



COOPERATIVE RESEARCH CENTRE FOR COAL IN SUSTAINABLE DEVELOPMENT
Established and supported under the Australian Government's Cooperative Research Centres Program

**MANUFACTURE OF LOW-GRADE ZEOLITES FROM FLY ASH FOR
FERTILISER APPLICATIONS**

RESEARCH REPORT 91

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June 2008



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Executive Summary

The beneficial use of ash from coal consumption is an important requirement for the sustainable use of coal. The CCSD research program on *By-products and Waste Utilisation* was initiated to focus on research that offered prospects to use large tonnages of fly ash.

This study is a final report on the Centre's research to develop low grade zeolites from fly-ash for use as fertilizer in bulk agricultural applications. It provides information on the production of zeolite product prepared from flyash and includes some preliminary tests of its application to enhance the efficacy of plant growth. A summary of the doctoral thesis that established a chemical basis to produce the zeolite from ash is also provided as an appendix to the report.

In this work, fly ash was converted into zeolite using an improved hydrothermal method with optimised H₂O/Al molar ratio. It was found that the optimum ratio is 57.4 where the main product is analcime zeolite. The zeolite, in the forms of both K- and Na-zeolite, was subjected to trials of plants (canola, spinach and wheat) growth in pots using two types of soils, namely grey Bassendean sand and yellow gravely loamy sand (Collie soil). When planted in Bassendean sand, Spinach and wheat grow better at 1 and 2 wt% of K and Na-zeolite addition sand while canola only grows better at 1 wt% K-zeolite addition. When the zeolites were added to a more fertile Collie soil, there is an apparent beneficial effect on canola, spinach and wheat at all 3 levels of additions of both types of zeolite. Cadmium and Mercury were detected on the dried shoots of Spinach and Wheat planted on zeolite added soils but their concentration is still within FAO and WHO recommended levels. The Cadmium and Mercury levels decrease as higher percentages of zeolites were added to the soils.

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1. INTRODUCTION

A promising new approach to the utilisation of fly ash is to convert it into a value-added product like zeolites. Zeolitic minerals are hydrous aluminosilicates that in the soil environment can be considered very stable. Zeolite considerably raises the Cation Exchange Capacity (CEC) of soils thus making it suitable for agricultural/horticultural applications. The zeolite is able to freely exchange certain plant nutrients, acting to significantly improve fertiliser utilisation. Cationic nutrient ions, such as those of calcium, magnesium, potassium, sodium and particularly ammonia are exchanged in this way.

Coal fly ash has a similar chemical component to zeolite but they have different crystal structure. Majority of fly ash components are amorphous phase with small amounts of crystalline phases which are generally mullite and quartz. Therefore, there is a possibility of synthesising zeolite-like materials from the fly ash.

There are three methods to convert fly ash into zeolite [1]. The first method is conventional direct hydrothermal conversion from a mixture of fly ash and alkaline solution (normally sodium hydroxide or potassium hydroxide solution). The method was also used by Inada et al. [2] on two different types of Japanese fly ashes and the main product was zeolite P1 and hydroxosodalite. Many other researchers [3-7] also employed this method. This is a single step and the simplest method but suffers from low fly ash conversion to zeolite as pointed by Singer and Berkgaut [8]. Only about 50% of fly ash converted into zeolite P and/or hydroxysodalite.

The second method is carried out through fly ash fusion followed by a hydrothermal reaction as reported by several researchers [5, 9, 10]. In the fusion step, fly ash powder is mixed with fusion chemicals (NaOH or Na₂CO₃) and fused at high temperature (typically 550 °C) to convert fly ash into soluble sodium silicate and sodium aluminate. Then it is followed by dissolving the soluble fused products in an alkaline solution and reacted under hydrothermal condition. The method has high fly ash conversion into zeolite and can be directed to a certain type of zeolite by adjusting the hydrothermal reaction condition. However, the use of the high temperature fusion step makes this method very energy intense.

Both methods were regarded as only partially convert fly ash into zeolite by Hollman et al [11]. For this reason, Hollman et al developed a two steps procedure, the third method, which starts with silicone extraction from fly ash followed by hydrothermal reaction of the extracted silicone solution with the addition of aluminate solutions in certain ratio. This method produced high purity zeolitic products and can produce certain phase of zeolite by controlling the chemical composition and reaction conditions. A similar method to that of Hollman et al with membrane extraction process was reported by Tanaka et al. [12, 13].

Although the direct method was regarded as the worst in terms of zeolite purity produced from the fly ash, the simplicity and single step method makes it more favourable in converting fly ash into low grade zeolites but suitable for use in agricultural areas such as control released fertiliser and soil amendment. The method and the proposed application in agricultural areas have been thoroughly investigated by Elliot [14] using various Australian fly ashes as well as bottom ashes. While Elliot reported a successful conversion of various fly ashes and bottom ashes into agricultural grade zeolite, the reaction conditions used in the preparation are far from economical due to very large water to aluminum (H₂O/Al) ratio and the zeolites were never tested as soil amendments or controlled release fertiliser.

Water plays very an important role in hydrothermally zeolite synthesis. It is a medium for zeolite components such as aluminium, silicone, cations and templates to react and

crystallised under certain temperature and pressure. To quantify the amount of water in the synthesis, it is commonly reported as a relative proportion to other chemicals involved in the synthesis. For example Elliot [14] used the ratio of water to aluminium (H_2O/Al) to quantify the water. Others may use silicate to water (SiO_2/H_2O) or water to sodium oxide (H_2O/Na_2O) ratio.

Elliot used high H_2O to Al ratio ($H_2O/Al = 400$) to ensure that high crystalline zeolite was formed from fly ash. Although it can produce zeolites, the high H_2O to Al ratio will restrict the production rate because the maximum amount of liquid to be placed into any given hydrothermal reactor should be less than 2/3 of its total volume to avoid an excessive pressure build up due to phase change of liquid (hence is water) into gas. Excessive use of water may also create problem due to the large amount of wastewater that requires treatment before disposal. Therefore, it is important to minimise the amount of water used in the zeolite synthesis from fly ash.

This paper reports our latest attempts to reduce the H_2O/Al ratio, yet being able to produce high yields of zeolite. The zeolite thus produced was then tried in a series of pot tests on canola, spinach and wheat as a soil amendment as well as controlled release fertiliser.

2. EXPERIMENTAL

2.1. Fly Ash Sample

The fly ash was collected from Collie Power Station in Western Australia. Physico-chemicals properties of the ash are given in Table 1.

Table 1: Chemical and Physical properties of Collie coal - fly ash [14]

Chemical	% mass	Mineral	% mass
SiO ₂	52.3	Quartz	14.10 ± 0.50
Al ₂ O ₃	33.8	Mullite	10.70 ± 0.90
Fe ₂ O ₃	15.4	Hercynite	3.84 ± 0.40
CaO	1.9	Hematite	1.07 ± 0.10
MgO	1.3	Magnetite	0.54 ± 0.90
Na ₂ O	0.63	Glass (amorphous)	69.70 ± 1.01
K ₂ O	0.88		
TiO ₂	1.4		
Mn ₃ O ₄	0.15		
P ₂ O ₅	1.4		
SO ₃ ⁼	0.1		
SrO	0.27		
BaO	0.49		
LOI	0.4		
Total	110.42		
		Other	% mass
		Relative Density ^{*)}	2.40
		BET Surface Area	12.93
		D50 (µm)	12.1
		Unburned Carbon (LECO)	1.78

^{*)}AS3583.5 determination of relative density (uses Kerosene)

Based on the mineral composition, it has been calculated that the amorphous phase of the fly ash contains 49.1 wt % SiO₂, 19.6 wt % Al₂O₃ and 16.8 wt % Fe₂O₃.

2.2. Zeolite Syntheses

The zeolite syntheses were conducted using two types of reactors, namely, a teflon[®] lined stainless steel reactor (300 mL total capacity) for trial syntheses to optimise the process conditions and a 1.8 L teflon[®] lined Parr[®] autoclave for large scale synthesis. The trial

syntheses were carried out at 140°C for 24 hours without agitation, except for trials No. 1 to 3. The H₂O/Al ratios were varied between 25 and 420 while keeping the amounts of other ingredients constant. The experiment conditions for the trial syntheses are given in Table 2.

The large scale zeolite syntheses were carried out under the optimum conditions found from the trial syntheses under which a high zeolite yield was achieved at the lowest H₂O/Al ratio in the trials. All zeolite products were separated from the reaction solution by filtering using No. 41 Whatman filter paper straight after the reaction was terminated. The solid residue left on the filter paper was washed with double distilled water until the pH of the filtrate was between 8 and 9. The solid was then dried in an oven at 105 °C for 12 hours. The zeolite thus synthesised was called Na-Zeolite.

Table 2: Experiment conditions

Trial No	H ₂ O/Al mole ratio	T (°C)	t (hours)
1	419.1	150	24
2	209.5	140	24
3	209.5	120	24
4	167.6	140	24
5	179.6	140	24
6	419.1	140	24
7	209.5	140	24
8	104.8	140	24
9	41.9	140	24
10	26.2	140	24

2.3. Preparation of K-Zeolite

K-Zeolite was prepared from the Na-Zeolite by ion exchange. The Na-Zeolite was stirred in 0.5 M KNO₃ solution for 6 hours with the ratio between the mass of zeolite to the volume of KNO₃ solution set at 1:5. The zeolite was filtered without washing, and dried at 105 °C for 12 hours.

2.4. Characterisation

The zeolite products were characterised using X-ray diffraction for phase analysis and Scanning Electron Microscopy for morphology analysis. All X-ray analyses were carried out using a Siemens D 500 diffractometer with Cu K α radiation generated at 30 mA and 40 kV. The cation exchange capacity of both raw fly ash and zeolite products were determined using the ammonium chloride method [15].

2.5. Pot plant trials

The pot plant trials were carried out using three plant species, namely, canola, spinach and wheat, and two Zeolite products, namely, Na-zeolite and K-zeolite, applied at 0, 1, 2 and 5% to two soil types, namely, a yellow gravelly loamy sand from the Collie region (Boyup Brook, Western Australia) and Bassendean sand. The top 10 cm of the respective soil types were used. Gravel and debris were removed by sieving the soils through a 2 mm stainless steel sieve and the < 2 mm soil fraction used in the experimentation. All pot trials were conducted in a glasshouse facility located at the Muresk Institute, Northam, Western Australia. The temperature was maintained close to 25°C \pm 3°C to maximise growth.

2.5.1. Pots and basal nutrients

A total of 1.8 kg of air-dried soil was added to free-draining plastic pots (measuring 15 cm deep by 15 cm diameter). For each crop, basal amounts of N, P, K, Cu, Zn, B and Mo was applied per kg soil to all pots, for example as follows: 100 mg K as K_2SO_4 , 1.2 mg Cu as $CuSO_4 \cdot 5H_2O$, 1.0 mg Zn as $ZnSO_4 \cdot 7H_2O$, 0.24 mg B as H_3BO_3 , 0.05 mg Mo as $Na_2MoO_4 \cdot 2H_2O$. All treatments received a total of 160 mg N/kg for each of the three crops with the N applied in solution as ammonium nitrate (NH_4NO_3) and split over three applications; prior to sowing and at 10 and 20 days, respectively. Monocalcium phosphate [MCP; $Ca(H_2PO_4)_2 \cdot H_2O$] was used as the inorganic source of P and was thoroughly mixed dry into the soil at a rate of 150 mg P/kg.

2.5.2. Sowing

Soils were watered to a gravimetric soil water capacity (GSWC) as determined for each soil type (using deionised water) and then allowed to incubate in the glasshouse for 7 day prior to sowing. The GSWC was determined as the amount of water remaining after 24 h in the top 5 cm of soil in a 50 cm high free draining soil column covered with plastic wrap to prevent evaporation. The moisture content is determined by drying soil samples at 105°C for 48 h.

For each consecutive crop, where canola or wheat was used, ten seeds of each species were sown in each pot. The seeds were pre-germinated two days prior to sowing. Plants were thinned to five plants per pot at the 2.5 leaf stage, leaving the five most median sized plants. Spinach was purchased as seedlings and 3 plants planted in each pot and thinned to 2 healthy plants after the first week. Pots were made up to GSWC using deionised water at least every second day and the position of pots re-randomised.

2.5.3. Plant measurements and harvest

For each crop, plants were harvested at 30 DAS (Days after Sowing) by cutting the shoots at ground level and then drying at 70°C for 48 h in a forced draught oven. The dried plant matters were weight to measure the growth.

3. RESULTS AND DISCUSSIONS

3.1. Zeolite synthesis

The zeolite syntheses were performed in three parts. The first part of the syntheses was aimed at refining the reaction condition to obtain zeolite from fly ash based on our previous method [14]. Including in the first part is trials 1 to 4. The second part was aimed at optimising H_2O/Al ratio at the best conditions found from the first part. Including in this part is trials 5 to 10. Then, the optimised H_2O/Al ratio and reaction condition were applied to the large scale zeolite production.

X-ray diffractograms of products from the first part of syntheses are shown in Figure 1. No zeolite peaks appear on the diffractograms under the trials 1 and 3 conditions. Meanwhile, peaks of zeolite P appears on the diffractograms of the products of trials 2, 4 and 5.

In trial 1, the reaction was carried out at $H_2O/Al = 400$ and using a lower NaOH concentration. In this trial, the Collie fly ash was practically not converted into any types of zeolite as shown by diffractogram of trial 1 in Figure 1. The diffractogram only shows peaks of mullite and quartz, which are the main crystalline phases found in the fly ash. The same results were also obtained in trials 3.

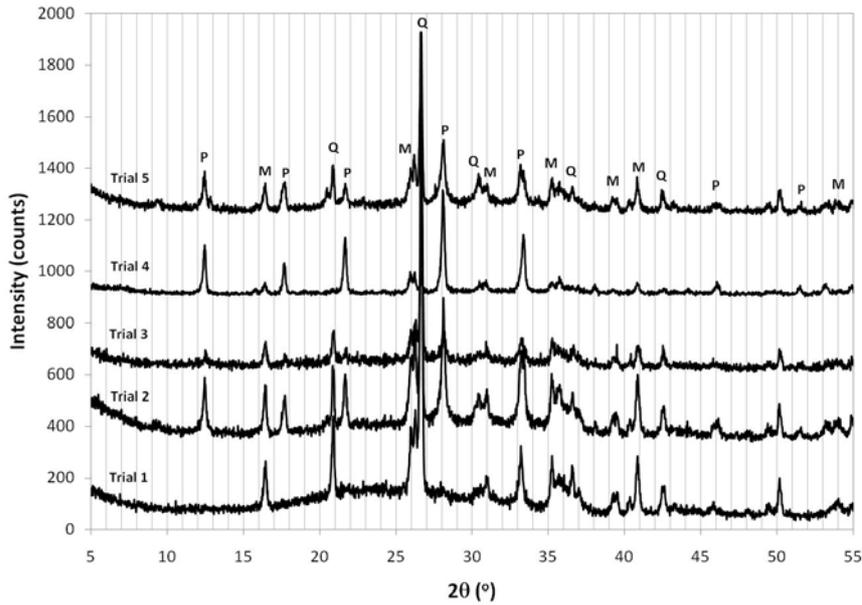


Figure 1: X-ray diffractograms of zeolite products from Collie coal fly ash in various H₂O/Al ratio. **P** = Zeolite Na-P, **M**= Mullite and **Q**= Quartz.

In trials 1, the zeolite phase was not formed probably because of the alkalinity of the solutions was not strong enough to dissolve silicone and aluminium components from the fly ash particles due to their relatively lower initial pH. Even though trial 1 was carried out at higher temperature, there was no indication that the ash particles were dissolved in the solution system. On the other hand, trial 3 was carried out at higher initial pH but the low reaction temperature (120 °C) did not seem to be high enough to initiate the dissolution of silica and alumina components.

The low solubilisation of silica and alumina from the ash particles is evidenced by the results of electron microscopy analysis of trial 1 product as shown in Figure 2. The figure shows a fly ash particle with an initial stage of crystal growth on its surface. Crystals growth on an ash particle where its components were formerly dissolved in the solution and then followed by crystal precipitation and growth on the left over surface.

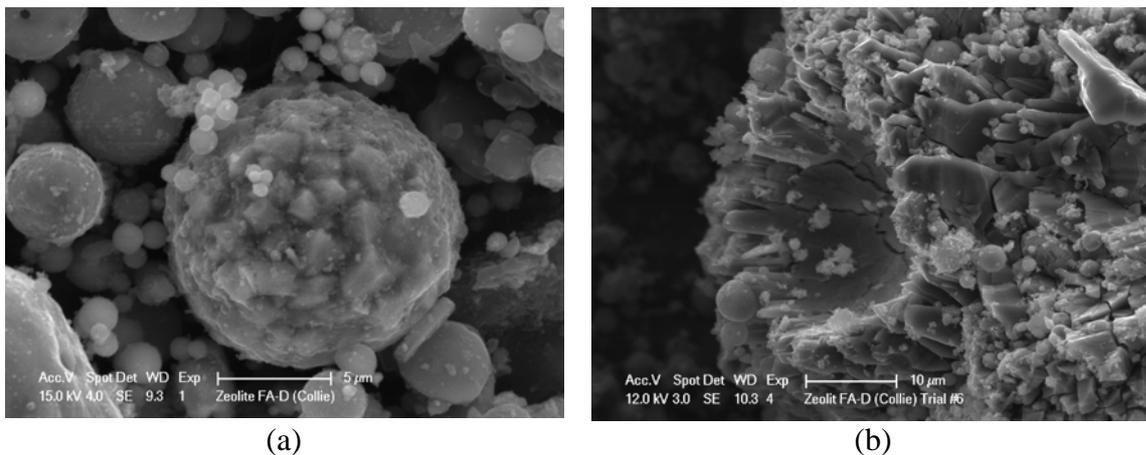


Figure 2: (a) An early stage of zeolite crystal formation on a surface of fly ash particle. (b) A trace of partly dissolved fly ash particle where new crystals (zeolites) being grown on it

As discussed by Iler (page 56 of [16]), the dissolution of silica will be altered when there is aluminium or iron ions in the solution. Both elements are the second major components in Collie coal fly ash. As a result, although the high pH favours the silica dissolution, the coexistence of aluminium and iron ions decreases the solubility of silica and thus reduces the possibility of zeolite formation. A high H_2O/Al ratio was ineffective since the high water content also favours the solubilisation of aluminium and iron

To improve the solubility of silica and overcome the effect of aluminium and iron ions in the solution, a higher pH and temperature are needed to provoke the zeolite formation. For these reasons, trials 2 and 4 were run with a high initial pH but at a lower H_2O/Al ratio. It was very interesting that these trials produced zeolite. Furthermore, trial 4 only left a minor amount of un-reacted mullite and quartz with no evidence of amorphous phase to exist (see Figure 1, Trial 4).

In trial 5, where the H_2O/Al is between those in trials 3 and 4, peaks of zeolite phase (Zeolite P) are clearly seen although peaks of mullite and quartz are still dominant. The diffractogram of trial 5 shows that reducing the amount of water by a factor of two increases the amount of zeolite produced. The trend was followed when water amount is halved of that in trial 5 as shown by diffractogram of trial No. 4. The diffractogram shows very little residue of mullite and quartz, and zeolite P peaks becomes very dominant. The high fly ash conversion into zeolite in trial 4 can also be seen on its electron microscope image as shown in Figure 3.

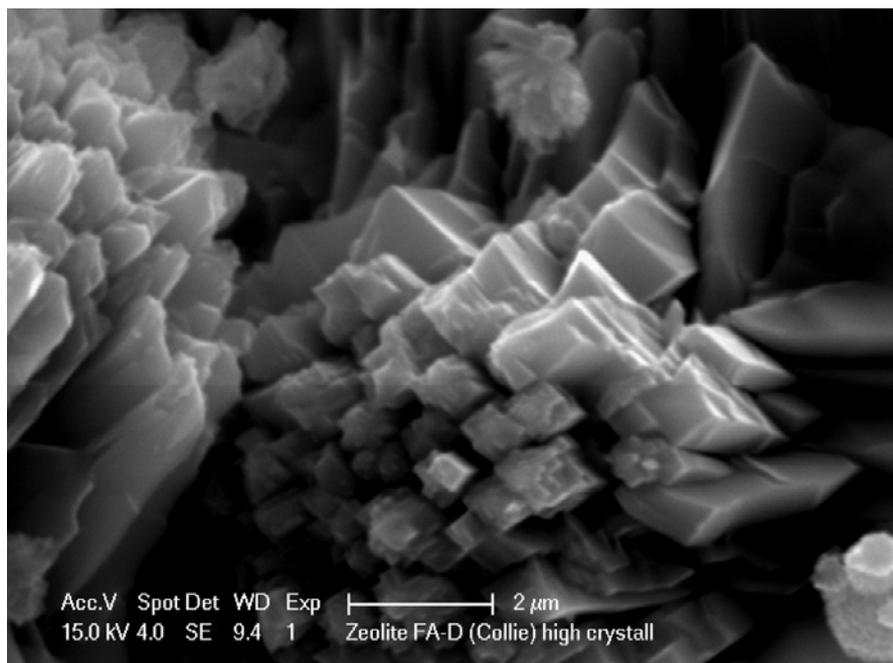


Figure 3: Highly crystalline phase of zeolite formed under trial 4 condition.

3.1.1. Effect of reducing H_2O/Al ratio

The effect of reducing H_2O/Al ratio was investigated systematically in the second part of the zeolite syntheses (trial 6 through to trial 10). Figure 4 shows the diffractograms of the products of these trials, together with those of trials 1, 4, and 5 for comparison. Trial 6 was carried out at exactly the same composition as that of Elliot [14] while trials 7 to 10 at decreasing H_2O/Al ratio.

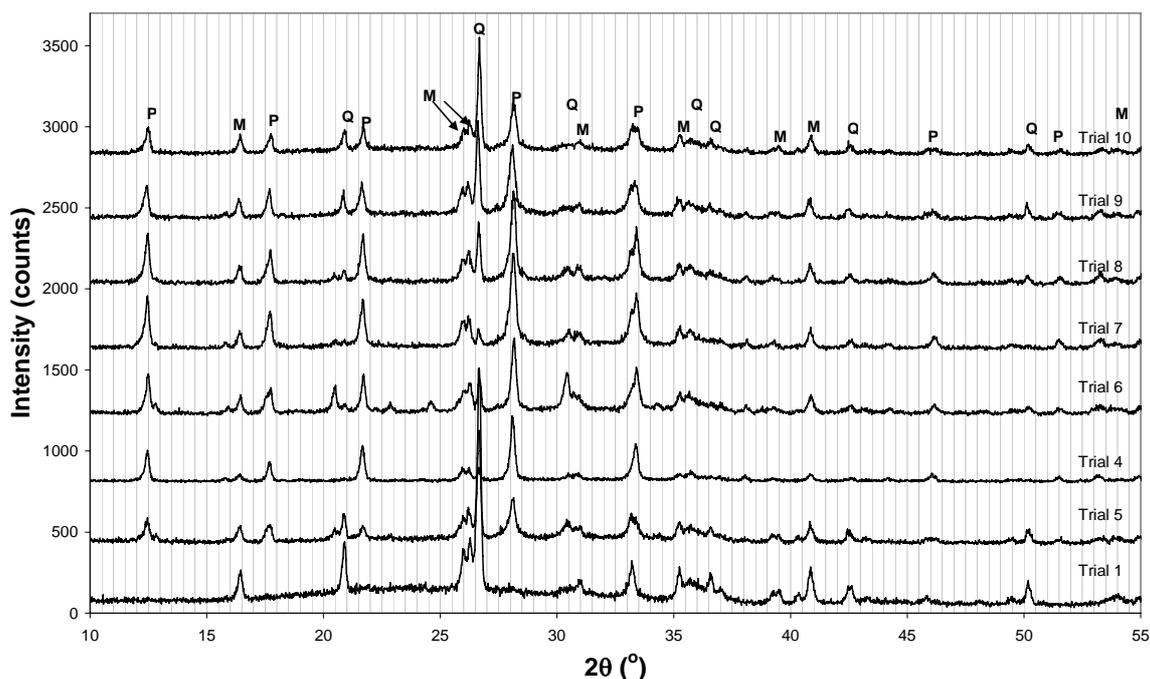


Figure 4: X-ray diffractograms of zeolite products from Collie coal fly ash in various H_2O/Al ratios. **P** = Zeolite Na-P, **G**= Gismondine, **M**= Mullite and **Q**= Quartz.

All trials in this part produced zeolite P, some amounts of zeolite P1 (Gismondine type) and un-reacted mullite and quartz. There was no evidence of amorphous phase left in each trial indicated by no broad background intensity from 15 to 35° of 2θ as those found in diffractogram of trial 1.

Figure 4 shows an increasing amount of zeolite P produced in the trial and reaches a peak in trials 7 and 8, as evidenced by characteristic peaks of zeolite P at around 13.5° and 28° 2θ . In trial 9 in which water was further reduced, there was less zeolite product than in trial 8 and more unreacted fly ash material. It is shown by lower intensity of characteristic peaks of zeolite P and higher intensity of peaks of mullite and quartz. It means that under this condition, there was not enough water available to induce the dissolution of Si and Al from the fly ash and crystallised into zeolite.

A semi quantitative analysis of the product using $\alpha-Al_2O_3$ (corundum) as an internal standard in the diffraction analysis gives a relative phase composition of the products of these trials (Figure 5). The figure shows that more zeolite products were produced when H_2/Al ratio was reduced from 419 to 105, then the zeolite productivity decreased at $H_2O/Al = 26$ (trial 10)

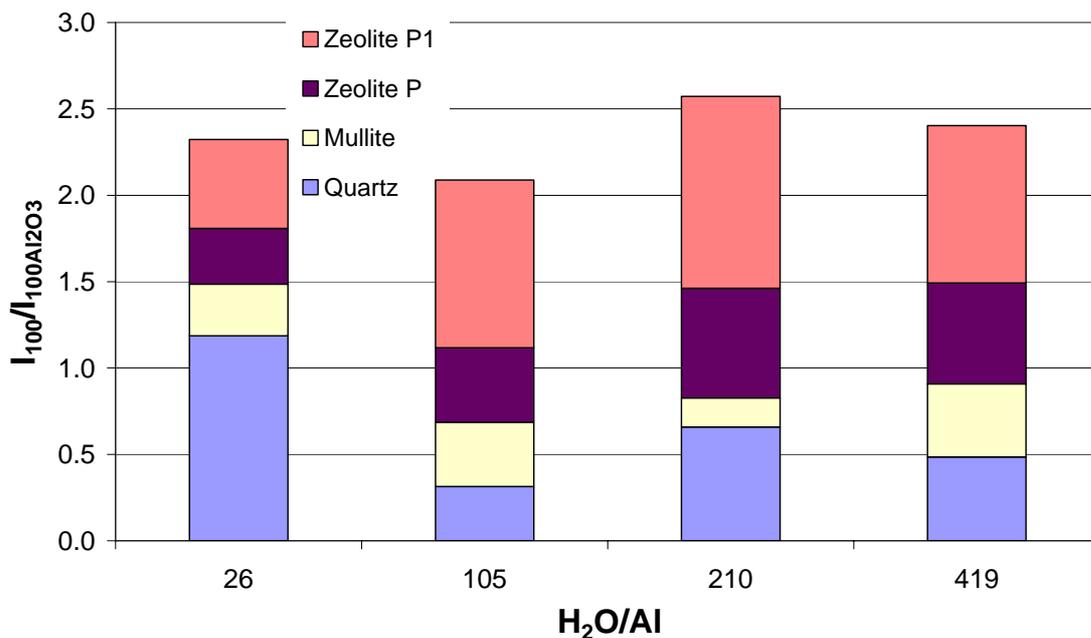


Figure 5: Composition of crystallisation product as a function of H₂O/Al ratio

3.1.2. Large scale zeolite synthesis

Results from trials 1 to 10 reveal that the optimum H₂O to Al ratio is that falling between trials 7 and 9 (H₂O/Al between 209.5 and 41.9). However, one should remember that no agitation was given during the hydrothermal reaction. As the reaction/crystallisation occurs via dissolution of Si and Al from the fly ash particles followed by crystallisation, agitation will alter the reaction either by increasing the solubility of silicone and aluminium or delaying the crystallisation process. The Parr 1.8 L vessel that will be used to produce kilograms of zeolite has an agitator while being able to maintain high pressure condition. For this reason, further optimisation need to be done using the Parr reactor.

To maximise the zeolite produced while maintaining high fly ash conversion into zeolite, a reaction composition in between trials 8 and 9 was chosen, i.e. the ratio of H₂O to Al was 57.4. Due to the low water content in the reaction, an agitator was used throughout the hydrothermal process with a speed of 200 rpm. At the end of the reaction, the speed was reduced to 50 rpm. Reaction without agitation using the Parr reactor was also investigated to replicate the condition applied to the 300 mL reactor without agitator.

X-ray diffraction analysis of the resulting zeolite synthesised using the Parr reactor is given in Figure 6. When the reaction was carried out without agitation, the product is similar to the product in trial 8, i.e it contains zeolite P and some amounts of un-reacted mullite and quartz. A dramatic improvement in the zeolite product was shown when the reaction was carried out with agitation. Under exactly the same reaction conditions and reactant composition, those with agitation produced a single phase of analcime, one of the high temperature phases of zeolite [17].

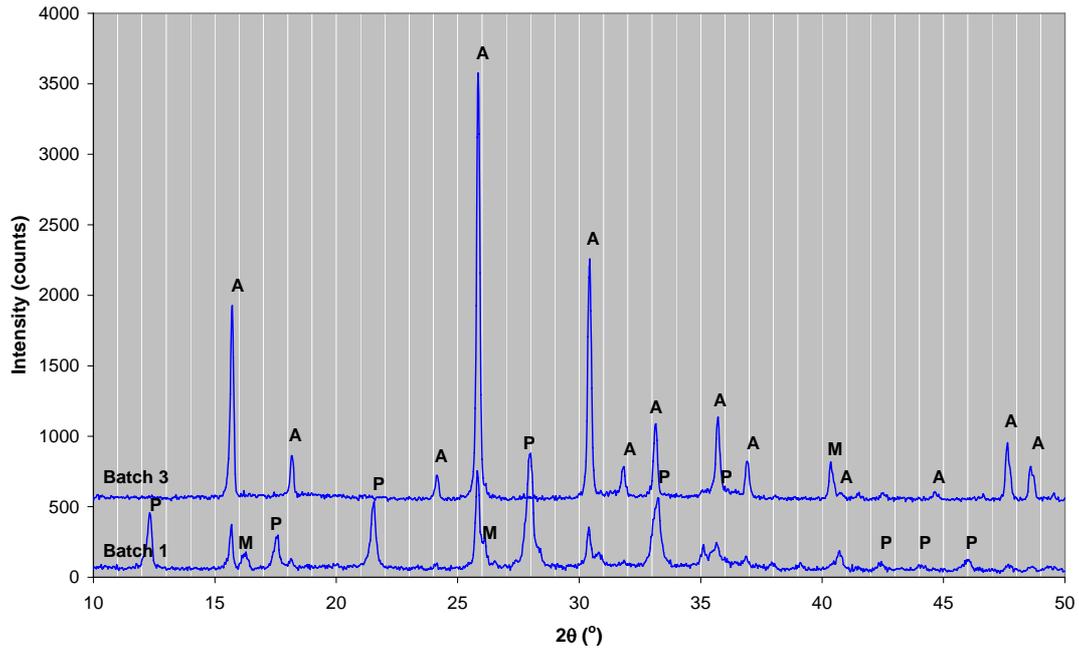


Figure 6: Zeolite product from optimised reaction condition using the 1.8 L reactor shows a high conversion of fly ash materials into Analchime and zeolite P. Batch 1 was carried out without any agitation while batch 3 with agitation.

It has been shown that when the reaction condition between trials 8 and 9 was used together with agitation, single phase zeolite, i.e analchime, is the only zeolite product found in the product. The same product as well as XRD crystallinity was also produced at trial 8 with agitation. However, when in trial 10 with agitation, the product started to change as shown in Figure 7. In this run, zeolite P becomes the only zeolite phase produced and there were some un-reacted fly ash particles represented by mullite and quartz peaks.

Semi quantitative analysis of zeolite products with the X-ray diffractograms in Figure 7 is given in Figure 8. It is again shown that the synthesis condition between trials 8 and 9, i.e synthesis with H₂O/Al ratio of 57.4, is the optimum reaction condition to make zeolite from Collie coal fly ash and will be used throughout in this research.

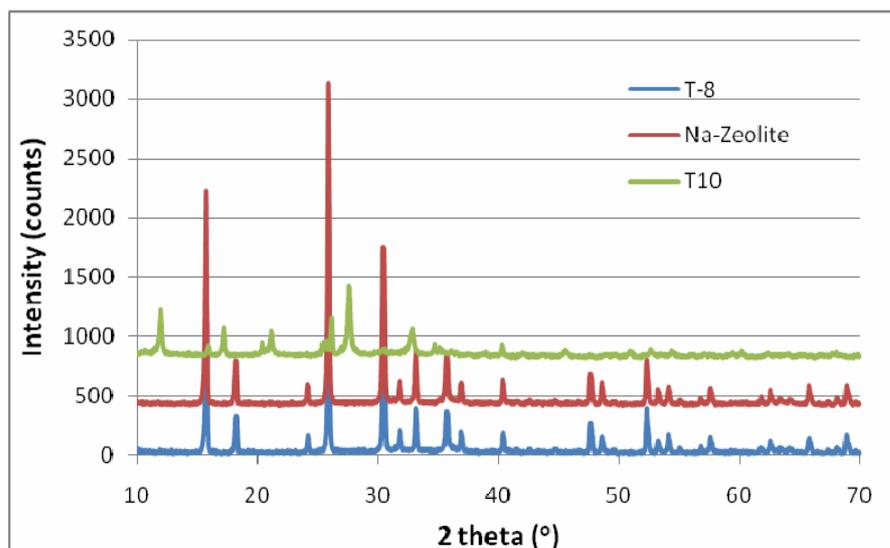


Figure 7: Comparison of zeolite produced from reaction under agitation using condition in trial 8 (T-8), trial 10 (T-10) and condition between trial 8 and 9 (Na-Zeolite).

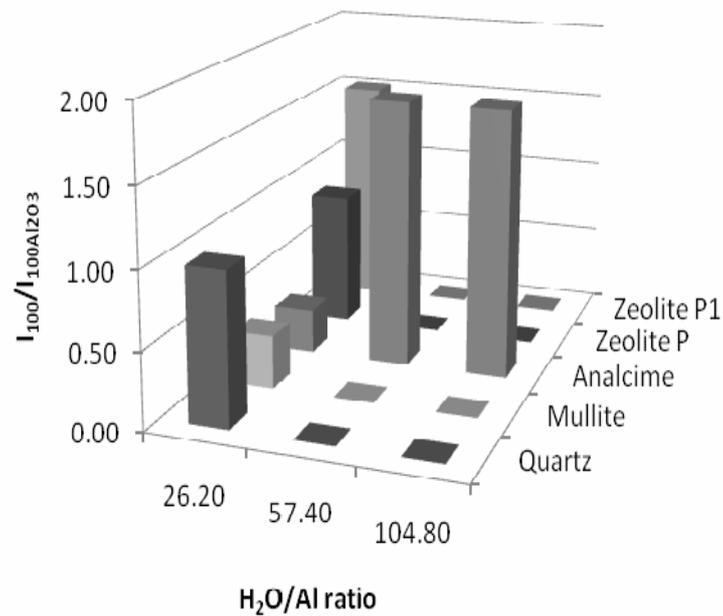


Figure 8: Composition of crystallisation product as a function of H₂O/Al with agitation. XRD phase composition search/match result is given in Figure 9.

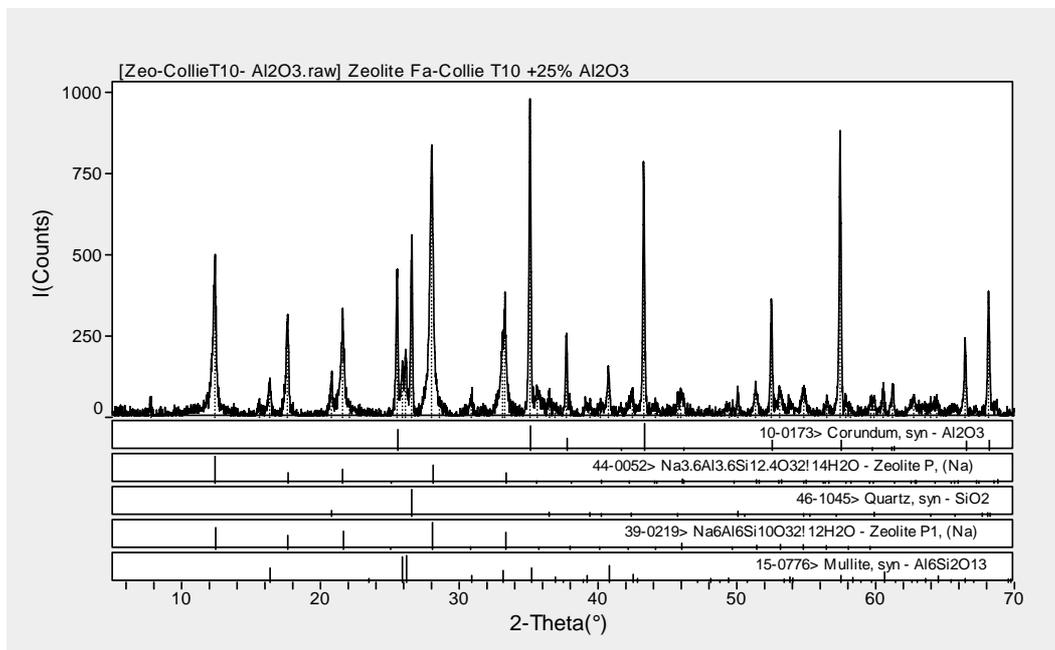


Figure 9: Diffractogram of products using trial 10 condition with agitation. Al₂O₃ was added into the product as an internal standard.

3.1.3. Effect of reaction time on the zeolite product

In order to further optimise the large scale zeolite synthesis, the optimised reaction condition mentioned in the previous section was tested at shorter reaction time, i.e 12 and 4 hours. Figure 10 shows diffractogram while Figure 11 shows the relative composition of zeolite produced at 4, 12 and 20 hours of hydrothermal reaction.

Extra peaks shown in the diffractograms at the 12 and 4 hours runs (compared to the 20 hours) belong to the zeolite P phase. Small peaks at 2 theta between 26 and 26.2° are specific peaks of mullite phase, which, together with quartz, are the main crystalline phases found in the fly ash. No quartz peaks and amorphous phase are visible in the diffractogram. The Figures show almost all fly ash particles were converted to zeolite even when the crystallisation was run for only 4 hours. It means that to make zeolitic phase from fly ash suitable for low grade zeolite utilisation such as for controlled release fertiliser, a crystallisation time of 4 hours is sufficient.

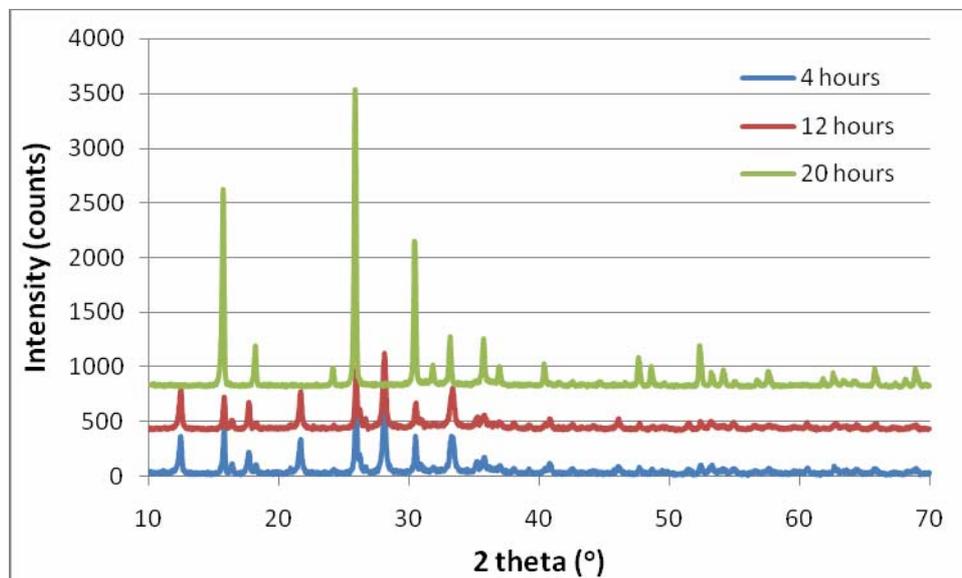


Figure 10: Effect of hydrothermal reaction time on the formation of zeolite from fly ash.

