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A Framework for Synergy Evaluation and Implementation in Resource Based Industries

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material that has been accepted for the award of any other degree or diploma in any university.

Signature: ………………………

Date: 26/10/2016

Abstract

Resource based industries have considerable impacts on the environment ranging from the depletion of non-renewable resources, landscape damage, emission of greenhouse gases and solid wastes. Industrial ecology offers long-term solutions that aim at achieving zero waste through reducing virgin resource use, increasing efficiency and formation of closed loop cycles. One potential tool of industrial ecology is industrial symbiosis through the utilisation of waste or by-products with neighbouring industries as feed material. Nonetheless, the implementation of industrial symbiosis has been mostly through the collaboration of industries with few studies encountered in literature that encourage identification of new symbiotic relations. Most of the current research has focused on sustainability studies that are performed on already existing industrial interaction (synergies).

The current research aims at developing a framework for new synergy evaluation and implementation incorporating process engineering concepts with sustainability principles. The specific objectives of accomplishing the research are: 1) to apply process engineering principles for developing resource synergies; 2) to conduct waste analysis, waste processing paths design, and optimization through laboratory scale experimentations and computer simulation; 3) to conduct life cycle assessment to identify opportunities for green process design; and 4) to assess the sustainability of green processes from social, environmental and economic aspects.

Firstly, using process knowledge a generic outlay was developed to encourage greater co-ordination between industries within a specific region. Possible by-products from particular industries were categorised according to their chemical composition. Recipient industries that had potential for industrial symbiosis were then identified from their feed requirements. Utilisation of the developed generic outlay to the Kwinana Industrial Area (KIA) highlighted the potential of utilising several by-products. Two of them have been used as case studies for the thesis and they are nitrogen oxides tail gases and phosphogypsum (PG).

NO_x absorption was analysed through simulation in Aspen Plus v8.4. PG reduction study was undertaken through the aid of laboratory experimentation and simulations. Optimisation for the use of sodium salts in the laboratory experimentation was done by analysing the effects of three variables (temperature, mixing speed, mole ratio of reagents to PG) on the reaction yield. The mass and energy balances determined from experiments and simulations were used to create the LCI for the life cycle assessment of the different process options. The LCI was fed into Simapro 8.03 software where the LCA studies were determined using data from the Australian LCI database. Environmental impacts considered from the LCA were global warming potential (GWP), eutrophication potential (EP), solid waste and water use for both case studies. Acidification potential (AP) was also considered for the NO_x absorption case study.

Overall, the best process option for the NO_x absorption and production of KNO_3 fertiliser was the use of H_2O_2 as oxidant and $Ca(OH)_2$ as absorbent. As for the PG reduction case study, none of the options were found to have lower environmental impacts compared to conventional paper production (sodium salts as reagents) or ammonium sulphate fertiliser production (ammonium salts as reagents). This was mostly attributed to the high water use in the reduction-oxidation stage. The only process option that was deemed suitable for reduction of PG was the one that utilised Na_2CO_3 as reagent.

The last objective undertaken was the determination of the economics of each process option and the social analysis of the profitable options. Economics was performed through the aid of Aspen Plus Economic Analyser v8.4 to estimate all the capital costs, operating costs and the proceeds from sales. In the NO_x absorption case study, none of the process options was found to be profitable due to the cost of using oxidants. As for the PG reduction case study, utilising sodium based reagents were found to be similar to the ammonium based options, where the cost of NaOH reagent made it not to be profitable compared to the use of sodium carbonate as reagent. The social benefits of setting up the PG reduction plant using sodium carbonate was found to create more employment opportunities, conserve land and energy resources for the future generation, reduce local and regional environmental pollution that can result health impacts and offer reduced PG stockpiled.

Therefore, the framework has shown that the establishment of new industrial synergies or symbiotic networks from both organic and inorganic wastes could be achieved with the aid of process engineering and sustainable principles. This is by a pragmatically selecting the most suitable pathway (environmentally and economically) for transforming the wastes to valuable products, which could be used to develop industrial symbiosis, which addresses the challenges of Industrial Ecology by reducing the overall environmental burden of an industrial system to provide services to the society. The result is closed looped systems that in the long term will help to conserve virgin resources and reduce the environmental impacts of heavy industries.

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List of Publications Arising from this Thesis

Published papers in refereed scholarly journals

1. Mohammed, Feisal Ali, Biswas, Wahidul K., Yao, Hong Mei and Tadé, Moses Oludayo, 2013. Assessment of industrial by-product synergies from process engineering and sustainability principles. Progress in Industrial Ecology: an international journal (PIE). 8 (3):156-165.
2. Mohammed, Feisal Ali, Biswas, Wahidul K., Yao, Hong Mei and Tadé, Moses Oludayo, 2016. Identification of an environmentally friendly symbiotic process for the reuse of industrial by-product – an LCA perspective. Journal of Cleaner Production. 112 (4): 3376-3387.

Published peer-reviewed conference papers

1. Mohammed, Feisal Ali, Yao, Hong Mei, Tadé, Moses Oludayo and Biswas, Wahidul, 2013. A framework for synergy evaluation and development in heavy industries, in Nee, A. Y. C., Song, B., Ong, S. K. (ed), Re-engineering manufacturing for sustainability, 20th CIRP International Conference on Life Cycle Engineering, Apr 17-19, 2013, pp. 591-595. Singapore: Springer.

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Annotations

ACD -	Acid mine drainage
AP -	Acidification Potential
CAPEX -	Capital expenses
CO_2-e -	CO_2 equivalent
DSS-	Decision support system
Ea -	Activation energy
EDX -	Energy-dispersive x-ray
EIP-	Eco-industrial parks
EP -	Eutrophication Potential
EPA -	Environmental Protection Agency
GHG -	Greenhouse gases
GWP -	Global warming potential
HAP -	Hydroxyapatite
ICP-AES -	Inductively coupled plasma atomic emission spectrometer
IE -	Industrial ecology
KIA -	Kwinana Industrial Area
kWh -	Kilowatts per hour
LCA -	Life Cycle Assessment
LCI -	Life Cycle Inventory
MFA -	Material flow analysis
MINLP-	Mixed integer non-linear programming
Mt -	Million tonnes
MVR -	Modified reaction model
NORM -	Natural occurring radioactive materials
OPEX -	Operating expenses

PG -	Phosphogypsum
PO_4^-- e -	Phosphate equivalent
rpm -	Revolutions per minute
SCR -	Selective Catalytic Reduction
SNCR -	Selective Non-Catalytic Reduction
SLCA -	Streamlined LCA
TGA -	Thermogravimetric analysis (TGA)
wt% -	weight percentage
w/v -	weight per unit volume
w/w -	weight over weight basis
XRD -	X-ray Diffractometer

Chapter 1 Introduction

This chapter introduces the objectives set out in conducting the PhD studies. It begins with a background of environmental considerations in industry from reactive responses to environmental legislation to the sustainable approaches of industrial ecology and industrial symbiosis. Thereafter, the objectives and significance of the research is described before presentation of the thesis outline.

1.1 Background

Traditionally, the main objective of resource-based (process and mineral) industries has been economic considerations where the set aim is the minimisation of production costs thereby maximising profits (Alexander *et al.*, 2000). However, industrial activities bring considerable environmental impacts. These include landscape damage, depletion of non-renewable resources from extractive operations (Azapagic, 2004), and emissions from minerals processing in the form of toxic greenhouse gases and large amounts of solid wastes (Broadhurst & Petrie, 2010). The gaseous emissions have resulted in the well-known phenomena of global warming. Solid waste emissions also bring considerable concerns over the long term from the leaching of metals and hazardous salts resulting from processing operations. These affect ecological health, bio-diversity and socio-economic well-being of local communities (Broadhurst & Petrie, 2010).

With global warming awareness, environmental factors based on legislative constraints become necessary to be incorporated as an objective (Guillén-Gosálbez, 2011). The reactive responses of companies to legislation mean end-of-pipe solutions are always sought to meet set requirements. These include minimizing leaching, noise pollution and substance release (Driussi & Jansz, 2006,) all which are remediation and treatment procedures. However, due to the ever changing and stringent government legislation coupled with exorbitant end of pipe solutions, the process industries have to rethink of their approach from scratch. This is where pollution prevention techniques were developed such as waste minimization (Barrett *et al.*, 2011; Mauricio & Karen, 1999; Chang & Hwang, 1996) and the 3Rs concepts (reduce, reuse and recycle). Introducing pollution reduction objectives in resource industry operations saw the innovation of new technologies which are mostly addons to existing facilities (Guillén-Gosálbez *et al.*, 2008), or retrofitting of existing operations and units (Tan & Cruz, 2004). However, end-of-pipe techniques and re-design are all short term strategies for environmental compliance.

There is hope, from the development of effective industrial ecology strategies through the aid of life cycle assessment (Seager & Theis, 2002) including eco-efficiency, cleaner production and industrial symbiosis (Basu & van Zyl, 2006; Gerber *et al.*, 2011; Verhoef *et al.*, 2006). Industrial ecology is the study on the material and energy flows between industrial systems and the resultant effects on the environment (Rosenthal, 2004; Urmila, 2005). The above mentioned strategies, currently being implemented globally, are long term ones that aim at achieving zero waste through reducing virgin resource use, increasing efficiency and formation of closed loop cycles.

Industrial symbiosis (synergy) remains an untapped potential with some developed methodologies and tools that have few industrial applications (van Beers, 2009). It involves the interaction of industries whereby wastes and by-products of an industry are re-utilised by others so that both can be effectively minimized. In order to be effective, industrial symbiosis is involved with industries that are clustered together within a locality so that overall savings of transport and resource availability are achievable (Chertow, 2007). With a varied group of industries clustered together, there is potential to attract new industries which can source their raw materials from the wastes of other industries and their wastes can also find use within the industrial clusters, thereby enhancing further synergy developments. The aim is to form closed loops whereby material streams are maintained within the industrial system, and the contact with the surrounding environments is greatly reduced (Faria & Bagajewicz, 2011; Luo & Uan, 2008).

The resource industries are one of the most pollutive in terms of emissions and waste generation. Therefore, it is an ideal focus for industrial synergy development which aims at reducing pollution in these industries through energy efficiency, water recycling, and waste re-use by other industries. However, most of the current research on the same in resource based industries has primarily focused on the application of sustainability principles to existing synergies (Kurup *et al.*, 2005; van Beers, 2009). The application of the same principles in identifying and developing further industrial synergies has not witnessed much effort. Therefore, one of the highlights of the thesis at hand will be the development of a sustainable framework with the incorporation of process engineering concepts for the evaluation and implementation of potential synergies.

The presence of industrial interactions and already developed synergies (van Beers et al., 2007), plus the close proximity makes Kwinana Industrial Area (KIA) the most ideal case study for the research. As with elsewhere in Australia and globally, the KIA is facing sustainability challenges on various fronts, including water and energy scarcity, climate change, an aging workforce, and growing community sustainability expectations. According to the previous research (van Beers, 2008), four areas can be considered for further focus: the use of inorganic mineral wastes, enhancing by-product synergies, waste water utilisation and energy economy. These areas are where the proposed framework has been applied to in order to aid in furthering the closed loop system and in the long run achieving zero waste.

