

Sustainability Assessment of Symbiotic Processes for the Reuse of Phosphogypsum

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ABSTRACT

The conversion of by-products to resources is a novel approach for enhancing circular economy through increasing the lifecycle of resources, however, it does not always achieve sustainability outcomes. A life cycle assessment has been conducted to assess the economic and environmental implications of the conversion of phosphogypsum, which is a by-product from phosphoric acid manufacture, to useful resources such as paper and fertilizer. The current research found that the phosphogypsum based paper and fertilizer are neither environmentally nor economically better than conventional products due to the raw materials used that leads to higher environmental impact and economic cost. However, phosphogypsum based products offers some social benefits such as additional employment creation and enhanced intergenerational equity. Further investigation into chemical process design in terms of reagent selection for precipitation reactions is needed to achieve the economic and environmental feasibility of the products based on these by-products.

Keywords: Solid by-products, industrial symbiosis, triple bottom line analysis

1. INTRODUCTION

Phosphoric acid is mainly utilised in the production of phosphate fertilisers, which means it is vital for crop production and of key economic importance. More than 90% of phosphoric acid produced worldwide is derived from the wet acid process (Tayibi et al., 2009) the phosphate rock digestion by sulphuric acid. However, the major by-product from phosphate rock digestion by sulphuric acid is phosphogypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) as described through Equation 1.



This process generates about 5 tons of phosphogypsum (PG) for every ton of dry phosphoric acid. Due to the presence of natural occurring radioactive materials and heavy metals, only a small amount of PG is able to be reused in soil amendment, or as a resource for building materials, fertilizers, etc. The rest is stockpiled as waste.

Solid waste brings considerable concerns over the long term from the leaching of metals and hazardous salts. Various processes have been investigated for the separation of radionuclides and heavy metals from phosphogypsum. The most suitable process is the use of 4-7% H₂SO₄ solution (Todorovsky et al., 1997; Valkov et al., 2014). The use of sulphuric acid as leachate is more economical because it is one of the raw materials used for phosphate rock digestion and would add minimal capital costs based on the low percent solution required for leaching. The separation of the radioactive materials leaves a rich calcium sulphate bulk that can be used as a resource. For the extraction of sulphate in PG, the most widely adopted methods are the thermal decomposition of calcium sulphate (bulk of PG) (Ma et al., 2012; Yang et al., 2013; Zheng et al., 2014; Wang et al., 2014) and precipitation reactions via suitable reagents (Aagli et al., 2005; Abu-Eishah et al., 2000; Cárdenas-Escudero et al., 2011; Mulopo & Ikhu-Omoregbe, 2012; Ennaciri et al., 2013; Zhao et al., 2014). Thermal decomposition requires very high reaction temperature in a reduction atmosphere, such as carbon, carbon monoxide, nitrogen, etc. Equation 2 is a typical reaction of phosphogypsum with carbon monoxide. With the increasing of temperature, the reaction rate increases.



Precipitation reactions can form valuable sulphates and calcium by-product salts, providing a high potential reusing of PG. The formation of sodium sulphates from use of sodium based reagents could be utilised as a feed in paper production or a sulphate source for other important industrial sulphate compounds like potassium sulphates. The use of ammonium based reagents produces ammonium sulphate that could be utilised as a fertilizer. On the other hand, calcium oxide from precipitation with NaOH or other reductants (e.g. sulphur and hydrogen through thermochemical decomposition) could be utilised as a lime feed for other industries (for example in production of mortars) (Zheng et al., 2014; Romero-Hermida et al., 2014). Calcium carbonate by-product from the

use of sodium carbonate as a precipitating reagent could be used in acid mine drainage treatment to control acid wastes and also leaching of the acid wastes underground (Mulopo & Ikhu-Omoregbe, 2012).

Apart from chemical industries, PG has been used as construction materials due to its cementitious properties (Rashad, 2017). The other significant work reported in the literature (Mousa & Hanna, 2013) for the conversion of PG is the use of a mixture of 85% phosphoric acid and ammonia solution that results in the production of hydroxyapatite (HAP), which possesses a similar ratio of Ca/P in human bones. Therefore, the HAP formed has the potential to be used for bone and tooth implants.

Salts produced from waste PG can be a potential feedstock alternative to neighbouring industries via industrial symbiosis. For industrial symbiosis, there are a limited number of research which predominantly considered synergy development without adequately considering its sustainability implications.

The conversion of by-products or wastes to resources could potentially conserve land, avoid the use of finite non-renewable resources and the loss of biodiversity (Biswas and Cooling 2013), but this conversion may have social, economic and environmental implications which need to be assessed. For example, Fatimah and Biswas (2016) found that the use of recycled and used parts for manufacturing remanufactured alternator could meet the environmental objective of sustainability due to energy intensive recycling processes and therefore the maximum use of used components were considered as an improvement strategies. Catlin and Wang (2013) concluded that recycling options may not be sufficient to save natural resources, or at least does not always yield the maximum environmental benefit. Thus, El-Assaly and Ellis (2015) confirms that economic and environmental assessments of any by-products for use in infrastructure applications are essential for assessing the overall sustainability aspect of the by-product utilization.

The aim of this study is to apply process engineering principles for developing synergies or symbiotic pathways on the reuse of PG and to assess the sustainability of these pathways from social, environmental and economic objectives. Suitable reagents for different precipitation reaction

processes of PG were selected. A number of symbiotic pathways were proposed. Life Cycle Assessment (LCA) has been conducted on selected pathways/options and social implications were also evaluated. The current research is distinctive in a way that it investigated if the conversion of cheaper by-product to useful products through industrial symbiotic pathways could offer triple bottom line sustainability benefits.

2. METHODS AND MATERIALS

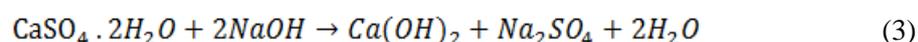
The following steps have been conducted to assess sustainability of the symbiotic process for the use of phosphogypsum by-product in paper and fertilizer production.

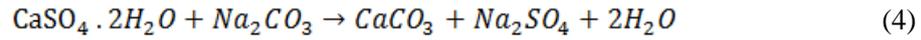
2.1 Phosphogypsum Conversion through Precipitation Reactions

In order to extract the sulphur from PG, various studies have been conducted on the double displacement reaction of PG with group 1 alkali metal salts and ammonia salts (see supporting information Table A1). The selection of reaction reagent is based on the effectiveness and economical availability.

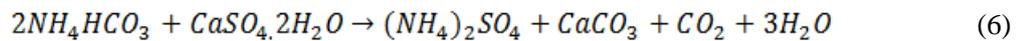
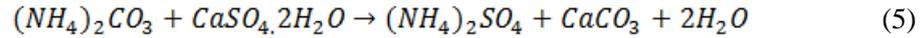
The use of potassium hydroxide and carbonate salts offer potential for the conversion of PG and formation of potassium sulphate, however, the price of the precipitating salts is higher in comparison to the product, which instead can be derived cheaply from abundant natural ores. Studies have investigated the use of the chloride as a cheap potassium resource for sulphate precipitation (Aagli et al., 2005; Abu-Eishah et al., 2000), however, the main drawback with the use of potassium chloride is the formation of double salts such as syngentite and penta-salt, which impede the precipitation reaction. Economic viability issues make potassium salts not suitable for our pathway selection.