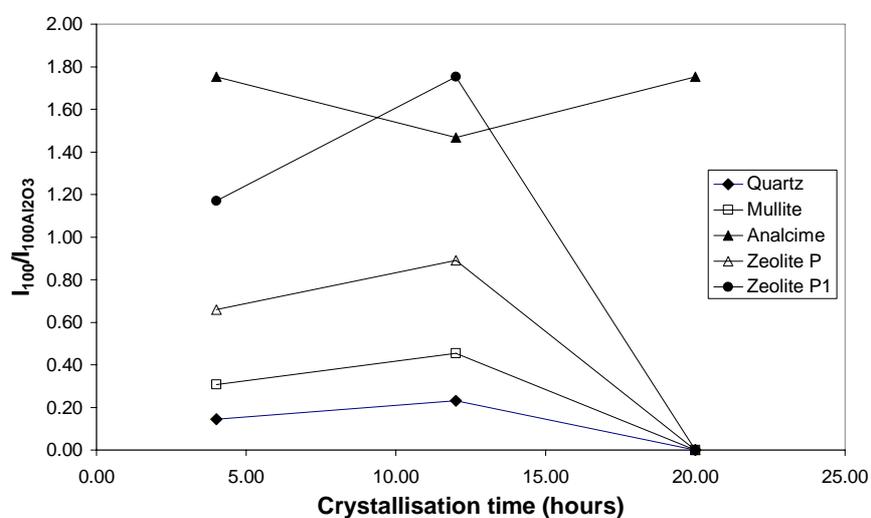


Figure 11: Quantitative analysis on the effect of reaction time to the zeolite formation

3.2. Pot test trial results

3.2.1. Characteristics of the zeolite, sand and soil

All zeolite used in the pot plant trial was synthesised according to the optimum condition aforementioned. They are highly crystalline and in the form of very fine powder where the particle size is similar to the parent fly ash as shown in Figure 12. Other characteristics of the zeolite, fly ash and the the soils, the yellow gravelly loamy sand (hence call as soil or Collie soil) and Bassendean sand used in the pot plant experiments are given in Table 3

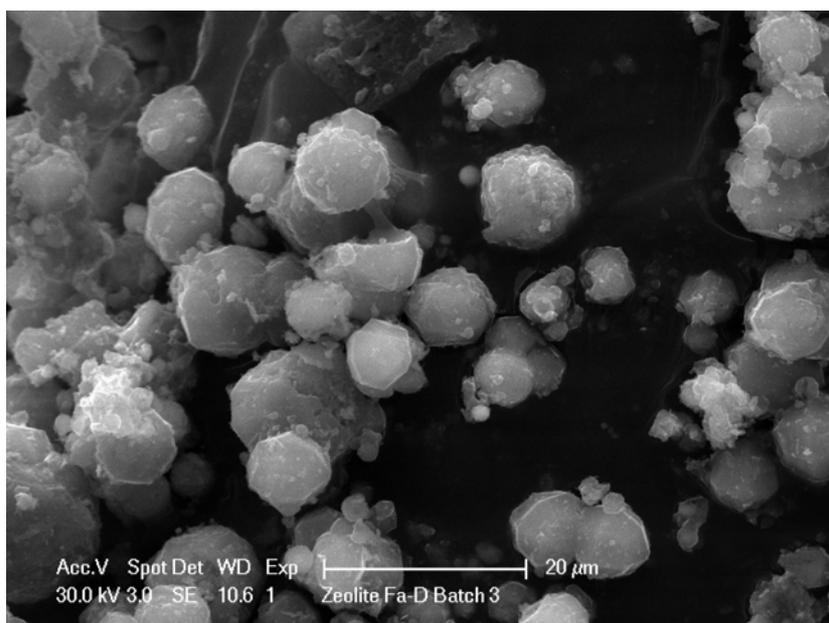


Figure 12: Electron microscope image of zeolite made from fly ash using the optimum synthesis condition.

Table 3: Characteristics of zeolites, Bassendean sand, Collie soil and fly ash

Parameters	Na-Zeolite	K-Zeolite	Sand	Soil	Fly Ash
pH (H ₂ O)	10.5	9.9	6.8	6.2	5
CEC (NH ₄ Cl) me%	31 ^a	35 ^a	1 ^a	7 ^a	2 ^a
EC (1:5) mS/m	88	440	1	4	94
Toxic Heavy metals (mg kg⁻¹)					
As	<1	2	<1	<1	11
Cd	0.48	0.27	<0.05	<0.05	0.4
Hg	0.09	0.09	<0.05	<0.05	0.18
Pb	65	54	<0.5	2.4	51
Se	<1	<1	<1	<1	6
Exchangeable cations (me%)^b					
Ca	3.04 ^a	3.66 ^a	0.06 ^a	3.00 ^a	3.33 ^a
Mg	1.54 ^a	1.49 ^a	0.03 ^a	0.79 ^a	1.06 ^a
K			<0.02	0.15 ^a	0.04 ^a
Na			<0.02	0.08 ^a	0.83 ^a

^a 1 M NH₄Cl at pH 7; ^b mm % = milliequivalent per 100 g sample

Table 3 shows that Bassendean sand and Collie soil have very low electrical conductivities (EC) and cation exchange capacity (CEC), and neutral to slightly acid pH. Electrical conductivities (EC) of Bassendean sand and Collie soil are about one order of magnitude lower than the fly ash and both Na- and K-zeolites. Their toxic heavy metal contents are also very low except for the lead concentration in Collie soil. Bassendean sand has the lower exchangeable cations while Collie soil has similar exchangeable Ca and Mg to the fly ash and the Na and K-zeolites and higher exchangeable K than the fly ash. The low CEC, EC and exchangeable cations of Bassendean sand indicate that the sand is infertile.

In contrast to Bassendean sand and Collie soil, the pH, CEC and EC of the Na and K-zeolites are very high. The high pH of the zeolite suggests its ability to exchange its Na^+ or K^+ with H^+ from the water, since the zeolites have high cation exchange capacities, being 31 and 35 for Na and K-zeolite, respectively. The exchange capability also contributes to the electrical conductivity (EC) because the zeolites can introduce cations to the water being used to measure the EC. Exchangeable Ca and Mg of the zeolites are also high, similar to those of Collie soil. They also have very high exchangeable Na and K due to the nature of the synthetic Na and K-zeolites. While the zeolites have everything to improve the soil properties, they also contain one order of magnitude higher concentration of toxic heavy metals than Bassendean sand and Collie soil, which have been carried forward from the fly ash. The toxic heavy metals in the Na and K-zeolites are very similar to those in the fly ash with As and Se seeming to have been leached out during the zeolite synthesis.

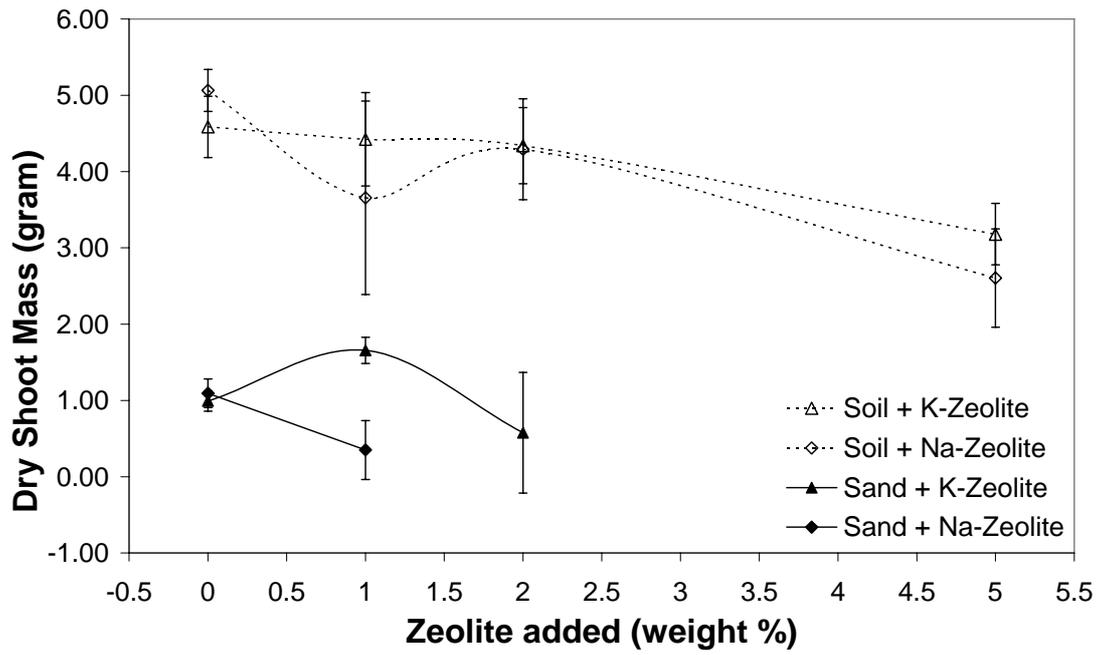
3.2.2. The growth of the crops

The pot trial results are featured in Figure 13. In the figure, the pots were arranged from left to right in the order of increasing the amount of zeolite added into the soils so as to show the effect of zeolite addition into the soils on the growth of canola, spinach and wheat.

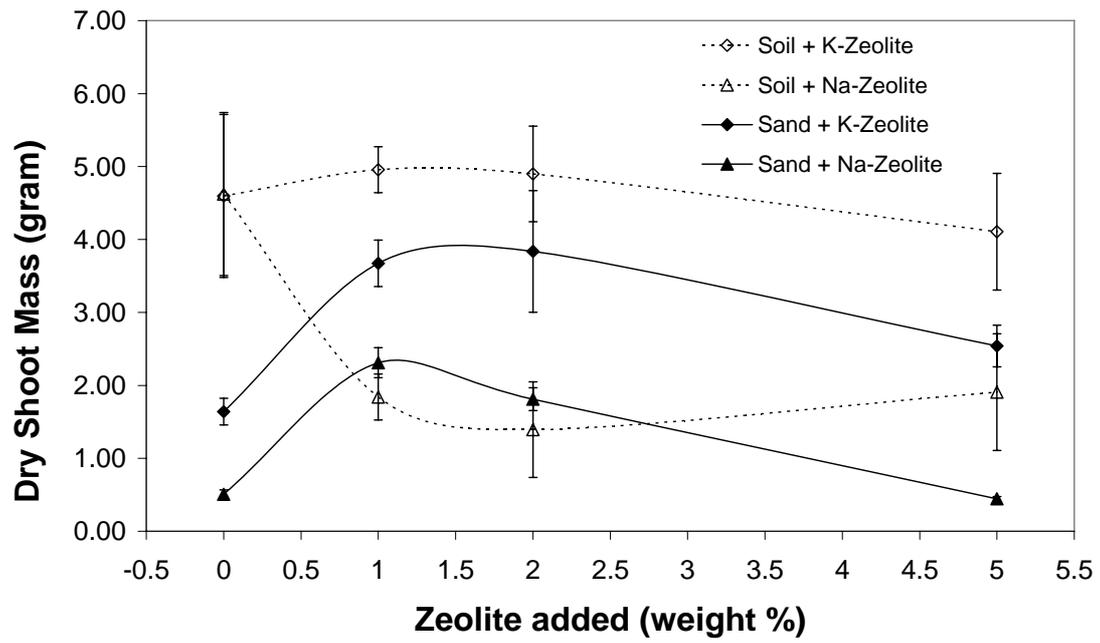
The effect of zeolite addition was clearly shown on spinach and wheat when they were planted in Bassendean sand. The crops grow better at 1 and 2 wt% of zeolite additions for both K- and Na-zeolite. However, apparent improvement to the growth of canola has only been found at 1 wt% K-zeolite addition and an adverse effect on the growth was found when adding Na-zeolite at any dosage and K-zeolite at more than 2 wt % to the soils. The zeolites also improved the growth of canola, spinach and wheat when they were added to the more fertile Collie soil as clearly shown in the photos.

	Grey Bassendean Sand	Yellow Gravelly Loamy Sand
Wheat		
Na		
K		
Spinach		
Na		
K		
Canola		
Na		
K		

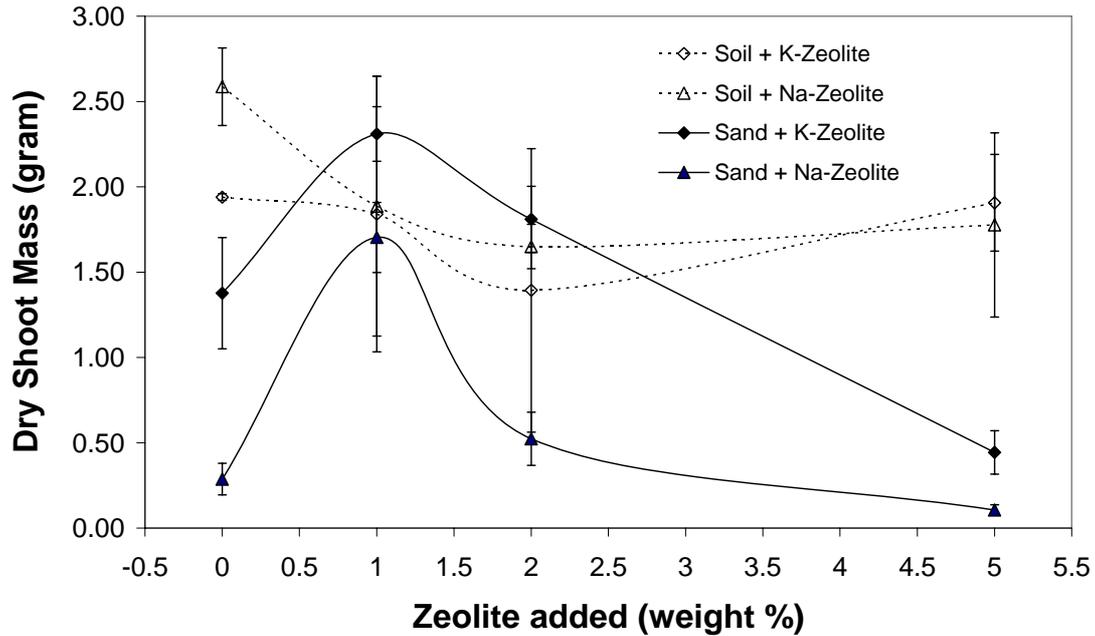
Figure 13: The pot plant trial results of K- and Na-zeolite. For each set of photos, the pots were arranged (from left to right) as 0% (control pot), 1%, 2% and 5%.



(a)



(b)



(c)

Figure 14: The mass of dried shoots of (a) Canola, (b) Spinach and (c) Wheat at different levels of zeolite added into the soils.

The growth of the crops in the soils with different zeolite additions can be represented by the mass of the crop dried shoots. Figure 14 shows that both K- and Na-Zeolites improve spinach and wheat growth when they were added at a dosage between 1 and 2 wt % to the sand. Canola also grows better in K-zeolite added sand but it is restricted only at 1 wt% addition. An observable beneficial effect can be seen when the zeolites were added to the Collie soil at any level on canola, spinach and wheat.

Canola and spinach require greater nutrient (such as nitrogen, phosphorus and sulphur) input than other crops [18]. Nitrogen is one of macronutrient greatly needed by canola and spinach. When soil's nitrogen is low, nitrogen fertiliser is added to the soil. The nitrogen fertiliser added is in the form of ammonia nitrate. Zeolite added to the soil can adsorb the ammonium ion from the fertiliser via an ion exchange reaction, releasing its cation (either Na or K, depends on the zeolite being used). When the zeolite added is Na-Zeolite, sodium will be released to the soil in exchange of ammonium ion resulting in a nitrogen-deficient state and excessive sodium content in the soil. The same process can also occur when using K-Zeolite. However, potassium ion released from the zeolite is required by canola while sodium is not.

3.2.3. Heavy metals in the soils and crops

Heavy metal pollution is a serious problem for agriculture and health when the metal concentrations are high. Some crops such as wheat, soy bean and peanuts can highly accumulate the heavy metal in their shoots [19].

Zeolites in this research were made from fly ash. It is known that fly ash may contain trace amounts of toxic heavy metals such as Lead (Pb), Mercury (Hg), Arsenic (As), Cadmium (Cd) and Selenium (Se). The metals might still exist in the zeolite although it is believed that these toxic metals are not incorporated into zeolite [2].

As listed in Table 3, the concentrations of the toxic heavy metals in the zeolites were carried forward from the fly ash and they are one order of magnitude higher than those in Bassendean sand and Collie soil. Therefore, when the zeolites were added into the soils, the increase of its concentration is expected.

Although the concentrations of the toxic heavy metals in the zeolites is relatively high, zeolite addition to the soils has been shown not to increase the heavy metal concentrations in the dry biomass of the plants investigated. The analysis results of the concentrations of the toxic heavy metals in the zeolite added soils show that the heavy metal concentration is undetectable except for Pb (lead), which is shown to increase as the zeolite added increases. Table 4 and Figure 15 show the lead concentrations in zeolite added soils.

Table 4: Lead in soil samples

Zeolite Added (wt%)	Lead in Soil, mg kg ⁻¹			
	Grey Bassendean Sand		Yellow Gravelly Loamy Soil	
	Na-zeolite added	K-zeolite added	Na-zeolite added	K-zeolite added
0	0.8	0.5	2.3	2.6
0	0.5	0.5	2.2	2.4
0	0.5	0.5	2.3	2.3
1	0.7	0.7	3	3.1
2	1.8	1.3	4	3.8
5	3.1	3.5	5.7	5.8

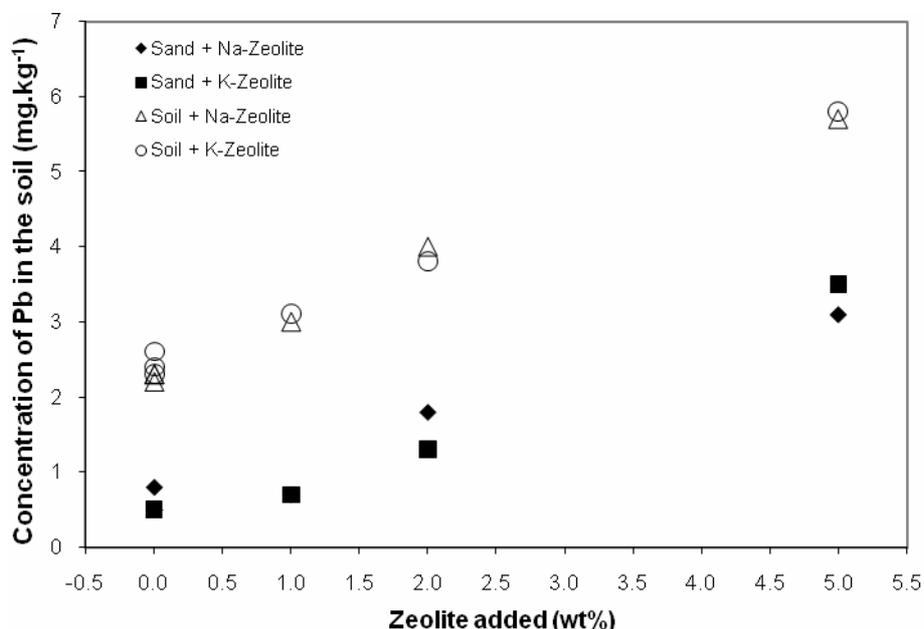


Figure 15: Heavy metals concentration in the soil and sand after plants' harvest. Only Lead (Pb) was detected while other heavy metals were below the detection limit.

Figure 15 shows that zeolite addition to the sand and soil increases the Lead concentration. The increase linearly correlates with the amount of zeolite added into the soils. However,

although a high lead concentration was found in the zeolites and zeolite added soils, Lead was not found in the dried shoot mass of all crops tested in this work as shown in Table 5.

In contrast to the soils, the toxic heavy metal concentrations in dried shoots of canola, spinach and wheat did not follow the zeolite addition and is apparently independent of the heavy metal concentrations in the soils. For example, although there were relatively high Lead concentrations in the zeolite added soils, no Lead was detected in the dry mass of the crop shoots. Arsen (As) and Selenium (se), the two of toxic metals found to be below the detection limit in the zeolite added soils, were not found in the crops either. However, Cadmium (Cd) and Mercury (Hg) were found in the dry shoot biomass of canola, spinach and wheat even when no zeolite was added into the soils and their concentrations in the soil are very low.

Table 5: Heavy metals found in Canola, Spinach and Wheat

Zeolite added (wt %)	Cd (mg kg ⁻¹)				Hg total (mg kg ⁻¹)			
	Collie Soil		Bassendean Sand		Collie Soil		Bassendean Sand	
	Soil K-Z	Soil Na-Z	Sand K-Z	Sand Na-Z	Soil K-Z	Soil Na-Z	Sand K-Z	Sand Na-Z
Canola								
5%	0.51	0.21	- ^{*)}	- ^{*)}	0.14	0.05	- ^{*)}	- ^{*)}
2%	0.43	0.19	0.09	- ^{*)}	0.18	0.08	0.06	- ^{*)}
1%	0.45	0.29	0.1	0.09	0.09	0.14	0.11	0.1
0%	0.36		0.22		<0.05		0.19	
Spinach								
5%	0.11	0.21	0.35	0.05	0.1	0.09	0.08	0.12
2%	0.14	0.23	0.28	0.07	0.06	0.06	0.09	0.09
1%	0.15	0.35	0.35	0.09	0.1	0.04	0.11	0.08
0%	0.56		0.16		0.12		0.07	
Wheat								
5%	0.16	0.08	0.05	- ^{*)}	0.13	0.08	0.13	- ^{*)}
2%	0.16	0.14	0.04	0.02	0.12	0.06	0.14	0.12
1%	0.18	0.17	0.06	0.05	0.12	0.13	0.04	0.13
0%	0.19		0.39		<0.05		0.12	

Na-Z = Na-Zeolite; K-Z=K-Zeolite; ^{*)} insufficient dried shoot sample

The Cadmium level in spinach found in this test is within the range reported on vegetable grown in Metropolitan Boston and Washington DC [20]. The Cadmium level was reported in the range of 0.9 to 2.6 mg kg⁻¹. It is also still within permissible level by WHO and FAO (0.3 mg kg⁻¹) as reported by Bahemuka and Mubofu [21].

The zeolite addition to either sand or soil apparently reduces the heavy metal contents in spinach and wheat except for spinach planted in the K-zeolite added Bassendean sand. This is contrary to the fact that the heavy metal (Lead) concentration in the soils increases with increasing the amount of zeolite added. This phenomenon can only be explained if the zeolite retains the heavy metals inside its lattice structure.

4. CONCLUSIONS AND RECOMMENDATIONS

Water content, expressed as the H₂O/Al molar ratio, plays a very important role in hydrothermal conversion of Collie coal fly ash to zeolite. It is found that the optimum H₂O/Al ratio is 57.4. The main zeolite product produced under the optimum condition is analcime. It is also found that four hours hydrothermal reaction is sufficient to produce fertiliser grade zeolite which contains a mixture of analcime, Zeolite P and Zeolite P1, from Collie fly ash.

Addition of up to 5 wt% zeolite into yellow gravelly loamy sand (Collie soil) apparently showed some observable beneficial effect on the growth of canola, spinach and wheat, except on spinach at 5 wt% Na-zeolite addition. On the other hand, when the zeolite was added to grey Bassendean sand, spinach and wheat grow better at 1 and 2 wt% zeolite additions, both in sodium and potassium form. Overall, K-zeolite addition gives better spinach and wheat growth than Na-zeolite.

In contrast to spinach and wheat, zeolite addition at almost all levels dwarves the canola planted on Bassendean sand. Only at 1 wt% K-zeolite addition the canola grows better.

The zeolite might adsorb and retain Nitrogen which is highly required by the canola and spinach, causing nitrogen deficiency in the soil. The nitrogen was added into the soil in the form of ammonium nitrate fertiliser where the ammonium ion can be adsorbed by the zeolite added by ion exchange mechanisms.

Only Lead was found at an insignificant figure in the soil added with zeolite and its concentration increases as the zeolite addition increases. However, Cadmium and Mercury were detected in the dried shoots of spinach and wheat even without zeolite addition. Nevertheless, their concentrations are within FAO and WHO recommended levels. It is also interesting that Cadmium and Mercury levels decrease as higher percentage of zeolite was added into the soils.

ACKNOWLEDGEMENTS

The project was supported by the CRC for Coal in Sustainable Developments (CCSD). We would also like to express our gratitude to Collie power station for supplying the fly ash sample and Mr. Adam Hyland for technical assistance in some zeolite preparations.

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APPENDIX

Industry Summary Report from Thesis

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**AN INVESTIGATION INTO THE HYDROTHERMAL PROCESSING OF
COAL FLY ASH TO PRODUCE ZEOLITE FOR CONTROLLED RELEASE
FERTILISER APPLICATIONS**

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Curtin University of Technology

May 2006

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1 Executive Summary of Thesis

The doctoral thesis and associated work looks at the issues behind fly ash utilisation in the broader sense^{A1}, evaluates the potential markets for zeolite products in Australia^{A2}, and assesses the established science behind producing zeolite materials from fly ash^{A3}.

The experimental component of this research examines the hydrothermal process for producing zeolites suitable for agricultural application from coal fly ash starting materials, including the relationship between operating conditions, the reactivity of ash components, and zeolite types produced, zeolite properties desirable for controlled release fertilisers^{A2}, optimal production conditions, and economic implications^{A5}.

The vision of this work is to redesign the zeolite production process to incorporate coal fly ash as a raw material, taking advantage of fly ash properties and hydrothermal chemistry to increase productivity and reduce costs^{A4}.

The hydrothermal treatment process was studied through the control of reaction temperature (T), reaction time (t), the Si/Al mole ratio (n), the pH, the Si/Al mole ratio (n), the cation type (M), the pH, the H₂O/Al mole ratio (p), and the M⁺/Al mole ratio in excess of unity (m), where MnO₃ was used to control 'm' independent of pH.

A systematic quantitative refinement method was developed using 'Rietica' to characterise the mineralogy of fly ash and hydrothermal treatment products, resulting in substantially more information regarding the transformations taking place than has previously been available in the study of the synthesis of zeolites from fly ash. This in conjunction with SEM has provided unprecedented detail regarding the reactivity of fly ash components, namely glass, quartz, and mullite phases, as well as the independent role of M⁺ and OH⁻ within the hydrothermal system, and the encapsulation of fly ash reactants by products.

The experiments conducted demonstrate and for the first time quantify the dependency of gel formation and zeolite crystal growth processes on M⁺ and OH⁻ concentrations and temperature. The results show that optimising these processes is best targeted in the continuous presence of zeolites with fly ash reactants. Manipulation of M⁺ and OH⁻ concentrations and temperature are used to balance the suppression of fly ash dissolution while enhancing crystallisation to minimise the encapsulation of reactants by products and increase the productivity of hydrothermal treatment process. The study shows that these are the key variables that must be optimised to improve its economic viability, which is key to its possible future implementation.

It is believed that the experimental study conducted, adds value to the understanding of the synthesis of zeolites from fly ash. Avenues for increasing productivity and reducing costs have been identified. The study forms the basis for future research to progress the successful synthesis of zeolites from fly ash for application in bulk use agricultural applications.^{A6}

2 Introduction

Coal-fired power is the primary source of electricity in Australia, providing 80% of electricity production. Coal fly ash is produced as a by-product of coal combustion, and its utilisation is at present realised by low technology applications, such as in cement and construction materials including mine backfills, soil stabilisation, engineered fills, and road base^{A1.1}. However, ca. 500 million tonnes of coal ash is produced globally each year, with only 34% effectively used (Manz 1997). During the year that concluded prior to the commencement of this doctoral study (2001) 11.7 million tonnes of fly ash was produced in Australia, of which only 32% was used in some way. The latest statistics (2004), reveal that 12.5 million tonnes was produced with only 35% utilised (ADAA 2006)^{A1.3}, with the remainder accumulated in landfills and ash dams^{A1.4}.

An overarching objective of the Co-operative Research Centre for Coal in Sustainable Development (CCSD) is to optimise the contribution of coal to a sustainable future. In the Centre's research program, this included targeting the energy and economic credits that may be available by finding options for the bulk (tonnage) use of fly ash. The doctoral thesis commenced with;

A study of the current state of fly ash utilisation within Australia and the world to identify the best technology opportunities capable of using very large tonnage of fly ash.

The low level of ash utilisation is inevitable due to inherently high transport costs for the relatively low value products produced, especially in Australia where a small population is spread over a large area. This makes it difficult for ash to compete with traditional raw materials^{A1.3.3}. This situation argues for more value-added high technology utilisation of fly ash as an effective means of overcoming the transport cost barriers.

There are a number of known fly ash utilisation strategies, see Figure 9.1, each having its own advantages and disadvantages, and some form of barriers. In the interest of selecting the right strategy to meet research objectives, the following concepts need to be considered, the strategy needs:

- to be high volume, capable of consuming a significant quantity of fly ash
- to be significantly value-added so that it is not inhibited by the transport cost barriers
- to be a new product or explore new applications or markets for fly ash, so that it is not
- inhibited by market inelasticity
- to be inhibited by significant technical barriers where research can make a difference

Under such criteria, zeolites and geopolymers prevail as viable candidates^{A4.1}.

The opportunity to use zeolite derived from fly ash in an application for agricultural purposes if viable, lends itself to a bulk application that requires the use of large tonnages. It would also have significant economic and environmental benefits;

Therefore, from the study of the primary objective (stated earlier), the thesis research focused on investigating the production of zeolites from fly ash

The fertiliser industry is a major industry in Australia. Fertilisers are consumed by agriculture, horticulture, floriculture and turf industries, as well as the gardens and lawns of households. The fertiliser industry is worth \$AU 2 billion per annum, however current fertilisers are rarely more than 50% efficient and, in some applications such as in sandy soils, their efficiency in delivering

nutrients to plants can be as low as 10%. Fertiliser not taken up by plants is washed through to the water table, rivers and waterways, or volatilised into the atmosphere^{A2.5}.

Zeolites can be produced from coal fly ash using chemical processing^{A3}, and they can then be used as controlled release fertilisers which supply nutrients to plants as they need it, making them more efficient, and longer lasting than traditional fertilisers^{A2.4}. As such have a considerable advantage in terms of economic, technical and environmental performance. The controlled release zeolite fertiliser market has the potential to be both a high volume and a high value market, with the potential to consume significant quantities of fly ash^{A2.2}.

From the foregoing analysis, the generic objective of investigating the production of zeolites from fly ash, was further refined;

To study the process of producing zeolite from fly ash for controlled release fertiliser applications with a focus on multiple products and cost minimisation.

Zeolite manufacture is not new^{A3.1}. Well established manufacturing plants exist which produce zeolites for industrial absorbers and adsorbents, ion exchangers, and catalyst applications, as well as water softeners in powder detergents, using calcined kaolinite or other more expensive aluminosilicate sources, and recent years have seen plants using fly ash come into service^{A3.3.1.3}. **These plants produce small quantities of zeolite at great cost, making them unviable for agricultural applications.**

There are many different types of zeolite, where some zeolites perform better than others for a particular application^{A2.1}. Understanding this and knowing how to control the production process to produce the desired zeolite product is critical for the identification and manufacture of a superior product. However there is a limited understanding of the processes and mechanisms of producing zeolites from fly ash^{A4.3}, especially zeolites suitable for agricultural applications.

The experimental objective for this doctoral study is therefore to;

Investigate the influence of ash properties, hydrothermal chemistry, and continuous processing on the hydrothermal synthesis of zeolite from fly ash.

Three hypotheses were proposed for study;

- i. Iron has low solubility at high pH, it will reduce glass phase reactivity proportional to its content in the glass, and low iron glass will be etched away leaving high iron glass and hematite, magnetite, and hercynite phases
- ii. OH^- controls the total solubility and dissolution rates of Al and Si, M^+ controls the type of zeolite product, and the rate of reaction, and together MOH and MNO_3 occupy soluble space, therefore the associated reaction chemistry.
- iii. The reaction solution could be maintained in a saturated state with dissolution from reactants in sync with crystal growth through a combination of (i) suppressing fly ash dissolution through the manipulation of M^+ and OH^- concentrations, and (ii) enhancing crystallisation through the manipulation of M^+ concentration and the ratio of zeolite to fly ash maintained within the reactor minimising fly ash encapsulation during gel precipitation

An experimental methodology was developed based on batch hydrothermal synthesis in conjunction predominantly with XRD and SEM analysis techniques to test hypothesis.

3 Relevance to Industry

The technical and philosophical achievements of the thesis are summarised both in the Executive Summary (Section 1), the Introduction (Section 2), and in Evaluation and Reflection (A6.3). This section explores the implication of the thesis results to zeolite fertiliser application of fly ash in general, and the relevance to ash producers and the coal industry in particular. To allow a deeper understanding of the science behind statements and conclusions, a detailed analysis of topics is also provided in the attached appendices.

The product successfully produced in the laboratory may be used as a fertiliser based on controlled release zeolite technology^{A2.4}. The pre-existing fertiliser markets within Australia^{A2.2} and the world with which this product may compete are so substantial in size that they can consume a significant percentage of Australia's annual ash production even with small market penetration, through a significantly value added product capable of overcoming the transport cost barrier to fly ash utilisation.

Appendices A2.3 to 2.5 explain how zeolite fertiliser products differ from their traditional fertiliser counterparts through superior efficiency and environmental performance

- Greater efficiency at delivering nutrient elements to crop
- Reduced emission of nutrients to environment and associated environmental impact
- Longer effective life

These advantages should help zeolite fertiliser products penetrate parts of the pre-existing fertiliser market.

The value of fly ash as a raw material in the synthesis of zeolites^{A2.3.1} is what makes this application relevant to ash producers and the coal industry in general. Any coal ash can be used to produce zeolites; however not all ashes perform equally.

For example;

- i. Low iron ashes perform better at producing zeolites than high iron ashes.
- ii. Very high quartz produces high Si/Al zeolites which is undesirable for fertilisers due to lower nutrient storage capacity than low Si/Al zeolites.
- iii. Under low pH production conditions, lower quartz and mullite containing fly ash perform better than high quartz and mullite ashes.

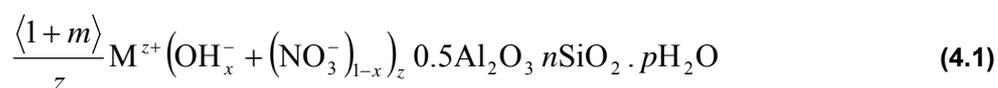
The benefit to power stations in investing in fly ash zeolite research and ultimately in a fly ash zeolite manufacturing plant lies in its capability to divert ash production away from ash dam, through a strategy which provides ongoing secure demand for ash, extending the operating life of ash dam.

4 Summary Results and Discussion

The following results and discussion are an important subset of typical outcomes taken from the thesis experimental program. For a more detailed discussion of all the results and their implications, the reader is referred to the full thesis document.

4.1 Hydrothermal Synthesis Methodology

Treatment conditions for the hydrothermal synthesis of zeolites from fly ash have traditionally been defined by the ratio of the volume of sodium hydroxide solution to the mass of fly ash, and by the concentration of sodium hydroxide in solution. However this method is incapable of distinguishing between the role of M^+ and of OH^- in the chemistry of hydrothermal treatment. To investigate these phenomena, a new method was developed and used, which makes use of MNO_3 , and where reaction conditions are defined by the mole ratios OH^-/H_2O , H_2O/Al (p), and m (the ratio M^+/Al in excess of stoichiometry), which are defined by the reaction mixture Equation (4.1) which is based on 1 mole of Al, where n is the Si/Al mole ratio (related to fly ash composition).



The decisive results of Section 4.3 demonstrate the independent role of M^+ and OH^- in the hydrothermal chemistry, therefore the value of this technique when studying the hydrothermal treatment of fly ash.

4.2 Identifying and quantifying the product

To illustrate the capacity of quantitative XRD technique to contribute to our understanding of the transformation processes taking place during hydrothermal reactions, the following examples are given.

Example A – HTP67 (SRC)

From characteristic peak location and relative peak intensities, major mineral constituents can be identified (qualitative result) see Figure 4.1. Using Rietveld refinement (using Rietica software program), the quantitative analysis of mineral components contained in sample can be calculated from the XRD pattern of internally standardised sample. See Figures 4.1 and 4.2.

From the XRD pattern of fly ash A (Figure 4.1), five mineral phases can be identified, where quartz and mullite are phases that contain Al and Si which are required for zeolite synthesis, while hematite, magnetite, and hercynite are iron phases (impurities). From the XRD pattern of hydrothermal treatment product (SRC), see Figure 4.1, four zeolite phases are identified, zeolite ZK-14, analcime, zeolite P1, and gmelinite.

From the quantitative results there was an approximate reduction of 74, and 30% in the composition of quartz and other phases as a result of hydrothermal treatment, while mullite concentration in product is 23% higher than in reactant. The hydrothermal treatment product (SRC) contains roughly 30% zeolite (see Figure 4.2). Quantitative results allow the direct

comparison of different hydrothermal treatment outcomes, therefore the performance of treatment conditions.