1.2 Objectives of the Research

The goal of this research is to develop a framework for new synergy evaluation and implementation; incorporating process engineering concepts with sustainability principles. It aims at investigating the potential of converting industrial by-products and wastes to useful resources for neighbouring industries and assessing sustainability implications. The specific objectives to obtain this goal are as follows:

a) Develop a theoretical framework encompassing green engineering principles, LCA, socio-economic analysis for evaluating synergies in an industrial area.
b) To apply process engineering principles for developing resource synergies in the Kwinana Industrial Area, a case study for this PhD research. One of the main benefits brought about by incorporating process engineering in synergy development is the ability to convert waste from an unwanted state to a desired one through processing. It also aids in identifying the most ideal industry compatible for synergy realisation through the waste processing pathway options.
c) To conduct life cycle assessment to identify opportunities for green process design through the assessment of environmental impacts and burdens avoided

from the development of identified synergies. The LCA will focus on the analysis of complete material streams of virgin resource up to the utilisation of the waste products by neighbouring industries through industrial symbiosis – cradle to gate approach.

d) To conduct waste analysis, waste processing paths design, and optimization through laboratory scale experimentations and computer simulation. The above mentioned categories/principles of sustainable engineering will be analysed for the synergy evaluation through g*reen process design and optimisation*. The focus on application of each of them will be through the design and optimisation of intermediary decomposing processes for wastes identified for synergy applications.

   Note: Decomposing process is one where wastes are chemically converted into different chemical compositions or compounds through addition of reagents in order to make them reusable.

e) To assess the sustainability of green processes from social, environmental and economic aspects. In order for the realisations for any synergy evaluations, the main factors to be considered will be economic and social. The environmental factors will be incorporated through the process design. Profit is the motive of every company yet there will be social obligations from government policies, local community demands and industry's integrity. Thus, to address these, economic (discounted cash flow analysis) and social assessment will be carried out. The outcomes of the assessments are what will motivate the stakeholders (industry, government and local community) to assess the fruition of any practical synergy implementation.

1.3 Significance and Contributions of this Study

Research on industrial ecology in resource industries has primarily focused on the application of sustainability principles to existing synergies. The incorporation of green process engineering application to the same industries will reduce resource scarcity and environmental degradation by converting wastes and by-products to useful resources. The overall contributions that will result from the research are:

- Encouraging Industrial and Academic collaboration – through industrial interaction, physical data and samples will be used to develop a real case model for synergy development.
- Application of the concept of industrial symbiosis to evaluate both inorganic and organic waste potential – most developed synergies in Kwinana have focused on inorganic wastes but organic wastes have been neglected. The research will bridge this gap by looking at both categories.
- Application of green process engineering for synergy realisations – the efficient optimisation, design and simulation of waste processing for re-use through sustainability principles incorporation is still at infancy and the research will aim at developing a green process for synergy visualisation.

1.4 Thesis Outline

The outline of the thesis is represented in Figure 1.1, which describes the contents covered in the 8 chapters that make up the thesis. An overview of each of the chapters is presented below:

- Chapter 1 introduces the scope and aims of the research.
- Chapter 2 highlights the current scholarly literature on nitrogen oxides flue gas control and phosphogypsum reuse, the two case studies identified through the developed framework in Chapter 3.
- Chapter 3 describes the details of the framework developed to encourage industrial symbiosis from the identification of waste or byproduct reuse options (to surrounding industries) through the application of process engineering and sustainability principles.
- Chapter 4 details the methodology employed in applying the framework to the two case studies. The methodology describes the steps applied for establishing industrial symbiotic links from experimental analysis, life cycle assessment, economic and social analysis assessment.
- Chapter 5 covers the application of the framework to the nitrogen oxides flue gas from nitric acid plants for their reuse in fertilizer production (potassium nitrate) through oxidation and absorption processes. It demonstrates the

employing of the methodology presented in Chapter 4 up until the life cycle assessment stage.

- Chapter 6 covers the application of the framework to phosphogypsum reuse potentials though redox reaction with suitable reagents for conversion into valuable products that could be used in paper or ammonium sulphate fertilizer production. Similar to Chapter 5, it follows the methodology covered in Chapter 4 up to the life cycle assessment stage.
- Chapter 7 discusses the economic and social analysis of the symbiotic linkages formed through the case studies employed in Chapters 5 and 6. This is to assess the economic profitability and social benefits as a result of the reuse of byproducts by neighbouring industries.
- Chapter 8 provides the conclusions of the thesis and recommendations for future work.

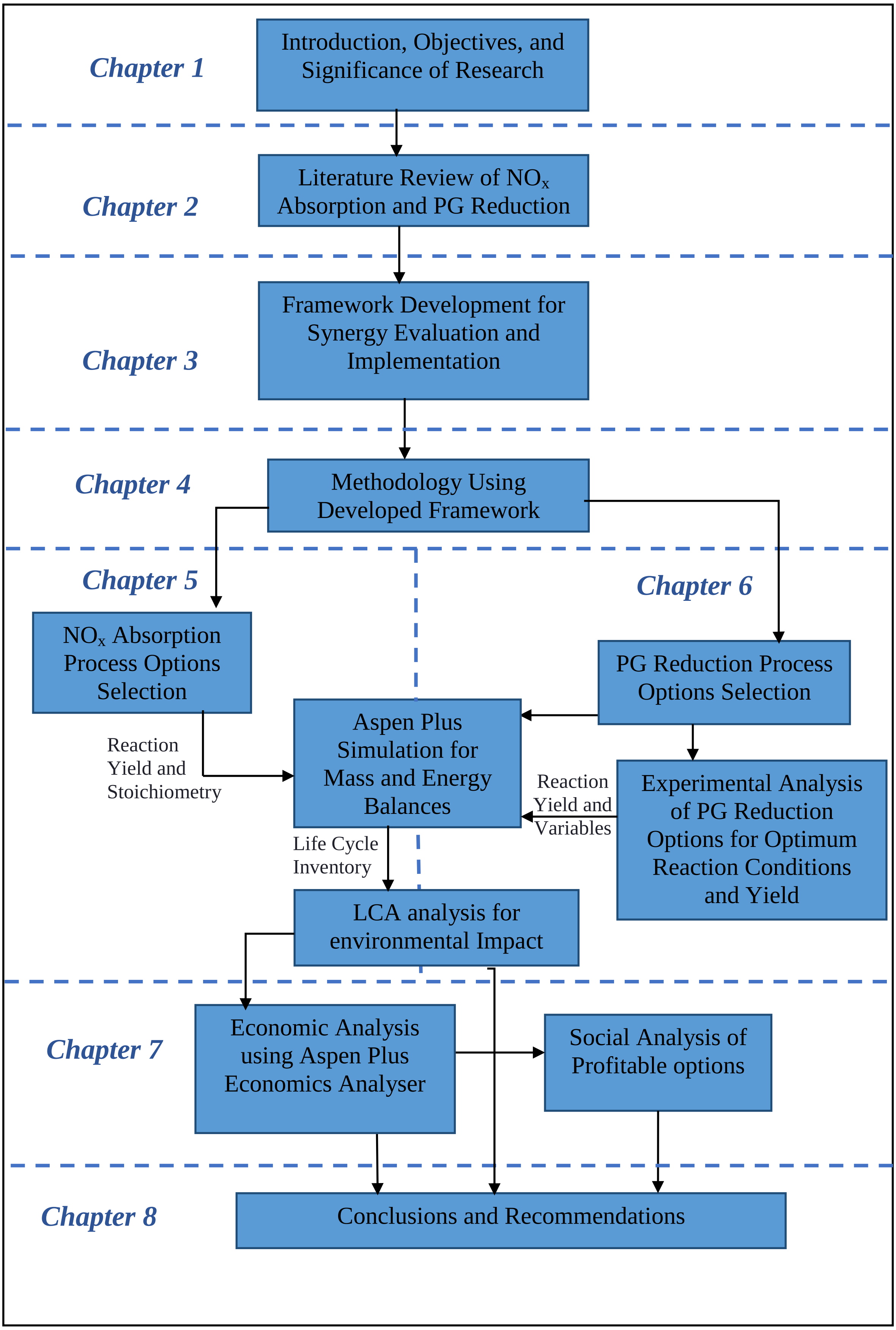

Figure 1.1 Thesis Outline

Chapter 2 Literature Review

2.1 Introduction

This chapter details the review of literary research work that has been performed on the two cases under investigation using the developed framework, i.e. nitrogen oxides (NO_x) absorption and phosphogypsum reduction. It begins with the various technologies that have been developed to control NO_x absorption before reviewing the different alkaline absorption and oxidation reagents that have been used to convert NO_x to valuable nitrates or nitrites. The review then elaborates on the different reuses of phosphogypsum through the use of various reductants to produce valuable products like calcium oxide and sulphur dioxide. Finally, it covers the use of redox reagents to reduce phosphogypsum while forming various valuable sulphates. Sections of the review have been adapted/ reprinted from the publications of Mohammed *et al.* (2013a) and Mohammed *et al.* (2016), with permissions from Copyright 2013 Springer (Appendix 1) and Copyright 2016 Elsevier BV (Appendix 3) respectively.

2.2 Nitrogen Oxide Tail Gases

Nitric oxide (NO) and nitrogen dioxide (NO_2), together known as NO_x, are harmful emissions produced primarily from the combustion of fossil fuels for energy generation in power plants and automobiles. Over 95% of NO_x emitted from the combustion of fossil fuels are NO (Chen *et al*., 2002). Another major source of NO_x emissions is from the manufacture of nitric acid, which is produced in bulk mainly for fertiliser and adipic acid production. The ratio of NO to NO_2 in NO_x emissions from nitric acid plants is equimolar i.e. one mole of NO_2 for every mole of NO emitted (European Commission, 2007). These gases are detrimental to the environment as they cause acidification of soil, water and air, visibility issues and health effects (Chen *et al.*, 2005; Pourmohammadbagher *et al.*, 2011).

There are various technologies that have been developed to control NO_x emissions, the most common of which are: Selective Catalytic Reduction (SCR); Selective Non-Catalytic Reduction (SNCR); and Alkali Absorption (Lee *et al.*, 2005). The SCR method incorporates the use of special catalysts to breakdown nitrogen oxides to nitrogen and oxygen gases. For tail gas comprising only nitrogen monoxide (NO), SCR is ideal with very high efficiencies. However, in the case of nitrogen dioxide (NO_2), higher temperatures of more than 400°C are required to effectively reduce them (Yoshikawa *et al.*, 1998). This is the major drawback of SCR as higher tail gas temperatures mean higher energy costs, which can make the process economically unviable. In addition, the capital cost of setting up the SCR technology and cost of catalysts and their regeneration are also highly expensive (Jakubiak & Kordylewski, 2011; Wang *et al.*, 2007).