Therefore, the precipitation reagents under consideration will be the sodium salts and ammonium salts. Sodium salts present potential for extracting sulphate from PG (Cárdenas-Escudero et al. 2011; Mulopo & Ikhu-Omoregbe, 2012; Romero-Hermida et al., 2014) following the chemical reactions of Equation 3 (NaOH as reagent) or Equation 4 (Na₂CO₃ as reagent).





Ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ and ammonium bicarbonate NH_4HCO_3 are the only suitable and common industrial ammonium salts for the precipitation of PG. Direct utilisation of NH_4HCO_3 was not encountered in literature. Nonetheless, it reacts similarly to $(\text{NH}_4)_2\text{CO}_3$ in precipitating PG (Equation 5) (Zhao et al., 2015). Thus, it is also considered along with $(\text{NH}_4)_2\text{CO}_3$ as one of the possible pathways (Equation 6).



2.2 Selection of Process Pathway Options

Based on the previous analysis, the reaction pathways selected are listed in Table 1.

Table 1. Different pathway options based on selection of precipitating reagents

	Reagents	Options	By-products	End Products
Sodium Salts	Sodium Hydroxide	Option 1.1	Sodium Sulphate	Paper/ detergent;
	Sodium Hydroxide and CO_2	Option 1.2		Calcium Hydroxide;
	Sodium Carbonate	Option 1.3		Calcium Carbonate
Ammonium Salts	Ammonium Carbonate	Option 2.1		Ammonium Sulphate;
	Ammonium Bicarbonate	Option 2.2		Calcium Carbonate

For the use of sodium salts as reagent for PG precipitation, Option 1.2 ($\text{NaOH} + \text{CO}_2$) was investigated for the potential use of lime water ($\text{Ca}(\text{OH})_2$ in water) to sequester CO_2 . When CO_2 is percolated through the lime water, it generates CaCO_3 as per the chemical Equation 7.



Figure 1 proposes the general pathway comprising the inputs and outputs of the different stages of PG reaction with precipitation reagents to the final products formed through industrial symbiosis/synergy. The overall process begins with the reaction of the sulphur present in the gypsum through the ion exchange with the aid of suitable precipitation reagents represented as 'XCO₃/ XOH',

where X represents either sodium or ammonium cations. After separation through centrifugation, the soluble sulphates formed are dried before they can be utilised for industrial symbiosis while the insoluble calcium precipitate salts (CaCO_3 and Ca(OH)_2) are removed as by-products.

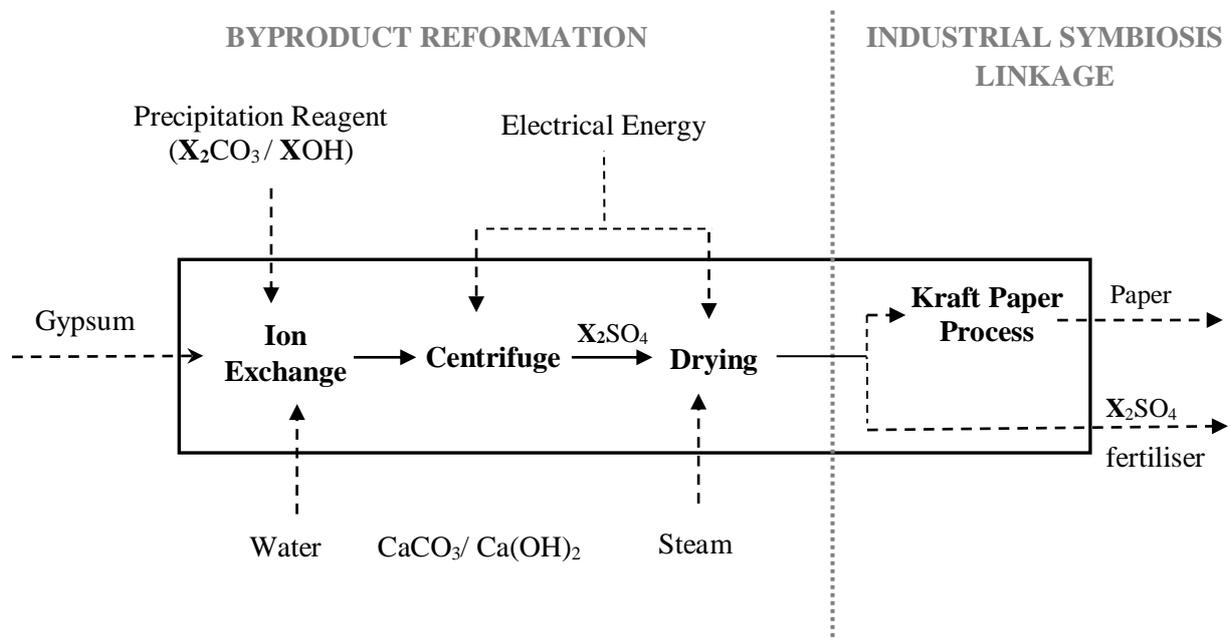


Figure 1 General process pathway for PG precipitation and industrial symbiotic linkage.

Ammonium sulphate formed from ammonium salts precipitation of PG is crystallized and dried for use as fertilizer. Sodium sulphate formed from the sodium salts, after thermal reduction, can be used in the paper production process as a source of sodium sulphide feed, which is produced from thermal reduction of the sodium sulphate using heat generated from black residue (spent digestion liquor) combustion. Sodium sulphide is used together with sodium hydroxide for the digestion of wood chips in order to separate lignin fibres from wood in order to make paper pulp that is used to produce paper. About 16.5g of sodium sulphate are used per kg of packaging paper, representing 1.65% of the total material requirement.

2.3. Environmental Life Cycle Assessment

Streamlined life cycle assessment has been adopted in this study. It takes a cradle to factory gate approach, which did not consider downstream activities such as transportation or product use (Biswas, 2014). According to International Organization for Standardization (ISO) 14040-44, LCA was

conducted in several steps (ISO, 2007): goal and scope definition; inventory analysis; impact assessment; interpretation.

The aim of this LCA was to investigate different phosphogypsum precipitation processes and to develop potential industrial symbiosis with the least environmental impacts. The indicators chosen below quantitatively provide an overall environmental outlook and were found to be the predominant impacts on chemical processing by other researches (Biswas & Cooling, 2013; Mohammed et al., 2016):

- a. Global warming potential (GWP) associated with the emissions from manufacturing, transportation and use of inputs at different stages of process under study.
- b. Eutrophication potential (EP) due to enrichment of nutrient level in water resource that the inputs and processes may cause.
- c. Solid waste impact resulting from the processing waste.

The values of other categories such as; human toxicity, land use, freshwater aquatic toxicity, etc., have been found negligible, therefore, were not reported here.

The functional unit determines the system boundary of the LCAs and was defined as:

- The sodium sulphate for production of 1kg packaging paper, or;
- The ammonium sulphate for production of 1kg ammonium sulphate fertilizer.

