact upon the planet.

There are other implications that would favour this product uptake. These include reduction of stored material in Bayer residue impoundments, and the reduction of

stored fly ash which is in significant excess to potential use in OPC (Sanjayan, 2011). There will also be a reduction of mining of virgin sand and aggregate in potentially environmentally sensitive areas. Finally, Bayer-derived geopolymers aggregates are 10 to 30% lighter than natural aggregates and will result in lower transport emissions and road network wear (assuming similar transport distances).

8.9 Global impact

Global impact is a wide-ranging evaluation and just the liquor bleed out rate is entirely optional depending on caustic price, impurity issues, alumina price, etc. However, a simplified assessment can be made based upon expectations and possible uptake.

For example, as an impurity removal process, the more impurity prone refineries would run a maintenance level of 0.08 kL/tonne of alumina product and a maximum possible (to shift operational positions) of 1 kL/tonne. Factoring in a level of uptake, since many refineries do not have impurity problems and processing requirements, it is suggested here that a value of 0.0125 kL of geopolymer feedstock be bled for each tonne of alumina product.

The International Aluminium Institute (IAI, 2013) estimates the global production of alumina in 2011 to be 92 million tonnes. This would provide 1.15 million kL of Bayer geopolymer feedstock at a density of 1.6, resulting in a mass of 1.8 million tonnes.

Now Bayer geopolymer feedstock liquor is utilised at about 25 wt% of the paste. That equates to about 7.4 million tonnes of binder.

8.10 Development of admixes and property modifiers

Admixtures are added to OPC concrete to enhance rheology or to minimise water, etc. These specialised products improve various properties to suit the application. The chemistry of geopolymers is very different to OPC and there is more caustic initially, hence OPC admixtures are unlikely to work as effectively.

The rheological properties of geopolymers may be modified with super-plasticiser but addition of water has been shown to be more effective (Sathonsaowaphak *et al.* 2009), suggesting the chemistry of OPC additives is not well suited to silicate-activated materials. Geopolymer slurry properties have been shown to be complex and very sensitive to chemical changes (Romagnoli *et al.* 2012). It is certain that the construction industry would require improvements to additives to make the formulations more forgiving and the product more robust in applicability.

As geopolymer concrete becomes entrenched in use over the next decade and admixtures become more refined to silicate activated chemistry, it is unlikely that the admixtures will be suited to Bayer-derived geopolymer because of the different starting chemistry. Standard geopolymers use a caustic silicate to activate an aluminium rich aluminosilicate. Bayer polymers use a caustic aluminate to activate a silicate rich aluminosilicate. Hence specific encouragement or co-development may be required to start such development of admixtures for Bayer-derived geopolymer.

It is recommended that this technology be publicised within the chemical manufacturing industry to encourage development and early market saturation. The size of the potential market is a driving force and direct co-development is also recommended.

8.11 Bayer-derived geopolymer conclusions

From this investigation it has been demonstrated that Bayer liquor can be processed to be suitable as an activator for the production of geopolymers. Other findings are listed below.

- There is significant opportunity for synergy between the alumina and geopolymer industries.
- Bayer-derived geopolymers are versatile in application.
- The potential volumes of Bayer-derived geopolymers may result in this material becoming a major construction material in the future.

- Bayer liquor feedstock is stable for days and even weeks at room temperature.
- Bayer-derived geopolymers can be cured at 70°C or with the addition of calcium oxide.
- Bayer geopolymers can be made to have significant strength up to 55 MPa.
- Bayer geopolymers can be utilised to manufacture mortar and concrete.
- Bayer geopolymers can be produced that are thermally stable at up to 1150°C.
- Bayer geopolymers have a very low embodied energy, similar to that of artificial or recycled aggregates.
- Bayer geopolymer can include other Bayer residue products such as Red Sand™.
- Bayer geopolymers require rheology modifiers to allow high slump applications.
- Bayer geopolymers can be recycled to make aggregate for use in geopolymer or OPC concrete with significant strength development.
- Bayer geopolymer can be made into light weight aggregates for the manufacture of light weigh concrete.
- Bayer geopolymers can be made into stabilised foam products by simple mechanical agitation.
- Bayer geopolymers are not a hazardous waste against DoE Landfill Waste Classification 1996.
- Bayer geopolymers are exempt from radiological control under ARPANSA (2011) and the Western Australian Radiation Safety Act (1975 – 1979).