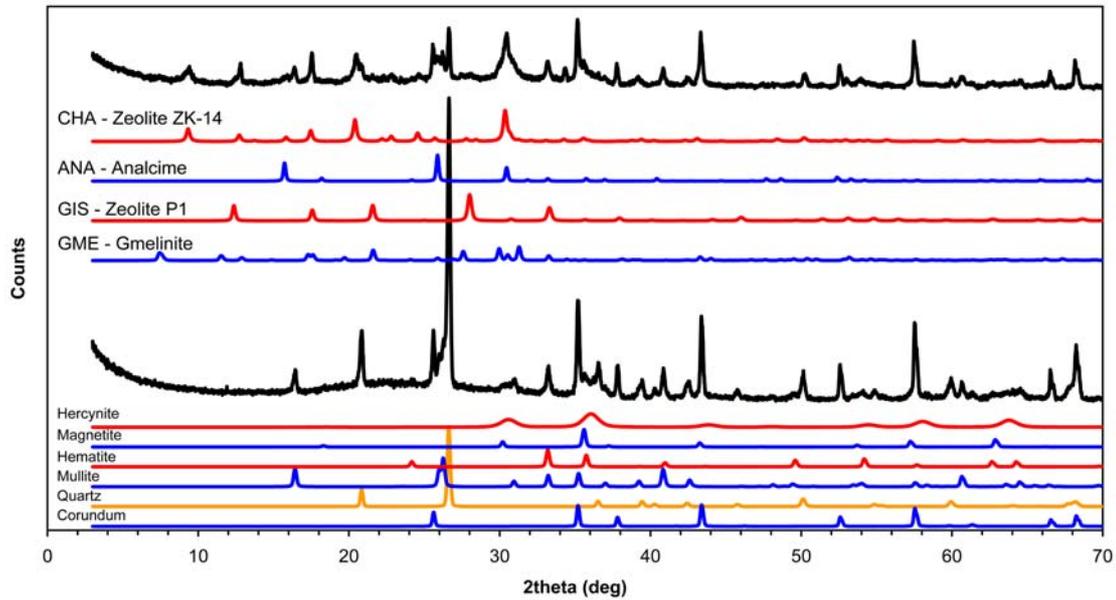


Figure 4.1 : XRD diffract-o-grams of fly ash A, HTP67 (SRC), and the individual mineral phases which they contain

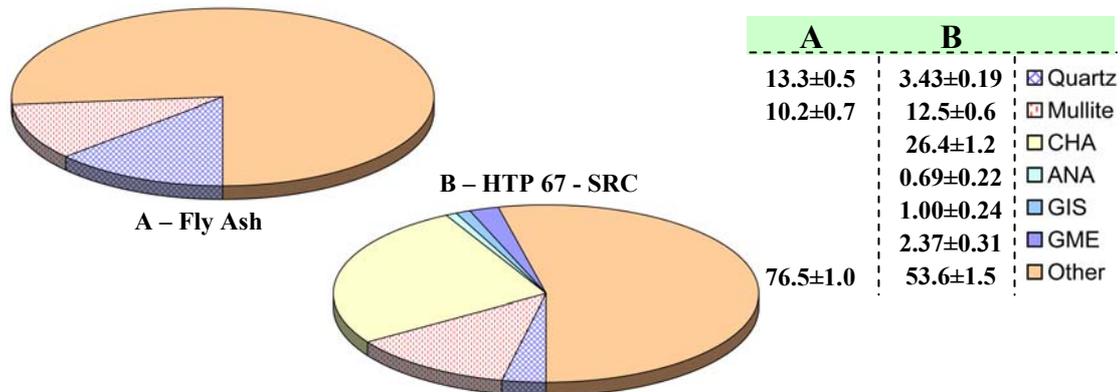


Figure 4.2 : Quantitative analysis of fly ash A and HTP 67 (SRC) samples using diffraction patterns illustrated in Figure 4.1 above

Example B – Peak Overlap

A number of zeolite products were produced from fly ash A using the non-agitated batch reactor over a range of pH conditions. The diffraction pattern for fly ash A and three of these products is presented in Figure 4.3, from which the following observations can be noted:

- The emergence of zeolite peaks resulting from hydrothermal treatment
- Increasing zeolite peak intensity with increasing reaction soup pH
- A shift in zeolites produced from sodalite to cancrinite with increasing pH
- A decrease in the quartz peak intensity with increasing pH

However there are limitations with direct peak comparison due to peak overlap between sodalite and cancrinite products. There are 4 major peaks which emerge (see Figure 4.3) at 2θ's of 13.96, 18.88, 24.30 and 27.49. The first and third of these peaks corresponds to the 011 and 112 *hkl*

orientations of sodalite, while all four peaks correspond to the 110 011 030 121 *hkl* orientations of cancrinite respectively. Rietveld refinement is needed to de-convolute these peaks. The quantitative mineral composition of products can be plotted as a function of operating conditions which is much more informative than a visual comparison of change between diffraction patterns, see Figures 4.3 and 4.4. From the quantitative results (Figure 4.4) we see:

- The relative consumption of quartz and mullite phases, and the reduction of “other” phase with increasing reactant pH
- The emergence of zeolite phases cancrinite and sodalite and their relative abundance as a function of pH

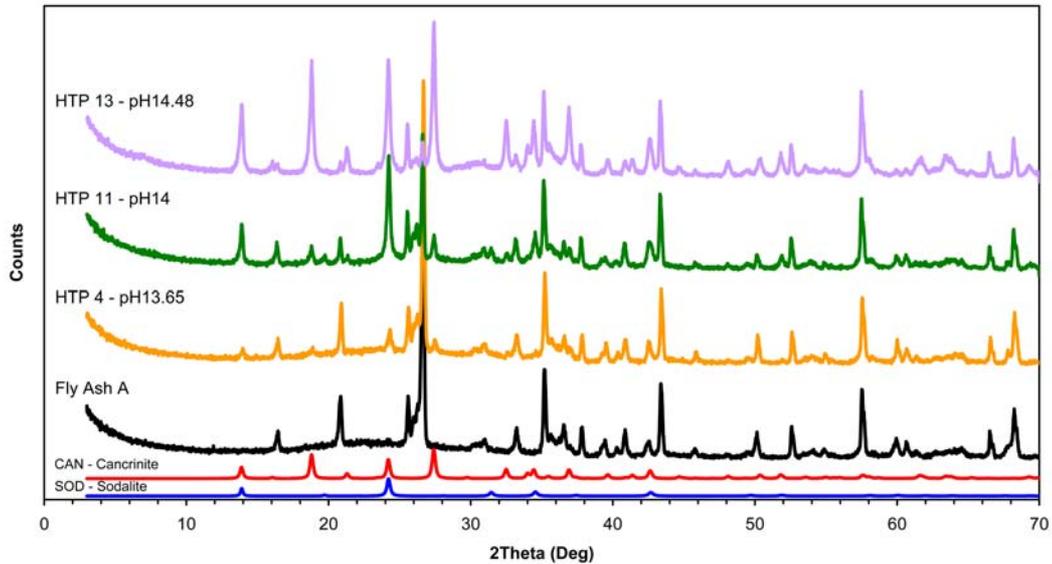


Figure 4.3 : XRD diffract-o-grams of fly ash A and hydrothermal treatment products HTP 4 (pH13.65m30), HTP 11 (pH14m30) and HTP 13 (pH14.48m30), as well as individual sodalite (SOD) and cancrinite (CAN) zeolite phases

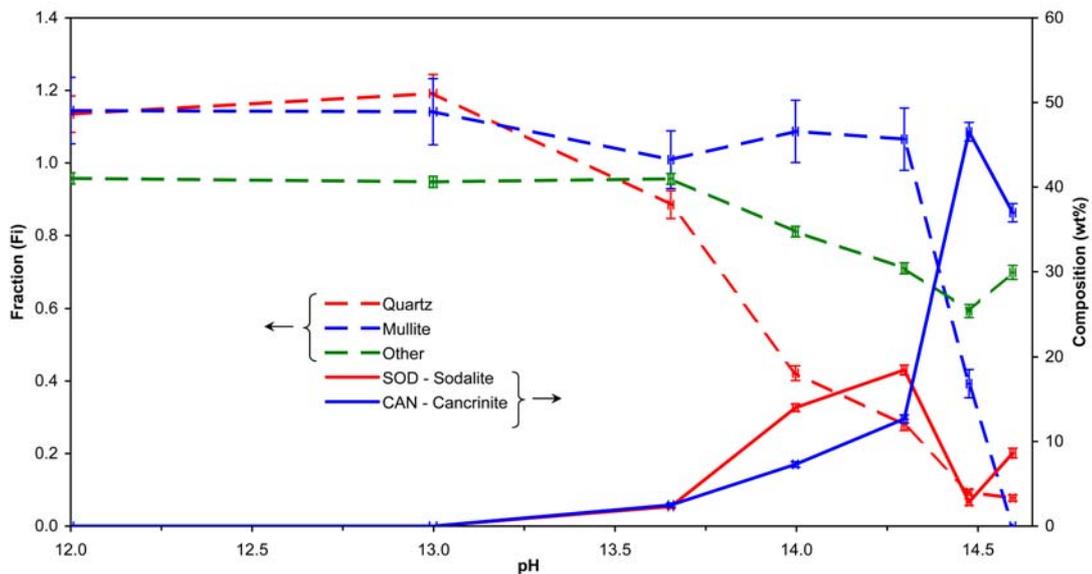


Figure 4.4 : Mineral compositional trends for hydrothermal treatment products* as a function of reaction pH

* HTP 8 (pH12m30), HTP 10 (pH13m30), HTP 4 (m30), HTP 11 (pH14m30), HTP 12 (pH14.3m30), HTP 13 (pH14.48m30)

4.3 Effect of pH, and ionic mole ratios (m and x)

From Figure 4.4, where m is fixed and pH is varied, the yields of zeolite produced and dissolution of reactants following hydrothermal treatment changes with changing pH. By comparison, from Figure 4.5, where m is varied and pH constant, the abundances and types of zeolite produced change with the changing m conditions. Clearly M^+ and OH^- play a different role in the overall reaction mechanism.

Previously Murayama, *et al.* (2002b; 2002a) investigated the substitution of NaOH for KOH and Na_2CO_3 while maintaining a constant concentration of M^+ in solution, and concluded that:

- The OH^- in alkali solution contributes to the dissolution of coal fly ash, while
- The Na^+ contributes to the crystallisation of zeolite P

In order to build on Murayama's work, and differentiate between the role of M^+ and OH^- within the chemistry of hydrothermal treatment, sodium hydroxide and sodium nitrate were used together to independently control the quantities of M^+ and OH^- within the hydrothermal system, in conjunction with quantitative XRD analysis of products produced. From the results presented in Figures 4.5 to 4.7, the following conclusions can be drawn:

1. The dissolution of reactants is most strongly correlated to the OH^- concentration, with increasing pH resulting in increased dissolution of glass, quartz, and mullite.
2. The types of zeolite produced are clearly most strongly correlated to m. Increasing m at constant pH increases the yield of a particular zeolite until a maximum is achieved, after which further increases in m result in a decrease in yield. CHA is produced and yields are optimised at $m < 10$, while SOD and CAN are produced at $m > 5$. For constant pH, CAN is favoured and optimised at low m relative to $x = 1$, while SOD is favoured and optimised at high m relative to $x = 1$
3. Since zeolite yields substantially increase with increasing m starting from $x = 1$ (at low m relative to $x = 1$). Considering that the additional MNO_3 is occupying soluble space, increased M^+ concentration must be increasing reaction rates.
4. The presence of MNO_3 clearly has two conflicting affects:
 - i. At low m, relative to $x = 1$, its impact on increased reaction rates dominates, with increased reaction rates removing dissolved Al and Si from solution faster allowing faster dissolution of reactants (glass, quartz, and mullite) and increasing overall yield.
 - ii. At high m, relative to $x = 1$, the occupation by MNO_3 of soluble space dominates reducing the dissolution rates of reactants (glass, quartz, and mullite) and total solubility of Al and Si, since reaction rates are also proportional to Al and Si concentrations in solution, the total dissolution of reactants and yield of products is reduced
5. OH^- concentration does influence the relative yields of zeolite phases produced at constant m. Increasing pH at constant m increases the yield of a particular zeolite until a maximum is achieved, after which increasing pH results in a decrease in yield. Different zeolite phases have optimal yields at different pH ranges, where the optimal pH for $CHA < SOD < CAN$. For SOD, isoclines of constant m show a decrease in the pH of optimal yield at constant m for increases in m from $x = 1$ at low m relative to $x = 1$, after which the pH of optimal constant m yield increases with increasing m; two possible causes are proposed:
 - i. The changing OH^- concentration changes the dissolution of reactants, changing the Si/Al ratio in solution influencing the relative yields

- ii. The changing OH^- concentration changes the rates of dissolution of different zeolite products to different extents changing the relative equilibrium yield ratios between different zeolite products

The following Figures (4.5 to 4.7) provide an extensive summary of the production and yield of several zeolite product phases from fly ash and their response to key process variables.

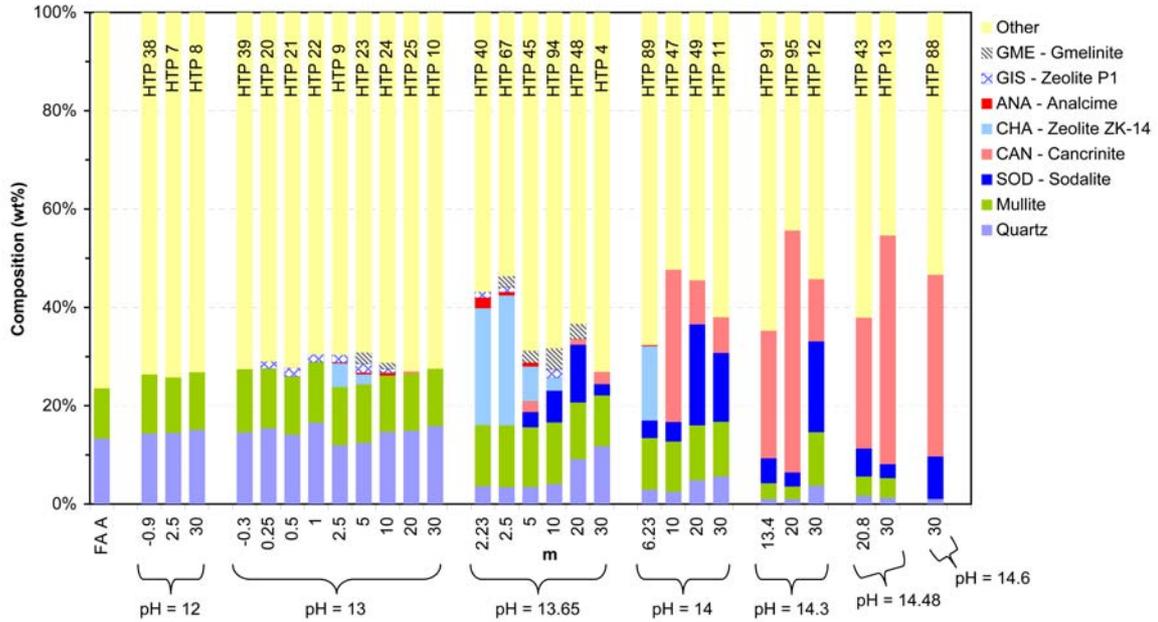


Figure 4.5: Mineral compositional trends for hydrothermal treatment products as a function of m, grouped according to constant pH

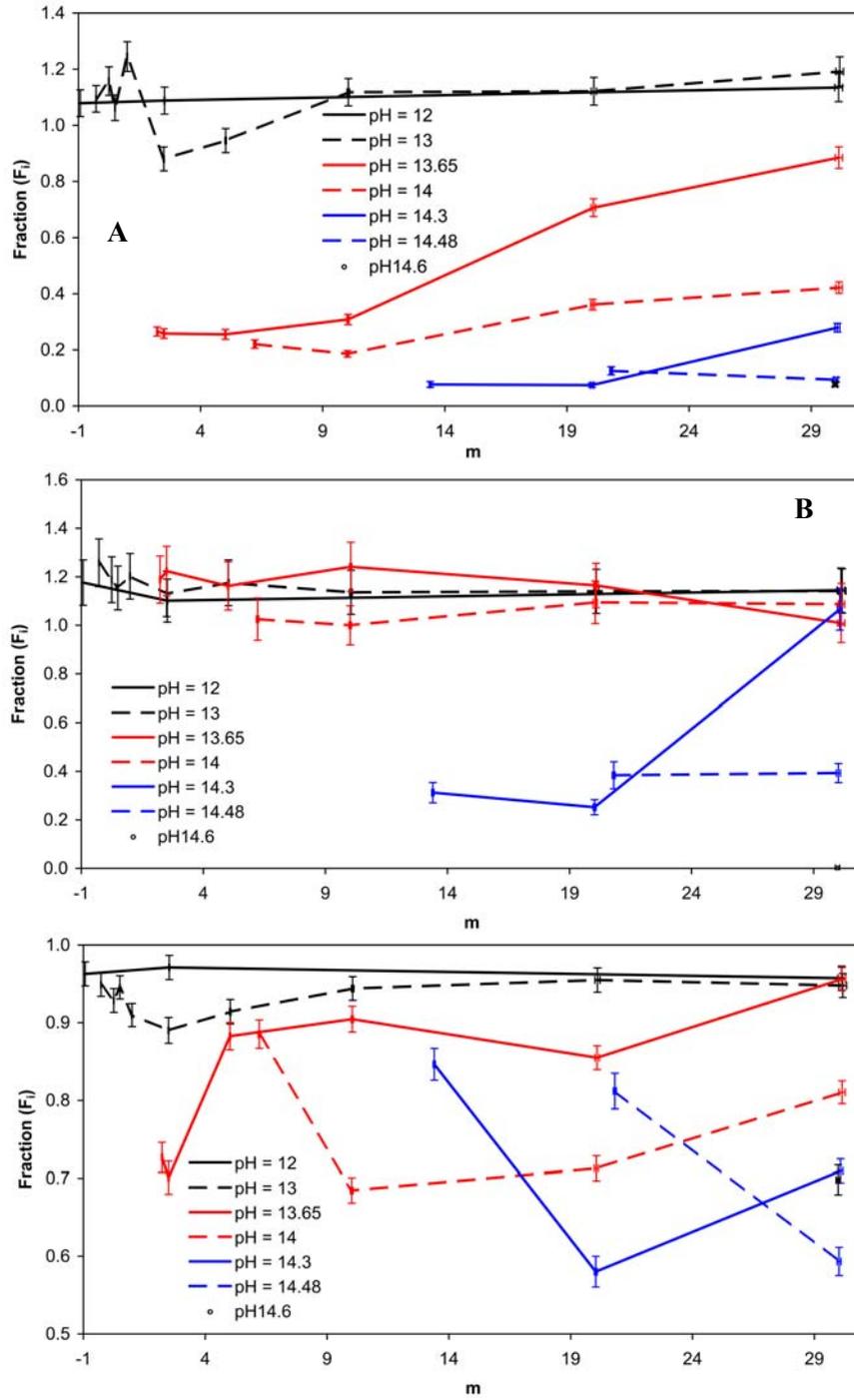


Figure 4.6: Component composition expressed as a fraction of original component composition in fly ash, and as a function of m , for A) Quartz, B) Mullite, C) Other

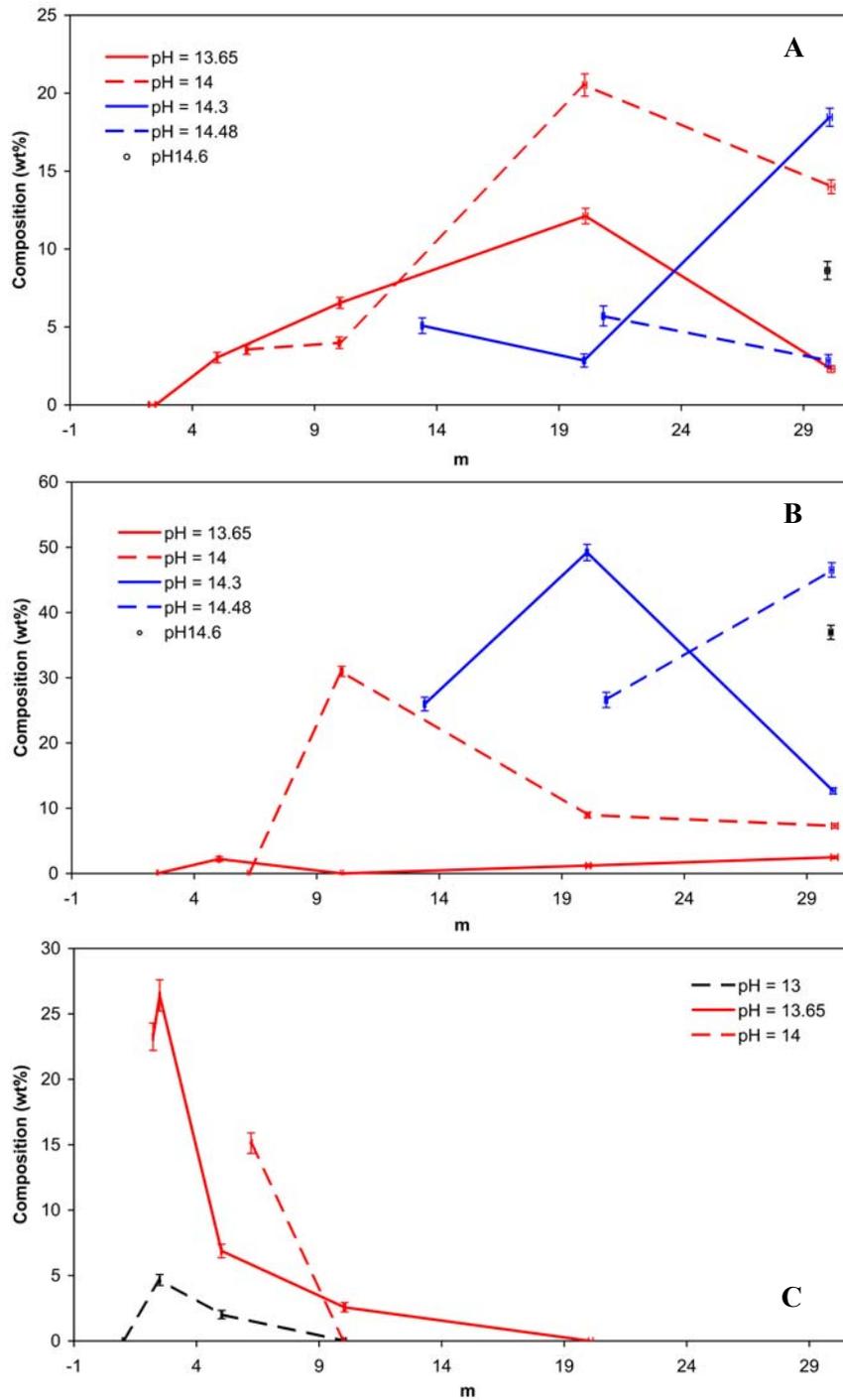


Figure 4.7: Composition of zeolite phases in products, as a function of m, for A) SOD, B) CAN, C) CHA

4.4 Hydrothermal Treatment Product Morphology

An insight into the transformations which have taken place during hydrothermal treatment can be gained from the analysis of reactant and product morphologies.

Quartz particles are often large and subsequently have small contact surface areas with reactive solution; however following hydrothermal treatment, significant signs of internal etching are present (see Figure 4.8), which is a testament to their reactivity, and which suggests that some quartz phases are more reactive than others, and dissolve significantly faster.

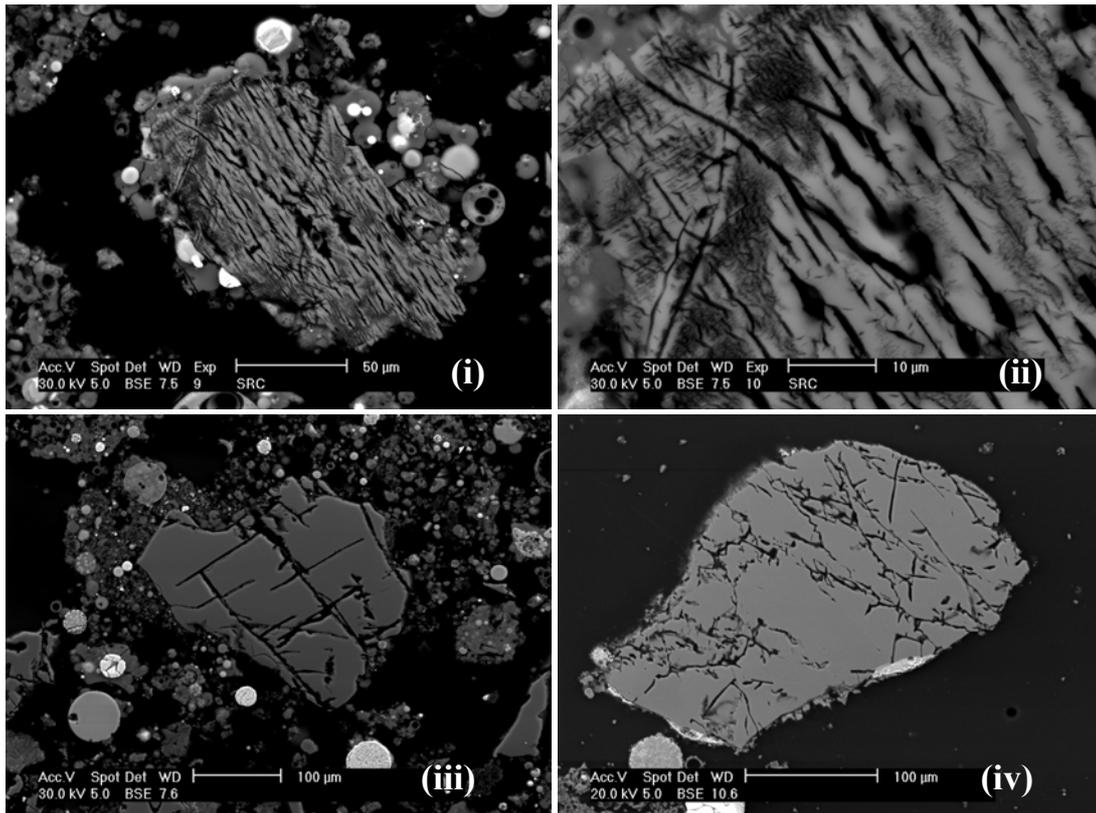


Figure 4.8: Particle cross sections viewed under SEM for i to iii) HTP 3 (SRC), and iv) HTP 11 (pH14m30), illustrating the etching of quartz phase which has occurred during hydrothermal treatment

Ghosts of fly ash particles remain where glass has been completely etched away to reveal mullite crystals which retain the overall morphology of original fly ash particle (see Figure 4.9). This demonstrates that the significant presence of iron previously demonstrated to be present in the glass phase (see Thesis), has not prevented its dissolution. The dissolution of glass has exposed mullite crystals, which are small with high surface areas, to the hydrothermal solution. However no signs of dissolution are evident (under the reaction conditions of HTP 3 (SRC), HTP 13 (pH13.48m30) or HTP 28 (AshC)) which supports previous authors' claims that mullite is the least reactive of the major contributing aluminosilicate reactants.

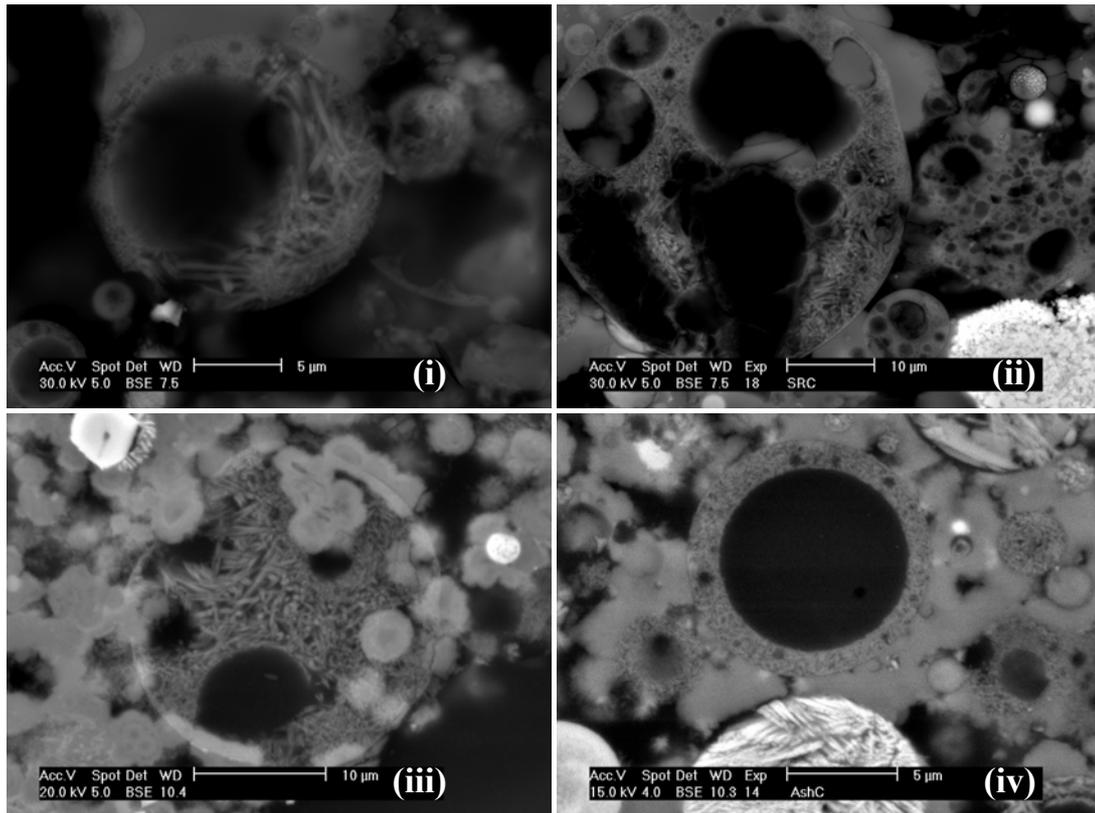


Figure 4.9: Particle cross sections viewed under SEM for i and ii) HTP 3 (SRC), iii) HTP 13 (pH14.48m30), and iv) HTP 28 (Ash C), illustrating the morphology of unreacted mullite present in hydrothermal product

From an inspection of the light contrast phases (high atomic number, e.g. high iron), free iron phases often occur in spherical like clusters, which indicate these phases originated as part of spherical fly ash particles where the more reactive phases have etched away (see Figure 4.10). This reactive phase (probably glass) is in close proximity to high iron phases, and subsequently is expected to contain significant iron which has not inhibited its dissolution. There is no evidence that iron mineral phases are dissolving.

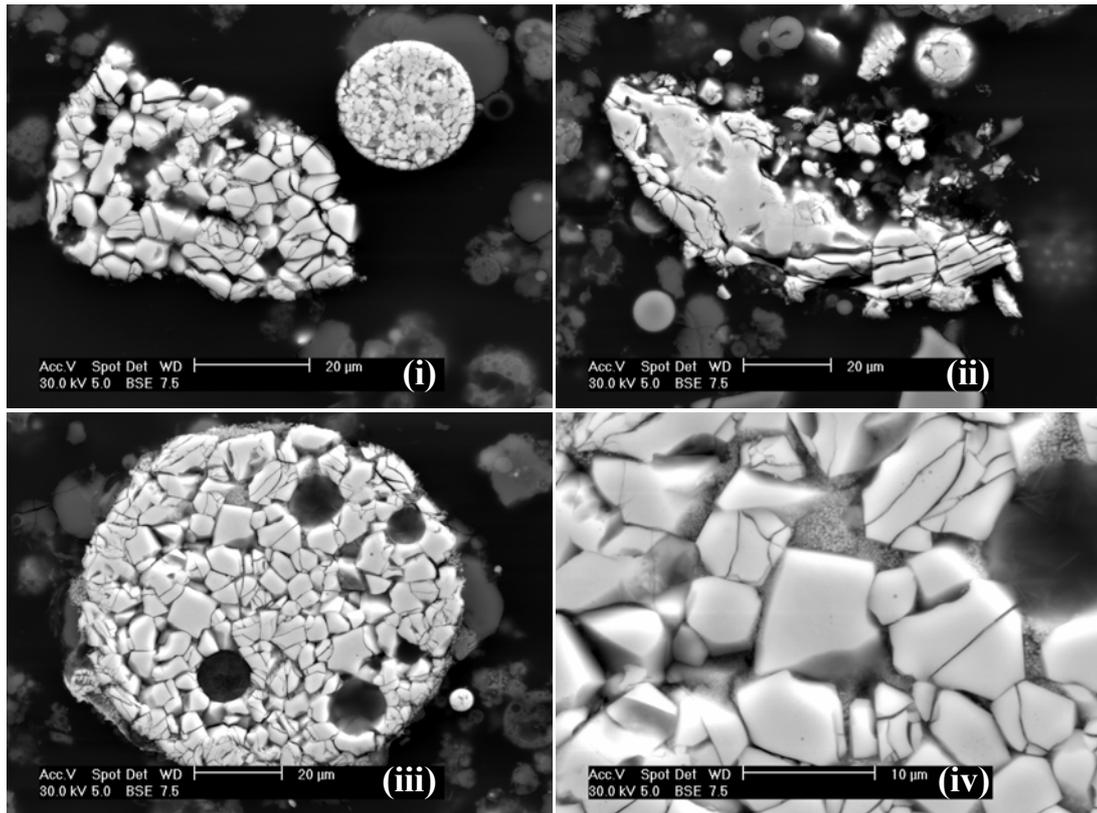


Figure 4.10: Particle cross sections viewed under SEM for HTP 3 (SRC) illustrating the morphology of unreacted iron mineral phases present in hydrothermal product

The notion that increased iron content in glass reduces its reactivity is supported by the growth rings of zeolite product in HTP 13 (see Figure 4.11), where initial zeolite growth at the centre of particles has low atomic number (low iron) and last stages of growth (outer most growth rings of zeolite particles) have significantly higher atomic number (high iron). Consequently high iron glass must be dissolving near the end of hydrothermal treatment.

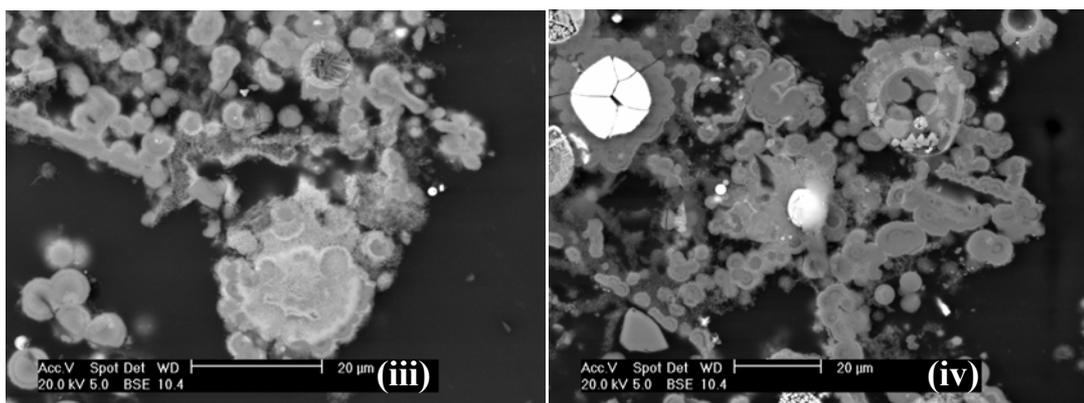


Figure 4.11: Particle cross sections viewed under SEM for i to ii) HTP 11 (pH14m30), and iii to iv) HTP 13 (pH14.48m30), illustrating the morphology of hydrothermal phase binding with unreacted fly ash to form aggregated product, produced under high pH conditions

From the un-seeded treatments (see Figure 4.12) the primary location for sodium enriched phases were spread over the outer surfaces of unreacted particles, some which are thick, see Figure 4.12(ii), and some thin, see Figure 4.12(iii and iv).

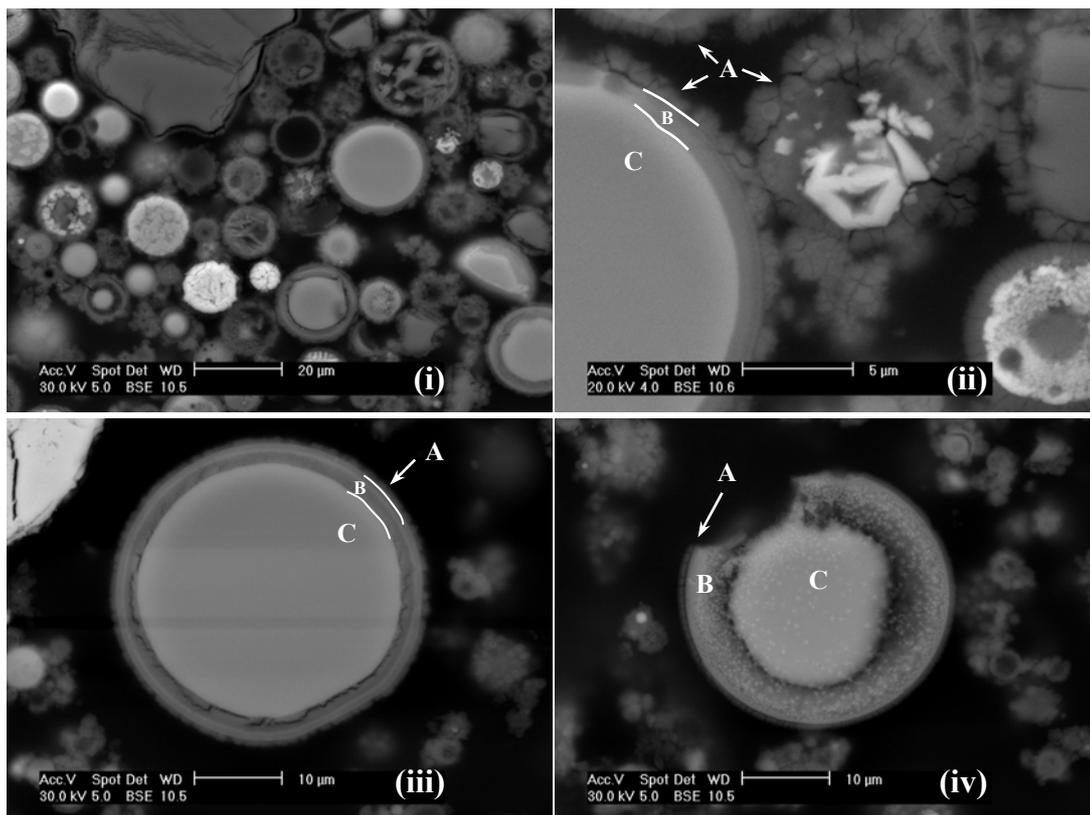


Figure 4.12: Particle cross sections viewed under SEM for HTP 64 (T80pH14m10), illustrating morphological features of un-seeded agitated hydrothermal treatment products, including A) sodium containing product phases, B) regions of etched reactant, and C) unreacted fly ash core

By seeding the hydrothermal system, the primary location for sodium enriched phases has shifted with the significant presence of product faces independent of unreacted fly ash phases (see Figure 4.13), although product phases are still present on the external surfaces of unreacted ash particles.

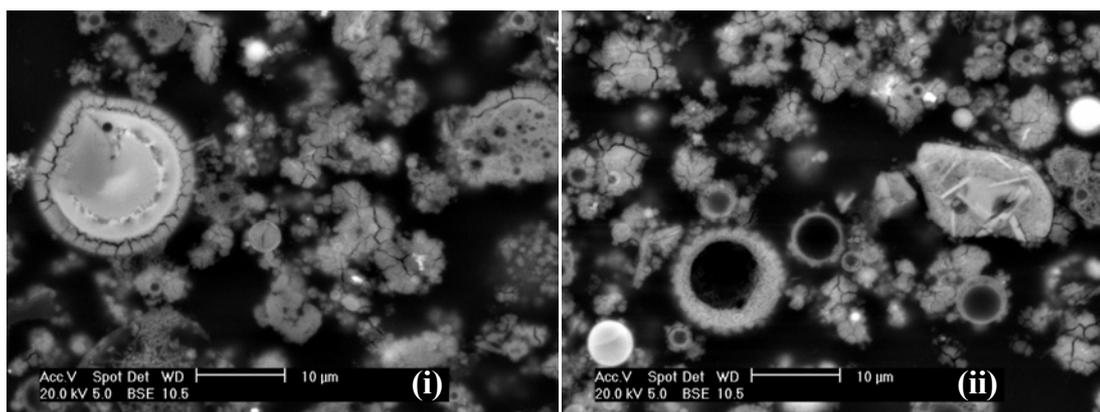


Figure 4.13: Particle cross sections viewed under SEM for HTP 106 (105-s-T80pH14x1) illustrating morphological features of seeded agitated hydrothermal treatment products

4.5 Trace Elements

The concentration of trace elements is of particular importance to the application of fly ash for environmental reasons (see Section A1.4). A comparison of trace element concentrations in fly ash samples and natural references is given in Table 4.1, and for hydrothermal treatment products following various hydrothermal conditions covering a range of different zeolite phases in Table 4.2.

Table 4.1 : Trace element analysis for fly ash (ppm)

Element ^[A]		Soil ^[B]	Shale ^[B]	Crust ^[B]	Fly Ash A	Fly Ash B	Fly Ash C
Elements of greatest concern							
Arsenic	As	7	13	1	6.0	11	14
Boron	B	30	130	10	20	20	40
Cadmium	Cd	0.6	0.3	0.2	0.5	1.0	1.5
Mercury	Hg	0.1	0.18	0.08	0.07	0.17	0.13
Molybdenum	Mo	1	2.6	1.5	12.5	18	20
Lead	Pb	20	25	13	52	78	101
Selenium	Se	0.4	0.5	0.05	<5	5.0	5.0
Elements of Moderate Concern							
Chromium	Cr	55	90	100	150	150	200
Copper	Cu	25	40	55	82	112	126
Nickel	Ni	20	68	75	254	268	266
Vanadium	V	80	130	135	146	150	156
Zinc	Zn	70	120	70	187	306	371

[A] Classified according to environmental concern as presented by Clarke and Sloss (1992) [B] (Sloss, et al. 1996)

Table 4.2 : Trace element analysis for a selection of hydrothermal treatment products (ppm)

Element ^[A]		HTP9	HTP11	HTP13	HTP27	HTP28	HTP53	HTP57	HTP67	HTP76
Elements of greatest concern										
Arsenic	As	1.0	<1.0	<1.0	1.0	<1.0	1.0	<1.0	<1.0	3.59
Boron	B	<20	20	40	20	<20	20	40	20	
Cadmium	Cd	0.5	0.5	<0.5	1.0	1.5	0.5	<0.5	0.5	1.13
Mercury	Hg	0.04	0.05	0.06	0.1	0.05	0.04	0.05	0.09	1.01
Molybdenum	Mo	2.5	2.5	1.5	1.5	1.0	2.0	3.0	2.0	3.61
Lead	Pb	45	49	30	66	76	38	45	41	51.5
Selenium	Se	<5	<5	<5	<5	<5	<5	<5	<5	3.02
Elements of Moderate Concern										
Chromium	Cr	150	200	150	150	150	150	200	150	184
Copper	Cu	77	79	55	98	94	67	78	76	52.6
Nickel	Ni	248	270	258	282	256	240	286	256	173
Vanadium	V	96	98	36	46	34	84	96	68	67.9
Zinc	Zn	176	196	180	303	330	157	185	189	95.1

[A] Classified according to environmental concern as presented by Clarke and Sloss (1992)

The elements most significantly elevated in fly ash are Molybdenum, lead, and selenium. Hydrothermal treatment resulted in some elements being significantly reduced in concentration (As and Mo), some were slightly reduced (Hg, Pb, Cu, V), some stayed constant (Cr, Ni, Zn), and some were already at or below the detection limit of analysis (B, Cd, Se). Most of the elements of greatest concern have been reduced in concentration to or below their average levels in soil, shale, or crust.