Contained in this boundary were two stages, the precipitation reaction and the product drying.

The life cycle inventory (LCI) consisting of inputs and outputs of different stages of the symbiotic relationship pathways are presented in Tables 2 and 3. The efficiency of PG precipitation for each of the precipitating reagents is assumed to be 90% based on published data in Table A1. The source of inputs for the development of the LCIs have been based on their availability from the relevant industries within Kwinana Industrial Area (KIA), Western Australia. In instances where inputs could not be sourced within KIA, regional and national industries were firstly explored for availability of required inputs before looking at overseas markets. It should be pointed out that variation in PG property will affect the assessment results. The conclusions drawn from this research is only applicable to the particular type of PG under study in Western Australia.

Table 2 Life Cycle Inventory for 1 kg Packaging paper formation using Na₂SO₄ as sodium based reagent.

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
CaSO ₄	3.3	g/kg	CSBP	0
Option 1 (Precipitation reaction with Sodium Reagents)				
Option 1.1				
<i>NaOH Reagent Use</i>				
Water for dilution of NaOH to 1M solution	0.05	L/kg	Water Corporation, Perth	0
NaOH	1	g/kg	Coogee Chemicals, Perth	2
<i>Drying</i>				
Steam required for Na ₂ SO ₄ concentration	0.1	kg/kg	On site	0
Electrical energy for Na ₂ SO ₄ crystallization	0.002	kWh/kg	On site	0
Option 1.2				
<i>NaOH Reagent Use with CO₂ Carbonation</i>				
Water for dilution of NaOH to 1M solution	0.05	L/kg	Water Corporation, Perth	0
NaOH	1	g/kg	Coogee Chemicals, Perth	2
CO ₂ for carbonation of CaO by-product	1	g/kg	CSBP Fertilizer Plant, Perth	0
<i>Drying</i>				
Steam required for Na ₂ SO ₄ concentration	0.1	kg/kg	On site	0
Electrical energy for Na ₂ SO ₄ crystallization	0.002	kWh/kg	On site	0
Option 1.3				
<i>Na₂CO₃ Reagent Use</i>				
Water for dilution of Na ₂ CO ₃ to 1M solution	0.025	L/kg	Water Corporation, Perth	0
Na ₂ CO ₃	2.5	g/kg	Penrice Soda Products, Adelaide	2700
<i>Drying</i>				
Steam required for Na ₂ SO ₄ concentration	0.03	kg/kg	On site	0

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
Electrical energy for Na ₂ SO ₄ crystallization	0.001	kWh/kg	On site	0
By-product 1 (from Option 1.1)				
Ca(OH) ₂	1.6	g/kg	On site	0
By-product 2 (from Option 1.2 or Option 1.3)				
CaCO ₃ (Option 1.2)	2.1	g/kg	On site	0
CaCO ₃ (Option 1.3)	2.2	g/kg	On site	0

Table 3 Life Cycle Inventory for 1 kg (NH₄)₂SO₄ formation using Ammonium based reagents.

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
CaSO ₄	1.27	kg/kg	CSBP, Perth	0
Option 2 (Precipitation reaction with Ammonium Reagents)				
Option 2.1				
<i>NH₄HCO₃ Reagent Use</i>				
Water for dilution of NH ₄ HCO ₃ to 1M solution	17	L/kg	Water Corporation, Perth	0
			Consolidated	
NH ₄ HCO ₃	1.33	kg/kg	Chemical Company, Adelaide	3500
CO ₂ emitted as by-product	0.33	kg/kg	On site	0
<i>Drying</i>				
Steam required for (NH ₄) ₂ SO ₄ concentration	18.2	kg/kg	On site	0
Electrical energy for (NH ₄) ₂ SO ₄ crystallization	0.36	kWh/kg	On site	0
Option 2.2				
<i>(NH₄)₂CO₃ Reagent Use</i>				
Water for dilution of (NH ₄) ₂ CO ₃ to 1M solution	8.6	L/kg	Water Corporation, Perth	0
(NH ₄) ₂ CO ₃	808	g/kg	Consolidated	3500

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
			Chemical Company, Adelaide	
<i>Drying</i>				
Steam required for (NH ₄) ₂ SO ₄ concentration	9.3	kg/kg	On site	0
Electrical energy for (NH ₄) ₂ SO ₄ crystallization	0.36	kWh/kg	On site	0
By-product (from both Options)				
CaCO ₃	0.76	kg/kg	On site	0

Three life cycle inventories were investigated, i.e. NaOH (Option 1.1), NaOH with waste CO₂ (Option 1.2) and Na₂CO₃ (Option 1.3). For symbiotic development, formed Na₂SO₄ could be used in a neighboring industry as a source of sodium sulfide (Na₂S) for digesting lignin during paper production. In Option 1.2, sequestration of CO₂ from CSBP plant exhaust into the Ca(OH)₂ water solution was utilized, which produced CaCO₃ as final product. The two main reagents used in Options 1.1, 1.2 and 1.3 (Table 2), the NaOH and Na₂CO₃, could be sourced easily from Coogee Chemicals (at KIA) and Penrice Soda Products (Osborne, South Australia) respectively.

The (NH₄)₂SO₄ product produced from Options 2.1 and 2.2 (Table 3) could be utilized directly as fertilizer or mixed with other salts in a nearby fertilizer company to produce compound fertilizers. Both the reagents, (NH₄)₂CO₃ and NH₄HCO₃, could be sourced from Consolidated Chemical Company from Melbourne, Victoria.

Data from the LCI were incorporated into SimaPro software to estimate the global warming, solid waste and eutrophication impacts. The Australian Life Cycle Inventory (AusLCI) Unit Processes and Ecoinvent 3 emission databases were used in conducting the LCI analysis [19]. When local databases are not available in the software, new databases were generated with information gathered from the literature to represent Australia's situation. The energy and material inputs in the LCI were

then linked to corresponding emission libraries to estimate the aforementioned environmental impacts.

2.4. Economic and Social Analysis

Comparison of economics of the different pathways was made through the Economic Analyser software in Aspen Plus v8.4. Aspen Economic Analyser has been widely used for economic analysis (Hunpinyo et al., 2013; Hammer et al., 2013; Jiang & Bhattacharyya, 2017) due to its powerful cost estimation capability. The following indicators were considered relevant for assessing the social implications of aforementioned symbiotic relationships (Taelman et al., 2016; Chapman et al., 2016; Guenther-Lübbers et al., 2016). These indicators have also been applied in research work of similar by-products performed previously in Kwinana (Biswas & Cooling, 2013).

- a. Employment Opportunity – a measure of the potential job opportunities that could be created by the proposed plants that could be filled by people in the surrounding communities per ton of by-product produced.
- b. Intergenerational Social Equity –the substitution of a ton of virgin resource with a ton of by-product produced from the proposed decomposing plants through industrial symbiosis that aids in conserving resources for the future generations.
- c. Avoided Land Use – the benefits obtained from utilising the waste or by-product, especially the reduced land area per square metre for stockpiling the waste PG per ton of by-product produced.