The SNCR method utilises reductants to react with the oxygen atoms in nitrogen oxides thereby reducing them to nitrogen gas, water and CO_2 (Zabetta *et al.*, 2005). Hydrocarbons, generally methane, are one of the most widely used reductants for SNCR methods. The use of hydrocarbons is equally effective at lower tail gas temperatures for NO_x reduction as the SCR methods. However, the use of hydrocarbons results in the production of CO_2, a green-house gas. Furthermore, there is additional expense associated with using hydrocarbons. The use of urea and ammonia can replace the use of hydrocarbons to lower costs. However, urea is affected by temperature – lower temperatures affect efficiency, while ammonia has high capital costs for setup (Javed *et al.*, 2007; Nguyen *et al.*, 2008).

The direct reduction method entails the scrubbing of tail gases through a liquid medium to absorb the nitrogen oxides. Water and alkali/alkali earth oxides solutions are the main liquids employed for the absorption. Alkali absorption has the advantage of being economically cheaper in comparison to SCR and SNCR (Jakubiak & Kordylewski, 2012; Fang *et al.*, 2013). Additionally, the acidic nature of NO_x facilitates reaction with the alkaline bases to produce neutral salt by-products that can be recovered and utilised as a valuable resource for industries such as fertiliser, glass making, explosives and pigment (Thomas & Vanderschuren, 2000).

However, NO is a highly stable compound that does not react easily with absorbents. Therefore, oxidants are used to enhance NO absorption by oxidising it into soluble NO_2 that is readily absorbed by suitable absorbents. The presence of NO_2 in equimolar amounts, as from NO_x emissions in nitric acid plants, facilitates NO_x absorption with the formation of mainly nitrites and small amounts of nitrates (Patwardhan & Joshi, 2003). Oxidants are thus utilised to oxidise both NO and NO_2

to higher nitrogen oxides before absorption with alkaline solutions in order to convert any nitrite by-product salts into nitrate salts.

2.2.1 Alkaline Absorbents Used for NO_x Scrubbing

There are numerous studies that have assessed the use of various absorbents for NO_x tail gas abatement associated with the production of a range of economically valuable by-product salts. Table 2.1 presents some of the absorbents that have been utilised for NO_x absorption from literature. The use of sodium hydroxide (NaOH) or calcium hydroxide ($Ca(OH)_2$) as absorbents for the reduction of NO_x has been widely studied, particularly for the formation of respective nitrates and nitrates (Pradhan & Joshi, 1999; Pradhan & Joshi, 2000; Zhang *et al.* 2008; Patwardhan & Joshi, 2003). Fang *et al.* (2013) have investigated the use of urea with potassium permanganate ($KMnO_4$) for NO_x and SO_x emissions abatement from coal plants. Ammonium sulphate by-product is produced from the absorption process.

Sun *et al.* (2011) have investigated the use of low grade pyrolusite slurry with low MnO_4 concentration in combination with ozone for NO_x absorption and realised high manganese extraction in the form of $Mn(NO_3)_2$ as by-product, thereby transforming low grade ore to a valuable resource.

Table 2.1 Different absorbent efficiencies for NO_x removal

Absorbent	**Oxidant**	**Potential NO_x Removal Efficiency and Condition**	**References**
Ammonium Hydroxide (NH_4OH)	None	90-95%	Kuropka, 2011; Zhang *et al.*, 2008
Ammonium Sulphite ($(NH_4)_2SO_3$))	Ozone	93%	Wang *et al.*, 2013
Calcium Hydroxide ($Ca(OH)_2$)	None	85% (363K)	Chen *et al.*, 2010
$Ca(OH)_2$	Calcium hypochlorite ($Ca(OCl)_2$)	65%	Kuropka, 2008
Calcium Sulphite ($CaSO_3$)	None	73% (293K)	Chen *et al.*, 2002; Wang *et al.*, 2012
Potassium Carbonate (K_2CO_3)	None	<90%	Huang & Dang, 2011; Kuropka, 2011; Zhao *et al.*, 2009
Potassium Hydroxide (KOH)	None	>95%	Kuropka, 2011; Zhang *et al.*, 2008
Pyrolusite slurry (22% MnO_2)	Ozone	82%	Sun *et al.*, 2011
Sodium Chlorite ($NaClO_2$)	Sodium Hypochlorite	85% (323 K)	Zhao *et al.*, 2010

Absorbent	**Oxidant**	**Potential NO_x Removal Efficiency and Condition**	**References**
	(NaClO)		
Sodium Hydroxide (NaOH)	None	95% (308K)	Zhang *et al.*, 2008
NaOH	Ozone (O_3)	95% (298K)	Jakubiak & Kordylewski, 2012
NaOH	$NaClO_2$	95% (323K); 72% (318K)	Chu *et al.*, 2001; Jin *et al.*, 2006
Sodium Sulphide (Na_2S)	Ozone	95%	Mok & Lee, 2006
Sodium Sulphite (Na_2SO_3)	None	92% (293K); 99% (298K)	Chen *et al.*, 2002; Wang *et al.*, 2012
Na_2SO_3 and Na_2S	Ozone	95%	Mok, 2005
Water in oxidant solution	Hydrogen Peroxide (H_2O_2)	91% (310K)	De Paiva & Kachan, 1998
Water in oxidant solution	Sodium hypochlorite (NaClO)	92% (293–323K)	Mondal & Chelluboyana, 2013

2.2.2 Use of Oxidants for NO Oxidation to NO_2 and Higher Nitrogen Oxides

There are various oxidants that have been used to oxidise NO and NO_2 into higher nitrogen oxides that can be easily absorbed by alkaline solutions due to their high solubilities. The most common oxidants identified in literature are hydrogen peroxide, ozone and oxychlorides (Zhao *et al.*, 2015; Jakubiak & Kordylewski, 2012; Skalska *et al.*, 2012a; Kuropka, 2011).

2.2.2.1 Hydrogen Peroxide

The use of hydrogen peroxide (H_2O_2) for the control of NO_x tail gases has been widely investigated in literature (Thomas & Vanderschuren, 1996). Most of the earlier studies concentrated on the dry oxidation of NO_x (gaseous state) through injection of a H_2O_2 mist into combustion flue gases at high temperatures (Collins *et al.*, 2001). At these temperatures, H_2O_2 decomposes to form highly reactive hydroxyl radicals ($OH^\bullet$) that oxidise NO into NO_2, and NO_2 into higher nitrogen oxides that can be easily absorbed by various solvents due to higher solubilities (Kasper *et al.*, 1996).

The optimum temperature for uniform H_2O_2 decomposition and thus higher oxidation of NO_x was evaluated to be about 500°C (Kasper *et al*., 1996; Zamansky *et al.*, 1996; Collins *et al.*, 2001). The effect of different mole ratios of hydrogen peroxide to NO was studied on the oxidation of efficiency. Zamansky *et al.* (1996) obtain 90% NO oxidation at H_2O_2:NO of 1.5:1, Kasper *et al.* (1996) obtained a 75% NO oxidation at H_2O_2:NO of 1.6:1 and Collins *et al.* (2001) obtained a 90% NO oxidation at H_2O_2:NO of 0.97:1. Kasper *et al.* (1996) attribute their low conversion rate to destruction of OH^- radicals at reactor walls, an effect attributed to higher H_2O_2:NO mole ratio (1.6 in this case) than that of optimum conditions (0.5 -1 H_2O_2:NO). Zamansky *et al.* (1996) used methanol as an additive that also oxidises NO while being reduced to CO, while Collins *et al.* (2001) investigated optimum injector location and H_2O_2 atomisation to reduce destruction of the $OH^\bullet$ radicals. This is the reason the latter two authors had higher NO oxidation than Kasper *et al.* (1996).

NO_x tail gases from chemical industries like nitric acid, nitrocellulose and adipic acid plants are mostly released at lower temperatures – from ambient to above 30°C

(Thomas & Vanderschuren, 1998). The use of dry oxidation becomes unfeasible for these types of NO_x flue gases because of the temperature difference, and thus most of the recent research has investigated the use of liquid phase oxidation of NO_x at low temperatures using hydrogen peroxide (Cooper *et al.*, 2002; Myers & Overcamp, 2002; De Paiva & Kachan, 2004).

Analysis of the effect of different H_2O_2 concentrations on NO_x oxidation concluded that there was no increase in oxidation with an increase in H_2O_2 concentration but oxidation occurred according to stoichiometry, which is based on the concentration of NO_x in flue gas ((Thomas & Vanderschuren, 1996).

The acidification of H_2O_2 solution during oxidation through the addition of either sulphuric acid or nitric acid was found to increase the oxidation of NO_x. This was because the acids facilitated H_2O_2 oxidisation of NO to NO_2 and oxidation of nitrous acid formed through absorption to nitric acid (Thomas & Vanderschuren, 2000; Liémans *et al.*, 2011)

The effect of temperature on the oxidation and absorption was found to decrease with an increase in temperature. Thomas and Vanderschuren, (1998) attribute this to the reduction in interfacial area of reaction and the fact that NO oxidation is lower with increased temperature meaning higher soluble nitrogen oxides like N_2O_3 and N_2O_4 are not produced at higher temperature.

2.2.2.2 Oxychlorides

Various oxychlorides have been investigated in literature for the oxidation of NO_x. The most common are chlorine dioxide gas (ClO_2), sodium chlorite ($NaClO_2$) and sodium hypochlorite (NaOCl) (Chen *et al.*, 2005; Mondal & Chelluboyana, 2013; Guo *et al.*, 2013).

In the presence of acidic conditions (low pH) such as HCl, $NaClO_2$ solution decomposes to ClO_2 gas which is the main species responsible for oxidising NO into HNO_3 (Yi *et al.*, 2011). ClO_2 gas can also be formed from reacting sodium chloride and sodium chlorate ($NaClO_3$) in concentrated acid (Deshwal *et al.*, 2008). Thus, $NaClO_2$ use is analogous to ClO_2 gas as oxidants. Temperature was found to influence the oxidation ratio of these oxidants with a corresponding increase in NO oxidation with increase in temperature up to an optimum of 50°C (Yi *et al.*, 2011).

At temperatures above 50°C, the oxidation rate decreased due to limiting mass transfer from gas phase to liquid phase caused by the negative effect of increased temperature on the exothermic reaction of NO oxidation (Zhao *et al.*, 2011b). In contrast, when $NaClO_2$ is mixed with NaClO in a molar ratio of 0.5:1, NO oxidation increased with increasing temperature up to 120°C and 74% oxidation, beyond which gas solubility decreased and hence reduction in NO oxidation (Zhao *et al.*, 2012). In order to reduce the cost of expensive $NaClO_2$, investigation of the addition of NaOCl found that at an optimal mixing of NaOCl: $NaClO_2$ in 4.1:1 and temperature of 50°C, greater than 90% NO oxidation could be achieved through use of cheaper NaOCl (Zhao *et al.*, 2011a).

When NaClO is used as an oxidising agent and dissolved in water, HClO is the main active species formed, which is responsible for NO oxidation and NO_2 absorption, requiring an optimum pH range of 5-6 for its formation (Chen *et al.*, 2005). Mondal and Chelluboyana (2013) analysed the effects of temperature on oxidation of NO with NaClO and established that an increase in temperature causes a corresponding increase in oxidation rate up to 40°C. Further increase in temperature resulted in lower oxidation rates, which the authors attributed to unwanted side reactions that led to formation of NO. In order to decrease the side reactions that led to NO formation, Chen et al (2005) analysed the effects of different NaClO concentrations at ambient conditions and found that increasing NaClO concentrations increased both NO oxidation and absorption while limiting side reactions. However, the oxidation and absorption rates could only be increased up to the stoichiometric balance of NaClO and NO_x to be absorbed (Kuropka, 2011).