However trace element content is not as important or of as much importance as trace element mobility. To evaluate trace element mobility, leaching tests were performed on a selection of fly ash and natural reference samples, and on selected hydrothermal treatment products, presented in Tables 4.3 and 4.4 below.

From the fly ash leaching results it appears, with the exception of mercury, that all elements of concern listed are significantly mobile and cause for concern, and based on aluminium mobility, the dissolution (reactivity) of fly ash is in part responsible.

Table 4.3 : Trace element leaching analysis for a selection of fly ash and natural reference samples ($\mu\text{g L}^{-1}$)

		Clay ^[A]	Sand ^[B]	Zeolite ^[C]	Fly Ash A	Fly Ash C
Analysis Conditions^[D]						
Mass ^[F]		5.021	5.045	5.034	5.029	5.063
Volume ^[G]		100	100	100	100	100
pH ^[H]		4.87	4.87	4.97	4.87	4.97
Elements of greatest concern^[E]						
Arsenic	As	1.66	4.34	2.64	10.4	8.73
Boron	B	130	20	<10	90	165
Cadmium	Cd	<0.1	<0.1	0.16	5.4	14.2
Mercury	Hg	<0.02	<0.02	<0.02	<0.02	0.04
Molybdenum	Mo	0.1	1.0	<1	110	74
Lead	Pb	0.7	1.1	1.3	1.2	0.9
Selenium	Se	<0.2	<0.2	0.02	28.5	29
Elements of Moderate Concern^[E]						
Chromium	Cr	16	10	0.8	17	14.8
Copper	Cu	7.4	1.6	1.0	82	107
Nickel	Ni	6	6	9.1	58	146
Vanadium	V	3	3	0.5	23	17.4
Zinc	Zn	43	64	9	160	290
Bulk Reference Elements						
Aluminium	Al			205		2690
Iron	Fe			<10		30

[A] Collected from the bank of Swan river at Lilac Hill Park, Guildford, Perth on 14/06/2005 [B] Collected from the bank of Canning river at Salter Point, Salter Point, Perth on 14/06/2005 [C] Natural zeolitic material sourced from mine at Werris Creek in New South Wales, product name "zelbrite", pool filter media 15kg bag, manufactured in Australia by Zeolite Australia LTD, web: www.zeolite.com.au and www.zelbrite.com. [D] USEPA 1311 (TCLP Leach) procedure, [E] Classified according to environmental concern as presented by Clarke and Sloss (1992) [F] Sample mass (g) [G] Fluid extraction volume (mL) [H] pH of Extraction Fluid

From the results of leaching tests performed on hydrothermal treatment products (Table 4.4) it is clear that with the exception of HTP's 57 and 75 the trace element mobility of elements in products is lower than that of fly ash, and that the mobility of elements from agitated hydrothermal reactor products (HTP's 104, 106, and 108) are lower than the natural reference samples given in Table 4.3.

Table 4.4: Trace element leaching analysis for a selection of hydrothermal product samples ($\mu\text{g L}^{-1}$)

HTP	4	9	13	28	53	57	68	75	97	104	106	108
Analysis Conditions ^[A]												
Mass ^[B]	1.034	1.040	1.072	1.504	5.099	0.983	1.497	1.513	1.072	1.492	1.512	5.043
Volume ^[C]	20	20	20	20	100	20	20	20	20	20	20	100
pH ^[D]	4.87	4.87	2.93	4.97	2.93	2.93	4.97	2.88	4.87	4.97	4.97	4.87
Elements of greatest concern ^[E]												
As	3.32	2.65	1.56	<0.2	1.56	1.56	5.59	53.8	1.83	<0.2	<0.2	1.71
B	20	<10	<10	10	130	20	100	100	<10	20	<10	20
Cd	1.0	0.1	2.8	0.07	0.3	4.1	0.07	1.05	<0.1	0.02	0.05	<0.1
Hg	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	3.7	2.5	2.7	7	6.9	0.2	12	124	4.5	6	11	11.5
Pb	0.2	<0.1	0.2	<0.2	0.1	1.3	<0.2	0.4	<0.1	<0.2	<0.2	<0.1
Se	14.2	13.3	5.9	10.3	30.9	5.5	4.2	40	20.0	1.35	0.62	2.06
Elements of Moderate Concern ^[E]												
Cr	9	8	16	6.0	13	42	20	44	10	7.5	8.9	14
Cu	6.1	5.7	19	0.6	11	126	0.8	1.0	0.3	0.1	0.1	0.2
Ni	97	24	60	7.2	47	185	10.9	5.0	1	1.4	6.5	0.4
V	23	4	4	2.9	25	3	58	484	8	2.1	1.8	7
Zn	46	35	88	<1	74	570	<1	4	18	4	<1	14
Bulk Reference Elements												
Al				61			<1	32000		243	6	
Fe				<10			<10	620		<10	<10	

[A] USEPA 1311 (TCLP Leach) procedure, [B] Sample mass (g), [C] Fluid extraction volume (mL), [D] pH of Extraction Fluid, [E] Classified according to environmental concern as presented by Clarke and Sloss (1992)

For comparison with the fertiliser industry in Australia, Table 4.5 lists typical trace element concentrations for single superphosphate in Australia, which has comparable trace element compositions to the hydrothermal treatment products listed in Table 4.2. In addition the contaminants in phosphate fertilisers are present as inorganic salts (McLaughlin, *et al.* 2000) making them significantly more mobile than their zeolite counterparts.

Table 4.5: Concentrations (in ppm) of elements in single superphosphate in Australia, taken from McLaughlin, *et al.* (2000)

Element	Range	Mean
Cd	20 – 49	40
Cr	20 – 78	61
Cu	10 – 201	28
F	9600 – 17400	14300
Pb	2 – 71	19
Mo	0.1 – 3.2	0.5
Ni	1.4 – 7.5	3.9
Zn	269 – 488	393

In Australia regulations vary from state to state. Cadmium is the main focus of regulatory control in fertilisers, with limits ranging from 10 ppm for non-phosphorous fertilisers to 500 ppm for phosphorous fertilisers. In Queensland Hg is limited to 2 ppm and Pb to 50 and 500 ppm for phosphatic and trace element fertilisers respectively (McLaughlin, *et al.* 2000). From these limits, and the trace element analysis of hydrothermal treatment products (see Table 4.2), it does not appear that trace elements will present a significant barrier to the utilisation of fly ash zeolites as fertilisers.

Given the high mobility of aluminium in HTP 75 and Fly ash C and corresponding high trace element mobility, it is reasonable to conclude that stable non-reactive phases are desirable as products, for safe application in agriculture. Clearly some products perform better than others,

and given the importance of trace element in agriculture, trace element composition and mobility should be determined and considered on a case by case basis prior to application in Agriculture.

The hydrothermal treatment process reduces the trace element concentrations from initial concentration present in fly ash as previously demonstrated. A consequence of this phenomenon is the accumulation of these elements in the aqueous phase which is of particular relevance for processes utilising recycle loops of aqueous phase, and for disposal of aqueous waste streams.

To evaluate this phenomenon, the aqueous waste from the agitated hydrothermal treatment of fly ash with different p conditions were collected and analysed for trace elements using ICP-MS, the results are summarised in Table 4.6 below.

Table 4.6 : Trace element analysis for a selection of post synthesis hydrothermal solutions and reference solutions (ppb) ^[A]

		H ₂ O ^[B]	Rxn ^[C]	110	108	111	112
pH ^[D]			14.30 ^[E]	14.27 ^[F]	14.24 ^[F]	14.18 ^[F]	14.04 ^[F]
p			200	100	50	25	
Elements of greatest concern^[1]							
Arsenic	As	<0.10	0.358	11.3	22.6	43.5	101
Boron	B						
Cadmium	Cd	<0.10	0.129	0.172	0.214	0.534	0.355
Mercury	Hg	<0.10	2.61	0.733	1.20	1.25	1.76
Molybdenum	Mo	<0.10	16.3	31.8	59.4	122	267
Lead	Pb	0.145	0.496	6.96	6.31	32.2	15.8
Selenium	Se	0.464	0.886	5.40	11.0	20.2	46.7
Elements of Moderate Concern^[1]							
Chromium	Cr	0.575	1.43	3.93	2.80	2.38	2.63
Copper	Cu	1.12	0.783	3.66	2.52	2.70	2.40
Nickel	Ni	0.409	0.357	0.480	0.631	12.6	2.17
Vanadium	V	0.150	0.361	190	328	531	1066
Zinc	Zn	2.98	1.52	13.8	7.92	7.00	5.24

[A] 50 mL of filtrate from HTP 110, 108, 111, and 112, and 50 mL of reaction solution from HTP 110 recipe were collected (before washing were relevant) and made up to 1 L in a volumetric flask for analysis, results presented are for diluted solutions (multiply by 20 to get original concentration). Solutions were diluted to minimise reaction or precipitation, all solutions were analysed by ICP-OES, [B] Double distilled water used in solution preparation and dilutions, [C] Prepared using solution recipe for HTP 110, [D] Hydrothermal solution pH prior to dilution, [E] calculated from recipe, [F] based on titration of diluted solution, [G] Classified according to environmental concern as presented by Clarke and Sloss (1992)

Arsenic, Molybdenum, Selenium and Vanadium are extracted significantly into the hydrothermal solution, with waste stream concentrations of these elements increasing with decreasing p. This will need to be accounted for in the design and operation of any manufacturing plant.

5 Summary and Conclusions

A detailed exposition of the conclusions, recommendations and significance of this thesis study are provided in Appendix 6. The following paragraphs are taken from the thesis abstract, and provide a summary of these findings and conclusions.

During the year that concluded prior to the commencement of this PhD (2001) 11.7 million tonnes of fly ash was produced in Australia, of which only 32% was utilised in some way, near its conclusion, the latest statistics (2004), reveal that 12.5 million tonnes was produced with only 35% utilised in some way (ADAA 2006), with the remainder being accumulated in landfills and ash dams. This low level of ash utilisation in Australia is inevitable due to the combination of inherently high transport costs, and relatively low value products. This situation argues for more value-added utilisation of coal ash to overcome the transport cost barrier.

Zeolite synthesised from fly ash for agricultural application as a controlled release fertiliser, is a technology which offers considerable advantages in terms of economic, technical and environmental performance. This fertiliser market is both a high value and high volume market, with the potential to consume significant quantities of fly ash. Studies using natural zeolite have demonstrated significant improvements in fertiliser efficiency for zeolite compared to soluble salts.

This thesis looks at the issues behind fly ash utilisation in the broader sense, evaluates the potential markets for zeolite products in Australia, assesses the established science behind producing zeolite materials from fly ash, and examines the direct hydrothermal treatment process for producing zeolites (including analcime, cancrinite, zeolite ZK-14, and zeolite P1) from coal fly ash, including the relationship between zeolite types produced and operating conditions, desirable zeolite properties for controlled release fertilisers, optimal production conditions, economic implications, and avenues for future research.

The hydrothermal treatment process was studied through the control of reaction temperature (T), reaction time (t), the Si/Al mole ratio (n), the cation type (M), the pH, the H₂O/Al mole ratio (p), and the M⁺/Al mole ratio in excess of unity (m), where MNO₃ was used to control m independent of pH. A number of different zeolite types were produced from fly ash with a maximum zeolite yield of 57%. Due to impurities present in the fly ash, it is impossible to selectively synthesise pure zeolite of any kind using the direct hydrothermal treatment method, but this is adequate for the intended fertiliser applications.

A systematic quantitative refinement method was developed using Rietica to characterise the mineralogy of fly ash and hydrothermal treatment products, resulting in substantially more information regarding the transformations taking place than has previously been available in the study of the synthesis of zeolites from fly ash. This in conjunction with SEM has provided unprecedented detail regarding the reactivity of fly ash components, namely glass, quartz, and mullite phases, as well as the independent role of M⁺ and OH⁻ within the hydrothermal system, and the encapsulation of fly ash reactants by products.

Notably quartz is more reactive than mullite; however at a pH of 14.6 mullite is completely dissolved while quartz is not, probably due to the significantly smaller size of mullite crystals relative to quartz particles; and for small increases in m with constant pH starting from x = 1, the total yield of zeolite increases, and the yields of different zeolite types change from low to a maxima back to low as functions of both pH and m.

From the experiments conducted it appears that the processes of gel formation and zeolite crystal growth can be manipulated through the continuous presence of zeolites with fly ash reactants, and through the manipulation and control of M^+ and OH^- concentrations as well as temperature to balance the suppression of fly ash dissolution while enhancing crystallisation to minimise the encapsulation of reactants by products, increasing the productivity of hydrothermal treatment process, therefore improve its economic viability, which is key to its possible future implementation.

6 List of Publications and Proprietary Reports

- Elliot A.D., Yan H.M., Vuthaluru H.B., Zhang D.K., “A kinetic study of thermal decomposition of organic-rich wastes for fuel oil recovery”, 6th Asia-Pacific International Symposium on Combustion and Energy Utilisation, May 20-22, 2002, Kuala Lumpur.
- Alex Elliot, (2002), “The Value Added Utilisation of Fly Ash from Coal Fired Power Utilities”, Candidacy Report, University of Technology, Perth
- Elliot A.D. Zhang D.K., (2002), “Joint Course and Workshop on Ash Utilisation: Review”, Cooperative Research Centre for Coal in Sustainable Development, Review
- Elliot A.D. Rossiter A. Zhang D.K., (2003), “The Feasibility of Producing Low-Grade Zeolites from Australian Fly Ash”, Cooperative Research Centre for Coal in Sustainable Development, Internal Report
- Elliot A.D. Zhang D.K., (2003), “Australian Coal Ash – A Valuable Resource: Current State and Future Directions”, Cooperative Research Centre for Coal in Sustainable Development, Internal Report
- Elliot A.D. Zhang D.K., (2003), “Fly Ashes Produced in Collie, Western Australia, and their Potential Applications”, Cooperative Research Centre for Coal in Sustainable Development, Fact Sheet
- Alex Elliot, Hongwei Wu and Dong-ke Zhang , (2004) “Value-Added Utilisation of Coal Combustion By-Products: Zeolites from Fly Ash and its Agricultural Applications”, International Committee for Coal Research (ICCR) Conference, China
- Dong-ke Zhang and Alex Elliot, (2004) “Australian Coal Ash – A Valuable Resource for Value-Added Utilisation: Current State and Future Directions”, International Committee for Coal Research (ICCR) Conference, China
- Elliot A.D., Zhang D.K., (2004), “The Scientific Basis for the Production of Zeolites from Fly Ash”, Cooperative Research Centre for Coal in Sustainable Development, Internal Report
- Rossiter A., Elliot A.D., Zhang D.K., (2004), “An Assessment of Environmental, Health and Safety Impacts of Coal Ash and Ash Utilisation”, Cooperative Research Centre for Coal in Sustainable Development, Internal Report
- Wu H., Elliot A.D., Rossiter A., Zhang D.K., (2004), “Economic Analysis of Manufacturing Aggregates from Fly Ash”, Cooperative Research Centre for Coal in Sustainable Development, Published Report
- Elliot A.D., Zhang D.K., (2004), “Zeolite Synthesis from Australian Coal Fly Ash – Hypothesis, Methodology, and Preliminary Results”, Cooperative Research Centre for Coal in Sustainable Development, Internal Report
- Elliot A.D., Zhang D.K., (2005), "Controlled Release Zeolite Fertilisers: A Value Added Product Produced from Fly Ash", World of Coal Ash, Kentucky, USA, April 11-15.
- Elliot A.D., Zhang D.K., (2005), “Zeolite Fertiliser Manufacturing Plant: Process Flow and Mass Balance”, Cooperative Research Centre for Coal in Sustainable Development, Internal Report
- Elliot A.D., (2005), “Designer Fertilisers from Coal Waste”, Australasian Science, 26(9), 24-26.

7 List of Symbols

Cation Exchange Selectivity (Equations 2.1 to 2.3, Section A3.3)

- X_i – Ionic Fraction, where $X_i = \frac{\text{Equivalent Moles of Cation } i}{\text{Sum of Equivalent Moles of all Cations}}$
 z_i – Ionic Charge, where $z_i = \text{Charge of Cation } i$
 K_i^j – Selectivity Coefficient
 α_i^j – Separation Factor
 A, B – Cations
 Z^- – Represents a single unit charge of framework structure

Pseudo Rate Equation (Equation 2.4, Section A3.5)

- $r_{M^{z+}}$ – Rate of positive change in concentration for species M^{z+}
 k' – Pseudo-reaction rate constant
 $[M^{z+}]$ – Concentration of species M^{z+} in solution
 n – Reaction rate constant

Hydrothermal Treatment Conditions

- T – Temperature
 t – Time
 n – Si/Al mole ratio
 M – Cation type
 p – $\frac{H_2O}{Al}$ mole ratio
 m – Excess $\frac{M^+}{Al}$ mole ratio = $\frac{M^+}{Al} - 1$, ranges $m \geq -1$, and where M^+ is per unit charge equivalent
 x – The mole ratio $\frac{OH^-}{(OH^- + NO_3^-)}$, ranges $0 \leq x \leq 1$

Yields and Fractions

- Y_i – Yield of component i , grams of component i in product per gram of fly ash used
 F_i^Y – Yield of component i expressed as a fraction of original amount in fly ash, grams of component i in product per gram of that component in fly ash
 x_i^j – Composition of component i in sample j , weight percent
 F_i – Composition fraction, ratio of composition of component i in product (wt%) to the composition to the composition of that component in fly ash reactant (wt%)

8 Glossary

General

ca.	– <i>circa</i> , around
e.g.	– for example
LPG	– Liquid (or Liquefied) Petroleum Gas
p.a.	– per annum

Concepts and Ideas

CCB	– Coal Combustion by-product
CCP	– Coal Combustion Product
CCP	– Cumulative Cash Position
CCW	– Coal Combustion Waste
DPBP	– Discounted Payback Period
FCI	– fixed capital investment
NPV	– Net Present Value
PBP	– Pay Back Period
PVR	– Present Value Ratio
ROROI	– Rate of Return on Investment

Organisations, Institutions, Entities and Events

ACAA	– American Coal Ash Association
ADAA	– Ash Development Association of Australia
AU	– Australia
CCUJ	– Center for Coal Utilisation Japan
ecoba	– European Coal Combustion Products Association
EPA	– Environmental Protection Agency
UK	– United Kingdom
US or USA	– United States of America
WOCA	– World of Coal Ash

Techniques and Equipment

BSE	– Backscattered Electrons
CEC	– Cation Exchange Capacity
CES	– Cation Exchange Selectivity
DTA	– Differential Thermal Analysis
EDS	– Energy dispersive spectroscopy
FTIR	– Fourier Transform Infrared
ICP	– Inductively Coupled Plasma
MAS NMR	– Magic-angle Spinning Nuclear Magnetic Resonance
MS	– Mass Spectrometry
OES	– Optical Emission Spectroscopy
SEM	– Scanning Electron Microscopy
TCLP	– Toxicity Characteristic Leaching Procedure
TEM	– Transmission Electron Microscopy
WDS	– Wavelength Dispersive Spectroscopy
XRD	– X-ray Diffraction
XRF	– X-ray Fluorescence

Sample Related

Note; these are not used as abbreviations rather as condition codes, where the individual letters of the code were selected to give the code meaning.

FA	– Fly Ash
HTP	– Hydrothermal Treatment Product, used when referring to a hydrothermal treatment product designated by a number
SRC	– Standard reference conditions, used in reference to the hydrothermal treatment conditions used to produce sample.

*Framework Structures**

ANA	– Analcime
CAN	– Cancrinite
CHA	– Chabazite
EDI	– Edingtonite
EMT	– EMC-2
ERI	– Erionite
FAU	– Faujasite
GIS	– Gismondine
GME	– Gmelinite
JBW	– Na-J (Barrer and White)
LTA	– Linde Type A
LTL	– Linde Type L
MAZ	– Mazzite
MER	– Merlinoite
MOR	– Mordenite
NAT	– Natrolite
OFF	– Offretite
PHI	– Phillipsite
SOD	– Sodalite

* A full updated list of framework structure types and associated codes is posted by the International Zeolite Association at <http://www.iza-structure.org/databases/>

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Appendix 1 Fly Ash Utilisation

A1.1 Fly Ash: A history of waste and resource perceptions

From a power generation perspective fly ash is a waste, while from a coal utilisation perspective we see fly ash as a resource and an opportunity yet to be fully realised and exploited. Sustainable development requires this secondary resource to be fully utilised.

Although ash ponds are the main destination for fly ash there is a long history of beneficial utilisation (where fly ash has provided a useful service), which has increased quite significantly in recent years. A brief history of early beneficial utilisation of fly ash precedents are outlined in Table 9.1 below, with Australian precedents highlighted in blue, and demonstrates the value of fly ash, particularly in cementitious applications.

Kalyoncu (2001b) lists three classifications for fly ash used in the USA, the first definition was given by environmental regulators and classified fly ash as coal combustion wastes (CCWs), this was changed to coal combustion by-products (CCBs), and now stands as coal combustion products (CCPs) a title pushed by power industry, ash marketers, and ash users. This illustrates how societies changing awareness of sustainability has manifested itself in recognising fly ash as a resource (what was once considered a waste is now considered a resource). This idea of fly ash as a resource is a key to maximising its exploitation.

Fly ash exhibits a wide range of properties, some of which make it a useful resource for use in valuable products. Fly ashes capacity to reduce overall green house gas emissions, of the processes which utilise it as a substitute for raw materials, is an attribute which could play a key strategic role for the coal industry in the form of green house gas displacement credits should green house gas trading systems be implemented. Fly ash is a resource whose full potential is yet to be realised and fully exploited.

Table 9.1: A brief history of fly ash utilisation

27 BC to 14 AD	The life of Marcus Vitruvius Pollio, whose treatise <i>De Architectura</i> , describes the use of volcanic ash in concrete ^[A] . Pollio named this ash “pulvis puteolanis” after the town Puteoli (now Pozzuoli) near mount Vesuvius, where it was found ^[B] . Here we find the origins of the word pozzolana to describe natural cementitious materials
1914	Anon (1914) publishes the results of the first study on coal combustion ashes, and makes the link between the similarity of coal combustion ash and natural pozzolana ^[C]
1918 to 1920	The Onieda street (now known as East Wells) power plant was used as the pilot plant in the development of pulverised coal combustion ^[D] as part of the Milwaukee Electric Railway and Light Co. ^[E]
1921	The Milwaukee Electric Railway and Light Company’s Lakeside power plant is the world’s first plant designed exclusively to burn pulverised coal ^[F] and is the first to burn pulverised coal exclusively ^[E]
1934	Pulverised fuel ash first considered for use in concrete by (McMillan and Powers 1934) in the Proceedings of the American Concrete Institute ^[G]
1937	Davis, <i>et al.</i> (1937) first identified pulverised fuel ash as a natural pozzolana ^[7] , and introduced the term “fly ash” into literature, in the Proceedings of the American Concrete Institute ^{[G] [H]}
1938	A compilation of fly ash concrete pavements were used by the sanitary district of Chicago ^[I]
1946	The Chicago Fly Ash Company is the first to market fly ash, which is sold as a construction material for concrete pipe ^[J]
1948 to 1953	120,000 tonnes of fly ash was used in the construction of the Hungry Horse Dam ^[K]
1949	First recorded use of fly ash in Australia. Fly ash was imported from Chicago, Illinois USA for use in grout for the Prepakt shafts in the Tumut I Power Station as part of the Snowy Mountains Hydro-Electric scheme ^[L]
1950	First investigation of fly ash as a pozzolan in Australia was carried out on East Perth Power Station fly ash ^{[L] [M]}
1950 to 1970	Approximately 100 major dam projects in the USA made use of fly ash concretes with fly ash contents as high as 50% ^[K]
1959	The first use of Australian fly ash in cement, was for part of the spillway of the Keepit Dam in New South Wales ^[L]
1960	The Clatworthy Dam is the first large scale use of fly ash concrete in Britain, consuming 4000 tonnes of fly ash ^[I]
1966	The use of fly ash in cement becomes firmly established following the commissioning of Swanbank (Queensland) and Port Augusta (South Australia) power stations, with the commercial production of 25% fly ash 75% Portland cement blends ^[M]
1966	Australian standard introduced for fly ash as a mineral filler in bituminous concrete as a replacement for cement or lime dust ^[N]
1968	The National Ash Association was founded in the US, currently known as the American Coal Ash Association (ACAA)
1971	The first Australian Standard for using fly ash in concrete ^[L]
1972 to 1974	Completion of the Gordon river hydroelectricity project in Tasmania which consumed approximately 10,000 tonnes of fly ash transported 1500 km from South Australia ^[N]
1989	Founding of the Center for Coal Utilization, Japan (CCUJ)
1990	Founding of the European Coal Combustion Products Association (ecoba)
1991	Founding of the Ash Development Association of Australia (ADAA)

[A] (Cavanagh and Guirguis 1992), [B] (Idorn 1997), [C] (Dhir 1986) [D] (ASME 1980), [E] (WEC 2002), [F] (ASME), [G] (Bamforth 2001), [H] (Mukherjee and Kikuchi 1999), [I] (Butler and Baweja 1986), [J] (Kalyoncu 2001b), [K] (Kalyoncu and Olson 2001), [L] (Samarin, *et al.* 1983), [M] (Beretka and Nelson 1994), [N] (Ryan, *et al.* 1976)

No single utilisation option as outlined in Figure 9.1 will solve the fly ash problem, to achieve complete beneficial utilisation (zero ponded ash) an integrated fly ash utilisation program will be required which takes advantage of a number of different strategies. Strategy integration could help lower the impurity load of ash and therefore ash products, increasing total utilisation, and helping to significantly reduce the ecological footprint of coal.

Although the fly ash industry now refers to fly ash as a coal combustion product, at current rates of fly ash utilisation it is probably more appropriate to refer to it as a by-product. However if fly ash utilisation is increased toward 100% utilisation, then fly ash can truly be referred to as a coal combustion product.

A1.2 Fly Ash Utilisation Strategies

Fly ash exhibits a wide range of properties, some of which make it a useful resource for use in a number of different utilisation strategies. The utilisation strategies available for exploitation have been classified into groups according to their usefulness and economic value; see Figure 9.1, the shaded strategies are those currently employed in Australia. For non-beneficial use, fly ash is seen as having no value, and is generally an economic burden to the ash producer, e.g. landfill. In simple utilisation strategies, fly ash is the final product, e.g. agricultural products, or is blended to form the final product, e.g. blended cement. In advanced utilisation strategies, fly ash is processed to produce a final product, e.g. zeolites, or to extract a product from the ash, e.g. cenospheres.

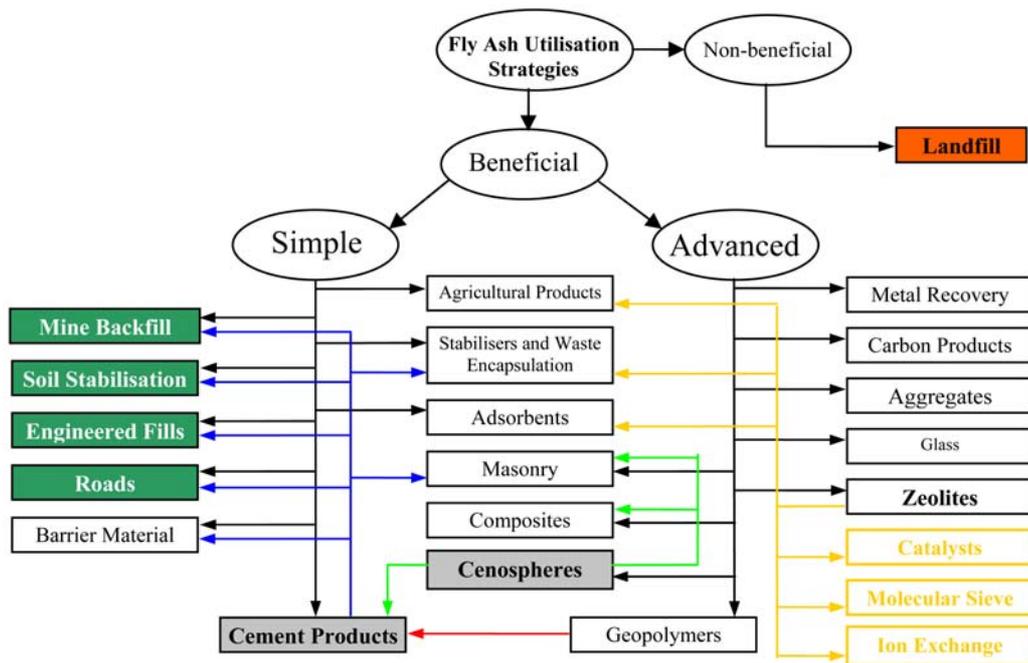


Figure 9.1: Relationships between different fly ash utilisation strategies

Of these strategies, a zeolite strategy is a high value strategy which is potentially also high volume through the use of zeolite products used in agricultural applications.

Non-beneficial Utilisation or Landfill

For landfill fly ash is essentially dumped, placed or compacted onto the surface of the land, in a valley, ravine or even in the sea. The form of landfill (pond or dump) affects the options available (solid, slurry or dense phase) for fly ash transportation (trucked or pumped) to landfill.

The water level, height of water above ground water and pH of water all affect leaching (Innes and Davis 1999). Clay liners may be employed to minimise the migration of trace elements into the environment.

Current World Market for Zeolites

Zeolites have a wide range of applications, which vary from small to large in scale. The world natural zeolite production was estimated to be 3.98 Mt for 2000 (O'Connor 2001), the distribution of this for known countries is given in Figure 9.2 below. The application of zeolites is divided 6:2:1 between building materials, agriculture, and others (O'Connor 2001).

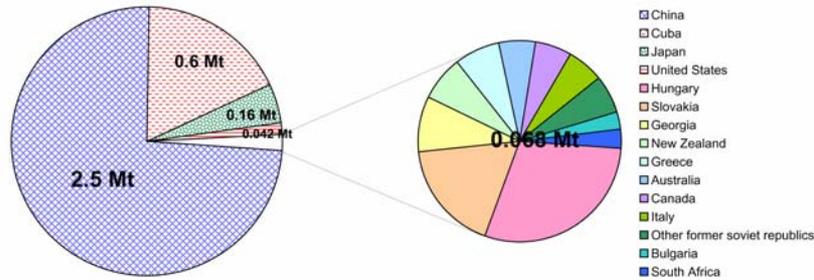


Figure 9.2 : Approximate distribution of the world known natural zeolite production for 2000, with total world production estimated at around 4 Mt, data from Virta (2001)

1.3 Mt of zeolite A were used globally in 2000 as detergent binders (O'Connor 2001), and 1.04 Mt of synthetic zeolite was consumed world wide in detergents during 1998 (Virta 2001), representing over 75% of the synthetic zeolite market. 117 kt of zeolite catalysts were produced globally in 2000, representing 55% of the global zeolite market on a value basis, and 85 kt of molecular sieves were consumed globally in 2000 (O'Connor 2001).

Horticultural applications are dominated by natural zeolites due to its low cost advantage, while industrial applications are dominated by synthetic zeolites which have superior and customisable performance advantages. Fly ash zeolites could potentially incorporate both these advantages. With potential applications in many market cultures, including agricultural, industrial, commercial and household sectors, and given the high value of natural zeolites relative to fly ash, see Figure 9.3 below, a zeolite strategy for fly ash utilisation has significant unrealised potential.

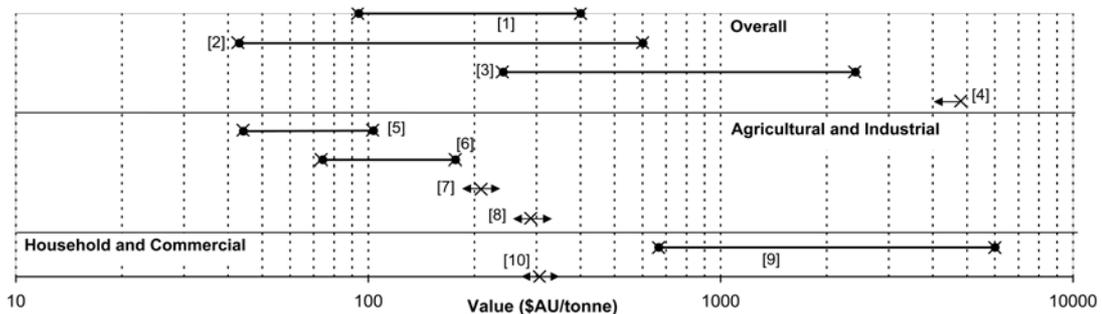


Figure 9.3 : Value of natural zeolites from various sources in both Australia, and the United States of America*

* Assuming an exchange rate of \$AU1 = \$US0.75, [1] General range in US natural zeolite prices (Virta 2002), [2] Price range for -425 μ m clinoptilolite in the US (Eyde 2002), [3] Price range for -425 μ m chabazite in the US (Eyde 2002), [4] Peak price for modified, extruded and activated clinoptilolite and chabazite products in the US (Eyde 2002), [5] +425 μ m zeolites for industrial and agricultural applications in the US (Holmes 1994), [6] -425 μ m to -43.2 μ m zeolites for industrial and agricultural applications in the US (Holmes 1994), [7] Average sale prices for horticultural zeolites by Talon resources in Australia, based on information in (Talon 2001), [8] Average sale prices for industrial zeolites by Talon resources in Australia, based on information in (Talon 2001), [9] zeolites for

A1.3 Current State of Fly Ash Utilisation

A1.3.1 The World

Approximately 460 million tonnes of coal ash was produced globally in 2002, of which 33.5% was utilised (Manz 1997). Land and mine fill are the largest utilisation methods, contributing to over half of total world ash utilisation in 1992, see Figure 9.4 below, this represents a low value use for ash. The cement and concrete markets are major value added consumers of fly ash.

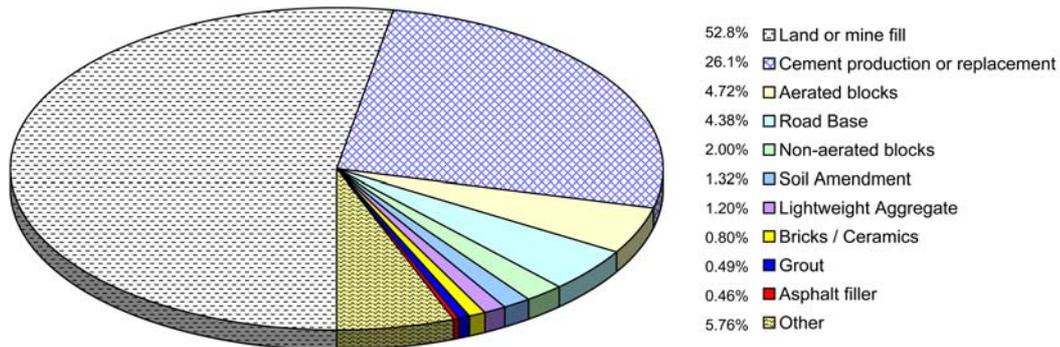


Figure 9.4: Contribution of utilisation strategies to world ash utilisation in 1992* (460 Mt ash produced, 33.5% utilised), data from Manz (1997)

Figure 9.5 below illustrates the total ash production and utilisation for all countries producing more than 4 million tonnes of pulverised coal ash in 1992. The data in Figure 9.5 has been ordered according to the percentage of valuable ash utilisation, where land and mine fill is considered to be non-valuable.

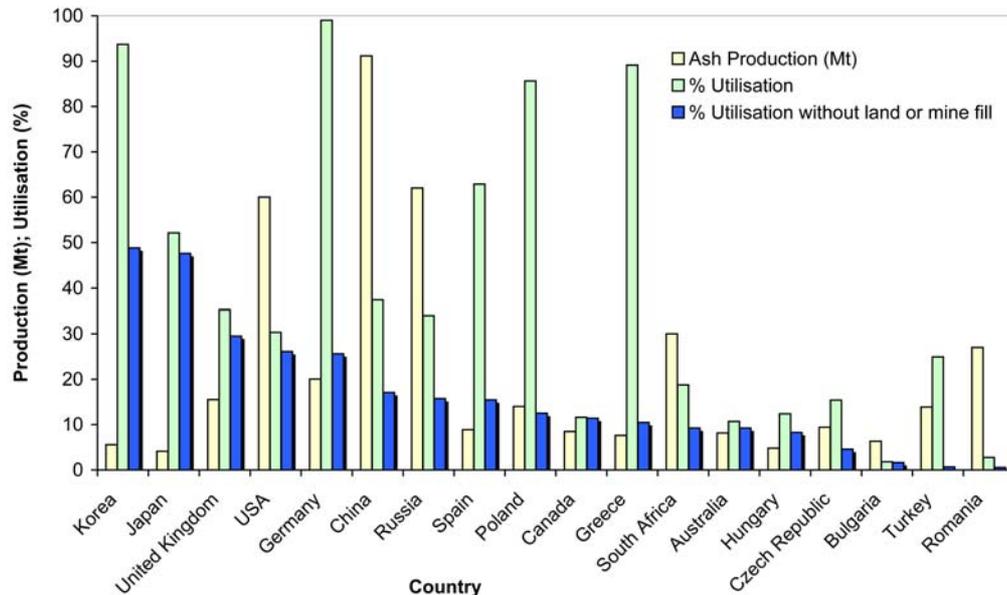


Figure 9.5: Combustion ash production and utilisation from countries producing more than 4 million tonnes in 1992*, data from Manz (1997)

consumer products (pet litter, fish tank media, or deodorant applications) in the US (Holmes 1994), [10] Average sale prices of zeolites for pet litter by Talon resources in Australia, based on information in (Talon 2001)

* Some countries data older and some newer than 1992, ranging from 1989 to 1994, these values are assumed to be roughly equivalent to 1992 values

Observations that can be made from Figure 9.5 are:

- Australia had one of the lowest ash utilisation rates, and one of the lowest valuable ash utilisation rates of the major ash producing nations
- Korea and Japan have the highest rates of valuable ash utilisation at nearly 50%
- Comparison of the reference countries (Japan, UK, USA, and China) to Australia reveals that Australia has the lowest percentage utilisation and percentage valuable utilisation of ash.
- Many European nations had very high utilisation rates, a low contribution to which is provided by valuable utilisation.
- Although some countries utilise nearly all ash produced (Korea, Germany, Poland, and Greece), none take full advantage of ash as a valuable resource
- Of the countries with a greater percentage of valuable ash utilisation than Australia, China is the highest ranking developing country

A look at steam coal consumption trends (see Figure 9.6 below) reveals that the USA, China, Japan, Australia, and the World have experienced an overall upward trend in consumption, while the UK and European Union have experienced a downward trend.

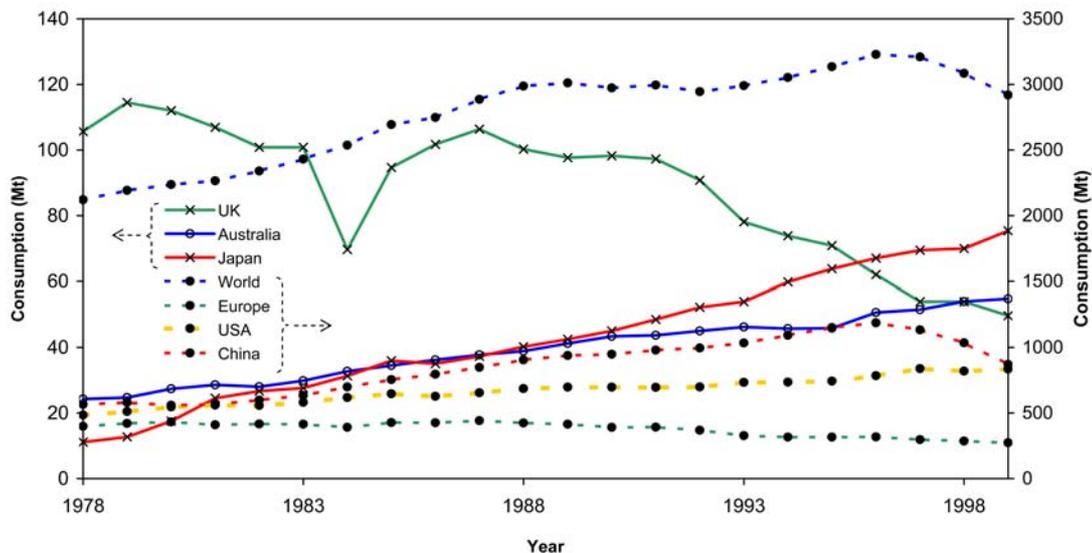


Figure 9.6: Historical trends in steam coal consumption by region, data from IEA (2000)

Mathematically speaking the rate of utilisation in Europe and the UK can be increased over time by keeping the total quantity of ash utilised constant, however for the USA, China, Japan, Australia, and the World as a whole, the utilisation percentage will only increase if the rate of increased utilisation exceeds the rate of increased ash production.