The above indicators were chosen as they cover the direct benefits that arise from the proposed processing plants to the surrounding community (Fatimah & Biswas, 2016).

3. ENVIRONMENTAL IMPACTS OF PATHWAYS

Four environmental impacts, including water use, global warming, eutrophication, and solid waste of the five alternate process pathways through LCA will be discussed.

3.1 Water Use

The basis for all the reagents used in this study for the precipitation reaction has been set as 1M of feed.

The findings of the study show that the highest water utilisation for 1 kg paper production results from both Options 1.1 and 1.2 with about 1.5L of water used for each, while water used for Option 1.3 is 1.3L (Figure 2). The major use of water is derived from the cradle to gate processes for the production of reagents even before they are used for the precipitation of PG. For Options 1.1 and 1.2, approximately 73% of water is attributed to reagent used, whereas for Option 1.3, it is 83% (see supporting information Figure A1). The other major water use is for diluting NaOH and Na₂CO₃ reagents to a molarity of 1 before they can be used for reaction. The water requirements in this stage accounts for 0.6% of total amount for Option 1.3, and 1.2% for Options 1.1 or Option 1.2.

The highest water use for the production of ammonium sulphate is attributed to Option 2.2 where 218.6L was required per kg of (NH₄)₂SO₄, while Option 2.1 requires only 31.5L. The water consumption patterns of Options 2.1 and 2.2 follow the same trend as Options 1.1 to 1.3 (Figure 3). The largest use of water for 1kg of ammonium sulphate production is derived from the reagent used (from the production processes of reagents before PG precipitation), which is about 81% for (NH₄)₂CO₃ (Option 2.1) and 95% for NH₄HCO₃ (Option 2.2) respectively. Similarly, water for reagent dilution is the other major consumption (17% for Option 2.1 and 5% for Option 2.2).

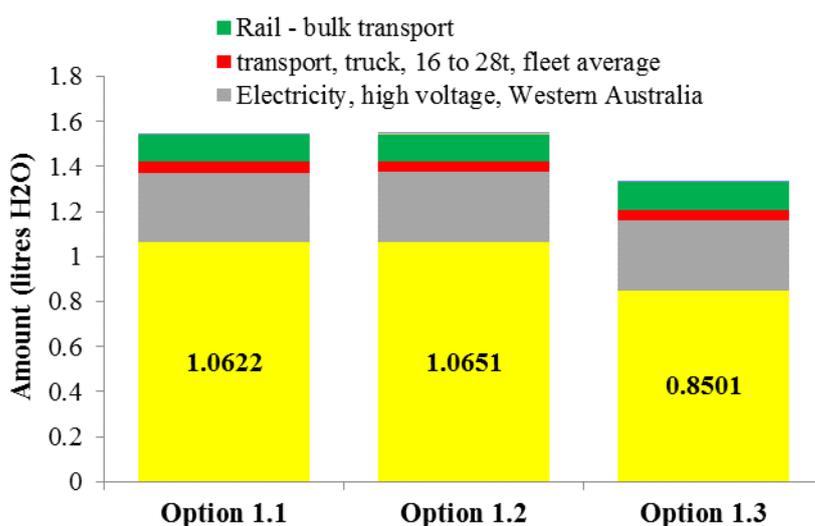


Figure 2 Water use breakdown per kg paper (values for only by-product sodium sulphates are represented in the figure).

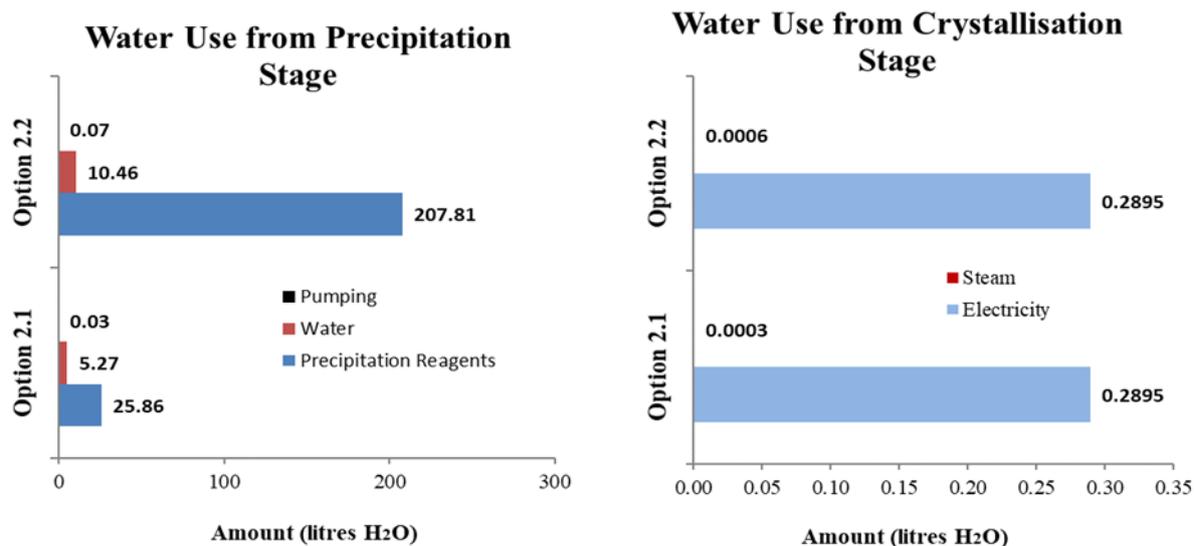


Figure 3. Water use from the precipitation and crystallization stages for production of 1 kg of ammonium sulphate.

The crystallization stage consumes the least water. Water used in this stage is for electricity consumption for drying water in the product. The amount of dilution water added to Options 1.1 and 1.2 for paper production is double that of Option 1.3. As for the production of ammonium sulphate fertilizer, there is twice more water used in Option 2.2 than in Option 2.1, which is attributed to the amount of ammonium ions present in the different ammonium salts. Thus, it can be summarised that water use decreases from Options 1.1 to 1.3 and increases from Options 2.1 to 2.2.

3.2. Global Warming Potential (GWP)

The major source of GWP for all process options is from the crystallization stage that utilizes energy for cooling and heating in order to dry the oxidized reagents (ammonium and sodium sulphates). This is attributed to the steam and electricity use. The study utilized steam generated from natural gas combustion. Electricity on the other hand is derived from the Western Australia (WA) electricity grid, which has about 95% of the generation derived from fossil fuels and the rest from renewable energy.

Whilst the use of Na₂SO₄ represents only 1.65% of the total material requirement for the production of packaging paper, the GWP does not correspond to the percentage of material used. Figure 4 shows that the overall GWP per kg paper from the use of Na₂SO₄ derived from PG are 0.1 kg

CO₂-e (7.7%) for both Options 1.1 and 1.2, and 0.06 kg CO₂-e (4.6%) for Option 1.3. The GWP contributions for steam use in the crystallization stage are 0.072 kg CO₂-e and 0.077 kg CO₂-e for Options 1.1 and 1.2 respectively. On the contrary, Option 1.3 (0.04 kg CO₂-e) has nearly half the GWP from drying than Option 1.1 and 1.2. As the molarity of all reagent solutions are similar, options utilizing two moles for reaction with a mole PG thus have twice the volume of water as opposed to options using one mole reagent for reaction. Thus, twice the amount of steam will be needed for evaporation and drying of solute products for Options 1.1 and 1.2 leading to higher associated GWP.