9 CONCLUSIONS

The utilisation of by-products holds negative connotations within the public consciousness, however, the reality is that by-product utilisation is both beneficial in application as well as maximising the public benefit obtained from the consumption of finite resources. Not using these natural resources is a waste. In this thesis, the author has evaluated a series of by-products from the Bayer process and reported on their application in a variety of different markets. Significantly a new concrete binding agent, Bayer-derived geopolymers (Bayer CreteTM, Bayer StoneTM, Bayer PolymerTM), has been added to the construction material menu.

An overview of the main conclusions from each section is described below.

Carbonated bauxite residue and Alkaloam®

Fine bauxite residue (red mud) can be processed to have a low pH through carbonation.

- The beneficiation of fine bauxite residue for use in iron manufacture will probably never be achieved. This assessment is made based upon the low total iron grades achievable and the high level of penalty elements. The additional need for capital to physically handle the fine residue is also problematic.
- Long term field trials successfully demonstrated that Alkaloam® is an alternative agricultural lime agent and allowed quantitative assessment of the pH elevating capacity. This added to the known phosphate control, soil wetting and water holding improvements, indicates that Alkaloam® is a significant soil ameliorant, particularly for sandy soils.
- Trials utilising carbonated bauxite residue in the construction of a reactive barrier suggest the process is meeting requirements but a different implementation design is required for further trials.

An assessment of Alkaloam® against various regulations was conducted with the following conclusions.

Table 9-1. Review of Alkaloam® against various regulations.

Regulation	Classification
WA Landfill Waste Classification	Landfill Classification I, Inert Landfill
Radiological assessment	Does not require radionuclide control
Dangerous Good	Not likely
Controlled Waste	No (Not a liquid and landfill Class I)
Hazardous Substance	No ($\text{pH} < 11.5$)
Contaminated sites HIL	Class D
Contaminated sites EIL	EIL triggered

Red Sand™

Coarse bauxite residue (sand) can be processed to have a low pH through carbonation and washed to have a low salt content. It is called Red Sand™ by Alcoa of Australia.

- It is possible to beneficiate Red Sand™ to produce low grade iron ore, however, the loading of penalty elements such as aluminium is very high. There is also a need for capital equipment for the beneficiation and to bleed the fine ores into furnace feed. This will result in the economics of processing Red Sand™ becoming uncompetitive in comparison to low grade iron ore.
- It is concluded that Red Sand™ will not be able to replace fine aggregate in concrete without significant use of admixtures and the results would still be inferior for handling concrete compared to using virgin sand. This may change as sources of natural sand diminish or are located at distance.
- Attempts to smooth the sharp angular nature of Red Sand™ were not successful.

- A long term field study has shown that Red Sand™ can be utilised as clean fill for top dressing of turf. There was minimal dust generation and no environmental impact beyond background levels or as a result from fertiliser application. Grass recovery was good and the sand held together well under sporting traffic. Drainage was noted to have improved and it was concluded that the use of Red Sand™ for levelling of the recreation oval was successful.
- Red Sand™ has been shown to meet the technical criteria for use as embankment fill and for use as sub-grade in road construction. Continued assessments will determine if it will also meet the requirements for use as sub-base in road construction.

An assessment of Red Sand™ against various regulations was conducted with the following conclusions.

Table 9-2.Evaluation of Red Sand™ against various regulations.

Regulation	Classification
WA Landfill Waste Classification	Landfill Classification I, Inert Landfill
Radiological assessment	Does not require radionuclide control
Dangerous Good	Not likely
Controlled Waste	No (Not a liquid and landfill Class I)
Hazardous Substance	No ($\text{pH} < 11.5$)
Contaminated sites HIL	Class D
Contaminated sites EIL	Triggers EILs

Red Lime™

The residue from a Bayer side-process called Causticisation produces a solid lime residue that can be collected. It is called Red Lime™ by Alcoa of Australia.

- A desk top assessment of Red Lime™ has shown that, with some additional processing, it could be part of the production feedstock for OPC manufacture. However, the market economics are tight for OPC and a new feedstock would

require additional holding bins and a drying circuit. The additional capital and operational expense make Red Lime™ uncompetitive at this time.

- A long term field trial has evaluated the use of Red Lime™ as a soil ameliorant. The fine particle size distribution and the variety of rapidly acting neutralising materials within Red Lime™ would appear to be well suited for such an application. The study has shown that the Red Lime™ modifies soil pH as required and there were no observed negative impacts.
- Red Lime™ would also appear suitable for acid sulphate soil remediation. The location of three sites for the production of Red Lime™ all lie within the Peel – Harvey region of Western Australia, a significant ASS region.