* Except India which has incomplete data. Data for Bulgaria, Hungary, Romania, and the United Kingdom is from 1989, and data from the Czech Republic is from 1993

A1.3.2 Australia

Fly Ash Production in Australia

To understand the relevance of fly ash as a resource in Australia both now and into the future, we need to look at coal's role in Australia's energy balance. Coal contributes the largest single portion to the total primary energy supply in Australia, as shown in Figure 9.7 below, and it dominates electricity production as shown in Figure 9.8 below.

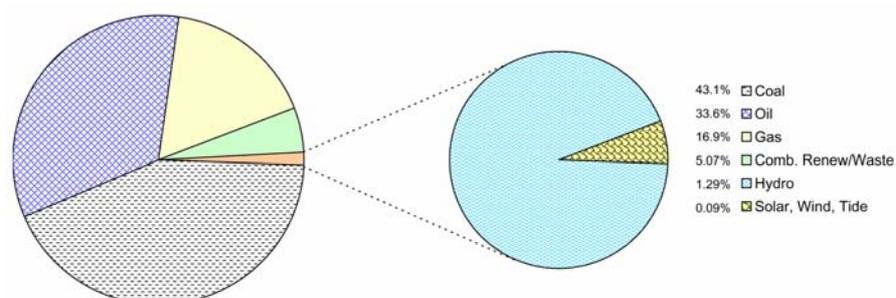


Figure 9.7: Distribution of total primary energy supply (TPES) (154.9 Mtce) by fuel within Australia for 1998, data from IEA (2000)

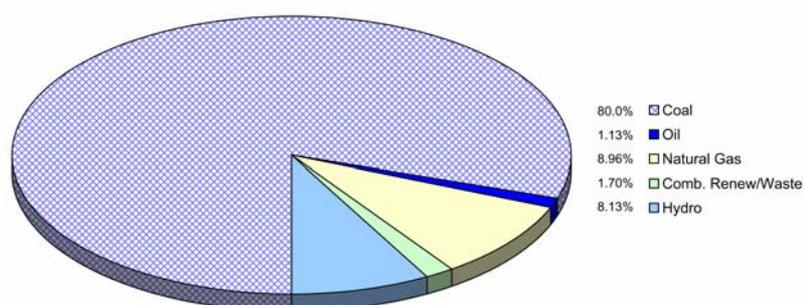


Figure 9.8: Share of total electricity generation (194.3 TWh) within Australia by fuel 1998, data from IEA (2000)

Black coals place in this energy consumption is illustrated in Figure 9.9 below, where a significant proportion of total coal use in Australia is from steaming coal, with over 90% of it being used to generate electricity (IEA 2000).

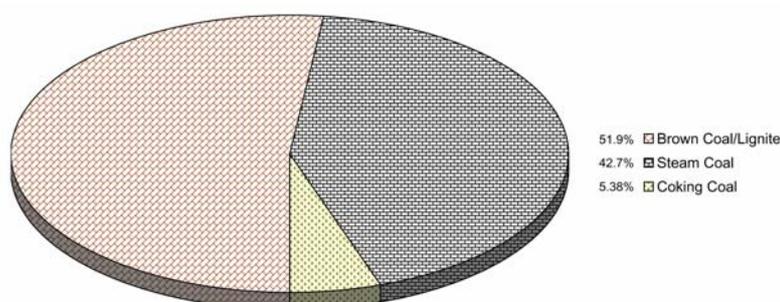


Figure 9.9: Contribution to total coal use (126.3 Mt) within Australia by type for 1998, data from IEA (2000)

The generation of electricity from coal will continue to grow over the next decade, although its share of electricity generation will diminish due to faster growth in natural gas electricity generation, see Figure 9.10 below.

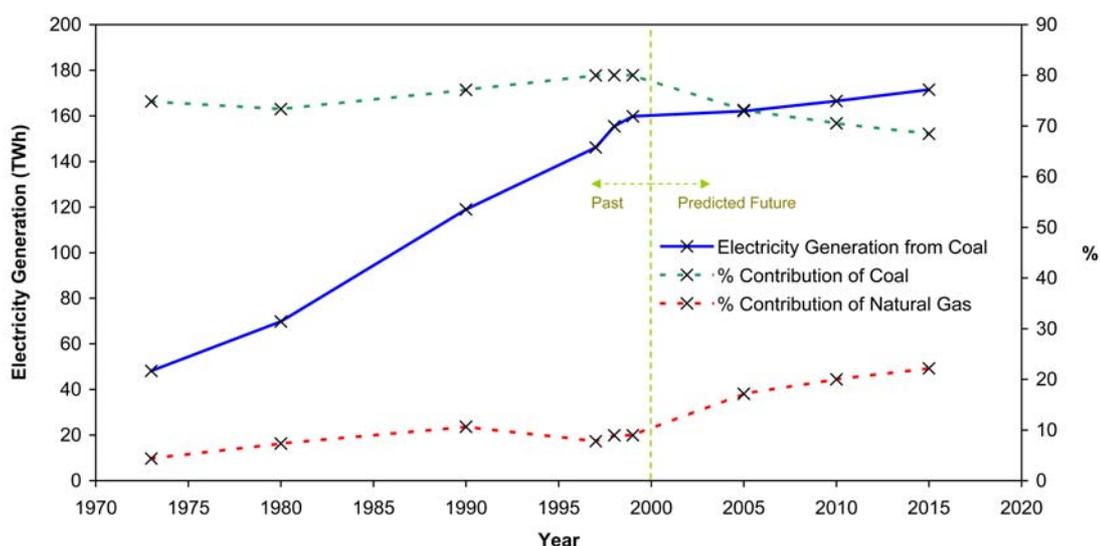


Figure 9.10: Past and predicted future electricity generation within Australia, data from IEA (2000)

Fossil fuels compose over 90% of Australia’s primary energy supply (see Figure 9.7), however in the medium to long term, oil and natural gas reserves will be depleted (see Table 9.2 below), and coal may have to fill some of this void.

Table 9.2: Australian and world demonstrated recoverable energy reserves

Energy Reserve	Life Expectance (Years)		
	Australia [A]	Australia [B]	World ^[B]
Brown Coal	820		
Black Coal	290		
Coal		297	227
Uranium	270		
Natural Gas	36	40.6	61.0
LPG	35		
Oil	13	10.4	39.9

[A] data from WEC (1998), [B] life expectancy is based upon year 2000 production rates, and reserves, data from BP (2001)

For the intermediate future steaming coal will continue to play a major role in Australia’s energy and specifically electricity needs. Fly ash as a resource will continue to be produced by current and future installed capacity for the lifetime of these facilities and will be available for utilisation.

Fly Ash Utilisation in Australia

Over the ten years from 1992 to 2002 the utilisation of ash within Australia has increased from 17.6% of 8.5 Mt to 32.3% of 12.5 Mt, where the increase in total ash utilisation is predominantly due to increases in land and mine fill utilisations. This shift in utilisation dynamics from cement dominated utilisation to land and mine fill utilisation is illustrated in Figure 9.11 below, where roughly 80% of total ash sales are for cementitious applications (see Figure 9.12), and where beneficial ash usage includes mine backfill, soil stabilisation, engineered fills, and road applications.

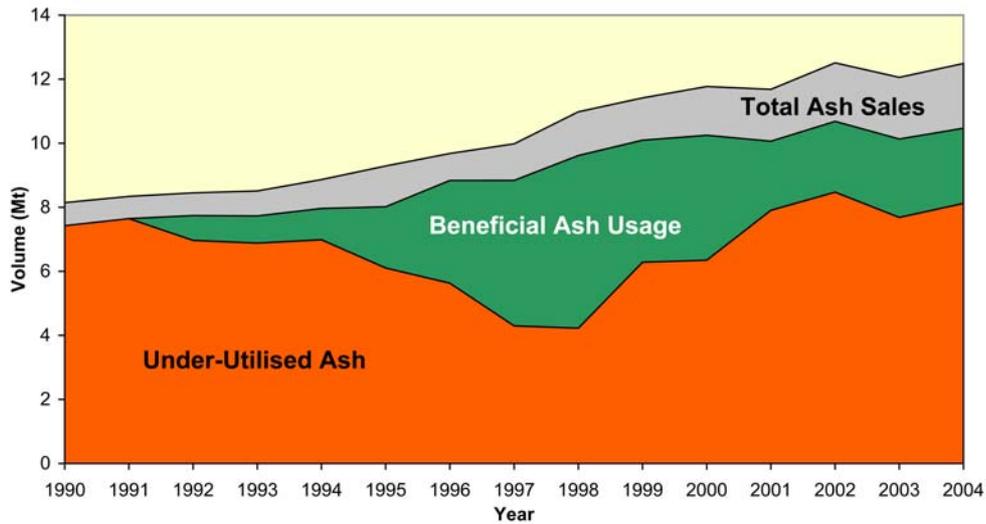


Figure 9.11: Trends in total Australian ash utilisation, where utilisation strategies have been classified into three groups according to their usefulness and economic value (ADAA 2006), as colour coded in Figure 9.1

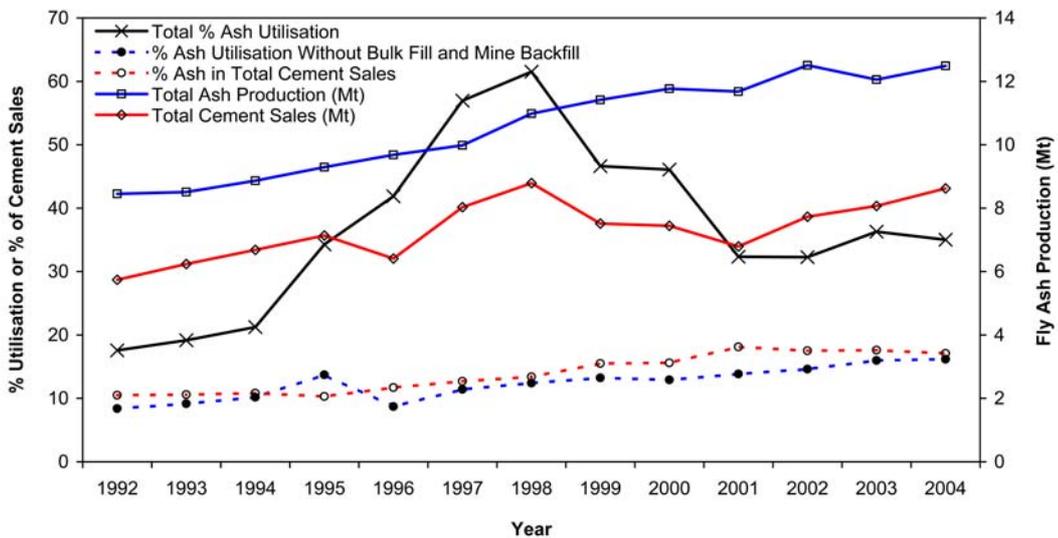


Figure 9.12: Historical trends of combustion ash utilisation within Australia, data from ADAA (2006)

Growth in valuable utilisation of fly ash has been slow, changing from 8.4 to 14.6% between 1992 and 2002, while growth in beneficial ash utilisation, predominantly land and mine fill, has been fast but unsustainable, growing from 0% to 49.1% of total fly ash production between 1991 and 1998, followed by a period of contraction to 18.8% in 2004, see Figure 9.11 above.

The average percentage of ash as a component of total cement sales has steadily grown over the last six years (see Figure 9.12); however there is a limit to how much fly ash the cement market can take. According to Innes and Davis (1999) it is 75-85% saturated, it will continue to grow, but is incapable of any major increase in its use of fly ash.

A comparison of Figures 2.20, 2.22, and 2.26 with 2.32, illustrates that the diversity of fly ash utilisation within Australia has simplicity akin to China, and is significantly less complex than the United States and the European Union. The nature of growth in fly ash utilisation within Australia is a function of driving forces, and paths of lowest resistance from the barriers that inhibit its utilisation, see Section A1.3.3.

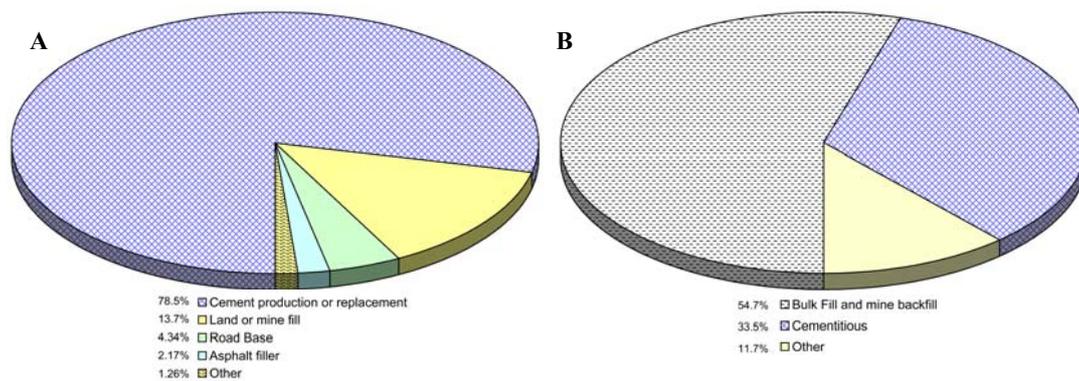


Figure 9.13: Contribution of utilisation strategies to A) 1992 combustion ash utilisation (8.2 Mt produced, 10.7% utilised), data from Manz (1997), and B) 2002 combustion ash utilisation (12.5 Mt produced, 32.3% utilised) within Australia, data from ADAA (2006)

A1.3.3 The Nature of fly ash utilisation barriers within Australia

By comparing the actual fly ash utilisation situation in Australia and around the world, an insight into the nature of fly ash utilisation barriers within Australia can be gained. Bricks and ceramics, lightweight aggregates, waste stabilisation and encapsulation, and mineral fillers were identified as viable utilisation strategies currently unexploited within Australia. Under these circumstances economics is the only significant barrier that can be inhibiting these strategies if any. These strategies represent the greatest potential to significantly improve upon current rates of fly ash utilisation in the short term.

Starting around 1994, there was a substantial acceleration in the rate of increased beneficial ash utilisation (bulk fill and mine backfill applications), see Figure 9.12. During the same period, growth in ash sales experienced average growth. The rapid growth in beneficial utilisation must reflect a reduction in the barriers associated with bulk fill and mine backfill utilisation strategies, and can be associated to deregulation within the electricity market, as well as activities of interest groups, in particular the Ash Development Association of Australia (ADAA). Bulk fill and mine backfill applications could potentially use all fly ash produced, however they are strategies of convenience and are not of any significant value.

Another application that has received widespread use outside of Australia is soil amendment. However technical and perceptual barriers related to trace elements do exist in agricultural applications of fly ash that would need to be addressed first before this strategy can be expected to play any significant role in Australia.

Other unexploited valuable utilisation strategies include adsorbents, metal recovery, carbon products, geopolymers, and zeolites. These strategies have technical, perceptual, and economic barriers which can be removed with research, development, education and demonstration; they could play a valuable role in the future for fly ash utilisation in Australia.

The low level of ash utilisation in Australia is inevitable, due to its high inherent transport costs, combined with relatively low-value applications of coal fly ash, and a small population spread over a large area, ensures that many ash utilisation strategies are not cost-effective. The cement market offers sufficient value adding to overcome the transport cost barrier, it will continue to grow, but is incapable of any major increase in its use of coal fly ash. This situation argues for more value-added utilisation of fly ash as an effective means of overcoming the transport cost barrier. New opportunities need to be created; this means new products, new applications, new markets, and new industries

A1.4 Environmental Considerations

When considering the environmental effects of fly ash, it is important to keep in mind that fly ash will be produced irrespective of whether it is beneficially utilised or not, and disposal rather than reuse carries the risk of future liability for ground water contamination or ash pond runoff. The environmental effects of fly ash utilisation strategies can be classified into a number of groups, illustrated in Figure 9.14 below.

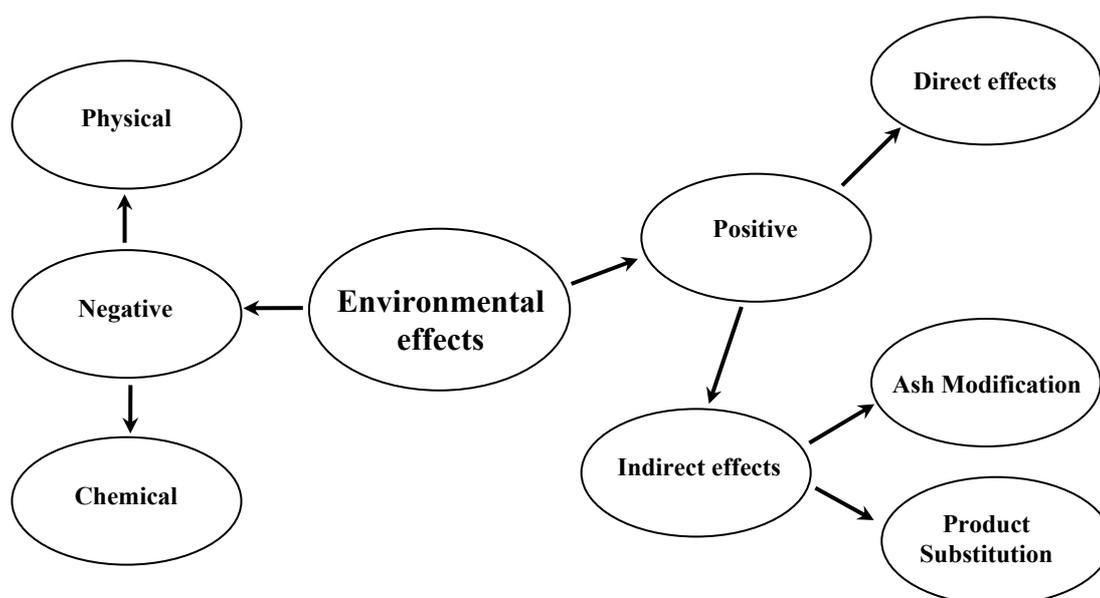


Figure 9.14: The environmental effects of fly ash utilisation strategies

For the power utility, increased fly ash utilisation and decreased landfill requirements, resulting in a decrease in associated environmental impacts, reduced use of fossil fuels and energy in the construction and operation of facilities, which all equate to financial savings to the power utility.

Physical

Fly ash landfill and stockpiles have a significant negative physical effect on the environment, where a large area of natural environment is destroyed to make way for these non-beneficial utilisation options, which then create their own artificial environment with a much lower or different diversity of life. Beneficial utilisation strategies also have a physical presence in the environment, however it is a presence that would be irrespective of whether fly ash was used or not.

Chemical

Chemical contamination of the environment occurs through the leaching of unnatural quantities of elements into the environment, and is related to exposure to water, the amount of contaminant, and the mobility of hazardous components.

Trace elements occur naturally throughout the earth (see Table 9.3 below), some elements are essential to life while others may become toxic in sufficient quantities, human activities often concentrate up these elements to levels which may be dangerous, however it is important to keep a sense of relative perspective with respect to trace elements

Table 9.3: Elements of concern in fly ash utilisation, and there typical concentrations (ppm) in soil, shale, and crust; adapted from (Clarke and Sloss 1992; Sloss, *et al.* 1996)

Element		Soil	Shale	Crust	Fly Ash
Elements of greatest concern					
Arsenic	As	7	13	1	180
Boron	B	30	130	10	220
Cadmium	Cd	0.6	0.3	0.2	230
Mercury	Hg	0.1	0.18	0.08	
Molybdenum	Mo	1	2.6	1.5	
Lead	Pb	20	25	13	530
Selenium	Se	0.4	0.5	0.05	20
Elements of moderate concern					
Chromium	Cr	55	90	100	250
Copper	Cu	25	40	55	250
Nickel	Ni	20	68	75	250
Vanadium	V	80	130	135	350
Zinc	Zn	70	120	70	600
Elements of minor concern					
Barium	Ba	500	550	425	
Cobalt	Co	10	20	15	
Germanium	Ge	1	2	1.5	
Lithium	Li	24	76	20	
Manganese	Mn	550	850	950	
Antimony	Sb	0.7	1.5	0.2	
Strontium	Sr	240	300	375	
Radioactive elements					
Radon	Rn			-	
Thorium	Th	9	12	7.2	25
Uranium	U	2.7	3.7	1.8	24
Elements of concern, but present only in very low concentrations					
Beryllium	Be	1	3	3	8
Tin	Sn	2	6	2	
Tellurium	Te			0.01	
Thallium	Tl	0.2	0.4	0.5	23

Heavy metal content is not as important as heavy metal mobility for ecological evaluation of fly ash (Nairn, *et al.* 2001). The mobility of hazardous compounds relates to contact surface areas, permeability, compositional distributions, and compositional phases present in ash product.

Many trace elements are locked into amorphous and crystalline phases and are not easily leached from fly ash (Nairn, *et al.* 2001). The mobility of metals from fly ash is greatly dependent on the leaching agent and pH (Cenni, *et al.* 2001). Therefore the effect of trace elements on the environment is dependent on local conditions.

For example in wet slurry landfill the fly ash is completely exposed to water which is stored above the water table allowing water to migrate. Fly ash has a large surface area, with a number of elements concentrated on particle surfaces, which allows for the quick leaching of these elements into the environment. A recent study by Peters, *et al.* (1999) found that a major period of selenium contamination in lake Macquarie has occurred in the last 30 years, the result of leaching from a nearby fly ash dam.

Zero discharge legislation and trace element leaching concerns have seen a move from slurry disposal to solid and dense phase disposal in Australia (Innes and Davis 1999). Mine site backfill is essentially landfill without a liner and concern exists over leaching into groundwater, in the US there is some strong opposition to mine backfilling (Innes and Davis 1999).

But how exposed to water are most beneficial utilisation strategies in their environment? The hydraulic conductivity of water through saturated compacted fly ash is typically 10^{-7} m s^{-1} or less (Palmer, *et al.* 2000), and flow only occurs when fly ash is saturated, therefore flow will only occur when fly ash is placed in areas below water (Sear 2001).

Road bases are protected by the asphalt that covers them, as is the fly ash within the asphalt. Adsorbents are usually housed during both storage and use, cement ceramics, bricks, glasses, and geopolymers have such low mobility that water would at worst sit or run over the surface, requiring great pressures and exposure times to move through, therefore these strategies pose little if any threat of contamination to the environment.

Positive – Direct effects

Agricultural products improve the properties of soil in a beneficial way for plant life, and may help convert barren sand to fertile soil. Absorbents can be used to recover hazardous components from waste streams, minimising the environmental burden that these wastes impose upon the environment. Seepage protection minimises the runoff of environmentally hazardous compounds in waste landfills and on the mine site, minimising the environmental impact that these operations have upon the environment.

These are some of the examples where fly ash products provide a service to the environment; however, these benefits are not exclusive to fly ash and could be provided by alternative raw materials.

Ash Modification

Some ash processing operations modify the ash significantly and can produce a new ash material with reduced trace element contents, and an associated reduced risk to the environment, which can be used in all non-cementitious applications. These processes include wet cenosphere recovery, wet carbon recovery, metal recovery, and ash upgrading.

Product Substitution

Product substitution affects the environment in three ways; by decreasing the burden on natural resources, by decreasing the use of energy (greater energy efficiency), and by lowering pollution.

Take cement as an example, the substitution of Portland cement with fly ash decreases the requirement for limestone and clay used to produce Portland cement, as well as all the fossil fuel used to extract, process, and transport limestone and clay to cement plant, and the fossil fuel used to make Portland cement from these materials, this decrease in fossil fuels represents a saving in energy and results in a level of greater energy efficiency and sustainability. This decrease in fossil fuel consumption results directly in reduced CO₂ emissions, also the substitution of fly ash for Portland cement decreases other pollutions and environmental impacts, which result from the mining of limestone and clay, and the manufacture of Portland cement.

Significant energy and processing, therefore CO₂, has been invested in producing fly ash. Coal-fired power stations are in the business of producing electricity, and fly ash is produced irrespective of whether it is used or not. By substituting fly ash for raw materials and products there is an associated reduction in CO₂ emissions from the mining, crushing, milling and processing which is avoided. This concept is echoed by Kalyoncu (2001a), and has been supported in principle for the majority of coal combustion products wide ranging applications, by the World Coal Institute (WCI 2000).

A recent case study by (Nunn, *et al.* 2001) found that for each tonne of cement clinker produced in Australia one tonne of CO₂ is emitted into the atmosphere. Therefore each tonne of fly ash displacing Portland cement will avoid approximately 1 tonne of CO₂ emission.

Appendix 2 Zeolites in Agricultural Application

A2.1 What is a Zeolite?

Zeolites are aluminosilicate minerals with a structure containing SiO_4 and AlO_4^- tetrahedra, linked together with adjacent tetrahedra sharing oxygen to form distinctive crystalline structures (framework structures), which contain large vacant spaces (cages) (see Figure 9.15 below) that can accommodate cations (Na^+ , K^+ , Ba^{2+} , Ca^{2+}), as well as large molecules and cation groups (H_2O , NH_4^+). The cations are distributed throughout the material and play a charge balancing role with the AlO_4^- tetrahedra.

The cage structures of zeolites are interconnected in three dimensions by channels of constant diameter (see Figure 9.15 below). Only molecules with a small enough molecular size to pass through these channels can enter the internal structure of the zeolite (geometrical selectivity). These void spaces can be filled with water (or other molecules), which can be driven off and reabsorbed without changing the framework structure.

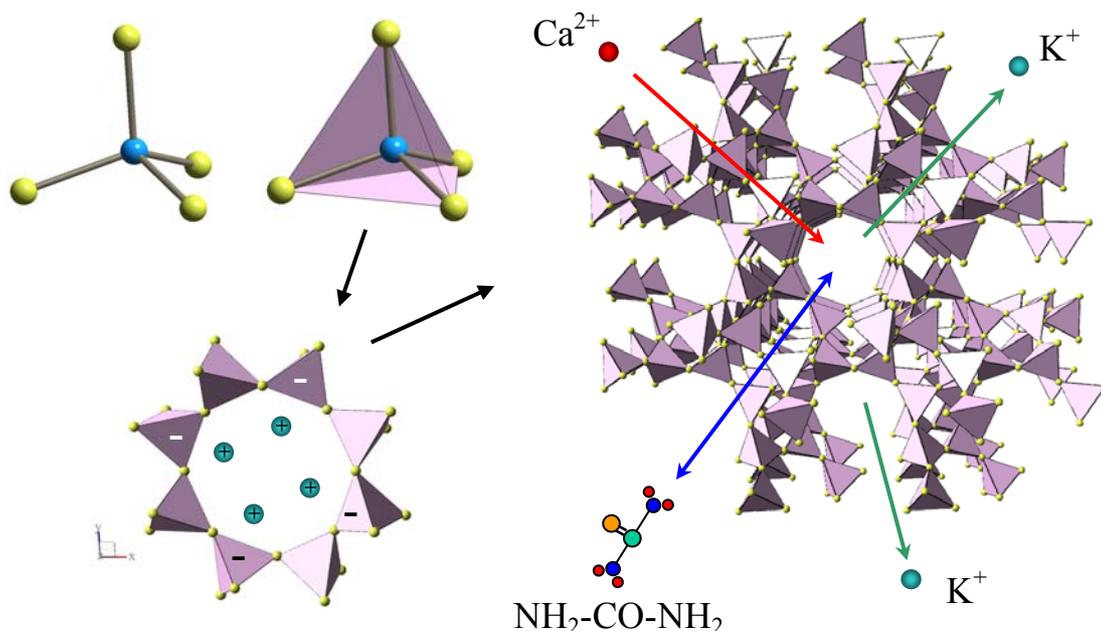


Figure 9.15 : Illustration of SiO_4 and AlO_4^- tetrahedra, the orientation of tetrahedra to form framework structures*, and external access to internal framework structure through channels

The charge balancing cations (Na^+ , K^+ , Ba^{2+} , Ca^{2+}) can be exchanged with other cations in aqueous solution, without affecting the aluminosilicate framework (see ion exchange capacity in Table 9.4 below).

* The framework structure graphic was created using chabazite crystal data (Smith, *et al.* 1963) and Balls & Sticks (Kang and Ozawa 2003) 3D chemical visualisation software

Table 9.4: Typical properties of some economic zeolites, adapted from Holmes (1994)

Zeolite	Typical unit cell formula	Framework structure ^[A]	Void volume (%)	Specific gravity	Channel dimensions (Å)	Cation exchange capacity ^[B] (meq/g)
Analcime	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$	ANA	18	2.24-2.29	2.6	4.54
Chabazite	$(\text{Na}_2\text{Ca})_6(\text{Al}_{12}\text{Si}_{24}\text{O}_{72}) \cdot 40\text{H}_2\text{O}$	CHA	47	2.05-2.10	3.7×4.2	3.81
Clinoptilolite	$(\text{Na}_4\text{K}_4)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	HEU	39?	2.16	3.9×5.4	2.54
Erionite	$(\text{Na}_2\text{Ca}_6\text{K})_9(\text{Al}_9\text{Si}_{27}\text{O}_{27}) \cdot 27\text{H}_2\text{O}$	ERI	35	2.02-2.08	3.6×5.2	3.12
Laumontite	$\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \cdot 16\text{H}_2\text{O}$	LAU	34	2.20-2.30	4.6×6.3	4.25
Mordenite	$\text{Na}_8(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	MOR	28	2.12-2.15	2.9×5.7	2.29
Linde A ^[C]	$\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48}) \cdot 27\text{H}_2\text{O}$	LTA	47	1.99	4.2	5.48
Linde X ^[C]	$\text{Na}_{66}(\text{Al}_{66}\text{Si}_{106}\text{O}_{364}) \cdot 264\text{H}_2\text{O}$	FAU	50	1.93	7.4	4.73

[A] Framework structure types are classified according to a capitalised three letter code [B] Calculated from unit cell formula, [C] synthetic phases

Different zeolites have different selectivity for different cations; a strong selectivity for a particular ion will see that ion preferentially exchanged into the zeolite, while the non-selective species is preferentially released from the zeolite into solution.

These properties distinguish zeolites as unique materials, and are important in their application. For example, large void space is important in animal nutrition, fertilisers, and pesticide applications where the zeolite acts as a carrier medium. Large ion exchange capacities are important in soil construction and repair, fertilisers, water softeners, waste stabilisation and encapsulation applications. Pore size is critical in pesticide and drug delivery applications where active ingredients must be free to enter and exit the zeolite structure.

For many applications, like controlled release fertilisers, most zeolites will suffice. However, not all zeolites were created equal; consequently some zeolites perform better than others for a particular application. Understanding this and knowing how to control the production process to produce the desired zeolite product is critical for the identification and manufacture of a superior product.

A2.2 Potential Products and Markets in Australia

A significant number of zeolite markets have been identified and classified into groups, see Figure 9.16 below. A rough evaluation of the potential of these markets to consume zeolite products in Australia is presented in Table 9.5, which clearly illustrate the potential for zeolite applications to consume significant quantities of fly ash through value added products.

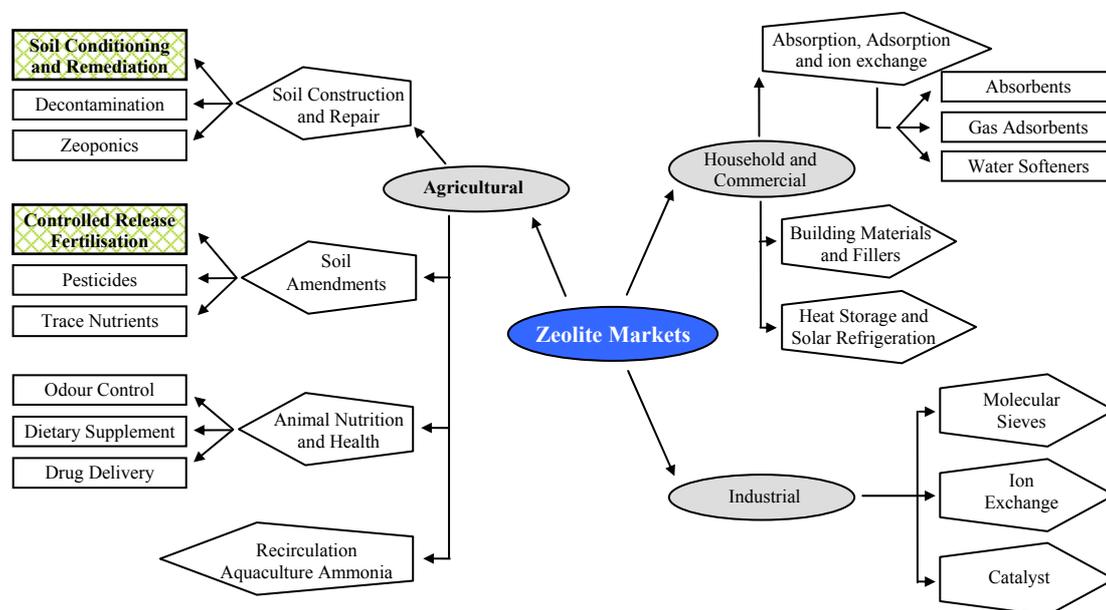


Figure 9.16: Classification of different zeolite markets

Table 9.5 : Potential zeolite markets in Australia^[A]

Market	Zeolite Value (\$AU t ⁻¹)	Market Demand ^[B] (kt p.a.)	Market Value (Millions \$AU p.a.)
Agricultural			
Soil Conditioning and Remediation ^[C]	150	1,500	225
Decontamination	150	30	4.5
Zeoionics	150	230	34.5
Controlled Release Fertilisation ^[D]	150	9,100	1,365
Pesticides ^[E]	500	107	53.5
Odour Control	150	228	34.2
Dietary Supplement	500	62	31
Recirculation Aquaculture Ammonia	150	3	0.5
Household and Commercial			
Pet Litter Media	150	42	6.3
Absorbents	500	0.3	0.15
Gas Adsorbents	150	200	30
Water Softeners	500	84	42
Building Materials and Fillers ^[F]	150	865	130
Heat Storage and Solar Refrigeration	2,000	150	300
Industrial			
Molecular Sieves	2,000	0.5	1
Ion Exchange ^[G]	150	1,281	192
Catalysts	2,000	0.7	1.4
Total		13,884	2,451

[A] This is a summary table, for the full justification of figures the reader is referred to the full thesis document [B] Assuming the following zeolite properties; a void volume of 35%, a cation exchange capacity (CEC) of 3.5 meq per gram of Na⁺ loaded zeolite on a dehydrated basis, and a specific gravity of 2.3. [C] High intensity agriculture (1,076 kt p.a.), floriculture (222 kt p.a.), home garden (potting mix, 115 kt p.a.), and Perth's publicly irrigated turf (55 kt p.a.). [D] Market demand for zeolite component of fertiliser product assuming that it supplies Australias total 1999 market requirements for potassium and nitrogen. [E] Pesticides glyphosate, atrazine, simazine, metham sodium, parathion methyl, chlorpyrifos, mancozeb, and captan. Assuming zeolite framework has sufficiently large pore size to accommodate pesticide molecules [F] Paint (80 kt p.a.), paper (240 kt p.a.), and polymer fillers (120 kt p.a.) as well as lightweight zeolite concrete (425 kt p.a.) where market is based on a 1% replacement of sand and stone (together comprise 85% of concrete) components of concrete for zeolite equivalents over total concrete market (~50 Mt). [G] Predominantly municipal sewage treatment (1,235 kt p.a.), also includes industrial waste water cleaning, aqueous arsenic wastes and arsenic treatment in waste gases.

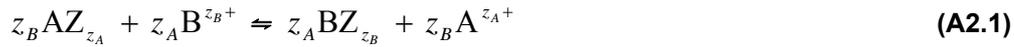
A2.3 Cation Exchange Selectivity (CES)

Cation exchange is a reversible chemical reaction between cations (e.g. plant nutrients Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+}) in the solid phase (e.g. zeolite) and in solution (e.g. water in soil), see Equation A2.1 below. The dynamics of this exchange will depend upon the selectivity of the zeolite and the types and quantities of cations present in the zeolite and surrounding solution.

For a non-selective zeolite, all cations are exchanged into the lattice and are released to maintain the same cation ratios in solution as in the zeolite. A dynamic equilibrium occurs where the zeolite behaves as a general ion buffer.

However by the nature of ion exchange reactions, ion exchangers always exhibit a greater selectivity or affinity for particular ions over others, and have an ordered selectivity sequence for cations (Khym 1974; Harland 1994), which is in part a function of cation and framework geometry and charge densities.

Under equilibrium conditions a cation that a zeolite has a high selectivity toward, will have a higher relative concentration (relative to a low selective cation) in that zeolite compared to the solution. The relative selectivity between any two cations is usually described by the separation factor (α_A^B), Equation A2.2, or the selectivity coefficient (K_A^B), Equation A2.3 below.



$$\alpha_A^B = \frac{(X_B)_Z (X_A)_{Aq}}{(X_A)_Z (X_B)_{Aq}} \quad (\text{A2.2})$$

$$K_A^B = \frac{(X_B)_Z^{z_A} (X_A)_{Aq}^{z_B}}{(X_A)_Z^{z_B} (X_B)_{Aq}^{z_A}} \quad (\text{A2.3})$$

(Khym 1974; Harland 1994)

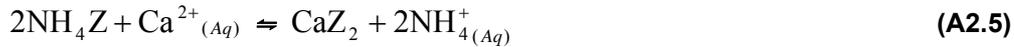
As a consequence of this phenomenon, in plant growth applications, zeolite dominated by exchangeable Na^+ may potentially have harmful effects through salinity poisoning, and zeolite deficient in K^+ , Ca^{2+} , and NH_4^+ can scavenge these ions from the soil and result in deficiencies of these nutrients that may stunt growth. Soil chemistry and zeolite properties must be taken into consideration for plant growth applications on a case by case basis so that a suitable zeolite can be selected for use.

A2.4 Zeolite Fertiliser Mechanisms

Various potential zeolite fertiliser products are possible, these products cover the three nutrient elements consumed the most in Australia, namely nitrogen, phosphorus, and potassium. There are three mechanisms through which zeolites facilitate the slow or controlled release of these nutrient elements; (1) nutrient cation exchange, (2) nutrient diffusion, and (3) nutrient mobilisation.

Nutrient Cation Exchange

A zeolite loaded with K^+ and/or NH_4^+ , and applied as a fertiliser onto the soil, will result in the exchange of K^+ and NH_4^+ ions from the zeolite to water in the soil in the zone of application, to maintain an equilibrium concentration in the soil governed by its selectivity as discussed in Section A2.3. As K^+ and NH_4^+ are stripped from the soil by plants, more is released by the zeolite to maintain this dynamic equilibrium between the soil and the zeolite, a controlled release process. In conjunction with the release of K^+ and NH_4^+ ions, other ions in the soil, such as Ca^{2+} will be exchanged into the zeolite lattice to maintain charge neutrality (See equations A2.4 and A2.5).



By controlling the selectivity of zeolite, the concentration of nutrients in solution can be controlled. By having fewer nutrients in solution at any one time, there is reduced loss through leaching or volatilisation, the efficiency of fertiliser application is improved, and the fertiliser lasts longer.

Once zeolite fertiliser has been consumed, the zeolite will remain and behave like soil conditioner. Nutrients are exchanged into the lattice when they are in excess in the soil (e.g. following the application of a soluble fertiliser), and are released when they are deficient in the soil to maintain equilibrium concentrations.

Urea Encapsulation and Diffusion

Urea is a nitrogen fertiliser that is very soluble in water, and can be occluded within the micro-porous structure of dehydrated zeolite when molten and crystallised at 132°C. The urea is protected from rapid leaching through its physical encapsulation within the zeolites framework structure, and is slowly leached into the soil by a diffusion process (Eberl 2002). The NH_4^+ released into the soil through this process will participate in the dynamic soil-zeolite cation equilibrium.

Mobilisation of Phosphate in Phosphate Rock – Zeolite Blends

Phosphate rock (calcium phosphate) can be physically blended with a zeolite fertiliser to act as a slow or controlled release phosphate fertiliser. Phosphate release is controlled by two reactions (i) ion exchange of Ca^{2+} into the zeolite in exchange for NH_4^+ and/or K^+ , where the removal of calcium from the soil system replaces insoluble calcium phosphate with soluble potassium and ammonium phosphates, making them more available to plants (Ming and Allen 2001; Pickering, *et al.* 2002), see Equation A2.6, and (ii) acid leaching of phosphate facilitated by the conversion of ammonium ions to nitrate ions through nitrification (Eberl 2002), see Equation A2.7. This fertiliser blend has a faster phosphate release than phosphate rock, and a lower solubility than super phosphate.



A2.5 Efficiency

There are various pathways through which fertiliser nutrients can be lost from the soil-water environment (see Figure 9.17), including leaching, volatilisation, runoff and erosion.