The presence of NaOH was found to hinder the oxidation of NO by $NaClO_2$ resulting in lower NO_x removal and is ascribed to the hindrance of ClO_2 formation by NaOH (Chu *et al.*, 2001). This is because the oxidation of NO by HClO and ClO_2 is affected by pH and occurs optimally at low acidic concentrations, pH of 4 to 6 (Chen *et al.*, 2005; Chien *et al.*, 2001; Pourmohammadbagher *et al.*, 2011; Krzyzynska & Hutson, 2012). Therefore, the addition of NaOH increases the pH and reduces the acidity of the solution thereby inhibiting NO oxidation by oxychlorides. However, after oxidation at low pH, the use of alkaline solutions such as NaOH is suitable because NO_2 absorption takes place at alkaline conditions of pH > 8 (Chien *et al.*, 2001). Similar findings were found for the use of H_2O_2 as oxidant, where there was increased oxidation due to facilitation of H_2O_2 decomposition to reactive hydroxyl ions under acidic conditions (Thomas & Vanderschuren, 2000; Liémans *et al.*, 2011). Thus, oxidation of NO should be done separately as a first step before the absorption with suitable alkaline reagents in a subsequent step or column.

2.2.2.3 Ozone

The oxidation of NO_x using ozone takes place in the gas phase due to the limited solubility of both NO and ozone (O_3) before absorption with water or alkaline solutions (Yasuda *et al.,* 2011). NO reacts very rapidly with ozone leading to its oxidation to NO_2 and an increase in ozone concentration causes a corresponding increase in NO oxidation (Mok *et al.*, 2005; Skalska *et al.*, 2009; Sun *et al.*, 2011). The optimum ratio for complete NO oxidation was evaluated experimentally to be a mole ratio of 1 for O_3/NO (Skalska *et al.*, 2012b). A greater than 1 O_3/NO ratio leads to the oxidation of NO_2 formed into higher oxides such as nitrate (NO_3) and dinitrogen pentoxide (N_2O_5) (Mok & Lee, 2006; Skalska *et al.*, 2012b).

Studies on NO_2 oxidation with ozone have shown that a mole ratio of 0.5 O_3/NO_2 is sufficient for total oxidation of NO_2 into higher nitrogen oxides (Skalska *et al.*, 2011, Stamate *et al.*, 2010). When both NO and NO_2 are present in the flue gas, as observed in tail gases from chemical industries, the selectivity of NO oxidation takes precedence and only when NO is completely oxidised can NO_2 oxidation take place (Stamate *et al.*, 2010). Evaluation of the optimum concentrations of ozone concentration with respect to NO_x (1 mole each for NO and NO_2) show that at least 2 mols of ozone are required for complete oxidation before absorption with suitable reagents (Stamate *et al.*, 2010; Skalska *et al.*, 2011; Jakubiak & Kordylewski, 2012).

Wang *et al.* (2010) studied the effect of ozone jet introduction on NO_x oxidation. A key finding on their study was that the flow of ozone affected the oxidation rate. Turbulent flow was observed to offer better interaction with NO_x through homogenous mixing, while at laminar conditions the uniformity in mixing was reduced due to symmetric flows, which resulted in lower oxidation ratios for NO_x. Jakubiak and Kordylewski (2011) analysed the effect of using different amounts of ozone introductory nozzles and evaluated that NO oxidation was improved with more nozzles when the ratio of O_3/NO was less than stoichiometry. This was because of homogenous mixing that improved the ozone and NO_x interaction. However, at

O_3/NO_x ratios higher than stoichiometry, the increased number of nozzles did not improve the oxidation. This could be due to higher flow rates (turbulent flow) that encourage better mixing according to the findings of Wang *et al.* (2010).

The effect of temperature on NO_x oxidation with ozone was determined to be negligible up to 160°C (Mok *et al.*, 2005) and in other studies up to 200°C (Wang *et al.*, 2007). However, beyond this temperature there was a decrease in oxidation resulting from the fact that ozone decomposes to oxygen at elevated temperatures, which reduces the amount of ozone used for oxidation (Mok *et al.*, 2005; Jakubiak & Kordylewski, 2011; Wang *et al.*, 2007). Mok *et al.* (2005) attribute the reduction in NO_x oxidation to incomplete mixture of ozone and NO_x, which reduces the oxidation reaction due to ozone slip that increases with temperature.

The next section covers literature review of the second case study analysed in this thesis, which is the reduction of phosphogypsum (PG) to obtain useful and valuable products that could be utilised for industrial symbiosis.

2.3 Recycling of Phosphogypsum for Industrial Symbiosis

Phosphoric acid is mainly utilised in the production of phosphate fertilisers, which means it is vital for crop production and of key economic importance. However, the major by-product from phosphate rock digestion by sulphuric acid is PG.

It is estimated that the production of 1 ton of P_2O_5 (phosphoric acid expressed as dry product) produces about 5 tons of PG through the phosphate rock digestion process or “wet acid” process (El-Didamony *et al.*, 2012). The world production of phosphoric acid in terms of P_2O_5 is provided in Figure 2.1.

From Figure 2.1, based on 2011 reported values, approximately 38 million tons (Mt) of P_2O_5 were produced annually for phosphoric acid production. More than 90% of phosphoric acid produced worldwide is derived from the wet acid process (Tayibi *et al.*, 2009), which translates to 170 Mt of PG produced based on the 2011 values.

Figure 2.1 Global Annual Production of Phosphoric Acid in terms of P_2O_5 (Source, PotashCorp. 2011)

2.3.1 Potential Reuse of Purified Phosphogypsum

About 15% of total produced PG is utilised in the production of building materials, soil amendment, fertilisers, etc. (Tayibi *et al.*, 2009). The rest of the PG is stockpiled as waste due to the presence of natural occurring radioactive materials (NORM) and heavy metals, which limit its reuse.

The typical concentration of radionuclides in Australian PG in Bq/kg is highlighted in Table 2.2 (IAEA, 2012). In comparison, the average natural background concentrations of soils in Australia contain between 5 - 60 Bq/kg for both uranium and thorium (Cooper, 2005). Tayibi *et al.* (2009) and El-Didamony *et al.* (2013) reported that United States EPA has banned any reuse of PG that exceeds 370 ^{226}Ra radiation of Bq/kg as it poses severe health concerns beyond that radiation limit.

Table 2.2 Average Concentrations of Radionuclides in Australian Phosphogypsum in Bq/kg (IAEA, 2012)

^{226}Ra	^{238}U	^{210}Pb	^{210}Po	^{232}Th
280–350	10–24	320–440	150–360	4–7

However, based on the IAEA (2012) data in Table 2.2, Australian PG has the potential to be reused. The radiation limit can be lowered further by pre-treatment of PG in order to remove the radionuclides present and any heavy metals.

There are various processes in literature that have been investigated for the reduction of the radionuclides and heavy metals to make PG reuse possible. Binnemans *et al.* (2015) and Tayibi *et al.* (2009) provided a comprehensive review of the separation of radioactive nuclides from PG before it can be utilised for other purposes. The most suitable process for the separation of radionuclides and heavy metals from PG is the use of 4-7% H_2SO_4 solution (Habashi, 1985, Todorovsky *et al.*, 1997, Jarosiński *et al.*, 1993, 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.

There are various processes that have been utilised for the extraction of the sulphate in PG. The two most widely reported methods in literature are the use of reductants and reduction-oxidation using suitable reagents.

2.3.2 The Extraction of Sulphate from Phosphogypsum

2.3.2.1 Use of Reductants

The use of reductants incorporates the thermal decomposition of calcium sulphate (bulk of PG) at elevated temperatures by the reduction of the oxygen atoms present in $CaSO_4$ to form either calcium sulphide (CaS) or calcium oxide (CaO) and sulphur dioxide gas (SO_2) depending on the temperature of decomposition. The most common reductants investigated for the reduction of PG are carbon and carbon monoxide.

(1) Carbon Monoxide

The use of carbon monoxide (CO) as PG reductant occurs in two stages, all of which are dependent on the temperature of reduction (Kuusik *et al.*, 1985). At temperature ranges between 800-960°C, PG is reduced to calcium sulphide (CaS) by CO that is itself oxidised to CO_2 (Kuusik *et al.*, 1985; Ma *et al.*, 2012). When the temperature range increases from 1000-1100°C, CaO and SO_2 are the principal products of PG reduction with CO (Kuusik *et al.,* 1985; Ma *et al.,* 2012).

The decomposition of PG with CO was observed to be about 100°C lower compared to reduction of natural gypsum with CO. This was assumed to be due to impurities present in the PG and its crystal structure that helped to lower the reaction temperature (Gruncharov *et al.,* 1985a). Further studies on the effect of different additives on PG reduction proved the assumption to be valid. When 5% $CaCl_2$ was added to PG, it reduced the starting temperature of decomposition to 790°C (by 10°C) (Ma *et al.*, 2012). $CaCl_2$ addition also increased the reaction efficiency, which was evidenced through a higher mass loss of PG at the initial reaction temperature. The addition of 5% Fe_2O_3 together with the $CaCl_2$ also enhanced the decomposition of PG by increasing the mass loss further by 1% compared to addition of $CaCl_2$ alone(Ma *et al.,* 2012).

The effects of different CO concentrations on the decomposition showed that as the concentration of CO reduced (in CO_2 carrier gas), CaO was the favoured product instead of CaS due to the inhibition of CO_2 on the reaction for forming CaS (Gruncharov *et al.,* 1985a).Thus, the reaction was rate-determined at high temperature with CO_2. The effect of heating rate was also found to affect the final product of PG decomposition. At high heating rates (25°C /min and above), reaction kinetics are affected leading to CaO formation, while at low temperatures CaS is favoured up to 1000°C (Kuusik *et al.,*1985).

(2) Carbon as Reductant

The reduction of PG with carbon takes place between 850-1080°C with formation of CaS from the reduction of PG and CO_2 gas (Strydom *et al.*, 1997). CO is initially formed from the oxidation of carbon, and later aids in the reduction of PG by being oxidised to CO_2 (Ma *et al.,* 2011). The reduction occurs through a series of step reactions as witnessed by the change in activation energy during decomposition (Strydom *et al.*, 1997). An inert environment is necessary for the redox reaction to takes place as any oxygen present interacts with carbon to form CO_2 at temperatures between 600-900°C, reducing the reduction of PG (Strydom *et al.*, 1997).

The most common source of carbon utilised for the reduction of PG in literature has been anthracite and high sulphur coal (Ma *et al.*, 2010; Zheng *et al.*, 2014). The use of oil shale has also been reported as a successful carbon source for reducing PG (Suyadal *et al.,* 1997).Temperature was found to play a major role in the decomposition efficiency irrespective of the coal or carbon source used for PG reduction. At 900°C and above, the appearance of SO_2 increases and reaches a maximum at 1100°C due to the full decomposition of PG to CaO. This is also facilitated by CaS reaction with $CaSO_4$ at high temperatures to produce CaO and SO_2 (Ma *et al.*, 2011; Zheng *et al.*, 2011). Heating rate affects how fast the temperature rises. A higher heating rate results in higher reduction rate due to increased CO production from coal gasification (Ma *et al.*, 2011; van der Merwe *et al.*, 1999).