An assessment of Red Lime™ against various regulations was conducted with the following conclusions.

Table 9-3. Regulatory evaluation of Red Lime™.

Regulation	Classification
WA Landfill Waste Classification	Landfill Class I or III, but does not require secure landfill
Radiological assessment	Does not require radionuclide control
Dangerous Good	Possible
Controlled Waste	No (Not a liquid and landfill Class I- III)
Hazardous Substance	Yes ($\text{pH} > 11.5$)
Contaminated sites HIL	Class D
Contaminated sites EIL	Red Lime triggers EILs

Bayer Geopolymer (Bayer Stone™)

Bayer liquor is a recirculating caustic aluminate solution that continually dissolves impurities from bauxite ore. Concentrating this liquor, adding fly ash and silica fume produces a rigid alumina-silicate (geopolymer) of high strength. This product has been called Bayer Stone™ or Bayer-derived geopolymer by Alcoa of Australia.

From this investigation it has been demonstrated that Bayer liquor can be processed to be suitable as an activator for the production of geopolymers. Other findings include the following.

- There is significant opportunity for synergy between the alumina and geopolymer industries.
- Bayer-derived geopolymers are versatile in application.
- The potential volumes of Bayer-derived geopolymers may result in this material becoming a major construction material in the future.
- Bayer liquor feedstock is stable for days and even weeks at room temperature.
- Bayer-derived geopolymers can be cured at 70°C or with the addition of calcium oxide.
- Bayer geopolymers can be made to have significant strength, up to 55 MPa.
- Bayer geopolymers can be utilised to manufacture mortar and concrete.
- Bayer geopolymers can be produced that are thermally stable at up to 1150°C.
- Bayer geopolymers have a very low embodied energy, similar to that of artificial or recycled aggregates.
- Bayer geopolymer can include other Bayer residue products such as Red Sand™.
- Bayer geopolymers require rheology modifiers to allow high slump applications.
- Bayer geopolymers can be recycled to make aggregate for use in geopolymer or OPC concrete with significant strength development.
- Bayer geopolymer can be made into light weight aggregates for the manufacture of light weight concrete.
- Bayer geopolymer can be made into light weight aggregates for the manufacture of road base.
- Bayer geopolymers can be made into stabilised foam products by simple mechanical agitation.

An assessment of Bayer geopolymer against various regulations was conducted with the following conclusions.

Table 9-4. Comparison of Bayer geopolymers against regulations.

Regulation	Classification
WA Landfill Waste Classification	Crushed material is landfill Class III, but does not require secure landfill
Radiological assessment	Does not require radionuclide control
Dangerous Good	Not likely
Controlled Waste	No (Not a liquid and landfill Class III)
Hazardous Substance	Possible. Need QA/QC to keep pH < 11.5
Contaminated sites HIL	Crushed material is Class A
Contaminated sites EIL	Crushed material triggers EIL

10 RECOMMENDATIONS FOR FURTHER WORK

It is apparent that several Bayer by-products are now beyond the need for further bench top investigation. They require commercial application and refinement in use.

The development of Bayer geopolymers is very different. It is clearly in the early stages of development with some applications in their infancy while others now require field trials. A series of recommendations are included below.

- The following aspects of Bayer-derived geopolymer are very interesting and could lead to very high value but small volume products and markets.
 - Light weight concrete (use of light weight geopolymer aggregate and geopolymer binder).
 - Ultra light weight concrete (production of foamed geopolymers).
 - Fire resistant concrete (apply geopolymer to tunnel walls for fire protection or even wooden objects).
 - Shot-crete and spray on products for pipe-work longevity. (apply geopolymer coating to the inside of degraded OPC concrete pipes to extend their service life).

It is recommended that other projects progress to field trial applications. These include:

- Production of Bayer geopolymer aggregate for road base construction.
- Production of Bayer geopolymer aggregate for use in OPC concrete.
- Production of Bayer geopolymer low slump concrete pre-form products such as pavers, barrier walls, blocks, etc.
- Liquor solidification for impurity removal and use as dust suppressant if residue impoundments.
- Detailed carbon credit and embodied energy assessment.

11 LIST OF APPENDIXES

1. Material Safety Data Sheets.
2. Additional data for Alkaloam®
3. Additional data for Red Sand™
4. Additional data for Red Lime™
5. Additional data for Bayer Geopolymer (Bayer Stone™)

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