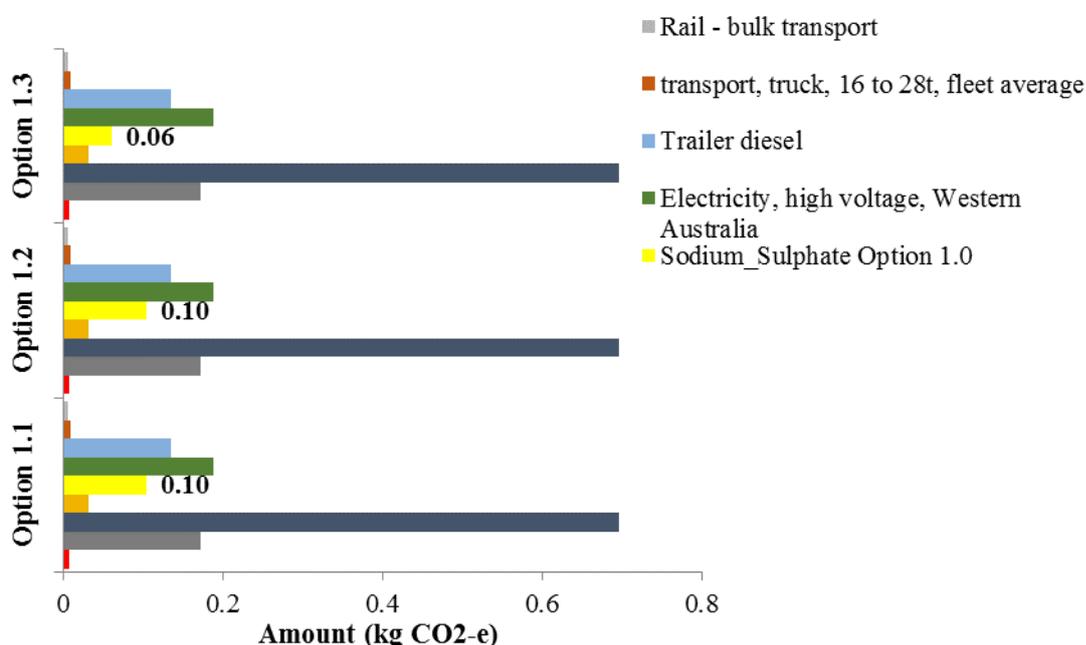


Figure 4 Global warming potential per kg packaging paper (values for only by-product sodium sulphates are represented in the figure).

The different reagents make a significant contribution towards total GWP in the precipitation stage, where over 93% of the GWP comes from (see supporting information Figure A2). Options 1.2 and 1.3 have the least GWP from production process. Options 1.1 and 1.2 utilize the same amount of NaOH as reagent; however, Option 1.2 also uses CO₂ for the carbonation of calcium hydroxide. The CO₂ use offsets about 0.01 kg CO₂-e of GWP as it acts as a CO₂ sink making Option 1.2 have a slightly lower GWP than Option 1.1.

For the GWP contribution from steam use in the crystallization stage, Option 2.2 (2.58 kg CO₂-e) is twice as that of Option 2.1 (1.31 kg CO₂-e) (Fig. 5). The difference in steam use arises from the

difference in concentration of ammonium ions present in the different options as was explained for water use. The GWP from electricity use in the crystallization stage for Option 2.2, on the other hand, does not follow a similar trend as GWP from steam use when compared with Option 2.1. This is mostly due to the endothermic nature of the process where heat is consumed in order for reaction to take place. This lowers the cooling requirement explaining the similar contributions of 0.176 kg CO₂-e GWP from electricity consumption between Options 2.1 and 2.2 (Figure 5). However, more heating energy (steam sourced) is supplied in order to enhance the reaction completion for Option 2.2 due to the endothermic reaction involved, which has already been incorporated in the GWP from steam use.

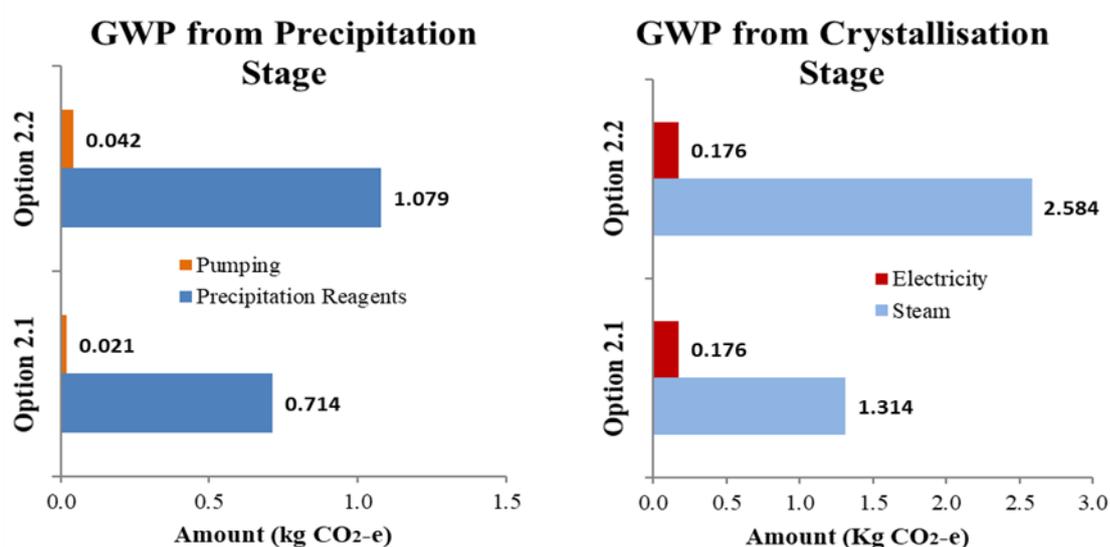


Figure 5 GWP from the precipitation and crystallization stages for production of 1 kg ammonium sulphate.

In the precipitation stage, the highest contribution of GWP arises from the processes involved in reagent production with Option 2.1 (96.2%) and Option 2.2 (97.1% of total GWP) respectively as highlighted in Figure 5. The high GWP is derived from the energy intensive Haber process of ammonia production in order to form the required carbonate and bicarbonate salts. Additionally, Option 2.2 has a higher GWP than Option 2.1 as twice the number of NH₄HCO₃ moles is required to react with a mole of PG as opposed to (NH₄)₂CO₃. Thus, the selection of reagents for precipitation of

PG also plays a role in determining the environmental effect from cradle to gate as emissions are passed on from the reagent production processes even before PG is precipitated.