The use of different mole ratios of carbon to PG was also found to affect the PG decomposition and final products formed. A higher PG to carbon ratio leads to increased SO_2 and CaO formation (Zheng *et al.*, 2014). On the contrary, with a lower PG to carbon ratio the formation of CaS is favoured, which then suppresses formation of SO_2 (Zheng *et al.*, 2011).

In order to improve the decomposition temperature further, several studies have investigated the selection of suitable catalysts to lower the initial decomposition temperature. The use of Fe_2O_3 catalysts reduced the initial reaction temperature from 850°C to about 750°C but did not affect PG reduction (Strydom *et al.*, 1997; van der Merwe *et al.*, 1999). The use of $FeCl_3$aided in lowering the initial decomposition temperature to 600°C while also helping to increase the SO_2 produced from PG reduction (Yan *et al.*, 2013). Similar to the use of $FeCl_3$, the addition of a small percentage of sodium dichromate ($Na_2Cr_2O_7$) and potassium dichromate ($K_2Cr_2O_7$) to carbon also enhanced the reduction of PG (Kale *et al.*, 1992).

(3) Other Notable Reductants

There are several other reductants that have been reported in literature for reducing phosphogypsum. They are hydrogen, sulphur and K-feldspar.

- *Hydrogen*

The reaction pathway for the reduction of PG with hydrogen (H_2) was established to be analogous with the use of CO as reductant, with the formation of CaO as final product of decomposition. However, unlike the use of CO the presence of CO_2 did not have any effect on the reaction of H_2 with PG (Gruncharov *et al.*, 1985b).

- *Sulphur*

The use of sulphur as a reductant of $CaSO_4$ has been investigated in laboratory studies and led to the production of SO_2 gas and CaO as end products (Yang *et al.*, 2013). The SO_2 formed could be utilised in the production of sulphuric acid. Additionally, the use of sulphur as reductant was established to reduce the energy required to convert $CaSO_4$ to SO_2 compared to coke (carbon). The added advantage of a lower reaction enthalpy means that it is more economical to utilise the SO_2 from sulphur reduction to reduce production costs if it will be utilised in the production of sulphuric acid (Yang *et al.*, 2013).

- *K-feldspar*

The use of K-feldspar for reduction of PG has been reported to take place at temperatures between 1100-1200°C (Wang *et al.*, 2014). An ion exchange between the K^+ and Ca^{2+} takes place at high temperature and PG ($CaSO_4$) is transformed to K_2SO_4 while the K-feldspar ($KAlSi_3O_8$) is reduced to $CaAl_2Si_2O_8$. Additional reactions between the SiO_2 present in the PG and $CaSO_4$ yield $CaSiO_3$, an important material for industrial insulations (Wang *et al.*, 2014).

2.3.2.2 Redox Reactions for the Utilisation of Sulphate in Phosphogypsum.

Another alternative to the use of reductants is the use of chemical reagents that can reduce the sulphate anion from the phosphogypsum through reduction-oxidation reactions (redox). This is based on the affinity of the anions by the redox reagent and normally performed through alkali and alkali earth metal salts. As PG is calcium based, the main redox reagents that can effectively reduce it are the group 1 alkali metals, predominantly sodium and potassium salts, and ammonia salts. Therefore, the redox reagents will be classified according to these two types of metal groups and ammonia salts.

(1) Sodium Based Reagents

There are limited publications in literature on the reduction of PG with sodium based reagents. The only two sodium salts investigated base on literature review for PG reduction are sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). The use of both as reductants results in the oxidation of sodium to sodium sulphate.

The use of NaOH reduces calcium sulphate in PG to calcium hydroxide (Cárdenas-Escudero *et al.*, 2011). Any trace elements in PG not removed from pre-treatment is adsorbed to $Ca(OH)_2$ (that is insoluble) leaving the waste water after sodium sulphate separation from the redox reaction free of toxic trace elements (Cárdenas-Escudero *et al.*, 2011). The use of the produced $Ca(OH)_2$ after PG reduction was investigated for making lime mortars to replace industrial lime. Initial tests on the produced mortars showed that they had a homogeneous and uniform finish with no cracks present (Romero-Hermida *et al.*, 2014). Thus, there is high potential for the replacement of industrial lime with that produced from PG reduction with NaOH.

The use of Na_2CO_3 on the other hand reduces PG to calcium carbonate (Mulopo & Ikhu-Omoregbe, 2012). This is because of the CO_3^{2-} anion in the Na_2CO_3 that replaces the SO_4^{2-} anion lost from PG through the redox reaction. The use of the resultant calcium carbonate by-product for acid mine drainage (AMD) showed that it had comparable results in neutralising AMD wastes compared to commercial calcium carbonate. Thus, the produced calcium carbonate by-product could potentially replace and reduce associated costs of purchasing high purity commercial $CaCO_3$ used in AMD treatment.

(2) Potassium Based Reagents.

Solubility plays a major role in the redox reaction between KCl and $CaSO_4.2H_2O$ as at high concentration of KCl, double salts such as syngentite and penta-salt ($K_2SO_4.5CaSO_4.H_2O$) form, which reduces the redox reaction (Abu-Eishah *et al.*, 2000). When the KCl concentration is reduced in comparison to the $CaSO_4.2H_2O$, there is a higher formation of potassium sulphate (K_2SO_4) due to reduction by KCl and lower formation of double salts.

When studies were performed with HCl instead of KCl, temperature was found to play a role in affecting solubility. Increase in temperature caused a corresponding increase in solubility (Abu-Eishah *et al.*, 2000). The reason for the high solubility is due to the conversion of SO_4^{2-} and Ca^{2+} into ionic form by HCl. The effect of addition of KCl to HCl (1:1 volume) was found to improve the redox reaction due to the increased PG ($CaSO_4.2H_2O$) solubility, which enhanced the chemical reaction between KCl and PG in the mixture of HCl and KCl (Aagli *et al.*, 2005). However, at a KCl concentration of greater than 130 g/L or 1.75M, the solubility of PG decreased even with an increase in temperature as KCl addition reduced the effect of temperature on solubility (Aagli *et al.,* 2005).

There are two additives, ammonia and isopropanol, that have been used in literature to inhibit the formation of double salts through unwanted side reactions between KCl and PG (Abu-Eishah *et al.,* 2000). Ammonia enhances the solubility of KCl while it crystallizes any K_2SO_4 formed due to decreased solubility in the presence of ammonia. However, at 35°C and higher the conversion rate decreased due to the evaporation of ammonia. The effect of longer residence time also affected conversion due to the reaction of ammonia with PG, which reduces the ammonia present in solution and hence favouring double salt formation (Abu-Eishah *et al.,* 2000). The presence of Isopropanol has similar effects of crystallising K_2SO_4 from solution. When K_2SO_4 is removed from solution, the formation of double salts is reduced as it cannot react with unreacted $CaSO_4.2H_2O$ (Abu-Eishah *et al.,* 2000).

Due to complexities of conversion with KCl, Ennaciri *et al.* (2013) investigated use of potassium carbonate as a redox reagent for PG conversion to K_2SO_4 and $CaCO_3$.

(3) Ammonia Based Reagents

There are only two literary works found on the use of ammonia reagents for the reduction of PG. The first was the use of ammonium carbonate solution formed from the dissolution CO_2 in ammonia, which reduced PG to $CaCO_3$ and was itself oxidised to ammonium sulphate ($(NH_4)_2SO_4$) (Zhao *et al.,* 2014). The effect of increased CO_2 partial pressure in the ammonium carbonate solution resulted in an increase in PG reduction. This is because the higher CO_2 pressure enhances the reaction rate to take place quicker and at a smaller residence time as mass transfer resistance from gas to liquid is reduced (Zhao *et al.,* 2014).

The other significant work reported in literature is the use of a mixture of 85% phosphoric acid and ammonia solution for the reduction of PG with production of hydroxyapatite (HAP), $Ca_5(PO_4)_3OH$, and ammonium sulphate as end products (Mousa & Hanna, 2013). An increase in the calcination temperature of this method of PG reduction increased the crystallinity of the HAP formed. Evaluation of calcium to phosphate ratio by energy-dispersive X-ray (EDX) showed that the ratio of the HAP formed from PG reaction with phosphoric acid had a similar ratio of Ca/P in human bones. The Ca/P ratio of human bones is 1.67, while that of HAP formed is

1.5 (Mousa & Hanna, 2013). Therefore, the HAP has the potential to be used for bone and tooth implants.

2.4 Summary

Based on the findings from literature, the application of absorption technology with the aid of oxidants for NO_x flue gas absorption can achieve both economic and environmental benefits by converting tail gas pollutions to useful and saleable by-products. The use of ammonium, sodium and calcium based reagents produces ammonium, sodium and calcium nitrates respectively all that can be utilised in the production of safety explosives for use in the mining industry. The ammonium nitrate could be also utilised as a fertiliser or constituent of compound fertilisers. Sodium and calcium nitrates could also be utilised as nitrate sources (through reduction) with other compounds such as potassium salts to produce valuable industrial nitrates like potassium nitrate (that could be used in fertiliser production).

There is also a high potential of reusing PG through the extraction of the sulphate anions (through redox reactions) to form valuable sulphates and calcium by-product salts as depicted from literature review. 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 fertiliser. On the other hand, calcium oxide from reduction with NaOH or other reductants (like sulphur and hydrogen through thermochemical decomposition) could be utilised as a lime feed for other industries (for example in production of mortars). The calcium carbonate by-product from the use of sodium carbonate could be used in acid mine drainage treatment to control acid wastes and also leaching of the acid wastes underground.

Thus, there is potential of converting waste PG to useful by-product salts that could offer cheaper feedstock alternatives to neighbouring industries through industrial symbiosis. Therefore, investigations of different reaction pathways for the formation of suitable by-products from NO_x absorption and PG reduction for industrial symbiotic linkage have been analysed as case studies in the current thesis. The results and analysis are prepared in Chapters 5 and 6.

Chapter 3 Framework for Synergy Evaluation and Development in Heavy Industries

3.1 Introduction

The chapter begins with a description of industrial ecology and symbiosis before providing a generic outline of typical industrial symbiotic relations. The generic outline is used as a first step in identifying potential by-products before introducing the methodology of the proposed framework. It continues with the introduction of the Kwinana Industrial Area (KIA), which was used as a case study for the implementation of this framework. A major part of this chapter has been adapted/ reprinted from the publications of Mohammed *et al.* (2013a) and Mohammed *et al.* (2013b), with permissions from Copyright 2013 Springer (Appendix 1) and Copyright 2013 Inderscience (Appendix 2) respectively.

3.2 Industrial Ecology

Industrial ecology (IE) is the study of material and energy flows between industrial systems, and their effects on the environment (Edward, 2004; Diwekar, 2005). It aims at achieving zero waste through the application of sustainable technologies such as green chemistry; increasing plant efficiency; and forming closed loop operations. Therefore, IE provides a long-term solution for maintaining a sustainable environment.