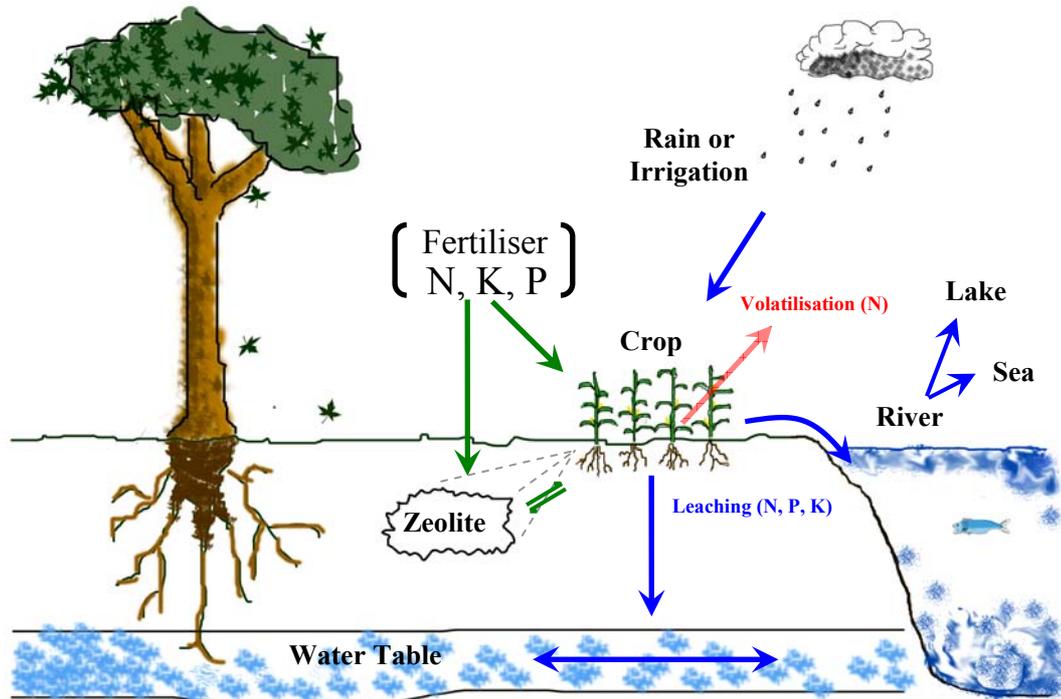


Figure 9.17 : Illustration of nutrient cation exchange between zeolite fertiliser and the soil-water environment

Nutrients contained within the zeolite do not take part in aqueous phase reactions or leaching, and are out of the reach of bacteria, so they will not be lost to leaching or vaporisation processes. Once released into the soil from the zeolite, nutrients will be available to these mechanisms of loss. Reaction rates are usually proportional to available concentration (see Equation A2.8 for a pseudo reaction); therefore by reducing the concentration of nutrients available for loss at any moment in time, the total loss over the lifecycle of fertiliser is reduced.

$$-r_{M^{Z+}} = k [M^{Z+}]^n \quad (\text{A2.8})$$

There are many local factors which influence the efficiency of a fertiliser, and it is rare for fertiliser use efficiency to exceed 50% for conventional fertilisers (Ming and Allen 2001). For example, Hollinger *et al.* (2001) found that 31% of nitrogen applied to the soil at a rate of 414 kg/ha in a market garden in the Hawkesbury-Nepean catchment near Sydney, runs into a nearby creek. And a study by the US EPA found that over 48% of N applied to container grown plants is leached (Robbins 2003).

The theory behind the mechanisms of nutrient delivery provided by zeolites and responsible for its greater efficiency relative to traditional soluble fertilisers has been presented previously in Section A2.4; however the following case studies from extreme leaching environments demonstrate this capability in practice:

- A experiment of nutrient leaching in 1.5 litres of potting medium found that over 90% of K from KNO_3 was leached from the soil apposed to 10% of K from K-Clioptilolite after 3 litres of leachate was collected (Hershey, *et al.* 1980)
- In another experiment, 1.5 litres of potting medium used to grow chrysanthemums was irrigated daily producing 200 mL of leachate. The control pots received soluble K at 234 ppm in irrigation water. To obtain an equal yield of chrysanthemums over 3 months, a once off application of 50 g of K-Clioptilolite was required at the start of the trial, which contains half as much K than was applied to control pots over 3 month period (Hershey, *et al.* 1980)
- A 42 day plant growth study for corn in sandy soil, involving a range of sand particle sizes, and a range of nutrient application rates, found that the nitrogen-use efficiency of NH_4 -Clioptilolite amended soils was > 95% as apposed to 10-73% for $(\text{NH}_4)_2\text{SO}_4$, while maintaining normal corn growth (Perrin, *et al.* 1998)

For the current situation with traditional soluble fertilisers, resources and energy have been invested in producing a product for which a significant percentage is lost. By using zeolite fertilisers, the consumer can save through improved efficiency, and be able to purchase less for the same result, or the same for a longer lasting effect, with an associated reduction in the ecological footprint of fertiliser application.

Appendix 3 Processes in Zeolite Production from Coal Ash

A3.1 Established Commercial Zeolite Synthesis Manufacture

Commercial molecular sieve manufacturing processes are classified into three groups listed in Table 9.6 below (fly ash is analogous to volcanic glass). These processes are performed as batch operations. The process flow for the Hydrogel process is illustrated in Figure 9.18, with the clay conversion process illustrated in Figure 9.19, and mass balances given in Table 9.7. Many applications require zeolites to be in the form of agglomerates or pellets; an example of an agglomeration process for zeolites is illustrated in Figure 9.20 below.

Table 9.6: Molecular sieve zeolite preparation processes, taken from Breck (1974)

Process	Reactants	Products
Hydrogel	Reactive oxides Soluble silicates Soluble aluminates Caustic	High purity powders Gel preform Zeolite in gel matrix
Clay Conversion	Raw kaolin Metakaolin Calcined kaolin Soluble silicate Caustic Sodium chloride Natural SiO ₂	Low to high purity powder Binderless, high purity preform Zeolite in clay-derived matrix
Other	Acid-treated clay Amorphous minerals Volcanic glass Caustic Al ₂ O ₃ ·3H ₂ O	Low to high purity powder Zeolite on ceramic support Binderless preforms

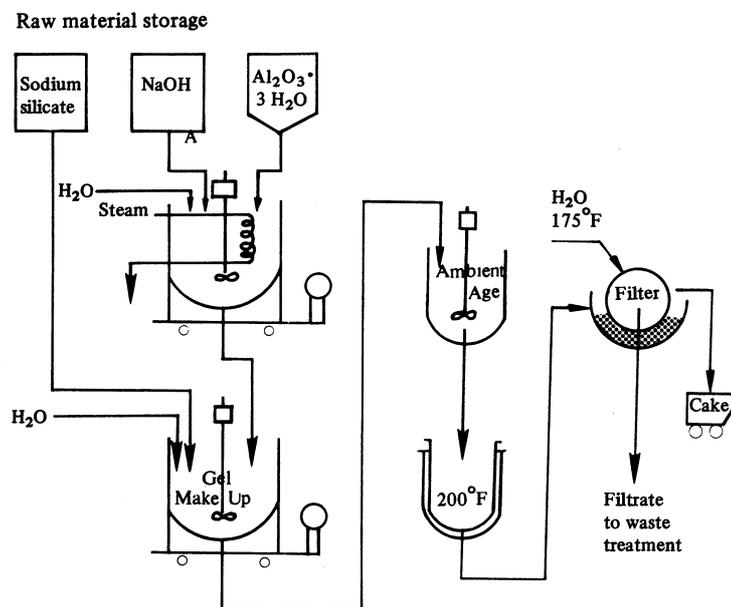


Figure 9.18: A schematic of the Hydrogel process, taken from Breck (1974)

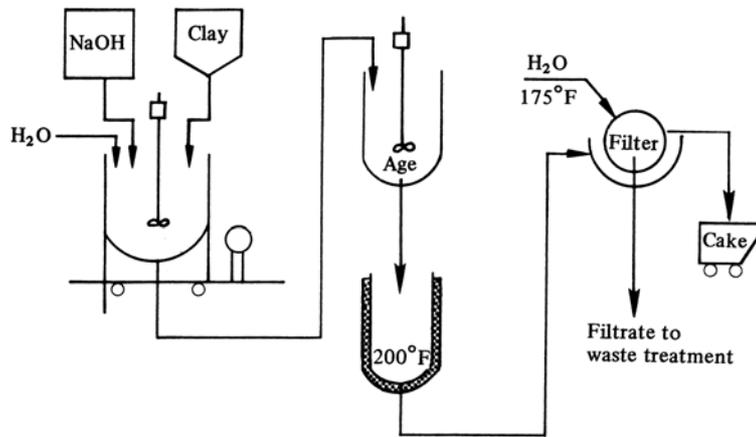


Figure 9.19: A schematic of the clay process, taken from Breck (1974)

Table 9.7: Mass balances to Figures 5 and 6, taken from Breck (1974)

Raw Materials	Hydrogel Process			Clay Process
	4A	13X	Y	4A
	Weight (To produce 1000lbs, dry basis)			
Sodium Silicate ^[A]	1350	2000	-	-
SiO ₂ powder ^[B]	-	-	1450	-
Aluminium Trihydrate ^[C]	575	500	340	-
Calcined kaolin ^[D]	-	-	-	800
Caustic, 50% NaOH	870	1600	1400	1100
Water	3135	7687	5300	3755
	Gel or reactant composition (moles) ^[E]			
Na ₂ O	2.04	4.09	4.0	2.0
Al ₂ O ₃	1.00	1.00	1.0	1.0
SiO ₂	1.75	3.00	10.6	2.0
H ₂ O	70	176	161	70

[A] 9.4% Na₂O, 28.4% SiO₂, [B] 95% SiO₂, [C] 65% Al₂O₃, 35% H₂O, [D] 44.8% Al₂O₃, 52.8% SiO₂, [E] Gel composition for Hydrogel process and reactant composition for clay process

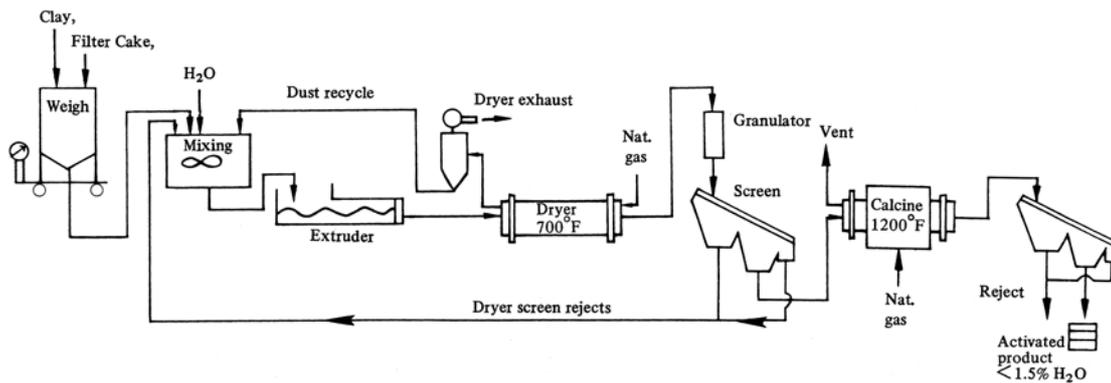


Figure 9.20: A schematic of the pelletization process, taken from Breck (1974)

A3.2 Zeolite Synthesis and Enhancement Processes from Coal Fly Ash

The objective of this chapter (outlined in Figure 9.21 below) is to illustrate the processes involved in the synthesis of zeolite from coal fly ash, as well as a summary of what research has been conducted in this field.

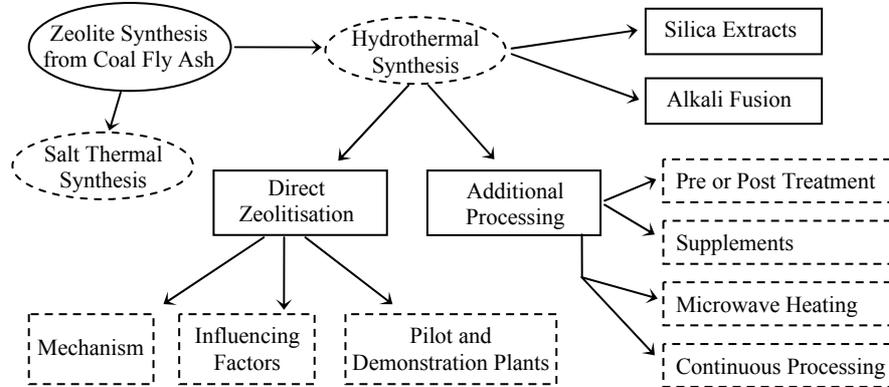


Figure 9.21: Outline of zeolite synthesis from fly ash

For hydrothermal synthesis, the zeolitisation of aluminium and silicon takes place in the presence of water at elevated temperatures. Varying the conditions of hydrothermal zeolite synthesis could be used to produce either (i) ~100% zeolite products or (ii) <95% zeolite product (low grade zeolite), which have superior properties to fly ash, at a lower cost than pure zeolite.

Many authors have investigated the hydrothermal synthesis of zeolite materials from coal fly ash as the starting material^{*}, for direct hydrothermal synthesis^[1-21], for hydrothermal synthesis using silica extracts^{[14][22-24]}, and for hydrothermal synthesis from alkali fused fly ash^{[14][25-29]}.

A number of different types of zeolite have been synthesised from fly ash by previous authors. They are classified according to synthesis method, base, and framework structure:

Direct Hydrothermal Synthesis Products

- Sodium Hydroxide
 - ANA – Analcime^[1-6]
 - CAN – Cancrinite^[1], Hydroxy-Cancrinite^[4-6]
 - CHA – Herschelite^[5]
 - FAU - Faujasite^{[5][7]}, Zeolite X^[8-11]
 - GIS - Zeolite P^{[1][7-8][12-16]}, Zeolite P1^{[2-6][9-10][17-19]}, Gobbinsite^[18]
 - GME – Gmelinite^[3]
 - JBW - Nepheline hydrate^[3-4]
 - LTA - Linde Type A^{[5][7][11-12]}
 - PHI – Phillipsite^[10]
 - SOD – Sodalite^[14], Hydroxy-Sodalite^{[1][4-6][8][13][15-16][19]}, Sodalite Octahydrate^[10]

^{*} [1] (Lin and Hsi 1995) [2] (Querol, *et al.* 1995) [3] (Querol, *et al.* 1997b) [4] (Querol, *et al.* 1997a) [5] (Querol, *et al.* 2001) [6] (Zeng, *et al.* 2002) [7] (Shih and Chang 1996) [8] (Mondragon, *et al.* 1990) [9] (Amrhein, *et al.* 1996) [10] (Scott, *et al.* 2001) [11] (Tanaka, *et al.* 2002) [12] (Catalfamo, *et al.* 1993) [13] (Singer and Berggaut 1995) [14] (Berggaut and Singer 1996) [15] (Murayama, *et al.* 2002a) [16] (Murayama, *et al.* 2002b) [17] (Steenbruggen and Hollman 1998) [18] (Mouhtariss, *et al.* 2003) [19] (Vucinic, *et al.* 2003) [20] (Belardi, *et al.* 1998) [21] (Mimura, *et al.* 2001) [22] (Moreno, *et al.* 2002) [23] (Hollman, *et al.* 1999) [24] (Moreno, *et al.* 2001) [25] (Chang and Shih 1998) [26] (Shigemoto, *et al.* 1993) [27] (Chang and Shih 2000) [28] (Rayalu, *et al.* 2000) [29] (Rayalu, *et al.* 2001)

- Potassium Hydroxide
 - CHA - Potassium Chabazite^{[5][9][17]}
 - EDI - Linde F^[4-6]
 - LTL - Linde Type L (K exchanged)^[20], Perliolite^[5]
 - MER – Merlinoite^[2], K-M^[4-6], Zeolite W (K exchanged)^[20]
 - NAT - Natrolite (K exchanged)^[21]
 - PHI – Phillipsite^[2-3], ZK19^[17]

Hydrothermal Synthesis Products using Silica Extracts

- Sodium Hydroxide
 - FAU - Zeolite X^[22-24]
 - GIS - Zeolite P^{[14][23]}
 - LTA - Linde Type A^[22-24]
 - SOD – Sodalite^[14], Hydroxy-sodalite^[22]

Hydrothermal Synthesis Products using Alkali Fusion

- Sodium Hydroxide
 - FAU – Faujasite^[25], Zeolite X^{[14][26-27]}, Zeolite Y^[28]
 - GIS - Zeolite P^{[14][25]}
 - LTA - Linde Type A^{[25-27][29]}

Note on Salt thermal Synthesis:

The salt thermal method for zeolite synthesis involves heating fly ash with a base (e.g. NaOH, KOH or NH₄F) and a salt (e.g. KNO₃, NaNO₃, or NH₄NO₃) as dry solids at 350°C for 12h producing sodalite and cancrinite zeolites (Park, *et al.* 2000b; a; Choi, *et al.* 2001). This technique has not been independently verified.

A3.2.1 Direct Hydrothermal Synthesis

Direct hydrothermal synthesis of fly ash is where the ash in its solid particulate form, without any prior chemical transformation, is combined with other reactants and treated hydro-thermally to produce a zeolitic product which contains both zeolite and un-reacted fly ash phases.

A3.2.2 Alkali Fusion

Alkali fusion is used to enhance the dissolution of fly ash. Alkali fusion involves heating fly ash with sodium hydroxide at 500 – 650°C fusing the two, and converting most of the ash into sodium salts (silicate and aluminate). The fused ash can then be dissolved in water and reacted by hydrothermal synthesis to produce zeolites*.

Shigemoto *et al.* (1993) found that mullite was only partially converted into aluminium silicate by alkali fusion. Berggaut and Singer (1996) improved the fusion process by adding a small quantity of water to the reaction mixture resulting in the complete decomposition of Mullite after 2h of fusion by improving the contact between NaOH and fly ash during fusion.

A3.2.3 Silica Extracts

Following a batch hydrothermal synthesis reaction the aqueous phase contains a significant quantity of dissolved silica. This solution can be recovered and used to produce pure zeolites using a sol-gel hydrothermal synthesis technique.

* The hydrothermal treatment of fly ash in 3.5M NaOH for 6 hours produced zeolite P with a cation exchange capacity of 250-300 meq/100g. The same fly ash was fused with NaOH (1g Fly ash with 1.2g NaOH), and following hydrothermal treatment for 4 hours, zeolite P was produced with a cation exchange capacity of 420 meq/100g (Berggaut and Singer 1996)

Hollman *et al.* (1999) prepared NaP1, NaX and NaA zeolites from silica extracts, representing an extra 85g of pure zeolite produced per kg of fly ash used in original batch hydrothermal synthesis. Aluminium-rich waste solutions from the aluminium-anodising industry can be used as the aluminium source in the hydrothermal synthesis of silica extracts to zeolites (Moreno, *et al.* 2002).

A3.2.4 Pre or post treatment

Acid treatment prior to hydrothermal synthesis can be employed to reduce the iron content of fly ash as well as metal oxides and trace elements. However no significant improvements in the properties of zeolite synthesised from fly ash following acid treatment have been observed (Rayalu, *et al.* 2001). The framework structure of zeolite P is broken (dissolved) by the action of protons (acid) at pH below 4 (Murayama, *et al.* 2003), therefore the post synthesis leaching of iron by acid treatment is not advantageous.

A significant portion of iron can be separated from fly ash using magnetic separation, which results in an increased yield therefore increased cation exchange capacity (Poole, *et al.* 2000; Rayalu, *et al.* 2001), the resulting magnetic product could be sold as a dense medium for gravity separations (Nairn, *et al.* 2001).

Carbon can be separated using froth flotation or electrostatic separation. However, unless this phase comprises a major volume of the fly ash, it is probably not economically advantageous.

Some applications of fly ash zeolite require post treatment to exchange the charge balancing cations from synthesis with cations vital for the application, using an ion exchange process where the zeolite is exposed to a concentrated aqueous solution of the appropriate cation. For example fertilisers require K^+ or NH_4^+ zeolites.

Some applications may require that the zeolite product be in a pellet or aggregate form. This could be done before or after synthesis. Pelletising prior to synthesis may affect the conversion and zeolite yield, although Garcia-Martínez, *et al.* (2002) produced zeolites Na-P1, analcime, cancrinite and sodalite from hydrothermal synthesis of fly ash briquettes with no loss in yield or disintegration of briquette.

A3.2.5 Supplements (making use of other waste resources)

Not all fly ashes have compositions (Si/Al ratio available) suitable for the synthesis of specific zeolite products, and if the correct composition cannot be achieved through blending, alternative sources of Al and/or Si for blending include incinerator ash, alkaline wastes from the alumina industry, slags from the iron industry, and silica fume.

A3.2.6 *Microwave heating*

By employing microwave heating of batch hydrothermal zeolite synthesis, the reaction time can be reduced from 24h when using conventional heating, to 30 min when using microwave heating (Querol, *et al.* 1997a; Querol, *et al.* 2001). This is due in part to microwaves capability to heat a batch to reaction temperature more quickly with a more homogeneous heat distribution therefore faster reaction and decreased batch time.

A3.2.7 *Continuous Processing*

Continuous processing will be very important for low cost production of zeolites, currently the synthetic zeolite industry is based on batch processing. The demonstration plant presented by Kikuchi (1999) is a continuous process, however the zeolite products were not identified, and no comparisons between continuous and batch processing were drawn. Amrhein *et al.* (1996) looked at reusing (recycle) the filtrates from hydrothermal synthesis of zeolites from fly ash up to 4 times without any observable detrimental effect.

A3.3 *Detailed Consideration of the Direct Hydrothermal Synthesis Process*

Direct hydrothermal synthesis of fly ash is where the ash in its solid particulate form, without any prior chemical transformation, is combined with other reactants and treated hydro-thermally to produce a zeolitic product which contains both zeolite and un-reacted fly ash phases.

A3.3.1.1 *Mechanism*

The mechanism for zeolite synthesis from fly ash in a batch hydrothermal synthesis process has three stages; 1) The dissolution of aluminium and silicon from fly ash, 2) The deposition of aluminosilicate gel on ash surface, 3) The crystallisation of zeolite from aluminosilicate gel (Murayama, *et al.* 2002b; a), see Figure 9.22 below.

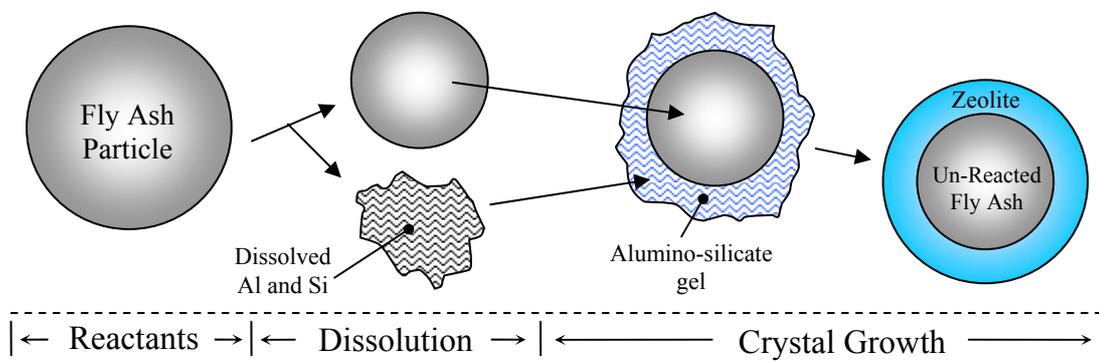


Figure 9.22 : Illustration of reaction mechanism for the batch hydrothermal conversion of fly ash to zeolite given by Murayama, *et al.* (2002b; 2002a)

Dissolution

The key sources of aluminium and silicon in fly ash are the 1) amorphous aluminosilicate glass, 2) quartz, and 3) mullite phases. The aluminosilicate glass phase is the largest and most unstable of these phases in the hydrothermal environment, and therefore has the highest rate of dissolution (Querol, *et al.* 1997b; Belardi, *et al.* 1998; Poole, *et al.* 2000; Murayama, *et al.* 2002b; a), which increases with decreasing silica concentration in the glass (Höller and Wirsching 1978), and is therefore the largest contributor to the zeolites produced. Quartz is less stable than mullite (Querol, *et al.* 1995; Singer and Berkgaut 1995; Querol, *et al.* 1997b; Poole, *et al.* 2000; Murayama, *et al.* 2002b; a), although quartz and mullite phases are significantly more stable than the glass phase to the extent that some authors report little to no reactivity for quartz (Mondragon, *et al.* 1990), and for mullite (Catalfamo, *et al.* 1993; Berkgaut and Singer 1996).

Aluminosilicate Gel, Nucleation and Crystal Growth

There are two prominent theories for primary nucleation in the hydrothermal synthesis of zeolites, developed through research into the sol-gel synthesis method, are i) nuclei form through homogeneous nucleation in solution, and ii) nuclei form through homogeneous nucleation in the gel phase (Figure 9.23 below).

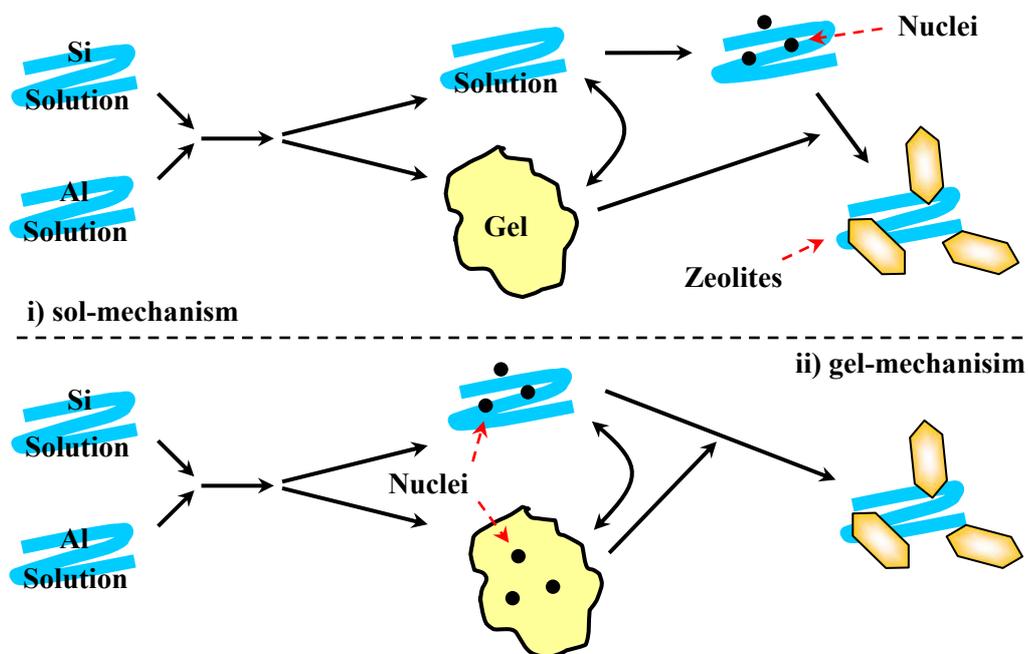


Figure 9.23: Illustration of alternative primary nucleation and crystal growth mechanism theories

For homogeneous solution nucleation mechanism during sol-gel synthesis, a gel forms following the mixing of aluminium and silicon solutions, producing a stable solution, see Figure 9.24 below. During ageing the concentration of aluminium and silicon in solution can increase through the dissolution of gel in conjunction with the formation and destruction of oligomeric species (including secondary building units), which can shift the solution into the metastable region and ultimately the labile region (Feijen, *et al.* 1994) where, it is speculated, nucleation can occur through the chemical aggregation of oligomeric species (Bell 1989; Feijen, *et al.* 1994). Oligomeric species are assumed to be at their greatest concentration within the diffusion boundary layer of the gel-solution interface, subsequently nucleation is expected to be greatest in these regions (McCormick and Bell 1989).

Numerous studies into the types of oligomeric species present in hydrothermal solutions have been conducted (McCormick and Bell 1989), using ^{29}Si Nuclear Magnetic Resonance (NMR) spectroscopy the types and quantities of oligomeric have proven to be sensitive to the pH and cation type of reaction solution (Bell 1989). However “there is, as yet, no direct proof for the participation of these species in zeolite nucleation and/or growth” (McCormick and Bell 1989); although recently Wakihara, *et al.* (2004) demonstrated that faujasite crystal growth proceeded through the direct incorporation of soluble aluminosilicate species equal to or smaller than the 6R oligomer species* using atomic force microscopy (AFM).

* The types and properties of oligomer species are described using codes, see McCormick and Bell (1989), and Bell (1989)

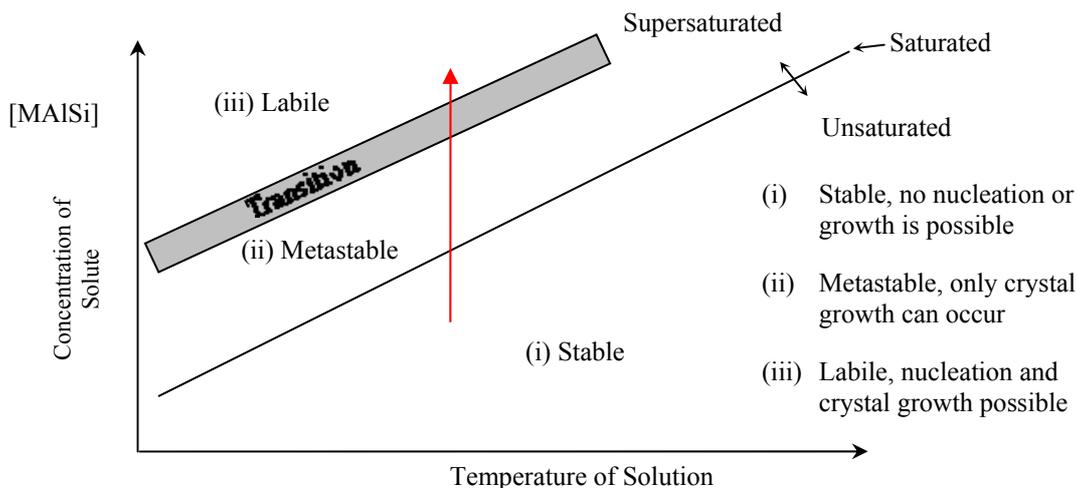


Figure 9.24 : Relationship between reactant concentrations and the crystallisation processes of nucleation and crystal growth, based on Feijen, *et al.* (1994)

For homogeneous gel nucleation mechanism during sol-gel synthesis, the initial mixing of aluminium and silicon solutions produces a supersaturated solution in which nuclei can form, and from which a predominantly amorphous aluminosilicate gel precipitates (Katovic, *et al.* 1989). During gel precipitation an initial number of nuclei are formed in both the aqueous and gel phases (Katovic, *et al.* 1989).

There are two effects occurring during gel ageing; i) new nuclei are formed in the gel phase, and ii) nuclei are released into solution during gel recrystallization (where small gel particles are dissolved and reprecipitated to form large gel particles (Katovic, *et al.* 1989). The types of nuclei favoured during precipitation and during gel ageing can be different and result in different types of zeolite being produced following gel ageing than without ageing (Katovic, *et al.* 1989).

There is a solubility equilibrium between the gel phase and solution (Zhdanov 1971), during crystallisation the nuclei in solution consume aqueous aluminium and silicon facilitating the net dissolution of gel phase releasing encapsulated nuclei accelerating crystallisation rate in turn accelerating gel dissolution (Katovic, *et al.* 1989).

The homogeneous gel nucleation mechanism is still under review (Thompson 2001). The presence of extraneous material in the solution can catalyse primary nucleation (Thompson 2001) consequently the presence of fly ash particles in the hydrothermal reaction system may have a significant effect on nucleation.

A3.3.1.2 Factors influencing zeolitisation

There are a number of different factors which influence the zeolitisation of fly ash, they include fly ash properties, base, temperature, time, cations, templates, water, ageing and seeding. Generally but not exclusively, direct hydrothermal synthesis is carried out between 70 and 200°C, 3 and 48 hours, 0.5 and 5 mol OH⁻ per litre of solution, 2 and 20mL of solution per g of coal fly ash, and usually with Na⁺ or K⁺ cations in the form of hydroxides.

Coal Fly Ash (Aluminosilicate source)

As the source for both silicon and aluminium for zeolite synthesis, the properties of fly ash will have a significant influence on the composition and quantity of these species liberated into solution and therefore the composition and yield of the zeolite produced.

The important components of fly ash are 1) Amorphous aluminosilicate glass, 2) Quartz, 3) Mullite, 4) Metal oxides (e.g. Na_2O , K_2O , and CaO), 5) Iron Oxides (e.g. Hematite and Magnetite), 6) Unburned Carbon, and 7) Trace elements

Highest synthesis yields $>80\text{wt}\%$ correspond to highest glass containing fly ash, the lower conversions (yields) are attributed to (i) larger contents of non-reactive phases (hematite, magnetite) in fly ash, and (ii) larger content of resistant aluminosilicate phases (mullite, quartz) (Querol, *et al.* 2001)

The crystallisation of zeolites can be split into primary and secondary crystallisation stages, where the primary crystallisation is fuelled by the amorphous aluminosilicate glass, while the secondary crystallisation is fuelled by the aqueous silica excess left by primary crystallisation and further extracts from quartz and mullite (Querol, *et al.* 1997b) (see Figure 9.25 below).

As the largest and most reactive aluminosilicate source, the glass phase has the greatest influence over the composition and type of zeolite produced. Fly ashes with similar bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have produced different zeolites under the same conditions, this is attributed to differences in the composition of glass matrix (Querol, *et al.* 1997b) (see Figure 9.25 below).

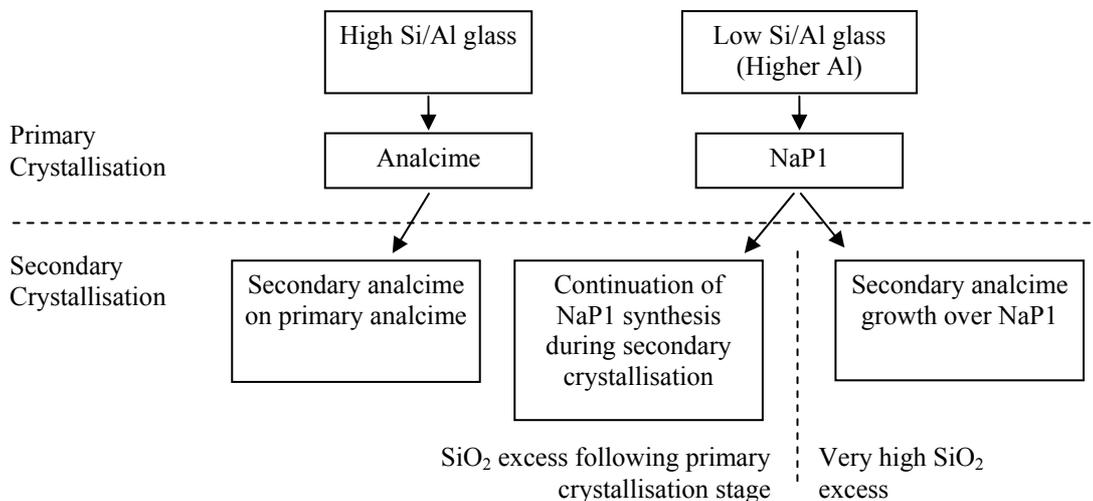


Figure 9.25: Illustration of the influence of glass composition on zeolite crystallisation, reproduced from description of findings given in Querol *et al.* (1997b)

The composition of silicon and aluminium in solution has a significant effect on the zeolite product formed. Generally higher temperature and higher Si/Al molar ratios favour zeolite P formation, lower Si/Al and temperature favour faujasite and zeolite A (Shih and Chang 1996; Tanaka, *et al.* 2002). Figure 9.25 above illustrates this for higher Si/Al solutions. By controlling the ratio of Si/Al in solution greater control over products formed can be realised.

The hydrothermal treatment product has significantly reduced Si content relative to fly ash (Lin and Hsi 1995), Tanaka *et al.* (2002) calculated that only 24% of the Si eluted from fly ash was

converted to Zeolite NaP1, with the remainder remaining in the effluent. This excess Si can be utilised by the addition of easily mobilised Al materials.

Many metal oxides are readily dissolved in hydrothermal media to produce cations in solution; the effect of charged species in solution is discussed later. Of particular interest is the effect of calcium content in fly ash material on the synthesis of zeolites, materials with a calcium content exceeding a critical level (3-5 wt% of fly ash), have a suppressing effect on the crystallisation of zeolites (in particular zeolite A) (Catalfamo, *et al.* 1997).

The magnetite phase is not altered (not affected) during the course of hydrothermal reaction (Querol, *et al.* 1995). The iron oxide and unburned carbon phases, which are not altered during hydrothermal synthesis, form part (impurities) of the zeolitic product; their presence in fly ash makes it impossible to produce a pure zeolite product.

Most anion forming elements are mobile and largely extracted into aqueous phase during hydrothermal synthesis (Steenbruggen and Hollman 1998), including As, Se (Steenbruggen and Hollman 1998), Mo (Amrhein, *et al.* 1996; Steenbruggen and Hollman 1998), B, and P (Amrhein, *et al.* 1996) (see Table 9.8 below). Cations forming heavy metals (e.g. Cu, Pb, Zn) remained in zeolite product (i) as precipitated hydroxides or (ii) absorbed into the zeolite framework (Steenbruggen and Hollman 1998).

Table 9.8: Extractable B, Mo, Cu, Ni, and Cd in fly ash before and after hydrothermal treatment (mg/kg), taken from Singer and Bergaut (1995)

Fly Ash		Se	Mo	B	Cu	Ni	Cd
1	Before	0.20	3.15	37.1	0.50	0.90	0.90
	After	<0.002	0.25	25.6	<0.002	0.05	0.05
2	Before	3.75	11.6	149.7	<0.002	0.05	0.05
	After	0.05	0.75	18.3	<0.002	<0.002	0.05

Base

In the reaction mixture, OH⁻ ions create an environment which mobilise Si and Al oxides into solution, OH⁻ ions control the concentrations of saturation and supersaturation which are a key to nucleation and crystal growth (Feijen, *et al.* 1994). The Si/Al ratio of solutions, gels and zeolites are strongly correlated with pH (Mariner and Surdam 1970), subsequently pH is often the primary means of controlling a products Si/Al ratio (Robson 1989). However different zeolite types generally crystallise within a narrow range of pH (Lechert 2001), and OH⁻ is consumed by the hydrothermal synthesis reactions.

The strength of this base is related to the cations it is coupled with, NaOH has a greater efficiency for dissolving quartz and Mullite than KOH (Querol, *et al.* 1997b), and NaOH solutions produce greater yields of zeolite than KOH solution (Querol, *et al.* 2001). The use of NH₄OH as base resulted in no change in the CEC compared to fly ash starting material (Amrhein, *et al.* 1996).

Increased pH will increase reactant concentrations in solution; this will accelerate the rate of nucleation and crystallisation (Feijen, *et al.* 1994). Dissolution is low at low OH⁻ concentration, and results in low zeolite yields (Murayama, *et al.* 2002b; a). Increasing NaOH concentration results in increased Mullite digestion (Querol, *et al.* 1997b), however increasing the NaOH concentration results in a greater increase in Si dissolution than the increase in Al dissolution from fly ash (Catalfamo, *et al.* 1993; Poole, *et al.* 2000), resulting in an increase in the Si/Al ratio

in solution which influences the gel composition and subsequently zeolite product type produced (Catalfamo, *et al.* 1993)^{*}.

Alternative fly ash mineralising agents have been investigated, including KF, NaF, NH₄F, NH₄-HF, and HF which were unable to produce any zeolites (Amrhein, *et al.* 1996). The use of carbonates as mineralising agents requires long reaction durations making them unviable for industrial application[†].

Temperature and time

The first phase to crystallise from solution according to Ostwald's rule of successive phase transformation is the thermodynamically least favourable phase, with time this phase will be followed successively with increasingly more stable phases (Goldsmith 1953; Barrer 1989; Feijen, *et al.* 1994)[‡], while increasing temperature increases the nucleation and growth rate of zeolite crystals (Feijen, *et al.* 1994), therefore the speed at which successive phase transformations take place. Coombs *et al.* (1959) found that equilibrium was not obtained for hydrothermal synthesis experiments even after 30 days, and according to Breck (1974), "true equilibrium may never be attained" during hydrothermal zeolite synthesis.