3.3 Eutrophication Potential (EP)

The eutrophication values (EP) are mainly associated with energy use and show similarities with GWP in both the precipitation stage and the crystallization stage for both sodium and ammonium sulphate production. Table 4 shows that the eutrophication decreases from Option 1.1 to 1.3 as electricity consumption decreases and increases from Option 2.1 to 2.2 as electricity consumption increases. The use of sodium sulphate by-products accounts for about 5% of the total EP for Options 1.1, 1.2 and 1.3. The EP from the production of ammonium sulphates from Options 2.1 and 2.2 are 0.004 kg PO₄^{-e} and 0.0044kg PO₄^{-e} respectively (Table 4).

Table 4. EP from the different Process Options for Na₂SO₄ formed (used in 1 kg paper production).

Stages		<i>Option 1.1</i>	<i>Option 1.2</i>	<i>Option 1.3</i>	<i>Option 2.1</i>	<i>Option 2.2</i>
Precipitation	<i>Water</i>	<i>1.29E-08</i>	<i>1.30E-8</i>	<i>6.47E-09</i>		
	<i>Pumping</i>	<i>4.43E-07</i>	<i>4.46E-07</i>	<i>2.21E-07</i>	<i>8.00E-06</i>	<i>1.70E-05</i>
	<i>Reagents</i>	<i>1.19E-05</i>	<i>1.19E-05</i>	<i>4.42E-05</i>	<i>2.41E-03</i>	<i>1.30E-03</i>
	Subtotal	1.23E-05	1.23E-05	4.44E-05	2.42E-03	1.31E-03
Crystallization	Steam	8.27E-05	8.91E-05	4.64E-05	1.51E-03	2.97E-03
	Electricity	4.20E-06	4.32E-06	1.93E-06	6.90E-05	6.90E-05
	Subtotal	8.69E-05	9.35E-05	4.84E-05	1.58E-03	3.05E-03
Total EP		9.92E-05	1.06E-04	9.27E-05	4.00E-03	4.36E-03

The eutrophication impacts from the use of reagents are different from GWP. This is because energy use alone does not influence the EP of reagents. The potential dissolution of carbonate and bicarbonate anions from reagents in water provides a ready source of dissolved CO₂ for which phytoplankton can utilise for respiration and food production via photosynthesis during the day

(Verspagen et al., 2014). However, increased CO₂ causes phytoplankton blooms that prevent sunlight penetrating shallow waters. This may cause death of other aquatic plants and corals that support other marine animals. Additionally, the phytoplankton reduce the dissolved oxygen in water bodies at night due to respiration, especially in large blooms, thereby lowering oxygen levels for other marine organisms.

In addition to CO₂ release, the ammonium reagents can also have potential effects towards eutrophication increase in phosphate and nitrogen nutrients from sources such as agricultural surface run off from fertilizer use also enhances phytoplankton growth (Beman et al., 2005).

3.4. Solid Waste

The major source of solid waste is from fuel combustion residue generated in the power plant (i.e. fly ash). This is due to the fact that all these energy intensive symbiotic processes depend on electricity from WA energy mix, which is dominated by coal and natural gas. Overall, the utilisation of by-product sodium sulphates for the production of 1kg paper has been found to reduce solid waste associated with traditional paper production (Figure 6), where the average amount of solid waste reduction from Options 1.1, 1.2 and 1.3 is 0.01 kg/kg of paper. This mostly stems from the use of the gypsum in the precipitation stage (see supporting information Figure A3) for sodium based options. For ammonium based options the total solid waste of Options 2.1 and 2.2 is reduced significantly resulting in the net negative production of solid waste produced per kg of (NH₄)₂SO₄ fertilizer produced (Figure 7). This is because gypsum utilisation to form symbiotic linkages offsets its accumulation as tailings or in residue dams.

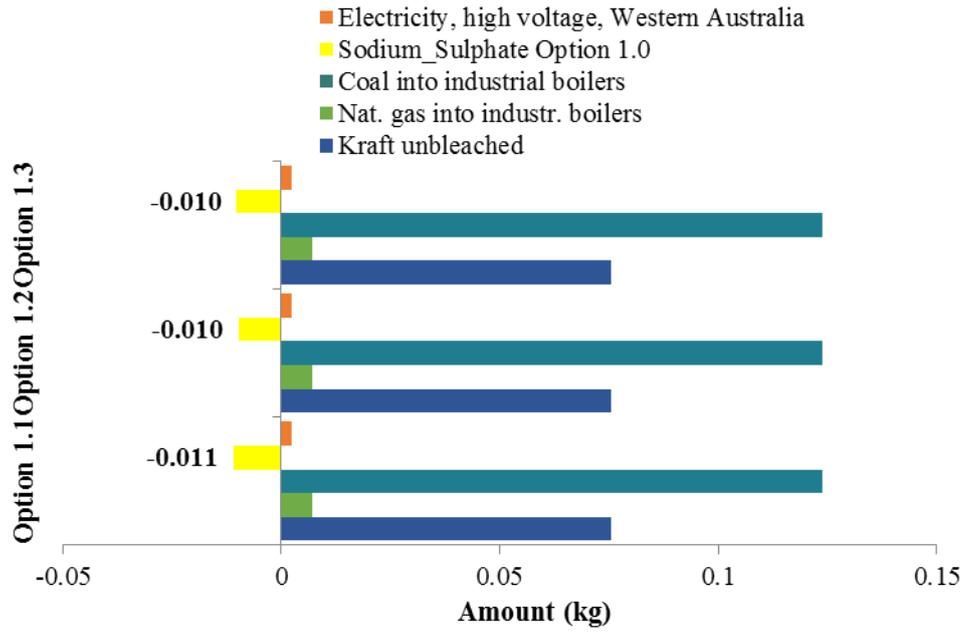


Figure 6 Solid wastes per kg packaging paper (values for only by-product sodium sulphates are represented in the figure).

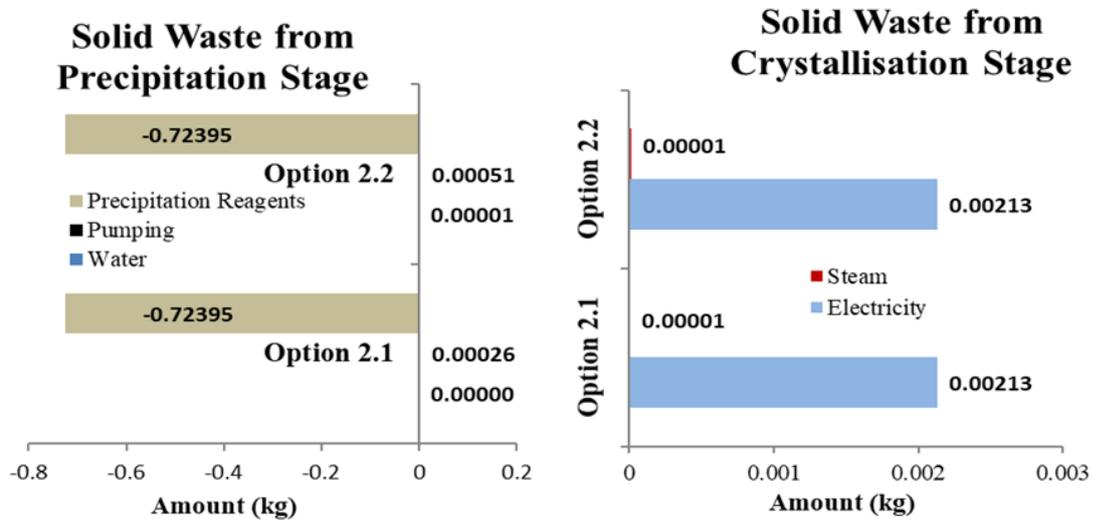


Figure 7 Solid Waste from the precipitation and crystallization stages for production of 1 kg ammonium sulphate.