Industrial symbiosis (synergy) is one of the branches or tools of industrial ecology that involves the exchange of by-products between neighbouring industries. In order to be effective, industrial symbiosis is built up among those industries that are clustered together within a locality so that overall savings of transport and resource availability can be achievable (Chertow, 2007). Furthermore, with a varied group of industries clustered together, there is potential to attract new industries to join in, thereby enhancing further synergy developments. The closed loop synergies maintain material streams within the industrial system and interaction with the surrounding environments is greatly reduced (Faria & Bagajewicz, 2011).

Research into IE has grown rapidly but has been primarily focused on a particular industrial zone or targeted at the conceptual design of new plants and processes (Nikolopoulou & Ierapetritou, 2012). There have been several IE studies on existing industries and the linkage of their wastes/ by-products to industrial symbiosis (Kurup *et al.,* 2005; van Beers, 2009; Biswas & Cooling, 2013). However, these studies did not take into account lifecycle analysis when assessing the environmental implications of synergies, and they have primarily focused on the application of sustainability principles to existing synergies. In addition, most of the current industrial synergies in use are seldom developed from organic streams.

In the methodology of environmental impact studies, a major tool used is the Life Cycle Assessment (LCA), which assesses the environmental impact of a product at each stage of its lifecycle (Diwekar, 2005). Despite this, the use of the LCA is restricted as it can only evaluate the environmental effects of a single process at any one time. To overcome this limitation, Gerber *et al.* (2011) developed a method whereby the LCA could accommodate various product uses and alternative processes. The idea of integrating process synthesis with a LCA applied in IE (Diwekar & Shastri, 2010) has created opportunities for process engineers to work closely with environmental scientists.

3.2.1 Methodologies Found in Literature for Aiding Synergy development

Several methodologies or frameworks have been reviewed in literature, which formulate strategies to aid the establishment of new synergies between industries. Zhang *et al.* (2015) provide a review of theories and methodologies on industrial symbiosis reported in literature. The authors evaluated that there are 3 ways that industrial symbiosis could develop between industries. The first is cooperation between industries for the mutual benefit of sharing by-products or other resources, thereby helping reducing expenses by obtaining input cheaply or exchanging water and energy. The second is advancement in technology of reusing by-products and wastes, which can facilitate their conversion into suitable form for use by relevant industries or sold to other industries by scavenger industries. The last and main factor encountered in literature for aiding development of industrial symbiotic linkages in industry has been from government legislation (Vargas & Halog, 2015; Zhang *et al.*, 2015). This has been mostly by setting up policies for existing industries to move from open looped to closed looped systems by changing processing technology to meet emission constraints or utilization of by-products for industrial symbiosis. This is witnessed by cement industries moving from wet processing to dry processing technology (Deja *et al.*, 2010; Vargas & Halog, 2015), and using by-products like fly ash or substituting fuels as a means of reducing CO_2 production burden from cement production (Feiz *et al.*, 2015a). Additionally, legislation is formulated for designing new eco-industrial parks (EIP) that foster industrial symbiosis between industries. This includes the UK Industrial Symbiosis Program (Velenturf, 2016), eco-industrial parks in South Korea and Japan (Fei *et al.*, 2015).

Legislation can also be used in attracting scavenger industries targeting particular industrial wastes in the EIP to convert them to products utilizing advanced technology. The products from waste conversion or processing could then be used by other existing industries and facilitate industrial symbiosis (Vargas & Halog, 2015).

Many studies in literature have analysed the success of industrial symbiosis networks that developed through cooperation of industries. However, there are limited methodologies or frameworks that have been reported to promote the development of new symbiotic links between industries from planning, identification, feasibility up to implementation (Behera *et al.*, 2012). The several methodologies or frameworks that have been encountered in literature, which formulate strategies to aid the establishment of new synergies between industries are subsequently elaborated below.

Golev *et al.* (2014) analysed the potential development of new synergies in Gladstone industrial area through the collection of material flows from existing industries. However, due to a lack of collaboration from many industries because of commercial secrets, the formation of new synergies in the existing industries was not evaluated. The main barrier the authors evaluated was government and industrial collaboration in overcoming technical and non-technical barriers like cooperation in evaluating potential new synergies.

Liu *et al.* (2015) have developed a three tier approach at linking industries through the facilitation of governments as facilitators through policy formulation. The first step aims at educating individual industries on cleaner production and industrial symbiosis practice so that they can be able to implement in their process plants.

Thereafter, the setup of organizational bodies is encouraged so that industrial collaboration can be realised. The second step involves identifying opportunities for industrial symbiosis links by collecting data on the waste and by-products of existing industries and also identifying existing symbiotic exchanges. The third step involves planning and analysing the feasibility of developing new symbiotic links through either introducing scavenger industries that can use wastes as feed or linking existing industries that could use wastes or by-products as feed. However, the three-tier approach assumes that new symbiotic linkages will be created through the collaboration of universities by analysing industries that can use the by-products or technologies that can be used to convert wastes and by-products to readily useful forms before industrial symbiosis can be realized. Additionally, there is no mechanism like LCA in the approach to show the viability of new symbiotic links from an environmental point of view through comparing the environmental burdens of products from symbiosis with conventional products.

Feiz *et al.*, (2015b) have developed a framework that aims at improving the environmental efficiency of cement industries by analysing existing technologies and their related CO_2 emissions. The material and energy streams of existing technologies are collected to make a generic outlook at which streams or by-products could be improved by recycling, use of by-products with other industries through industrial symbiosis, or technology and fuel substitution to reduce energy. However, the framework only targets cement industries and analyses improvements based only on CO_2 emissions, and the main industrial symbiotic linkage proposed in the case study example analysed is excess energy use with other industries and use of power plant fly ash as clinker replacement. Additional studies based on the review by Salas *et al.* (2016) show that use of material flow analysis (MFA) or LCA to analyse the environmental benefits of use of industrial symbiosis in cement production have used similar methodologies of substituting fuels used; exporting excess heat to other industries and use of substitutes like fly ash to reduce environmental burdens of clinker production.

Gerber *et al.* (2013) developed a methodology that aids decision makers by comparing the environmental and economic objectives of different processing options for a given waste or by-product in order to determine the most suitable using multi-objective optimization (mixed integer non-linear programming (MINLP)). The environmental implications (CO_2 emissions) of each process option are determined through LCA by analysing existing technology in the LCI database and where this cannot be found, flow- sheeting software are used to determine the mass and energy balances and this are fed to the LCA to determine environmental implications. The mass and energy relations, costs, and environmental implications are then modelled and fed into the MINLP to determine the most optimal configuration for each process for minimizing the objectives of economics and environmental impact though Pareto analysis (based on a given product output). Their methodology assumes the composition of wastes have been analysed and the relevant processing technologies to convert waste or by-products into a desired form have been investigated. Therefore, the details of these are then modelled and fed into the MINLP for optimization and then comparing the best processing options.

Horváth and Harazin (2016) have developed a framework based on a software decision support system (DSS) to aid local authorities' partner and facilitate industrial symbiosis development between new and/or existing industries in an industrial cluster. The DSS depends on the identification of wastes and by-product forms and classification that is provided by existing industries (open loop system) and then identifies opportunities for existing or new industries that could use the waste or by-products as input including necessary technologies. This is done by selection of a set of indicators such as availability of technology, financial benefits and demand and supply constraints to analyse the viability of the symbiotic linkage to potential industries for symbiotic linkage. However, for the DSS to work effectively the full cooperation of industries in providing waste and by-product assays is necessary. This may be a barrier as certain industries may refuse to disclose their waste assay due to trade secrets as witnessed firsthand when waste assays was sought at Kwinana industries in the current research and in the identification of potential synergies in Gladstone industrial area (Golev *et al.*, 2014). Additionally, the DSS does not consider the identification of environmental implications or benefits of products from identified potential industrial synergies and similar conventional products.

The approach of most of the encountered methodologies are the collection of material and energy stream data of whole processes from feed to wastes either through direct contact with relevant industries or through the aid of environmental reports from local councils that deal with the industries. The collected data of wastes is then matched to similar feed streams of industries that could use them through computer systems incorporating multi-objective optimisation or through experts in the field of industrial ecology.

However, most of the frameworks encountered in literature do not provide a comprehensive assessment of potential new synergies from the analysis of wastes or by-products compositions, the analysis of various post-processing options to identify the different products that wastes could be converted to meet feed requirements of surrounding industries. None of the frameworks also incorporate laboratory analyses to determine thermodynamic properties like process conversion efficiency or chemistry dynamics to determine flowsheet development. The data from laboratory analyses provides better input to aid simulations reflect the practicality of converting wastes as it also determines other factors like temperature and pressure that positively or negatively affect thermodynamics and process efficiency.

Additionally, the proposed framework aims at involving industries to provide their expertise in providing feedback on determined best pathways from laboratory and simulation analyses, such as designing variables or determining factors to improve process realisation based on experience. Furthermore, the proposed framework aids industries through involving academia in the setup of a pilot plant and researching ways to improve process operation and justify the practicality of scaling up production from previous analyses. The cooperation between academia and industry is a major proposal identified to overcome obstacles in developing the synergies (Dong *et al.*, 2016). This is not covered in the other frameworks, which only provide symbiotic potentials based on economic and environmental outcomes to industries, and leaves the industries to develop the synergies alone.

Thus, the aim of the current research is developing a framework that will incorporate both process engineering, sustainability principles and ultimately collaboration with industries to produce new and unexplored synergies. The involvement of process engineering in synergy implementation will essentially convert by-products to useful resources, and thus aid in achieving closed-loop systems.

3.3 Framework for By-product Assessment and New Synergy Establishment

There is a plethora of chemicals and products manufactured globally, largely supplied by Primary and major mineral processing industries. To this effect, a generic symbiotic relation between these industries is proposed as a first step in supporting the symbiosis evaluation in the proposed framework.

3.3.1 Premises of the Framework

The generic outlay in Figure 3.1 classifies industries into groups, based on manufacturing processes and product properties. The industries on the left side are identified as major sources of wastes/ by-products. In the middle of the figure, there are the core industries which generate most of the synergies. This is due to their ability to utilise the by-products of neighbouring industries as inputs, and their ability to provide by-products to other industries. The right side of the figure represents the industries that can form synergies by utilising by-products from other industries.