Increasing temperature results in increased mullite digestion (Querol, *et al.* 1997b), however it also results in a greater increase in Si dissolution than it increases Al dissolution from fly ash (Catalfamo, *et al.* 1993; Poole, *et al.* 2000), resulting in an increase in the Si/Al ratio in solution which influences the gel composition and subsequently zeolite product type produced (Catalfamo, *et al.* 1993)^{§**}.

Charged molecules and templates

Templates are structure directing species which increase the stability of particular aluminosilicate structures during zeolite synthesis depending on the properties of template (size and charge), and so have a significant influence on the structure and composition of zeolites produced (Flanigen 1973; McCormick and Bell 1989; Feijen, *et al.* 1994).

The use of sodium produces FAU, EMT, MAZ, and MOR framework structure types, while potassium produces LTL, ERI, and OFF framework structure types (Feijen, *et al.* 1994). Zeolite framework structures produced from fly ash (which contains a cocktail of cations) using NaOH solutions include FAU, LTA, GIS, ANA, SOD, and CAN, while KOH solutions have produced LTL, MER, PHI, CHA, and EDI framework structures.

* For NaOH concentrations less than 2 mol L⁻¹ zeolite P yield increases with increasing concentration, while for concentrations above 2 mol L⁻¹ zeolite P yield decreases with increasing concentration due to increased yield of hydroxysodalite (Murayama, *et al.* 2002b; a).

† Lin and Hsi (1995) were unable to produce zeolites from fly ash using Na₂CO₃ solutions, however Murayama *et al.* (2002b; 2002a) was able to detect trace levels of zeolite P following such synthesis. Hawkins *et al.* (1978) produced varying amounts of Clinoptilolite, Mordenite and Phillipsite from volcanic glass using 2 mol L⁻¹ CO₃²⁻ solutions with varying K:Na ratios, temperatures of 130°C or higher and reaction durations of two or more days

‡ For example when using NaOH in the hydrothermal treatment of fly ash, 4 hours of synthesis produced zeolite A while 6-8 hours produced zeolite P from zeolite A (Catalfamo, *et al.* 1997)

§ For example when using NaOH in the hydrothermal treatment of fly ash, between 70 and 130°C zeolite P was produced, while between 130 and 170°C analcime was produced (Lin and Hsi 1995). Generally higher temperature favour zeolite P formation, while lower temperatures favour faujasite and zeolite A (Shih and Chang 1996)

** In the KOH environment, zeolite KL is replaced with zeolite KW which is replaced by Kaliofillite with increasing reaction time or temperature (Belardi, *et al.* 1998)

In addition to being structure and composition directing species, cations also influence the rate of zeolite synthesis (McCormick and Bell 1989; Feijen, *et al.* 1994)*.

Solvent

Water acts as a template by its interaction with cations, in addition to its action as a solvating and hydrolysing agent (Feijen, *et al.* 1994). Water molecules also aid zeolite formation by filling void space which stabilises the structures (Barrer 1968; 1989; Feijen, *et al.* 1994).

Increasing the liquid to solid ratio in the hydrothermal synthesis of zeolites from fly ash was found to increase dissolution of mullite, quartz and the glassy matrix (Querol, *et al.* 2001), increase yield (Querol, *et al.* 1995), and decrease reaction rate (Querol, *et al.* 1995; Belardi, *et al.* 1998).

Ageing and Seeding

Both of these processes can significantly affect the reaction kinetics and the type of zeolite produced (Feijen, *et al.* 1994). Ageing results in the formation of semi-crystalline particles (nuclei) dispersed throughout the aqueous phase, their concentration increases with increasing periods of ageing prior to synthesis (Feijen, *et al.* 1994)[†], and an increased quantity of nuclei will decrease the average crystallite size in product (Barrer 1989). Seeding involves adding small particles of the desired zeolite product to the reaction soup, reaction starts with crystal growth, bypassing the induction and nucleation stages of synthesis (Feijen, *et al.* 1994)[‡], and typically results in increased crystallisation rates (Thompson 2001).

A3.3.1.3 Pilot and Demonstration Plants

Pilot and demonstration plants are of particular interest because they are a testament to how zeolites can be produced on a commercial scale; they facilitate improvement in the process, and produce large quantities of zeolite for application testing. Four references to such facilities have been cited in the literature made known to the authors.

1. A demonstration plant built by Nippon Steel in Japan produces a powder coal ash zeolite for ¥40,000/t, and fly ash zeolite pellets for ¥70,000/t (Sloss, *et al.* 1996)
2. A pilot plant study commissioned by the European Coal and Steel community has demonstrated a high degree of reproducibility between laboratory scale testing (g and kg scale synthesis performed in laboratory) and pilot scale (metric tonne sample size) processes (Querol, *et al.* 2001).
3. Details from a semi industrial scale coal fly ash zeolitisation experiment are presented by Kikuchi (1999); the process flow diagram is given in Figure 9.26 below. This plant produces 1.2 t/h of zeolite from 1.5 t/h of fly ash.
4. A commercial zeolite manufacturing plant is operated by Maeda Corporation, in Osaka Japan, which produces artificial zeolite products from fly ash, which are used in water-purification, heavy metal adsorption and deodorising applications (Maeda 2003).

* For example, for the hydrothermal treatment of fly ash using a fixed 3 hour reaction time and a fixed pH using a NaOH and KOH solution, increasing the sodium concentration results in increased zeolite P yield, and an increasing potassium chabazite yield for sodium concentration less than potassium concentration, starting from no potassium chabazite when sodium concentration is zero (Murayama, *et al.* 2002b; a)

[†] Following 12h of aging of NaOH fused fly ash, and hydrothermal synthesis at 100°C, Shigemoto *et al.* (1993) produced NaX with 62% yield, and NaA by enriching reaction mixture with aluminium, while Berkgaut and Singer (1996) produced NaX with CEC of 400 meq/100g, and without aging NaP was produced with CEC of 420 meq/100g

[‡] Following zeolite A seeding and aging of NaOH fused fly ash, Rayalu *et al.* (2001) produced zeolite A with 50-100% yield and a CEC of 290 to 560 meq/100g using hydrothermal synthesis at 90-105°C

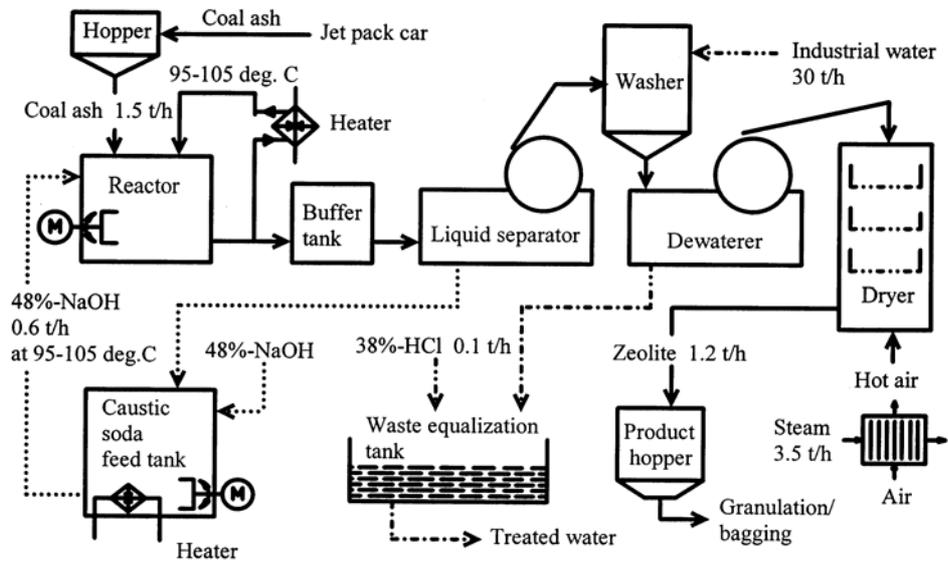


Figure 9.26: Process flow diagram of a 1.2 tonne per hour coal fly ash zeolitisation plant, reproduced from Kikuchi (1999)

Appendix 4 Justification for Research

The following sections document and justify the progressive evolution of project philosophy and direction which evolved over the course of PhD work.

A4.1 Fly Ash Utilisation

The objective of this work is to contribute to the arena of fly ash utilisation in a direction which has real potential to lead to the capability of significantly increasing fly ash utilisation. There are two broad avenues for research into fly ash utilisation, they relate to i) fly ash quality, and to ii) utilisation strategies.

A4.1.1 Ash Quality

Although fly ash quality may currently be an issue for some ash producers it is not preventing ash utilisation as a whole in Australia. For example the cement industry, which has strict quality requirements, is consuming close to all the ash it can.

The changing environmental and regulatory climate in Australia may lead to changes in boiler operation, fuel use, and emission mitigation technologies, with a major impact on ash quality Australia wide, which will threaten the current state of fly ash utilisation. Research into issues related to fly ash quality may help prevent such reductions in ash utilisation, however maintaining or improving fly ash quality can not contribute to a significant increase on the current state of fly ash utilisation.

A4.1.2 Utilisation Strategies

There are a number of known fly ash utilisation strategies, see Figure 9.1, each having its own advantages and disadvantages, and some form of barriers. In the interest of selecting the right strategy to meet research objectives, the following concepts need to be considered, the strategy needs:

- to be high volume, capable of consuming a significant quantity of fly ash
- to be significantly value-added so that it is not inhibited by the transport cost barrier
- to be a new product or explore new applications or markets for fly ash, so that it is not inhibited by market inelasticity
- to be inhibited by significant technical barriers where research can make a difference

By deduction, zeolites and geopolymers prevail as viable candidates, from which zeolites were chosen as the focus of this thesis.

A4.1.3 Refined Objective

A zeolite strategy for fly ash utilisation offers significant technical challenges worth tackling as part of a PhD, and is consistent with the philosophy of broad project objectives. Zeolites offer significant added value to overcome the transport cost barrier, and have application in a diverse range of products, including agricultural markets currently not exploited by fly ash, and potentially of high volume. Therefore zeolites have the potential to contribute to a significant increase in fly ash utilisation beyond its current state.

There are a number of different types of zeolites, offering a diverse range of applications. Like fly ash it is recognised that the current market for zeolite will not represent the full range of potential zeolite applications, nor will its current size represent its potential size. The revised objective is;

To study the potential products and markets for zeolites in Australia, and identify the best opportunities to support a zeolite fly ash utilisation strategy which has real potential to lead to the capability of significantly increasing fly ash utilisation.

A4.2 Zeolite Markets

A4.2.1 Zeolite Market Philosophy?

The following market requirements were identified previously as crucial in qualifying a fly ash utilisation strategy as a viable avenue for research:

1. to be high volume, capable of consuming a significant quantity of fly ash
2. to be significantly value-added so that it is not inhibited by the transport cost barrier
3. to be a new product or explore new applications or markets for fly ash, so that it is not inhibited by market inelasticity

Controlled release fertiliser and soil conditioner markets are the largest potential markets for zeolite in Australia (A2.2), they are high volume and capable of consuming a significant quantity of fly ash, and have sufficient value to overcome the transportation cost barrier.

Coal mines are often connected to power stations as well as major shipping ports with rail infrastructure to meet their transport requirements for domestic and export markets. A fly ash to zeolite manufacturing plant located in proximity to this infrastructure will be in a good position to export zeolite products around the world. Exploring international markets greatly increases the capacity for large economies of scale to be achieved, and can potentially contribute to significant if not complete utilisation of Australia's fly ash production.

Zeolite products all engage markets that are not currently employed by fly ash products. These markets are the domain of established products and practices, and consequently represent an environment where new zeolite products will have to compete for market share. Ultimately the achievable market size will be governed by:

1. Sale Price
2. Performance
3. Marketing

For the evaluation of potential market volumes and values, a sale price for zeolite fertiliser products was assumed which is cost competitive with established fertiliser products was assumed. Key factors associated with achieving such a competitive sale price include:

1. Capital requirements
2. Operating costs (in particular raw materials)
3. Economies of scale

Zeolite fertiliser and soil conditioner products offer superior environmental and application specific performance advantages which give them a competitive advantage.

Zeolites have significantly greater potential for profitability than most other fly ash utilisation strategies. To establish production infrastructure in the short term, the first markets exploited would need to be at the higher end of target markets (e.g. domestic and high intensity fertiliser markets, or hydroponics and potting mix soil construction markets), followed by a shift to all markets in the longer term.

A4.2.2 Zeolite Production Objective?

The objective of this work is to contribute to the arena of fly ash utilisation in a direction which has real potential to lead to the capability of significantly increasing fly ash utilisation. Zeolites produced from fly ash for application in fertiliser and soil conditioner markets have been identified as having the greatest potential to achieve this objective; however given

- that the principles behind the application of zeolite as a fertiliser and a soil conditioner are well known
- that performance based research has a prerequisite of products to benchmark
- the infancy of zeolite fertiliser technology and markets
- the importance and uncertainty in the current capacity to produce fly ash zeolite products at a competitive price

The revised objective is;

To study the process of producing zeolite from fly ash for controlled release fertiliser applications with an eye on multiple products and cost minimisation.

A4.3 Zeolite Production

A4.3.1 Considerations: Coal Fly Ash a Raw Material for Zeolite Synthesis

There are existing processes and raw materials for the manufacture of synthetic zeolites, this section is intended to layout from a technical and processing perspective what advantages can be gained from the use coal fly ash for the production of zeolites in general.

Disadvantages

- Contains some low reactivity components (quartz and mullite) which dissolve slowly
- Contains some impurities
 - Some of which form part of the products produced (e.g. iron oxides, unburned carbon)
 - Some of which are released into the base solution (e.g. As, Se, Mo, B, and P)

Advantages

- Already processed to a finely divided form appropriate for use (no crushing, grinding or clarification requirements)
- Aluminium and silicon already present predominantly in reactive glass phase, no additional calcination (energy intensive) required as in the case of clays
- Low value raw material relative to soluble silicates and soluble aluminates
- Large reliable raw material source with significant unused annual production and significant stockpiled reservoirs
- Geographically located close to major population centres and rural centres
- Size and location distribution of coal fly ash is analogous to potential size and location of zeolite markets
- Low synthesis temps (as low as 100°C) means that a process located near a power station (coal ash source) may satisfy most process heating requirements using low grade heat from the power station, in addition to all of its electricity requirements.

The disadvantages may prevent the application of a fly ash zeolite product in some specialised applications, depending on the production process (Direct and Alkali fused synthesis versus silica extracts synthesis methods), but do not prevent its application in large scale applications

such as agricultural* and waste processing applications. Overall there are certainly significant advantages in using fly ash which will help consolidate process economics.

A4.3.2 Knowledge Gaps

Fly ash, an aluminosilicate composite containing many impurities, is a non standard material with significant technical gaps regarding its use. A basic process flow for a zeolite processing plant using fly ash as the aluminosilicate source is presented in Figure 9.27 below which illustrates the configuration of various process options.

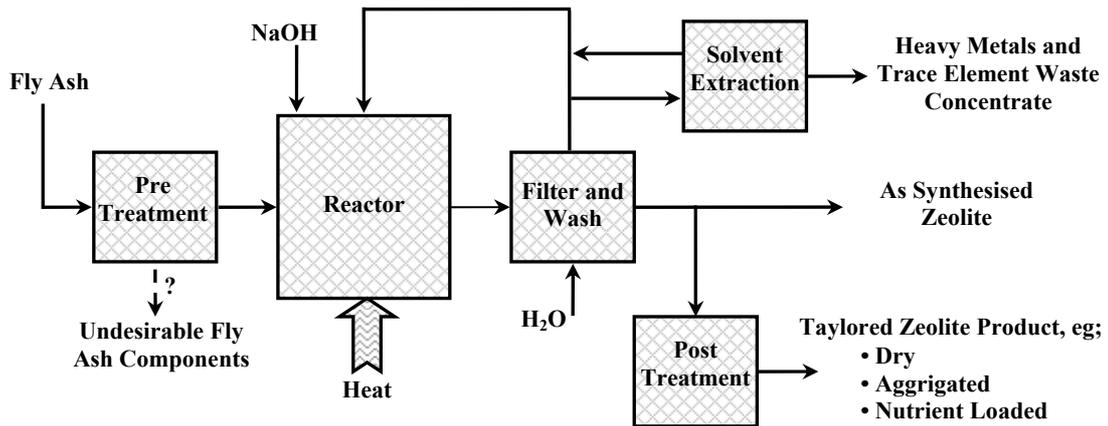


Figure 9.27 : Conceptual process flow diagram for a zeolite synthesis plant employing fly ash as the aluminosilicate source

The research path to commercial products is illustrated in Figure 9.28 below, with the essential stages represented by shaded diamonds. The clear diamonds represent non essential stages whose insight may increase our knowledge of the process allowing greater product control and higher quality products, and potentially cheaper operation.

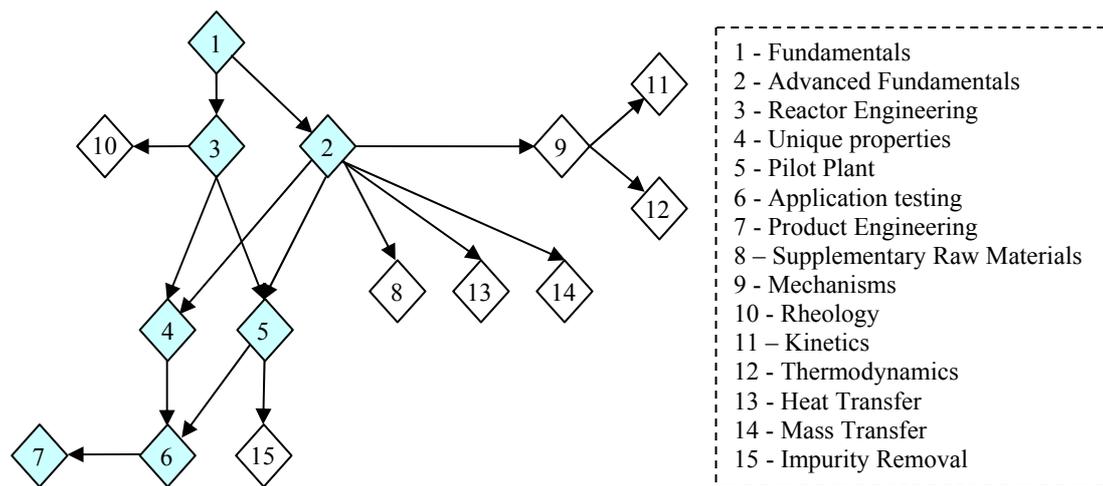


Figure 9.28 : Research path for the commercial production of fly ash zeolites

* Trace elements and heavy metals are of potential concern for agricultural applications and should be subject to investigation and verification

Broad explanations of the different stages which make up the research path illustrated in Figure 9.28 above:

1. The suitability of different Australian fly ashes (including ponded ash) in zeolite synthesis, identification of likely zeolite products and product quality, the development of a method for fly ash zeolite synthesis, and identification of optimal reaction conditions
2. Identification of the influence of fly ash components and properties on zeolite synthesis, developing pre-synthesis treatments, if required, to improve zeolite product quality, and modelling the integration of a zeolite strategy into other fly ash utilisation strategies
3. Investigation of continuous reactor configurations and design, resulting in the identification of most suitable reactor system for commercial synthesis
4. Identification of the properties unique to fly ash zeolites, and their effect on zeolites utilisation
5. Pilot plant and zeolite synthesis process demonstration; further process optimisation, development, and promotion of fly ash zeolites to potential markets
6. Application testing and demonstrations of fly ash zeolites improving the understanding of performance, cost effectiveness, and property requirements
7. Development of fly ash zeolites to meet specific product requirements, including changes to production conditions, and post synthesis treatments such as drying, aggregation and nutrient loading
8. Investigate the use of other waste materials (e.g. red mud) as supplementary raw materials in the synthesis of zeolite from fly ash
9. Investigate formation mechanisms and intermediate products of zeolite synthesis from fly ash to gain greater insight into the process
10. Investigate the effect of rheology on synthesis products
11. Investigate chemical kinetics (rate of reaction) of zeolite synthesis from fly ash to gain greater insight into the process
12. Investigate thermodynamics (equilibrium constant) of zeolite synthesis from fly ash to gain greater insight into the process
13. Investigate heat transfer effects upon zeolite synthesis from fly ash to gain greater insight into the process
14. Investigate mass transfer effects upon zeolite synthesis from fly ash to gain greater insight into the process
15. Investigate and design an impurity removal system from synthesis plant reaction liquors, and investigate the possible recovery of metals and compounds from impurity concentrates

A4.3.3 Experimental Objective

The direct hydrothermal conversion of fly ash to zeolite was chosen as the synthesis method to study, as it is perceived by the author to be the lowest cost method for producing zeolites, due to fewer processing steps and lower energy requirements than silica extracts and alkali fusion methods. In particular a continuous hydrothermal reaction system was identified as the most cost effective reactor configuration for producing zeolites from fly ash due to lower energy requirements, and higher capacity throughput than batch processing.

The situation summarised by Barrer and Cole in 1970 is as relevant today as it was then, especially in relation to the use of fly ash for zeolite production.

“The art of synthesizing molecular sieve zeolites has developed more quickly than the chemical science which would properly account for their formation in nature and in the laboratory from apparently simple aluminosilicate compositions”

(Barrer and Cole 1970)

To this end there are three questions whose study would contribute significantly to the science and subsequently improve the art of producing zeolite from fly ash;

1. How does fly ash heterogeneity in terms of phases (glass, quartz, and mullite) and composition (particularly iron) affect its performance as a raw material in zeolite synthesis?
2. What is the influence of hydrothermal chemistry on the performance of fly ash as a raw material?
3. What is the influence of continuous processing on the performance of fly ash?

The revised objective is;

To study the influence of ash properties, hydrothermal chemistry, and continuous processing on the hydrothermal synthesis of zeolite from fly ash.

Appendix 5 Conceptual Process Development and Mass Flows

The objective of developing a process flow sheet with mass balance based on ideal processes (perfect mixing, separation, equilibria etc, in a mixed flow reactor system) for a zeolite fertiliser manufacturing plant, is to illustrate how the manufacture of zeolite fertiliser from fly ash works in practical terms, roughly how big the component items of manufacturing plant are, and to facilitate the determination of crude ballpark economic figures based on simple and reasonable assumptions (see Section A5.1).

From the economic case study presented at the World of Coal Ash (WOCA) Conference in Kentucky (A5.1.1), we know that for economic viability at a competitive sale price constraints will exist on the operating conditions. The model presented here operates within these constraints, however differs on account of its increased complexity.

This model is based on a 300 kt per annum consumption of idealised fly ash (containing SiO_2 , Al_2O_3 and Fe_2O_3 only) based on ash produced in the Collie region of Western Australia which includes a substantial weight percent of iron (see Table 9.9). The process configuration used is presented in Figure 9.29. For simplicity the NaOH and KCl raw material and H_2O inputs are assumed to be pure. A list of all material property, equipment sizing, operating conditions and constraints, and equipment sizing outputs can be found in Tables 9.9 and 9.11. A full mass balance for all streams, including zeolite phase compositions is presented in Tables 9.12 and 9.13, and a summary of annual production statistics is presented in Table 9.14. The final packaged fertiliser product contains 9.45 wt% K^+ and 1.41 wt% Na^+ , where both Na and K are present as charge balancing cations in zeolite and as chlorides. The final packaged fertiliser product contains 4.7 wt% free moisture with a pH of 12.1.

Table 9.10: Equipment sizing constraints

Component	Equipment Capacity		Units
	Min	Max	
Solid bowl centrifuge	2	55	t h ⁻¹
Rotating drum dryer	5	900	t h ⁻¹
Vacuum filtration ^[A]	0.5	100	m ²
Dry solids hopper ^[B]	1	100	m ³
Agitated tank ^[B]	0.5	75	m ³
Reactor ^[B]	0.1	30	m ³
Open – liquids storage tank ^[B]	1	10000	m ³

[A] Using a factor relating filtration surface area to mass flow of 0.2 t h⁻¹ m⁻², [B] Assuming a fraction of total vessel capacity available for use of 0.8

Table 9.11: Equipment sizing results

Item		Total number ^[A]	Individual capacity	Units
Code	Description			
C01	Centrifuge ^[B]	3	40.6	t h ⁻¹
C02	Centrifuge ^[B]	3	43.6	t h ⁻¹
C03	Centrifuge ^[B]	3	44.5	t h ⁻¹
D01	Dryer ^[C]	3	5	t h ⁻¹
F01	Filtration and wash ^[D]	9	78.6	t h ⁻¹
F02	Filtration and wash ^[D]	6	89.8	t h ⁻¹
F03	Filtration and wash ^[D]	6	89.2	t h ⁻¹
H01	Solid NaOH storage hopper ^[E]	3	84.5	m ³
H02	Solid fly ash storage hopper ^[E]	12	94.7	m ³
H03	Solid KCl storage hopper ^[E]	4	76.7	m ³
M01	Reactor solution preparation tank ^[F]	6	41.5	m ³
M02	Re-slurry mixing tank ^[G]	3	34.4	m ³
M03	Re-slurry mixing tank ^[G]	3	34.1	m ³
M04	Nutrient loading tank ^[H]	9	51.1	m ³
M05	Nutrient loading tank ^[H]	9	54.6	m ³
M06	Nutrient loading tank ^[H]	12	62.2	m ³
M07	KCl solution preparation tank ^[I]	2	69.3	m ³
P01	Product packaging plant	1	58.4	t h ⁻¹
R01	Reactor ^[J]	18	25.5	m ³
T01	Water storage tank ^[E]	1	4050	m ³
T02	Recycle feed tank ^[K]	3	25.8	m ³
T03	Recycle feed tank ^[K]	3	25.6	m ³

[A] The total number of trains is calculated from reactor requirements, where the minimum number of reactors per train is 6, the centrifuges, dryer, vacuum filtration, and mixing tanks have a minimum requirement of one per train, and all other items have a minimum requirement of one item [B] Based on a 25 wt% moisture in solid concentrate and 100% solids recovery in solids concentrate stream, [C] Based on 5 wt% aqueous phase in product, [D] Based on a 20 wt% moisture in filter cake, [E] Based on a 48 hour storage capacity, [F] Based on a 2 hour storage capacity, [G] Based on a residence time of 1 hour, and a ratio of H₂O mass flow in streams T02-M02 and T03-M03 to that in stream R01-F01 of 0.5, [H] Based on a residence time of 4 hours, and a cation exchange selectivity of K over Na of 3 (see Equation A2.3), [I] Based on a storage capacity of 2 hours, a KCl solution concentration of 3 moles per kg, and a ratio of moles of KCl in stream H03-M07 to moles of Na in zeolite in stream F03-M04 of 1.2, [J] Based on a H₂O/Al mole ratio of 25 for reactants, a percent conversion of aluminium in fly ash of 60%, a pH14 reaction solution, and a residence time of 3 hours, [K] Based on a storage capacity of one hour

Table 9.12: Process streams – bulk flow (t h⁻¹)

Stream	Fly ash	Zeolite	H ₂ O	NaOH	NaCl	KCl	Total
Reactor section streams							
F01 – M01	---	---	92.2	3.73	---	---	95.9
F01 – M02	18.1	32.2	12.6	0.36	---	---	63.3
F02 – M03	18.1	32.2	12.6	0.16	---	---	63.1
F02 – T02	---	---	61	1.13	---	---	62.1
F03 – M04	18.1	32.2	12.6	0.04	---	---	62.9
F03 – T03	---	---	61	0.41	---	---	61.4
H01 – M01	---	---	0	5.07	---	---	5.07
H02 – R01	39.6	---	2.08	---	---	---	41.7
M01 – R01	---	---	92.2	8.8	---	---	101
M02 – F02	18.1	32.2	56.3	1.17	---	---	108
M03 – F03	18.1	32.2	56.3	0.46	---	---	107
R01 – F01	18.1	32.2	87.5	3.77	---	---	142
T01 – F03	---	---	17.3	---	---	---	17.3
T02 – F01	---	---	17.3	0.32	---	---	17.6
T02 – M02	---	---	43.8	0.81	---	---	44.6
T03 – F02	---	---	17.3	0.12	---	---	17.4
T03 – M03	---	---	43.8	0.3	---	---	44.1
Nutrient loading and product handling streams							
C01 – M05	18.1	32.9	17	0.0155	2.01	0.27	70.3
C01 – WH	---	---	45.5	0.0415	5.39	0.72	51.7
C02 – M04	---	---	49.9	0.0142	5.55	3.25	58.7
C02 – M06	18.1	33.6	17.2	0.0049	1.91	1.12	71.9
C03 – D01	18.1	34	17.4	0.0013	1.01	2.52	73
C03 – M05	---	---	50.2	0.0037	2.93	7.28	60.4
D01 – P01	18.1	34	2.74	0.0013	1.01	2.52	58.4
F03 – M04	18.1	32.9	62.5	0.057	---	---	114
H03 – M07	---	---	---	---	---	11.3	11.3
M04 – C01	18.1	32.9	62.5	0.057	7.4	0.99	122
M05 – C02	18.1	33.6	67.1	0.0192	7.46	4.37	131
M06 – C03	18.1	34	67.5	0.0049	3.94	9.8	133
M07 – M06	---	---	50.3	---	---	11.3	61.6
P01 – PFP	18.1	34	2.74	0.0013	1.01	2.52	58.4
T01 – M07	---	---	50.3	---	---	---	50.3

Table 9.13: Composition of zeolite phase at different stages of nutrient loading

Stream	Zeolite Composition (wt%)				
	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	H ₂ O
F03 – M04	46.9	19.9	12.1	0	21.1
M04 – C01	46.2	19.6	9.06	4.35	20.8
C01 – M05	45.2	19.2	4.91	10.3	20.4
M05 – C02	44.5	18.9	1.68	14.9	20
C02 – M06					
M06 – C03					
C03 – D01					

Table 9.14: Annual production statistics

Statistic	Value	Units
Fly ash consumption	300	kt
Fertiliser production (zeolite)	245	kt Zeolite
Sale price (zeolite)	160	\$AU per tonne of zeolite
Fertiliser production (total)	420	kt Total
Sale price (total)	93.3	\$AU per tonne of total product
NaOH consumption	36.5	kt
KCl consumption	81.4	kt
H ₂ O consumption	487	kt

Nitrogen based fertilisers could be produced using ammonium salts the same way as present in model, to lower overheads, the raw sodium zeolite could be used to extract ammonia from sewage waters, from aquaculture waters, from industrial waste streams of processes employing ammonia (like the Kwinana Nickel Refinery in Western Australia), and the resultant nitrogen containing zeolite used directly as a fertiliser, or after additional loading in a circuit using ammonium salts.

The potassium present in waste stream C01 – WH can be recovered using a high selectivity organic exchange resin which is regenerated using HCl, with the resultant KCl, HCl mixture injected back into vessel M04, where the HCl will neutralise NaOH, this will result in a product with neutral pH, as apposed to the pH 12.1 product in basic model. In addition water can be recovered from waste stream C01 – WH using reverse osmosis to significantly reduce volume of waste stream to a concentrated NaCl brine, as well as reducing the net input of fresh water.

For simplicity this model did not include minor and trace elements in the composition of fly ash. A significant portion of these elements will be liberated into solution from the fly ash in the reactor and accumulate within the process recycle loops. They can be removed from the system by employing a parallel solvent extraction circuit between F01 and M01 to produce small concentrate waste streams of these elements.

A5.1 Economic Modelling

To get an idea of the core relationships between economic viability and processing conditions, in particular reaction time and the H₂O/Al reactant mole ratio (p), a basic economic model was developed (A5.1.1) which formed the basis from which a more sophisticated process flow and mass balance model was developed (see Section Appendix 5), making possible more sophisticated economic analysis of the feasibility of process, as presented in A5.1.2.

A5.1.1 Basic Economic Model

To give a basic idea of the economic implications of processing conditions some crude economic calculations are presented below based on reasonable assumptions.

Assuming a 300 kilo-tonne per annum zeolite plant, which sells product for \$AU150 per tonne of zeolite, has an operating cost of \$AU100 per tonne, operates under a 30% corporate tax rate, with a 10 year double declining depreciation period, a 15 year project life span, and a 10% discount rate. For a present value ratio of 1, the fixed capital investment is \$AU100 million.

With a maximum reactor size of 30m³ (Garrett 1989), and assuming that 80% of this volume is available for solid and liquid reactants, 300 days of 24 hours continuous operation (continuous reactors), assuming that solids (fly ash, zeolite and sodium hydroxide) have a specific gravity of 2. Assuming a pH of 14.3, an x of 1 (see Equation 4.1), and an aluminium (Al₂O₃) composition equal to 25wt% of fly ash, where 1 tonne of zeolite is produced per tonne of fly ash. Then 20 reactors are required per hour of residence time per 100 units of p.

The 30m³ reactor cost \$US60,000 in 1987 (Garrett 1989). Using a ChE index of 324 in 1987 (Vatavuk 2002), and an extrapolated index of 404 for 2005 (Anonymous 2004), a location factor of 1.3 for Australia (Garrett 1989), an exchange rate of \$US0.75 per \$AU. Assuming a plant cost factor of 4, and that the reactor section of whole plant cannot exceed 10% of FCI, there is a 19 reactor limit. For a 3 hour residence time, p is limited to 32 which is equivalent to 11.3 g H₂O per g Al₂O₃ in fly ash.

A5.1.2 Process Based Economic Analysis

To gain a more sophisticated idea of the economic issues facing a zeolite fertiliser manufacturing process employing fly ash as the aluminosilicate source a process based economic case was developed.

The general economic inputs used are listed in Table 9.15, which in addition to equipment sizing (see Table 9.11) and annual production figures (see Table 9.14) calculated through process mass balances (see Section Appendix 5), was used to calculate the economic outputs presented in Table 9.16.

Table 9.15: General economic inputs

Variable	Value	Units
Sale price	160	\$AU per tonne of zeolite
Operating cost	100	\$AU per tonne of zeolite
Corporate tax rate	30	%
Operating life	15	Years
Period of double declining depreciation	10	Years
Discount rate	10	%
Exchange rate	0.75	\$AU/\$US
Location factor (Australia)	1.3	
Plant cost factor	4	
Reactor stage limit	10	% of FCI

Table 9.16: Economic outputs (Indices)

Index	Value	Units
FCI ^[A]	83.5	Million \$AU
PBP	6.33	Years
CCP	2.14	
ROROI	14.3	% pa
DPBP	11.1	Years
NPV	11.3	Million \$AU
PVR	1.13	

[A] Based on the quantity and size of reactors (see Table 9.11), the assumption that the total installed cost of reactors and support infrastructure is equivalent to 10% of FCI, using Equation 4.6 for reactor scale up, with reference reactor of 2.3 m³ (S_R) costing \$US 15,000 in the US for 1987 (C_R) at a cost exponent (n) of 0.53 (Garrett 1989). Using a ChE index of 324 for 1987 (Vatavuk 2002) and 404 for 2005 (Anonymous 2004), and using exchange rate, location factor, and plant cost factors listed in Table 9.15.

$$C = C_R \left(\frac{S}{S_R} \right)^n \quad (4.6)$$

(Garrett 1989)

This model assumes an operating cost of \$AU 100 per tonne of zeolite produced (245 kt of zeolite per annum). In the context of NaOH* and KCl† consumption figures (36.5 and 81.4 kt per annum respectively) this may be insufficient. However given Muriate of Potash (KCl, 60% K₂O equivalent) is selling locally as a fertiliser for \$AU395/tonne in 2002 (UFCC 2002), and the substantial efficiency of a zeolite based fertiliser there is room for sale prices higher than the \$AU 160 per tonne of zeolite assumed in model.

* Caustic soda flakes (99% NaOH) cost \$US 215 per tonne in 2002 (Anonymous 2002), alternatively natural soda ash (Na₂CO₃) could be sourced at \$US 69 per tonne in 2004 (Kostick 2005), but would require calcining to produce Na₂O consuming energy and emitting CO₂ as a decomposition product, as well as adding 30% to the weight of transport. Alternatively if NaOH is produced locally it can be purchased at a fraction of the cost as a 50wt% aqueous solution, or can be produced on site by electrolysis of sea water or brine from waste stream C01 – WH in process flow, and producing Cl₂ as an additional product.

† Murate of potash could be sourced in the USA for \$US 170 per tonne of K₂O equivalent f.o.b. mine in 2004 (Searls 2005), this represents \$US 107 per tonne of KCl. However to reduce overheads the bulk of potassium requirements (70%) can be met using a lower grade potassium source such as Sylvinitite (mixed NaCl, KCl), by reconfiguring nutrient loading section of process flow so that Sylvinitite sourced potassium is introduced into M05, with Murate of Potash sourced potassium introduced into M06 equivalents to current process flow configuration.

Appendix 6 Conclusions, Recommendations and Reflections

A6.1 Conclusions

A number of different topics have been covered and contributions made in this thesis, for clarity they have been broken up into nine components of relevance as illustrated in Figure 9.30 below.

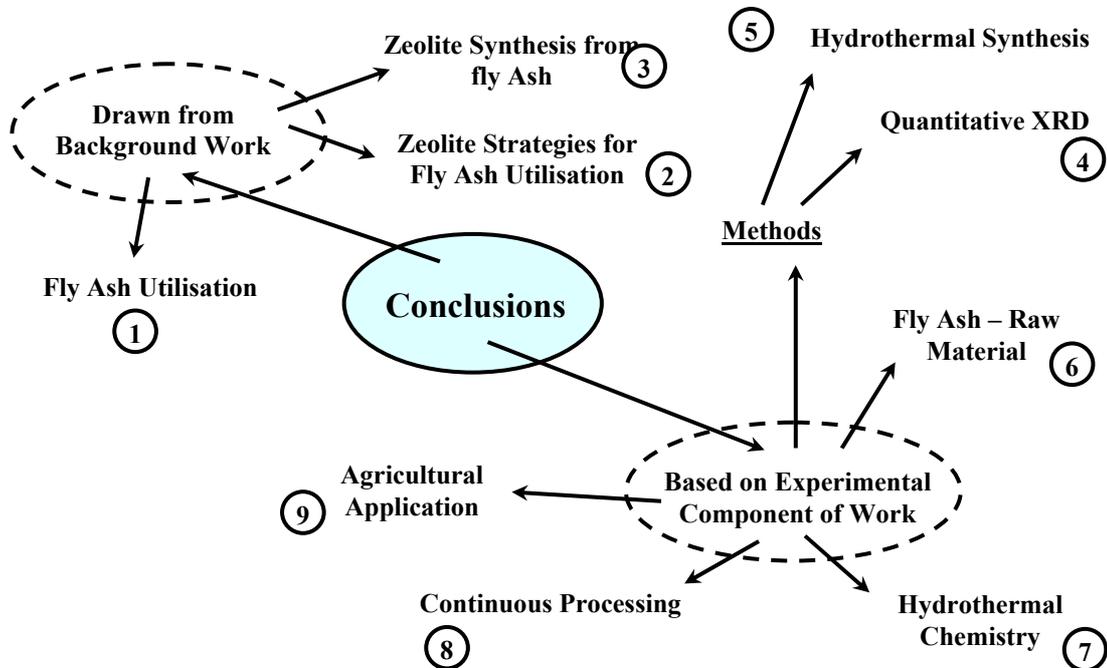


Figure 9.30: Classification of the nine key issues which constitute the conclusions

Fly Ash Utilisation

Near the conclusion of this thesis, the latest statistics (2004), reveal that 12.5 million tonnes was produced by Australian coal-fired power stations with only 35% utilised in some way (ADAA 2006). Numerous applications have been available for some time which are more than capable of consuming all the ash produced however they do not, this situation can be explained in terms of technical, economic and perceptual barriers. By removing these barriers, the subsequent fly ash utilisation can play an important role towards coal in sustainable development.

1. *Technical barriers can be overcome through research and development*
2. *Perceptual barriers can be overcome through education and demonstration*
3. *Economic barriers can be overcome by finding alternative products or markets, lowering production costs, increasing product value, or lowering transportation costs*

There are two broad avenues for research into fly ash utilisation, they relate to i) fly ash quality, and ii) utilisation strategies. To solve this problem, fly ash utilisation strategies need to be

1. High volume, capable of consuming a significant quantity of fly ash
2. Significantly value-added so that it is not inhibited by the transport cost barrier
3. Exploring new applications, products, or markets for fly ash, so that it is not inhibited by market inelasticity

Zeolite Strategies for Fly Ash Utilisation

Controlled release fertiliser and soil conditioner markets are the largest potential markets for zeolite in Australia, they are high volume and capable of consuming a significant quantity of fly ash, with sufficient value to overcome the transportation cost barrier, have significant potential to be exported, and can potentially contribute to significant if not complete utilisation of Australia's fly ash production.

Zeolite fertiliser and soil conditioner products offer superior environmental and application specific performance advantages which give them a competitive advantage; however, in spite of all the technical and environmental advantages, the success of this strategy is subject to a process design which can achieve a return on investment at a viable product sale price.