3.5. Comparative Environmental Assessment

The process that utilises sodium hydroxide (Option 1.1) as the reagent has the highest energy demand and a GWP of 1.35 kg CO₂-e/kg paper. On the contrary, the process that utilises sodium carbonate (Option 1.3) as reagent has the least energy demand (a GWP of 1.31 kg CO₂-e /kg paper).

The GWP, EP and water use for conventional paper from the Simapro 8.03 Australian LCI database is 1.25kg CO₂-e, 0.0021kg PO₄⁻-e and 0.6L respectively. In comparison, the contributions of Option 1.3 towards GWP, EP and water use are 1.31 kg CO₂-e, 0.0022 kg PO₄⁻-e and 1.3L. Apart from water use, the difference between conventional paper and by-product based paper from Option 1.3 is low for all other environmental impacts analysed. Therefore, Option 1.3 is the best option for symbiotic relation development.

The option with the highest energy demand for production of ammonium sulphate is the one that utilises ammonium hydrogen carbonate as reagent and thus contributes the highest GWP of 3.9 kg CO₂-e/kg fertilizer. In contrast, Option 2.1 that utilises ammonium carbonate as reagent has the least energy meaning it contributes the lowest GWP, which is about 2.2 kg CO₂-e/kg paper produced.

The findings of the ammonium sulphate fertilizer production from Simapro 8.03 Australian LCI database shows that the impacts of conventional ammonium sulphate are 0.48 kg CO₂-e, 0.00073 kg PO₄-e and 1.9L for GWP, EP and water use respectively. Option 2.2 that uses NH₄HCO₃ as reagent has a higher environmental impact compared with conventional (NH₄)₂SO₄ production. The GWP, water use and eutrophication index are about 85%, 608% and 11% greater. As for Option 2.1, it generates 2kg CO₂-e (or 409%) and 0.004 kg PO₄⁻e (or 841%) more GWP and EP. This makes Option 2.1 less environmentally friendly and unsuitable for industrial symbiosis development.

Thus, the LCA of multiple reaction pathways for PG precipitation has shown that pathways for the conversion of PG to ammonium sulphate (Options 2.1 and 2.2) are not suitable for replacing conventional fertilizer due to considerably higher environmental impacts. The most ideal way to convert PG is through precipitation with sodium carbonate for production of sodium sulphate (Option 1.3).

4. ECONOMIC FEASIBILITY OF PATHWAYS

The process options analysed for economic viability were Options 1.1, 1.2 and 1.3. The processes for the production of paper is not considered in the system boundary for economic analysis. Instead, the production of by-product Na₂SO₄ produced through a potential decomposing industry is the boundary considered for economic consideration. Additionally, a scenario where the NPV of the lifespan of the proposed industry equalled to double the value of capital investment (average of 5% profit on investment per year) was considered. This is to make the industrial plant attractive to investors, and the selling price per ton by-product determined will then be compared to the price of an equivalent conventional product amount. All costs in the economic assessment are in US dollars and represented as \$. Table 5 presents the economic results for the process option analysed, where the selling price (in \$/ton) of Option 1.1, 1.2 and 1.3 have been estimated to be \$141.58, \$159.00 and \$161.87 respectively. At the considered scenario (5% profit average return on the capital investment per year), the price of the by-product Na₂SO₄ for Options 1.1, 1.2 and 1.3 were 57.1%, 76.7% and 79.9% higher than conventional Na₂SO₄ (\$90/ton) respectively.

Table 5 Economic analysis of by-product cost for phosphogypsum case study

Pathway Options	Units	Option 1.1	Option 1.2	Option 1.3
<i>Total Project Capital Cost</i>	USD	6,46E+06	7,33E+06	3.28E+06
<i>Total Operating Expenses</i>	USD/Year	1.07E+07	1.08E+07	9,13E+06
<i>Total Raw Materials Cost</i>	USD/Year	8.58E+06	8.58E+06	7.24E+06
<i>Evaluated By-product Sale Price (With 5% returns on capital investment per year)</i>	USD/ton	223.02	238.78	161.87
<i>Plant Capacity</i>	tons/Year	25027	33222	49581
<i>CU S onventional product price</i>	USD/ton	90		

The main reason for the higher selling price of by-product Na₂SO₄ from all options is due to the high price of raw materials in order to return the 5% yearly profit considered. The price of the NaOH

absorbent is \$350/ ton while that of Na_2CO_3 absorbent is \$200/ ton. This explains why the options utilising NaOH (Options 1.1 and 1.2) have higher expenses leading to a higher product selling price.

A sensitivity analysis on Options 1.1, 1.2 and 1.3 was conducted to investigate the economic viability of varying plant production on the selling price of by-product Na_2SO_4 (Table 6). This was to determine whether economies of scale could help bring the costs down through higher product output and make these options economically viable in comparison with conventional Na_2SO_4 . The findings from the sensitivity analysis in Table 6 show that economies of scale lower the overall price of Option 1.1 from \$223.02/ton to \$197.90/ton when production capacity is quadrupled. This is because the LCC cost reduces from \$252.68 to \$227.12, which helps to reduce the price per ton by-product Na_2SO_4 produced. The same applies to Options 1.2 and 1.3, where the price of by-product Na_2SO_4 (\$/ton) is reduced to \$200.10 (from \$238.78) and \$139.14 (from \$161.87) respectively when production capacity is quadrupled. However, the price of by-product Na_2SO_4 after quadrupling plant capacity for Options 1.1, 1.2 and 1.3 are still 219.9%, 222.3% and 154.6% higher than conventional Na_2SO_4 .

1 **Table 6** Sensitivity analysis of by-product costs for phosphogypsum case study after varying plant capacities

Pathway Options	Units	Option 1.1 (Double Capacity)	Option 1.1 (Quadruple Capacity)	Option 1.2 (Double Capacity)	Option 1.2 (Quadruple Capacity)	Option 1.3 (Double Capacity)	Option 1.3 (Quadruple Capacity)
<i>Total Project Capital Cost</i>	USD	1.18E+07	1.92E+07	9.46E+06	1.28E+07	5.06E+06	6.84E+06
<i>Total Operating Expenses</i>	USD/Year	1.99E+07	3.85E+07	2.01E+07	3.88E+07	1.70E+07	3.26E+07
<i>Total Raw Materials Cost</i>	USD/Year	1.72E+07	3.43E+07	1.72E+07	3.43E+07	1.45E+07	2.89E+07
<i>Evaluated By-product Sales Price (With 5% returns on capital investment per year)</i>	USD/ton	208.63	197.90	213.73	200.10	147.48	139.14
<i>Life Cycle Cost (LCC)</i>	USD/ton	236.62	227.12	177.90	169.76	96.78	92.40
<i>Plant Capacity</i>	tons/Year	50054	100108	66444	132887	99161	198322
<i>Conventional product price</i>	USD/ton	90.00					

2 The primary reason for the price of by-product Na_2SO_4 remaining higher than that of
3 conventional Na_2SO_4 is due to the value of raw materials that contributes about 89% of total operating
4 expenses for all options analysed. The price of raw materials increases linearly with the increase in
5 production capacity. Therefore, it can be concluded that even with increase in production capacity, the
6 options for PG precipitation are not economically feasible as they cannot produce by-product Na_2SO_4
7 that is comparable or can compete with conventional Na_2SO_4 in terms of price for use in the
8 production of packaging paper. The application of carbon tax through an additional sensitivity
9 analysis was also not practicable as the by-product Na_2SO_4 increases the overall GWP impacts when
10 utilised for producing by-product paper compared to the impacts of conventional paper.