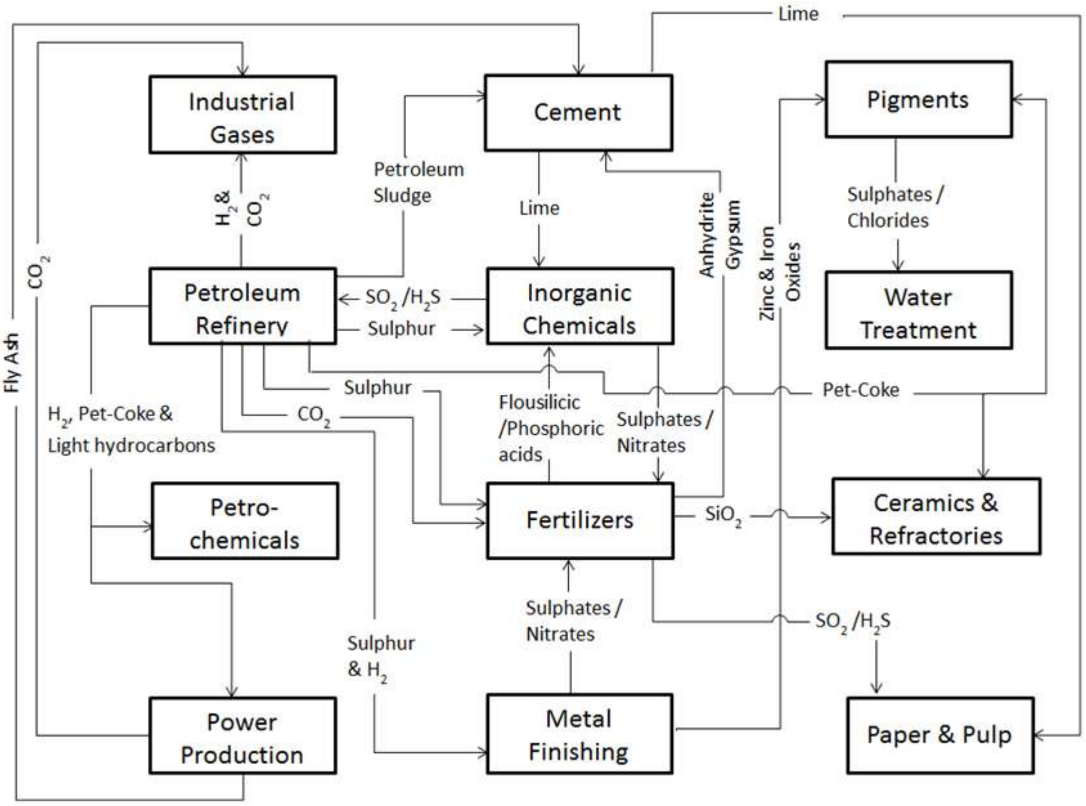

Figure 3.1 Generic industrial symbiotic relationship

Depending on the solvents /reducing agents used, different by-products are generated. The three most commonly used reducing agents are nitric, sulphuric and hydrochloric acid. Thus, many of the by-products produced are in the form of nitrates, sulphates or chlorides. Using the generic outlay above, one can firstly identify possible by-products from particular industries and also identify the recipient industries that have the potential to form synergies. The sustainability benefits of these by-product synergies can then be assessed and are discussed in the subsequent sections.

The purpose of this generic outlay is to promote the implementation of industrial symbiosis from local to regional levels. Therefore, instead of focusing on a single industrial area, greater co-ordination between industries within a specific region is proposed. However, challenges will be presented in the form of geographical proximity, and infrastructural constraints and their costs such as pipelines between industries and market changes. After the identification of potential by-products, the application of the framework will be carried out to investigate the practicability for synergy realisation.

3.3.2 The Sustainability Framework

The steps of the sustainability framework are highlighted in Figure 3.2, which shows the technical and sustainable aspects of synergy assessment. The potential by-products are firstly identified with the aid of the generic outlay. This is followed by an investigation into the available recipient industries that can form by-product synergies. After the establishment of synergy linkages, studies on their economic and environmental feasibility are assessed and then presented to relevant industries for feedback. Industrial workshops can then be organised to justify the suitability and practicality of synergies.

From the framework, objectives for practicable synergies were made and feed requirements for the recipient industry clarified. Thereafter, processing paths for effectively meeting the set objectives were assessed both theoretically via optimisation and simulation, and practically through laboratory experimentation with available industrial samples and data.

Sustainability and “green” engineering principles were further applied to the selection of the most suitable processing requirements for forming the symbiosis. This was complemented by a lifecycle analysis of environmental and economic objectives. Further necessary measures were taken via “green” engineering design to address any shortcomings regarding the environmental objectives. The results of the sustainability assessment will then be presented to relevant industries for feedback.

In the next stage, a pilot plant will be designed and implemented following set process synthesis and sustainable parameters. Based on the pilot plant results, improvement opportunities could be sought whereby more effective results could be obtained, or issues solved that might arise prior to deeming industrial application as suitable.

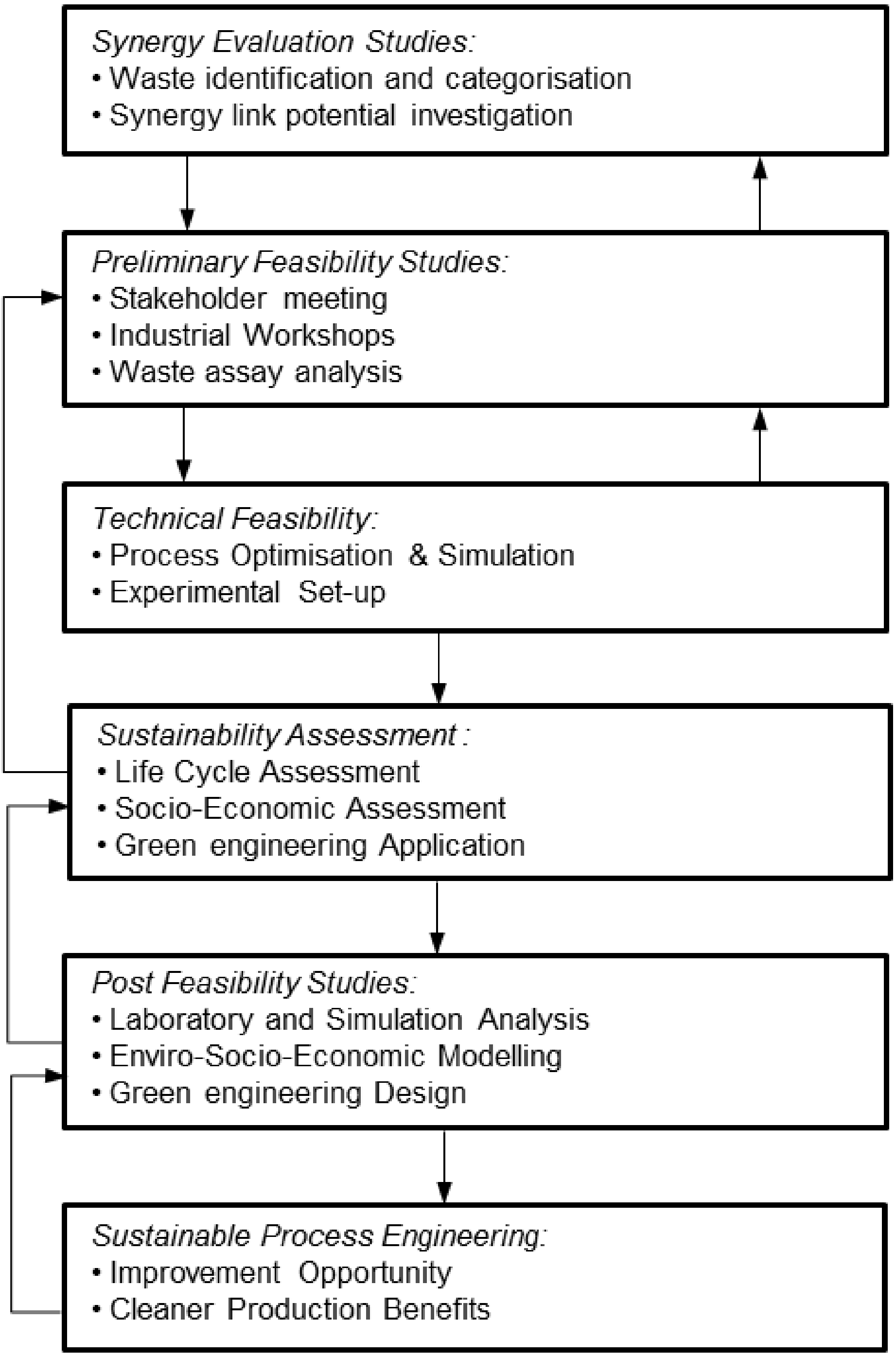

Figure 3.2 Framework for the evaluation and implementation of new synergies

The practical application of the framework was conducted on two case studies where identified potential symbioses at Kwinana Industrial Area (KIA) were made through by-product assessment and synergy pre-feasibility studies, which are presented in the next section.

The application of the framework beyond the sustainability assessment stage i.e. the pilot plant stage was not covered in the case studies due to limitation of time. The thesis only presents the results of the framework application up to the sustainability assessment stage, which are elaborated in chapters 5 and 6 using the case studies.

3.4 Case Studies at Kwinana Industrial Area (KIA)

KIA is by far the largest and most diverse industrial processing region (with supporting industries) in Western Australia. It consists of large inorganic mineral processing industries, chemical industries, an oil refinery, fertiliser manufacturer, and a number of other minor industries. This area is known for its many by-product synergies where materials and utilities are shared; wastes from one company are often inputs for another.

However, as with elsewhere globally, KIA is facing sustainability challenges on various fronts, including water and energy scarcity, climate-change, an ageing workforce, and growing community sustainability expectations. Sustainability studies at KIA have suggested four areas that can be further focused upon (Van Beers, 2008). These are: the use of inorganic mineral wastes, enhancing by-product synergies, wastewater utilisation and energy economy. The presence of various types of industries and their resultant by-product volumes within Kwinana are the main reason for choosing KIA as a case study.

3.4.1 By-product Identification

Through application of the framework at KIA, four by-products: petroleum coke, phosphate rock digestion off-gases, nitrogen oxides (NO_2) waste gases, and calcium chloride ($CaCl_2$) have been identified for their potential in the development of new relationship among industries. This identification has decided upon due to the amount of supply, the ease of post-processing or treatment, and the availability of candidate industries for symbiosis formations. The proposed synergies are presented in Figure 3.3 in red, with existing relations also depicted for reference.

As a result of preliminary synergy evaluation and pre-feasibility studies, it can be shown that with the application of industrial ecology, the by-products in question can be reused as feed materials by other industries.