Zeolite Synthesis from Fly Ash

Zeolite manufacture is not new. Well established manufacturing plants exist which produce zeolites for industrial absorbers and adsorbents, ion exchangers, and catalyst applications, as well as water softeners in powder detergents, using calcined kaolinite or other more expensive aluminosilicate sources, and recent years have seen plants using fly ash come into service. These plants produce small quantities of zeolite at great cost, making them unviable for agricultural applications.

To be viable, the zeolite production process needs to be redesigned to incorporate coal fly ash as a raw material, while increasing capacity, and reducing costs. To this end, a process for the continuous hydrothermal conversion of fly ash to zeolite using a sequence of mixed flow reactors in series will be required.

Quantitative XRD Methodology

The outcomes of hydrothermal treatments have traditionally been evaluated qualitatively from phase identification using XRD or quantitatively using CEC or individual XRD peak intensities. However CEC results can not distinguish between different zeolite phases and are a function of both zeolite yield and Si/Al ratio, and single peak correlations carry substantial experimental uncertainty, and peak overlap limitations, therefore a quantitative XRD method was developed using Rietica, which is capable of quantifying changes in the composition of quartz and mullite reactants, and zeolite products with changes in hydrothermal reaction conditions, revealing more information and allowing direct comparisons of the changes taking place with changing conditions, and has proved invaluable in distinguishing between and quantifying complicated crystalline products, and subsequently distinguishing between the roles of M^+ and OH^- in the chemistry of hydrothermal treatment.

This technique is still subject to significant uncertainty which introduces a bias in the results; some methods have been proposed which will help reduce these experimental uncertainties (see Section A6.3).

Hydrothermal Synthesis Methodology

Treatment conditions for the hydrothermal synthesis of zeolites from fly ash have traditionally been defined by the ratio of the volume of sodium hydroxide solution to the mass of fly ash, and by the concentration of sodium hydroxide in solution. However this method is incapable of distinguishing between the role of M^+ and of OH^- in the chemistry of hydrothermal treatment. To investigate these phenomena, a new method was developed and used, which makes use of MnO_3 , and where reaction conditions are defined by the mole ratios OH/H_2O , H_2O/Al (p), and

m (the ratio M^+/Al in excess of stoichiometry). The decisive results of Section 4.3 demonstrate the independent role of M^+ and OH^- in the hydrothermal chemistry, therefore the value of this technique when studying the hydrothermal treatment of fly ash.

Fly Ash – a Raw Material in Zeolite Synthesis

Fly Ash is a heterogeneous material, physically, chemically, and mineralogically. Established understanding within literature of the participation of different fly ash components towards the hydrothermal outcome is basic, and with respect to quartz and mullite, is often contradictory. Un-reacted fly ash particles can be identified within the hydrothermal treatment product using SEM, and unreacted quartz and mullite as well as total X-ray amorphous content can be quantified from XRD diffractograms. Therefore the participation of fly ash reactants towards the hydrothermal outcome can be evaluated.

Glass is the most reactive phase in fly ash. The significant presence of iron does not prevent the significant dissolution of glass by an alkaline hydrothermal solution. Increased iron content in glass reduces its reactivity, with high iron glass dissolving near the end of hydrothermal treatment. The higher the average glass phase iron content, the lower the overall yield of zeolites, where the dissolution of iron containing glass has resulted in iron containing zeolites, although it is not known how this iron is incorporated within the zeolite phase (within framework, as a charge balancing cation, or discrete nano-particles).

Quartz particles are often large and subsequently have small surface areas; however the appearance of significant internal etching following hydrothermal treatment is testament to their reactivity. The participation of quartz is a function primarily of its initial content in fly ash and its particle size.

The shrinking core dissolution of glass exposes mullite crystals, where a small with high surface areas, to the hydrothermal solution; the participation of mullite is in part a function of the particle size of the fly ash particles within which it is encapsulated. Mullite is less reactive than glass and quartz. However at pH14.6m30 (HTP 88), mullite completely dissolved while quartz did not, probably due to the substantially smaller size of mullite crystals relative to large quartz particles.

There is no evidence that iron mineral phases are dissolving, and as such are not considered to be contributing to the hydrothermal outcome.

Hydrothermal Chemistry

Different types of zeolite can be produced from fly ash by changing reaction conditions. Using quantitative XRD the influence of reaction conditions on the types and yields of zeolite and the different contributions of reactants can be quantified.

Most of these experiments were conducted using non-agitated reactors where mass transport and sedimentation profiles are a major limitation. All of the hydrothermal treatment conditions considered here were conducted at $p = 400$ to minimise these phenomena while still producing sufficient material for characterisation requirements; although these phenomena are still present they should be equivalent for all reaction conditions using the same ash. Therefore they do not impact on the study of these reaction conditions.

The influence of treatment conditions on hydrothermal outcomes which have been established in literature from qualitative experimental results, have been repeated here using quantitative XRD technique. Increasing reaction temperature results in increased quartz dissolution, decreased yields of “other” phases (iron mineral and X-ray amorphous phases), and increased yields of zeolite. Increasing reaction time results in increased zeolite yield and increased quartz dissolution, and the inclusion of different template cations changes the type and relative yields of zeolite phases produced.

The Si/Al ratio of the aqueous phase during hydrothermal synthesis has been established by previous authors as a significant influence on the types of zeolite produced. The quantitative mineral analysis of hydrothermal treatment products produced using different fly ashes was unable to identify any correlation between CHA and GIS yields and the Si/Al ratio (glass or bulk), with glass phase Fe₂O₃ composition, or with quartz or mullite contents in fly ash. The absence of any definitive correlations between the types and yields of zeolite produced and individual ash properties suggests that they are complicated functions of multiple properties.

The results of seeding experiments suggest that the role of seeds during hydrothermal treatment is more complicated than that described in literature. Under some conditions the addition of seed can have a significant impact on the types and yields of zeolite produced, while under other conditions the addition of seed had no observable effect. There is considerable scope for more research into the influence of seeding on the hydrothermal outcome.

In order to differentiate between the role of M⁺ and OH⁻ within the chemistry of hydrothermal treatment, sodium hydroxide and sodium nitrate were used together to independently control the quantities of M⁺ and OH⁻ within the hydrothermal system, in conjunction with quantitative XRD analysis of products produced. From the results it is clear that M⁺ and OH⁻ play a different role in the overall reaction mechanism, where:

6. The dissolution of reactants is most strongly correlated to the OH⁻ concentration, with increasing pH resulting in increased dissolution of glass, quartz, and mullite.
7. The types of zeolite produced are clearly most strongly correlated to m. Increasing m at constant pH increases the yield of a particular zeolite until a maximum is achieved, after which further increases in m result in a decrease in yield. CHA is produced and yields are optimised at m < 10, while SOD and CAN are produced at m > 5. For constant pH, CAN is favoured and optimised at low m relative to x = 1, while SOD is favoured and optimised at high m relative to x = 1
8. Since zeolite yields substantially increase with increasing m starting from x = 1 (at low m relative to x = 1). Considering that the additional MNO₃ is occupying soluble space, increased M⁺ concentration must be increasing reaction rates.
9. The presence of MNO₃ clearly has two conflicting affects:
 - iii. At low m, relative to x = 1, its impact on increased reaction rates dominates, with increased reaction rates removing dissolved Al and Si from solution faster allowing faster dissolution of reactants (glass, quartz, and mullite) and increasing overall yield.
 - iv. At high m, relative to x = 1, the occupation by MNO₃ of soluble space dominates reducing the dissolution rates of reactants (glass, quartz, and mullite) and total solubility of Al and Si, since reaction rates are also proportional to Al and Si concentrations in solution, the total dissolution of reactants and yield of products is reduced
10. OH⁻ concentration does influence the relative yields of zeolite phases produced at constant m. Increasing pH at constant m increases the yield of a particular zeolite until a

maximum is achieved, after which increasing pH results in a decrease in yield. Different zeolite phases have optimal yields at different pH ranges, where the optimal pH for CHA < SOD < CAN. For SOD, isoclines of constant m show a decrease in the pH of optimal yield at constant m for increases in m from $x = 1$ at low m relative to $x = 1$, after which the pH of optimal constant m yield increases with increasing m ; two possible causes are proposed:

- iii. The changing OH^- concentration changes the dissolution of reactants, changing the Si/Al ratio in solution influencing the relative yields
- iv. The changing OH^- concentration changes the rates of dissolution of different zeolite products to different extents changing the relative equilibrium yield ratios between different zeolite products

Bulk chemical analysis, quantitative mineral analysis, and SEM analysis together revealed the possibility* that the amorphous aluminosilicate gel precursor to zeolite synthesis is not completely converted to form zeolites, and is present in hydrothermal treatment products.

Continuous Processing

It has been hypothesised by the author that the fly ash encapsulation which results from gel precipitation could be minimised and potentially eliminated through a combination of (i) suppressed fly ash dissolution through the manipulation of M^+ and OH^- concentrations, and (ii) enhanced crystallisation through the manipulation of M^+ concentration and the ratio of zeolite to fly ash maintained within a continuous mixed flow reactor.

From the un-seeded treatments the primary location for sodium enriched phases were spread over the outer surfaces of unreacted particles. By seeding the hydrothermal system, the primary location for sodium enriched phases has shifted with the significant presence of product faces independent of unreacted fly ash phases, although product phases do still occur on the external surfaces of unreacted ash particles, this does support the principle of the hypothesis.

Decreasing pH decreases the rate of reactant dissolution, increasing m from $x = 1$ reduces reactant dissolution, increasing m from $x = 1$ substantially increases the total zeolite yield for m close to $x = 1$ condition, and under some conditions seeding increases zeolite yields. All of which support in principle the hypothesis for mitigating the reactant encapsulation limitation.

From reaction temperature experiments between 120 and 144°C there is a significant difference in dissolution with no significant change in zeolite yields, suggesting that reaction temperature may also be a tool in mitigating the reactant encapsulation limitation.

From an economically viable zeolite manufacturing plant operating in continuous mode, the hydrothermal system, (i) operates under steady state conditions, (ii) contains both reactants and products together in reactor at all times, and (iii) requires low p ($p \geq 30$).

Steady state conditions cannot be met in batch reactors, while the presence of both reactants and products at all times can be achieved using seeding. Preliminary treatments in the presence of the second two conditions[†] reveal that:

- The yield of zeolite per gram of fly ash is roughly the same for all p

* Where X-ray amorphous products can be either amorphous gel or X-ray amorphous zeolite

[†] Using agitated reactor system and reaction conditions of 4g of seed (HTP 76) at 80°C, pH14.3 and $x = 1$, for p 's of 25, 47, 100, 200, and 400 (HTP's 112, 111, 108, 110, and 109 respectively)

- The yield of zeolite in grams per batch increases with decreasing p

This work is preliminary, and there is plenty of scope for more comprehensive work into the mitigation of reactant encapsulation limitation.

Agricultural Application

Zeolite fertilisers show improved efficiency compared to traditional fertilisers, which means increased productivity and a reduced quantity of nutrients being leached into the environment. Using zeolite fertilisers produced from coal fly ash instead of traditional fertilisers will improve the current situation where:

- Significant energy and natural resources are invested in materials which are then wasted;
- There is an adverse environmental impact associated with the large scale stockpiling of coal ash in ash dams;
- The leaching of unnatural levels of nutrients into the environment has an adverse environmental impact, and an associated economic cost

From experimental results it is clear that different zeolite phases have different cation selectivity's, and therefore will perform differently as a controlled release fertiliser. Different zeolite fertiliser products* can be designed and produced to meet the requirements of specific applications. The types and yields of zeolites can be described as functions of operating conditions, from which an optimal process condition can be found for each zeolite type in conjunction with economic modelling. So that a manufacturing plant can produce a zeolite with properties optimised for a particular application, and by changing a few operating conditions zeolite for a different application can be produced.

The basic process and economic calculations presented in thesis highlight the following issues:

- A zeolite product produced using NaOH will always contain some Na even after successive nutrient loading stages
- The lower the selectivity for a nutrient the more difficult it will be to load it into zeolite and require a greater number of successive nutrient loading stages
- For economic viability there is a limitation on residence time (hours) and p (mole ratio H_2O/Al) within the reactor, roughly $pt \leq 100$ based on assumptions used in thesis
- The operating cost per tonne of zeolite produced is a major limiting factor in achieving economic viability at a competitive sale price

The ability to significantly increase the production capacity of a FCI over established practice, and potentially also reduce reaction temperature through the mitigation of reactant encapsulation limitation will contribute to making it viable to produce zeolite fertilisers from fly ash for bulk markets.

Fly ash zeolitic materials have a reduced overall trace element load and mobility as a result of leaching during hydrothermal treatment resulting in (i) a more environmentally friendly product, and therefore (ii) a more attractive product for use in agriculture relative to fly ash.

Most of the elements of greatest concern have been reduced in concentration to or below their average levels in soil, shale, or crust; and the mobility of elements from agitated hydrothermal

* For the bigger picture it is important to note that we are not looking at one product here, there is potential for many based on different types of zeolite, and blending with other compounds like phosphate rock, to control the chemistry of release, and so tailor fertiliser product for particular fertiliser applications.

reactor products are lower than the natural reference samples as tested. Some products perform better than others; as such, trace element mobility would have to be determined on a case by case basis prior to application in Agriculture.

A consequence of extracting trace elements from fly ash during hydrothermal treatment is the accumulation of these elements in the aqueous phase, and subsequent disposal of aqueous waste streams. This will need to be accounted for in the design and operation of any manufacturing plant.

Although this research focuses on the fertiliser application of zeolites, most experimental results presented in this thesis are relevant to all applications of fly ash zeolites.

A6.2 Recommendations for Future Work

A number of broad avenues for research relating to fly ash utilisation, various zeolite applications, and for zeolite synthesis using fly ash were presented in Appendix 4. However this section, as summarised in Figure 9.31, focuses more on research ideas which are a natural evolution of the methods and results of experimental component of this thesis.

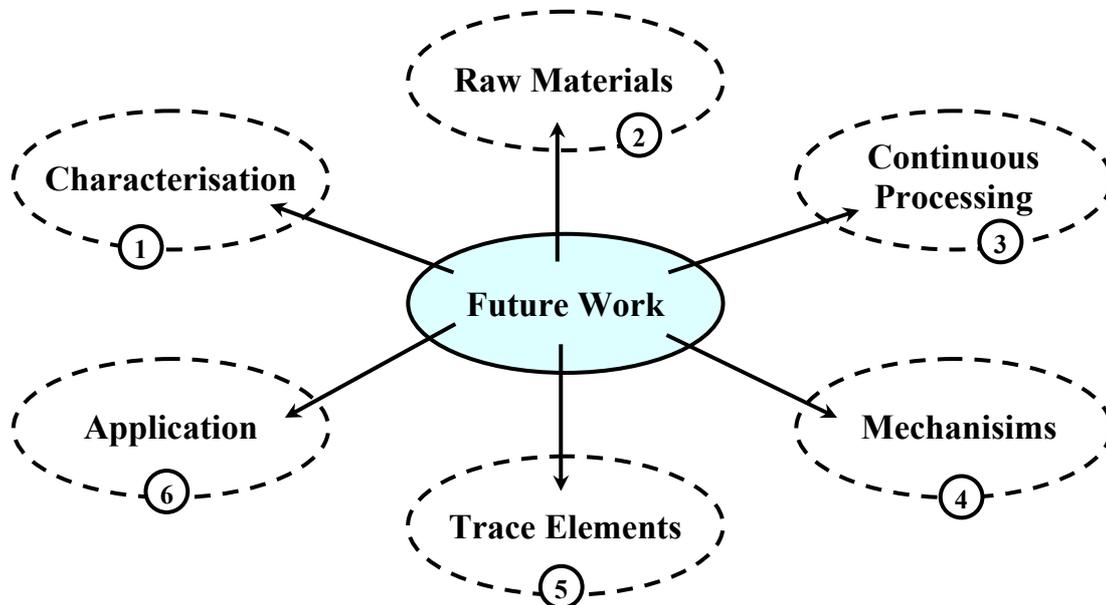


Figure 9.31: Illustration of the main topics for future work presented

The hydrothermal synthesis equipment used in this thesis was sufficient for the work done, however to take this work to the next level, including a closer study of the mechanisms, kinetics, and equilibriums, the major sources of avoidable uncertainty need to be eliminated, including temperature, water loss, sedimentation and residue sticking to reactor, through the use of better quality equipment. For application testing of zeolite products, reactor quality is not important, only the properties of zeolitic material used are relevant.

Characterisation - SEM

Using a stationary electron probe, while the sample is tilted, backscattered electrons can be channelled or diffracted by atomic planes, and subsequently imaged, appearing as a series of lines. This technique is referred to as electron backscatter diffraction (EBSD), two important uses are:

- Identifying crystalline phase by cross referencing EBSD pattern with quantitative chemical composition from EDS
- Orientation mapping, by determining EBSD patterns for an array of points, where the crystallographic orientation (texture) is calculated at each point from diffraction pattern.

(Prior, *et al.* 1999)

There is a size limitation for EDS and EBSD analyses, limiting what can be studied:

- For EDS (and WDS) the phase being analysed must be $> 1\mu\text{m}$ in size (3D) otherwise the result will include components from adjacent phases
- For EBSD the phase being analysed must have a single crystal orientation domain $> 1\mu\text{m}$ in size (3D)

(Prior, *et al.* 1999)

SEM-EBSD could be used to identify mineral phases in conjunction with EDS to quantify the elemental composition of that phase; together they give an idea of the distribution of composition for a phase, and an idea of the average phase composition (given a significant statistical sample of data points). The results could then be used to define phase composition used in quantitative analysis or as part of CES analysis to reduce experimental uncertainties.

An attempt was made to use EBSD in this thesis however carbon coatings were too thick to allow sufficiently strong patterns from zeolite phases to be obtained, and uncoated particles charged too much to get stable patterns. However since then the interpretation software has been upgraded, substantially improving its detection and identification capabilities. In addition mounting sample in a conductive resin would overcome the charging issue and negate the need for carbon coating.

Characterisation - XRD

Quantitative XRD using the Rietveld method provided the backbone of the research presented in this thesis; however it is still subject to significant uncertainty which introduces a bias into the results. This was not a problem in the current research where qualitative conclusions were drawn from the quantitative trends. However for future work which may require lower uncertainty including the study of X-ray amorphous phase composition, zeolite reaction kinetics and equilibria, this uncertainty needs to be reduced.

The uncertainty in quantitative XRD results could be reduced through the following techniques:

- Better knowledge of true zeolite composition for more accurate unit cell composition, XRD structural parameters, and therefore quantitative results. This could be achieved by grinding hydrothermal products into fine powder then using dense media to remove impurities like iron compounds and quartz to get a near pure zeolite material, which can be characterised using XRF and XRD with structural refinement, which can then be used for quantitative analysis. This method may also prove useful in identifying or refining the structure of the unknown hydrothermal product phase.
- Add tracer to reactants to minimise uncertainty leading to increased understanding of the transformations taking place, for example:
 - A mineral tracer would be useful for XRD, however it may be difficult to find suitable candidate which will not dissolve, or participate in hydrothermal chemistry by inducing seeding on mineral surfaces
 - Small particles of insoluble element which can be reliably and accurately quantified, like gold or platinum.
- Manually prepare 5-10 standardised fly ash A samples for XRD, run and perform quantitative analysis using refinement method of hydrothermal products to evaluate a more certain value for fly ash composition.
- Perform several XRD repeats of each HTP sample to reduce uncertainty in quantitative results
- Use a Cobalt X-ray source for XRD analysis to reduce X-ray adsorption by iron in sample leading to increased peak intensities for high iron samples*.
- Minimise the mineral heterogeneity of sample by using a fly ash starting material with minimal quartz and iron mineral phases, and clean fly ash to minimise the presence of

* Mass absorption coefficients for Cu Ka by Si, Al, and Fe are 48.6, 60.6, and 308 respectively, and for Co Ka by Si, Al, and Fe are 74.8, 93.3, and 52.8 respectively (Warren 1969).

other cations, like Ca^{2+} , which are incorporated into zeolite product and shift its composition away from the theoretical composition used in quantitative analysis

- Perform ion exchange on hydrothermal product to remove undesired cations prior to quantitative XRD determination

Cyclotron and neutron diffraction could be used for improved phase identification and refinement of hydrothermal products and purified zeolite phases. In addition synthesis experiments could be conducted in the presence of continuous neutron or cyclotron diffraction, to gather information on changes in reactants, intermediates, and products with time including possible quantitative composition and unit cell dimensions as a function of time. This will shed light on the formation of intermediate phases, on the role of gel in hydrothermal system, and on zeolite formation mechanisms.

Raw Materials

The experiments of this thesis have brought clarity with respect to the participation of fly ash components towards the hydrothermal outcome. Some ideas of how this understanding can be taken to the next level are presented.

To gain more information on the reactivity of mullite, smaller pH steps around the range where significant dissolution starts is needed. Conclusive evidence for the reactivity of iron phases could be gained by conducting experiments with p at and significantly greater than 1000, at high pH and a high temperature to ensure maximum dissolution. Using TEM on the solid product of these high p treatments, it may be possible to determine if new iron phases forming, and/or if existing iron phases are growing.

From SEM-EDS analysis conducted in this thesis it was demonstrated that iron was present in zeolite product particles, however the mechanism of its incorporation was not proven*. TEM can be used to differentiate between the incorporation of iron within zeolite mineral structure and/or as nano-particles. In addition, the CES experiments conducted could be repeated in a significantly acidic exchange solution to keep iron mobilised, should iron be exchanged from the zeolite into solution. However there may be an issue with acid reacting with iron mineral phases producing a false positive for the cation exchange of iron. To differentiate the source of iron, dense media or magnets could be used to produce two fractions for testing, 1) High iron mineral phase low zeolite fraction, and 2) Low iron mineral phases high zeolite.

To achieve better ash property control (reduced heterogeneity, and incremental property variation), and substantially increase the data set to help identify the relationships between fly ash properties and the types and yields of zeolite, the following property control methods can be employed:

1. Classify ashes into fractions according to a) density, and b) particle size
2. Blend different ashes and ash fractions (from the same and different ashes)

* Ratnasamy, *et al.* (1989) found consistant circumstantial evidence for the isomorphous substitution of iron into the faujasite lattice using X-ray diffraction (XRD), differential thermal analysis (DTA), Fourier transform infrared (FTIR) spectroscopy, and ^{27}Al and ^{29}Si magic-angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy characterisation techniques

Continuous Processing

A robust efficient and continuous “mixed flow reactor” process will be vital in achieving an economically viable manufacturing process for bulk applications. To this end a hypothesis was posed which puts forward a concept of how to improve the efficiency, therefore the productivity of synthesis process (see hypothesis 3 of Section 2). Individual components of the hypothesis were demonstrated through experimentation (see Section 4). Avenues through which this work can be further advanced are presented below.

Investigate the use of MOH, MNO_3 , temperature and seeding on the suppression of dissolution and enhanced crystallisation. To avoid the issue of unreacted reactant present in seeds used in the study of the role of seeding, purified zeolite phases separated from hydrothermal treatment products using dense media separations can be used as seed. To evaluate the influence of zeolite to fly ash ratio within the agitated reactor on the hydrothermal outcome, the following treatment conditions should be studied:

- Varying p with no seed
- Varying fly ash to seed mass ratio with a fixed p
- Varying p with fixed mass ratios of fly ash to seed

For a continuous “mixed flow” process, the most reactive components dissolve first therefore successive continuous reactors in series will be required to ensure less reactive components dissolve and contribute. A three-reactor continuous “mixed flow” system is proposed (see Figure 9.32). For the first stage where most reactive phases dissolve, reaction conditions desirable would slow dissolution and enhance crystal growth to minimise encapsulation of ash particles (low pH and x significantly less than 1). The second stage is maintained at balanced conditions, the same pH as the first stage but x slightly <1 to optimise dissolution and crystal growth since most reactive components have been consumed. For the third stage, the pH is raised to enhance dissolution of the least reactive components which remain. The actual treatment conditions employed will be constrained by the zeolite types to be produced.

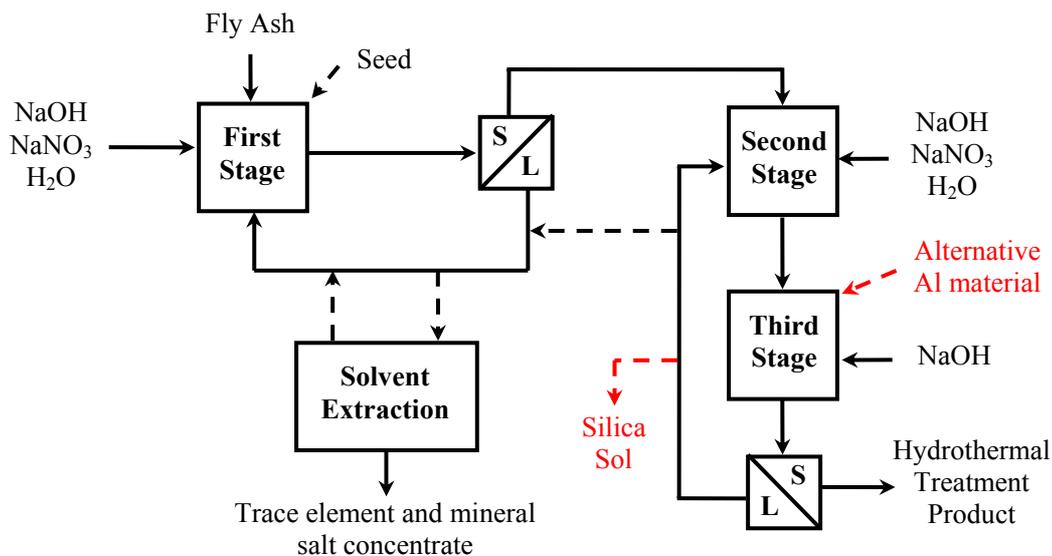


Figure 9.32: Proposed continuous three stage mixed flow hydrothermal reactor system for zeolite production from fly ash

It is hypothesised that dissolution in the first stage will be primarily of the reactive glass (high Al), and for later stages, if pH is not sufficient to dissolve mullite, dissolution will consist primarily of less reactive lower aluminium glass and quartz phases and subsequently have increased Si/Al ratio in solution. Some of this excess silicon can be bled from the third stage recycle and fed into the first stage recycle where there is plenty reactive aluminium; this has the benefit of bleeding leached elements upstream away from product. In addition alternative sources of aluminium could be added to the third stage, and/or a silica gel product could be bled from the recycle stream to make other products including zeolites through a sol-gel synthesis process.

Steady state conditions which occur in continuous processes cannot be reproduced in batch experimental reactors, however all other conditions can, for example the treatment of lower reactivity ash components which occur in the second and third stage of continuous process, illustrated in Figure 9.32, can be simulated using hydrothermal treatment products as the starting material.

Under batch (unsteady state) conditions, solution chemistry changes with time, results in an increased Si/Al ratio and reduced pH and M^+ concentration in solution with time, overall reaction chemistry can change significantly with time changing the types of zeolite which form at latter stages of synthesis.

It is in the low p to very low p where m approaches 0 or -1 that the difference between batch and continuous modes is most evident, concentrations will go from high levels to near zero over the course of hydrothermal treatment. This effect is minimised where all aqueous phase reactants are sufficiently in excess such that their consumption during the course of hydrothermal treatment has a minimal impact on their concentration.

Quantifying the changes which take place in hydrothermal outcomes as a function of time should yield information on the influence of changing conditions on outcomes. The use of NaOH, NaNO₃, and Al injections with time could further expand this understanding allowing reasonable prediction of the outcome of steady state conditions.

Hydrothermal Synthesis Mechanisms

Some synthesis mechanisms associated with raw materials and continuous processing were presented previously. More general mechanisms relevant to the direct hydrothermal conversion of fly ash to zeolite, whose study could improve our understanding of the synthesis process, and therefore the manufacturing process and zeolite property control include:

- i. Zeolite phase solubility, stability, and solution equilibria. By purifying different zeolites from hydrothermal treatment products using dense media, then combining blends of different zeolite types and ratios together in hydrothermal solutions with different pH, M^+ concentration, ratio of H₂O to zeolite, and temperature over a range of treatment times, and quantifying the composition of products.
- ii. The study of “other” composition in products, using XRF and quantitative XRD, has promising potential to reveal more information on glass reactivity and gel formation; however uncertainties need to be reduced for this to be reliable. Gel phase is of lower density than zeolite, therefore it can be separated using dense media with a finely ground sample. A purified sample of gel would allow a more detailed study of its properties.
- iii. Look at the influence of agitation speed, of continuous rotation in one direction or alternating direction, on the types and yields of zeolite produced.

Trace Elements

Trace element mobility is of particular relevance for hydrothermal products targeted at agricultural application. The trace element work conducted in this thesis was not comprehensive enough to correlate individual element mobility to individual zeolite or gel phases or yields or with treatment conditions. Such an understanding of this aspect of product properties may be beneficial to agricultural application.

For economic viability the hydrothermal solutions separated from solids need to be recycled. As a result, elements leached from ash during treatment will accumulate within the system. These elements will need to be removed from the system, which can be achieved through solvent extraction on a small fraction of the recycle as illustrated in Figure 9.32. To find a suitable exchange media, the test protocol illustrated in Figure 9.33 could be employed to test different solvent extraction agents and media.

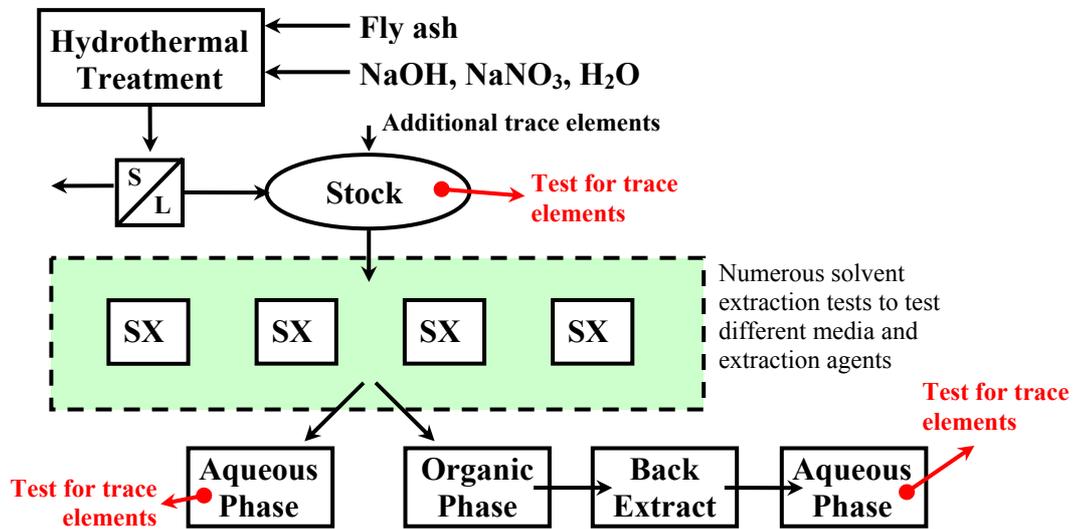


Figure 9.33: Solvent extraction test protocol

Trace elements are a major inhibitor to the direct use of unreacted fly ash in agriculture. Upgrading fly ash through a partial zeolite synthesis (hydrothermal treatment) will lower the impurity load, improve properties (water holding capacity and cation exchange capacity), and increase its value allowing its application as a soil amendment by overcoming the barriers associated with the amendment of soil using unaltered ash. However it is questionable whether such a process could be economically viable, to this end a comprehensive economic model would need to be developed to evaluate its viability.

Application

In theory, the equilibrium level of a nutrient maintained in the soil can be controlled with knowledge of typical soil solution composition for application and appropriate design of zeolite. The cation exchange selectivity is used to measure this performance theoretically, however if bulk elemental composition of hydrothermal product is used which includes unreacted reactants and other non-zeolite impurities it can introduce a considerable bias into the cation exchange selectivity calculated from exchange experiments. This uncertainty can be reduced by:

- i. Purify zeolite phase using dense media for more accurate XRF bulk chemistry resulting in more accurate cation exchange selectivity experimental results.
- ii. Expose unground hydrothermal product samples to exchange solution for a significant period of time then analyse exchanged solid using SEM-EDS to quantify the compositions of individual zeolite phases, and analyse equilibrium solution using IC or ICP, from which individual phase selectivity can be calculated.
- iii. Use a range of low iron fly ashes, classified and cleaned ashes, with fewer impurities to produce zeolite products with fewer impurities for CES experiments, so that more accurate CES values can be determined.

It would be useful to:

- i. Test the equilibrium times for nutrient loading as well as non-equilibrium concentration time curves to evaluate staging requirements, economic cost and performance trade offs for nutrient loading section of zeolite fertiliser production process
- ii. Address the health issue of fibrous zeolites and mullite through physiological testing

To evaluate actual zeolite fertiliser performance, application testing is required. Conducting controlled potplant experiments like those conducted by Hershey, *et al.* (1980), would be valuable in identifying actual fertiliser efficiency, leaching, and gaseous losses, and correlating them to application rates, nutrient types, zeolite types and selectivity's. This information would allow the identification of suitable products which could be related to operating conditions for which detailed economic modelling could be performed to evaluate the economic viability of potential products.

A6.3 Evaluation and Reflection

This project was born in an environment in which any zeolite application for fly ash utilisation is perceived as niche, exotic, and not worth allocating scarce resources toward, as a result there were considerable pressures (driving forces) to justify itself, which introduced a focus on applications, markets, economics, and a bigger picture appreciation of where zeolites fits into the fly ash utilisation mix, on top of the experimental objectives of my candidacy. This additional work has played an important role in the early stage of this thesis of work and as such, a significant portion has been included in this thesis.

This section documents the author's opinion of which components of work presented in this thesis (classified into topics, see Figure 9.34) constitute a significant contribution to fly ash utilisation and zeolite synthesis from fly ash research, and to science.

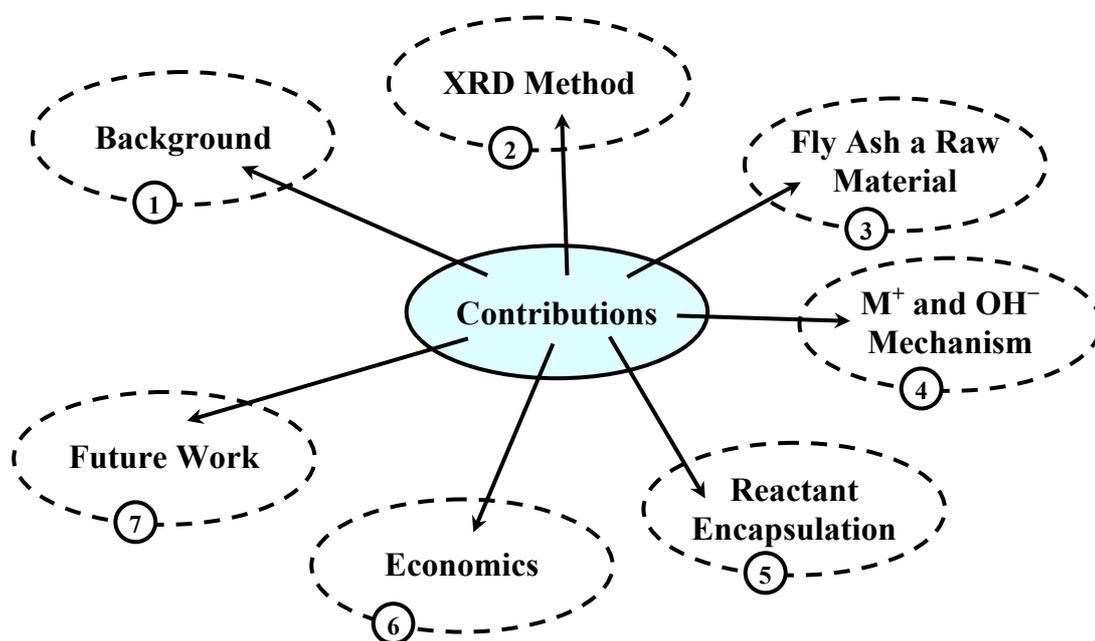


Figure 9.34: Illustration of the main contributions of thesis

Background

The scientific and philosophical principles and theories behind fly ash properties and applications, about the production of zeolites from fly ash and the application of zeolites in agricultural application are fragmented throughout scientific literature. As such a significant achievement of this thesis is to bring these concepts together to produce a general comprehensive overview of most aspects relevant to the fly ash zeolite fertiliser industry.

In particular the contrast between the current state of fly ash utilisation and the potential markets for fly ash zeolites in Australia and its philosophical implications shed the issue of fly ash utilisation in a new light.

XRD Method

Previous authors have been limited in their ability to study the transformations which take place during the hydrothermal treatment of fly ash due to limitations in the detail of information provided by the characterisation methods employed (CEC and qualitative X-ray diffract-o-gram comparisons).

Quantitative XRD analysis using full profile Rietveld analysis is a technique which can provide a significantly more detailed characterisation of reactants and products and therefore more detailed information on the transformations taking place.

This technique is well established within various fields of science, while, to the author's knowledge it has not previously been applied to the study of fly ash zeolites. A significant contribution of this thesis was the application of this technique to the study of zeolites produced from fly ash and the associated methodology developed to this end.

Fly Ash as Raw Material

Previous authors have presented basic observations of the dissolution of glass, quartz, and mullite, and they are on occasion contradictory. Only a few basic generalised qualitative relationships between reactivity and hydrothermal conditions have been cited by the author.

The use of quantitative XRD in conjunction with SEM analysis of particle cross sections has provided significant information on the transformations taking place during the course of hydrothermal treatment, and as trends over varying conditions, which bring considerable clarity to our understanding of fly ash component reactivity and as such is a significant contribution.

The use of particle cross sections in the study of mineralogy is substantially more informative than the study of particle surfaces for heterogeneous materials like fly ash and zeolites produced from fly ash. However, to the author's knowledge, the use of this technique in this work is also a first in the study of zeolites produced from fly ash.

Mechanism (M^+ versus OH^-)

An attempt to differentiate the role of M^+ and OH^- towards the outcome of the hydrothermal treatment of fly ash was previously conducted by Murayama, *et al.* (2002b; Murayama, *et al.* 2002a) which shed some light on the issue. However there were limitations with the technique employed. A new technique was developed to overcome these limitations, based on the use of NO_3^- and with conditions defined by the ratio of OH/H_2O , H_2O/Al and m (the ratio M^+/Al in excess of stoichiometry), and with outcomes quantified using quantitative XRD. From these experiments a significantly improved understanding of the role of M^+ and OH^- towards the overall reaction mechanism was gathered, and as such represents a significant contribution.

Mitigation of Reactant Encapsulation Limitation

Inspired by the description of gel encapsulation, provided by Murayama, *et al.* (2002b; Murayama, *et al.* 2002a), which occurs during the direct hydrothermal treatment of fly ash, and which retards further dissolution of ash particle; and by the possibility of controlling this phenomenon to minimise encapsulation and subsequently increase productivity, a mechanism was proposed based on suppressed dissolution and enhanced crystallisation in the continuous presence of zeolite to mitigate this problem.

Experiments were conducted to test this proposed mechanism over a range of hydrothermal treatment conditions using SEM to evaluate the outcomes. The results corroborate various individual elements of the proposed mechanism.

To the author's knowledge, this proposed mechanism is completely original and as such represents a significant contribution as do the corroborating experiments.

Economics

The purpose of the basic economic modelling work conducted was to provide a sense of perspective on the impact of hydrothermal conditions, on the economics, and subsequent viability of manufacturing zeolite fertilisers from fly ash. From the results it is clear that economic viability is far from assured*, with the process sensitive to operating costs particularly NaOH and KCl raw materials, and probably energy use which highlights the importance of:

- Economies of scale
- Continuous processing
- Aqueous stream recycles

And all other measures which can be taken to improve productivity. Therein lies the significance or value of studying fly ash component reactivity, the role of M^+ and OH^- toward hydrothermal outcomes, and the mitigation of reactant encapsulation, because each will contribute to our understanding of the direct hydrothermal conversion of fly ash to zeolite, with the potential to improve the productivity of producing zeolites from fly ash, and therefore its economic viability.

Recommendations for Future Work

Within the recommendations for future work are a number of innovative and original ideas of how to advance various aspects of the work conducted and ideas presented in this thesis to the next level, and as such is itself a significant contribution.

* For the high volume bulk market required to consume millions of tonnes of fly ash. However the pursuit of higher value fertiliser and other zeolite markets (300 to 600 \$AU per tonne) should be seen as the stepping stone required to establish the technology, with the lower value higher volume markets maintained as a longer term endgame.

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