11

12 **5. SOCIAL IMPLICATIONS OF PATHWAYS**

13 **5.1 Employment Opportunity**

14 The development of the proposed decomposing industry for the precipitation of PG creates
15 employment opportunities for people in the surrounding areas per single day of operation. The Aspen
16 Economic Analyser has estimated that irrespective of the size of the plant of all options considered for
17 economic assessment (Options 1.1, 1.2 and 1.3), two operators and a supervisor per shift will be
18 required during the normal operation of the plants. This is because all the plants will be automated
19 requiring less number of personnel to ensure proper operation. Considering that there are three shifts
20 per working day, there are opportunities for 6 operators and 3 supervisors to be employed in the
21 selected process pathways, a total of 9 skilled jobs. Additionally, during plant operation of the
22 proposed plant there are other employment positions created. These positions are in administration
23 where services of at least a receptionist, an accountant, several security guards (at least 6, with 2 per
24 shift) and an administrator are anticipated to be required. Thus, in total for any single day of
25 operation, it is envisaged that 18 employment opportunities will be required for the proposed plants.

26 The construction phase of the plants also presents numerous opportunities for employment as
27 both skilled and semi-skilled sets are required. Direct jobs resulting from construction include various
28 engineering roles required for supervising the construction and commissioning of the plant.
29 Contractors engaged in excavation, fabrication of plant equipment, plant setup, building of support

30 facilities such as pipes and roads are the other beneficiaries of direct jobs from construction. There are
31 also many indirect jobs resulting from construction and are linked to the supply chain of resources
32 used in construction. The incomes of the skilled jobs have been calculated by Aspen Economic
33 Analyser v8.4 to be USD\$58,440 and USD\$102,270 for an operator and supervisor respectively per
34 year. This is more than sufficient to meet all their basic needs and also have some savings. Thus, there
35 is a considerable benefit brought to the surrounding localities from the 9 skilled jobs created per ton of
36 by-product produced to replace conventional products through industrial symbiosis in the considered
37 case studies.

38

39 **5.2. Intergenerational Equity**

40 The proposed plant for the precipitation of PG with Na_2CO_3 is anticipated to reduce or preserve the
41 exploitation of natural sodium sulphate ores by 2.2 kg per ton of paper produced. However, the
42 embodied energy required for the conversion of PG is expected to be about 62.5GJs per ton of sodium
43 sulphate produced. This is 607% more embodied energy required than would have been used to
44 produce sodium sulphate via the Mannheim process (10.3 GJs) (Australian Life Cycle Inventory). This
45 was due to the intensive energy used for production of pure Na_2CO_3 used as reagent as opposed to the
46 Mannheim process, where Na_2SO_4 is produced as a by-product from hydrochloric acid production
47 resulting in a smaller environmental allocation. Most of the embodied energy used in the precipitation
48 of PG is utilised in the production process of the Na_2CO_3 reagent (24.6%) and the remainder is from
49 the steam generation using natural gas (68.4%). The Mannheim process has been used as reference as
50 there was no data on embodied energy derived sodium sulphate produced from natural ore.

51 **5.3. Avoided Land Use**

52 The recycling of PG is expected to reduce approximately 12000m² of land used for stockpiling of PG
53 based on the average plant operation of Option 1.1 that processes about 25,000 tons of PG annually
54 (or about 0.4m² per ton PG recycled). This result was based on the assumption that stockpiling is
55 made up to a metre in height and was calculated from the density of PG, 2.32 g/cm³ (dividing density
56 by metre height to get area). The reutilisation of PG for use as input by a surrounding industry through
57 industrial symbiosis is thus expected to save land that would actually be used for stockpiling PG. The

58 benefits of the avoided land use are that it could be reutilised for other economic benefits such as
59 expansion of the industrial plant or be sold for revenue generation. Additionally, there is a
60 considerable reduction of contamination of underground water sources or land from leaching of the
61 PG constituents.

62 **6. Conclusion**

63 In this research, analysis of different process options for the chemically decomposition of
64 phosphogypsum and use of resulting product for other manufactures were carried out. The findings
65 from LCA indicate that the phosphogypsum based paper and fertilizer are not environmentally
66 friendly in some aspects and also not economically profitable to conventional products.

67 Based on the findings from the research undertaken, it was found that solid wastes generated
68 for all options were offset from the utilisation of waste PG, but GWP, water use and EP of these by-
69 product based fertiliser and paper are higher than conventional products. Water use and electricity
70 consumption have been identified as the hotspots of these impacts associated with PG utilization.
71 There was no solution to alleviate the impact of water use, but the electricity generated from wind
72 mills instead of being supplied from an existing fossil fuel power plants of Western Australia could be
73 the best mitigation option considering the fact that the coastal area of WA has a large amount of wind
74 energy potential and the industries which are participating in the industrial symbiosis processes, are
75 also located on the coast (Biswas and Cooling, 2013).

76 Economic analysis evaluated that none of the process options for PG reduction were
77 economically profitable. This was due to the high cost of oxidants used in NO_x absorption, and the
78 high cost of ammonia reagents and NaOH reagents for PG reduction that offset gains from sales of
79 products formed. The introduction of economic instrument such as carbon tax has been found to make
80 emerging and new technologies cost-competitive for recycling or utilization of wastes and waste heat
81 applications (van Beers and Biswas 2008). However, the introduction of carbon tax is not possible to
82 enhance the viability of PG reduction as the GWP produced from by-product paper is more than that
83 of conventional paper. The most appropriate approach would be to conduct further research into

84 cheaper oxidant, reagents and symbiotic pathways that could potentially bring the overall cost
85 significantly.

86 Conversion of by-products, which is PG in this case study, to useful resources is inevitable
87 given the fact that the world is losing its carrying capacity and we are gradually running out of finite
88 non-renewable resources due to increased population growth, level of affluence and mechanization
89 processes. The sustainability assessment of this kind is important to put us in the right direction to
90 achieve the sustainability of these by-products utilization. From this aspect, LCA is a powerful
91 decision making tool to critically analyze the sustainability of industrial symbiosis involving
92 reuse/recycle and to propose strategies for sustainable by-product utilization.

93

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