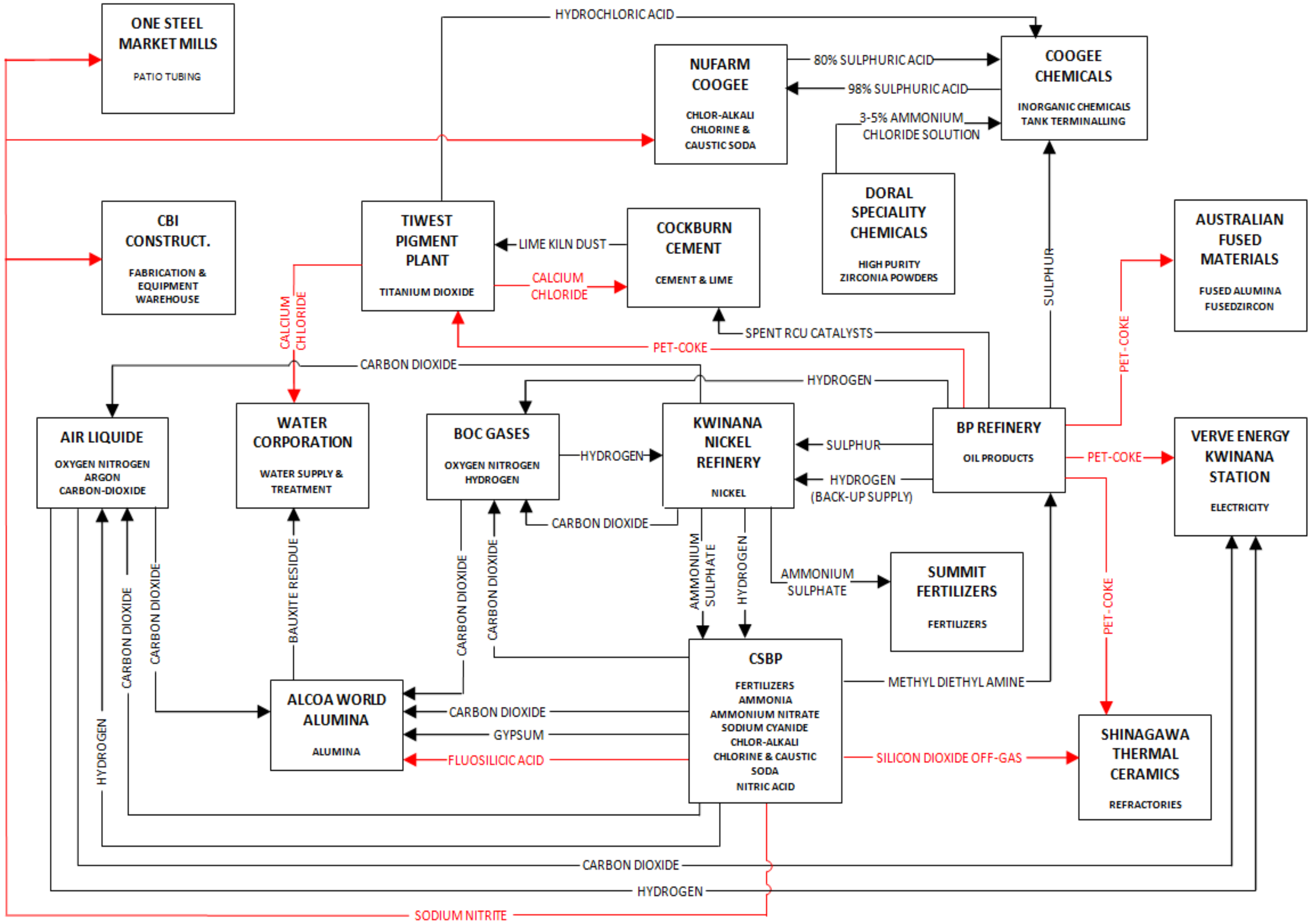

Figure 3.3 Current and Proposed Industrial Symbiotic Relations at KIA

3.4.2 Preliminary Sustainability Assessment

A hypothetical example, based on the triple bottom-line perspective was applied to the identified synergies in Kwinana. Typical results are summarised in Table 3.1. The sustainability implication of each identified relationship is also summarised in the table, and the socio-economic variables identified depend on the type of by-products analysed.

3.4.2.1 Petroleum Coke (Pet-coke)

Pet-coke has potential synergetic use as a feed material in the production of titanium dioxide pigment and the production of Zircon or the manufacture of silicon carbide as a constituent of thermal ceramics. Further potential, based on the calorific value (energy output) of pet-coke, is in electricity generation to supplement coal-fired plants. These uses can provide economic incentives from the sale of pet-coke and higher energy outputs. Pet-coke’s low volatile combustion matter and low ash content has social benefits in that health hazards to the surrounding population are reduced. The coke can also be mixed with low calorific coal to improve energy output, making the use of such coals more feasible (Predel, 2006). Although pet-coke is not used in large volumes at KIA, the reference to pet-coke synergy is used as an example to demonstrate the benefit of the by-product in areas where it is produced in large volumes.

Table 3.1 Sustainability Matrix of Identified Synergies

By-product	Further use	Preliminary Sustainability Assessment		
		Social	Economic	Environmental
Calcium Chloride	Dust Suppressant	Respiratory effects from fine dust avoided	Easy to contain dust and avoid fines from dust emissions	Chemical release due to dust containment avoided
	Waste water treatment	Less competition for water use from industries	Less water use from other sources saving on costs and avoiding fines from waste water	Release of toxic chemicals to environment and ground water contamination avoided
	Cement additive	Improved structure life leading to less burdens from tax to fix them	Reduction of alkalis increasing cement/concrete life	Avoids $CaCl_2$ release to marine environment
	SDOOL avoided disposal	Aesthetics and less effects from seafood derived from the SDOOL area	Fees from SDOOL disposal and monitoring costs avoided. Revenue from $CaCl_2$	Less chances of environmental effect by avoiding marine release
Petroleum Coke	Natural coke substitute	Not identified	Cheaper alternative	Less use of virgin resources
	Electricity generation	Less emissions meaning less health effects	Higher calorific value meaning less costs compared to other cokes	Lower CO_2 and toxic emissions to other cokes leading to less environmental effects
Nitrogen Oxides	Sodium nitrate production	Less acidic rain and adverse effects of nitrogen oxides to health by avoiding release	Fines resulting from emissions avoided, making savings to company. Revenue from the sale of ammonium nitrate	Less environmental burdens by avoiding nitrogen oxide emissions. Avoid virgin resource use through substitution or blending of ammonium nitrate with sodium nitrate in safety explosives
Phosphate Rock	Silicon dioxide supply to AFM	Less effects by avoiding long-term exposure to $SiO_{2,}$ minimizing health risks	Revenue from SiO_2 sales	Not identified

3.4.2.2 Phosphate Rock Digestion Off-gases

There are economic potentials for the use of acid SiO_2 off-gas at KIA. Flousilicic acid (H_2SiF_6) could be utilised as a resource to produce aluminium fluoride, which is useful for the production of aluminium metal from alumina. The challenge would be to attract investment in such an industry and incentives can be found in the availability of H_2SiF_6 acid and alumina in the vicinity. The SiO_2 produced could be sold as raw material to a Zircon manufacturer, supplementing the SiO_2 feed required for its production. In utilising SiO_2 to form synergies, there is a reduced risk of contact from the gas with the surrounding community. There is also a reduced risk to workers from long-term exposure during the working life of a phosphate digestion plant.

3.4.2.3 Nitric Acid Production Tail Gases

A suitable strategy that could be employed by a nitric acid plant at KIA to control nitrogen oxide emissions is the use of sodium hydroxide. It could be used in a series of counter current absorption processes to produce either sodium nitrite ($NaNO_2$) or sodium nitrate ($NaNO_3$) and water. This would effectively reduce its carbon footprint, but it can also form several synergies from the by-products formed from the process.

Sodium nitrate can be used for: (a) the manufacture of safety explosives for the mining industry; (b) as an agricultural fertiliser; (c) the regeneration of spent sulphuric acid from chemical manufacturing; (d) as a refining agent for air bubble removal in the glass and enamel industries. Sodium nitrite has uses analogous to sodium nitrate; mixtures of both are utilised in many applications. Sodium nitrite can be used for the synthesis of pesticides, as a de-scaling agent (oxide removal) for steel and as an additive to concrete in the fabrication and construction industry. These synergies can then improve the balance-sheets of the nitric acid plant. In addition, there are social benefits brought about by reduced nitrogen oxide emissions. These include lower health risks associated with inhalation that could cause respiratory failure and skin or eye burns from exposure to gases in high concentrations. Acidic rain brought about by the presence of gases in the air will also be lowered, which would further lessen health and environmental risks.

3.4.2.4 Calcium Chloride from Titanium Dioxide Pigment Plant

The potential uses of calcium chloride within Kwinana include:

- in water treatment as a flocculent for solid removal
- as a dust suppressant, or for the removal of unwanted water due to its hygroscopic or deliquescent nature (ability to absorb moisture)
- as a kiln additive during cement production where it controls and eliminates alkali content which causes unwanted expansive reactions in concrete.

One of the major challenges faced in Kwinana is the dust produced by several mineral processing industries, a cement manufacturer and a coal driven power station. $CaCl_2$ could be used to control and tackle this challenge. This would result in benefits to industrial operations and to the community around Kwinana. Environment conditions would also be improved with the eco-system being less exposed to various compounds contained in dust. The re-use of this by-product would also place a lesser burden on the marine environment where it is usually disposed of. For the company, there would be cost-savings on licensing and monitoring. $CaCl_2$ could also form synergies with the water- treatment and cement industries. This would have economic advantages for all companies involved in the synergies.

Based on the literature review undertaken, the existences of similar synergy implementations in practice have not been established. However, established technologies for capturing nitrogen oxide emissions from nitric acid plants, hydro-silicic acid and silicon dioxide off-gas from phosphate rock digestion are employed worldwide. The only remaining aspect is to establish synergy relations by determining the acceptable form of purity required by processes that may use them. Petroleum coke on the other hand, is a pure by-product and is used as a source of synthesised coke. It is actually sold as a product by refineries that produce it in bulk – mostly in North America and Europe. Synergetic relations are thus easier for implementation. The challenge however, would be with the synergy of the calcium chloride in terms of processing it to an acceptable standard for re-use. Nevertheless, its potential is great and thus its evaluation for implementation is warranted in the developed framework.

3.5 Summary

This chapter described the development of a generic outlay for linking wastes or by-products between industries as a first step in establishing potential industrial symbiotic relationships. This was done to explore the potential reuses of a particular waste or by-product to surrounding industries. The technical and sustainable aspects that formed the framework were presented. This ranged from the identification of various post processing options for converting waste into useful forms for other industries, optimisation through the development of experimental and simulation analysis, green process design through comparison of the different process routes analysed through LCA to determine the most environmentally friendly option, and finally economic and social assessment. The chapter then discussed the potential by-products that could be reutilised for synergy development in the Kwinana Industrial Area where petroleum coke, phosphate rock digestion off-gases, nitrogen oxides (NO_2) waste gases, and calcium chloride ($CaCl_2$), have been identified for their potential in the development of new relationship among neighbouring industries.

Chapter 4 Methodology

4.1 Introduction

The research methodology employed in order to achieve the objectives described in Chapter 1 - Section 1.3 is detailed in this chapter. It covers various stages in the implementation of proposed framework i.e. the feasibility study of post processing, experimental design and analysis, life cycle assessment, and economic analysis and social implication.

The general procedure carried out in applying the framework is represented in Figure 4.1 and consists of the following:

- Feasibility studies of post processing methods of treating the wastes or by-products into finished products that can be utilised by other industries as feed.
- Experimental analysis of the selected processing methods or options from the feasibility studies in order to ascertain the practicality of the processing methods.
- Development of process flowsheets from mass and energy balances obtained from experimental results and running simulation analysis for verification using Aspen Plus v8.4 software. Where experimental work could not be applied, the use of collected data from literature was utilised to develop the mass and energy balances.
- Environmental impact analysis through life cycle assessment of life cycle inventories developed from utilisation of processed by-product or waste from different processing options as feed by another industry for the production of 1kg of linked product from industrial symbiosis.
- Economic Analysis and social implications of processing options to compare the life cycle costing and social benefits of each process option. This will be used in determining the optimum option for industrial symbiotic development.

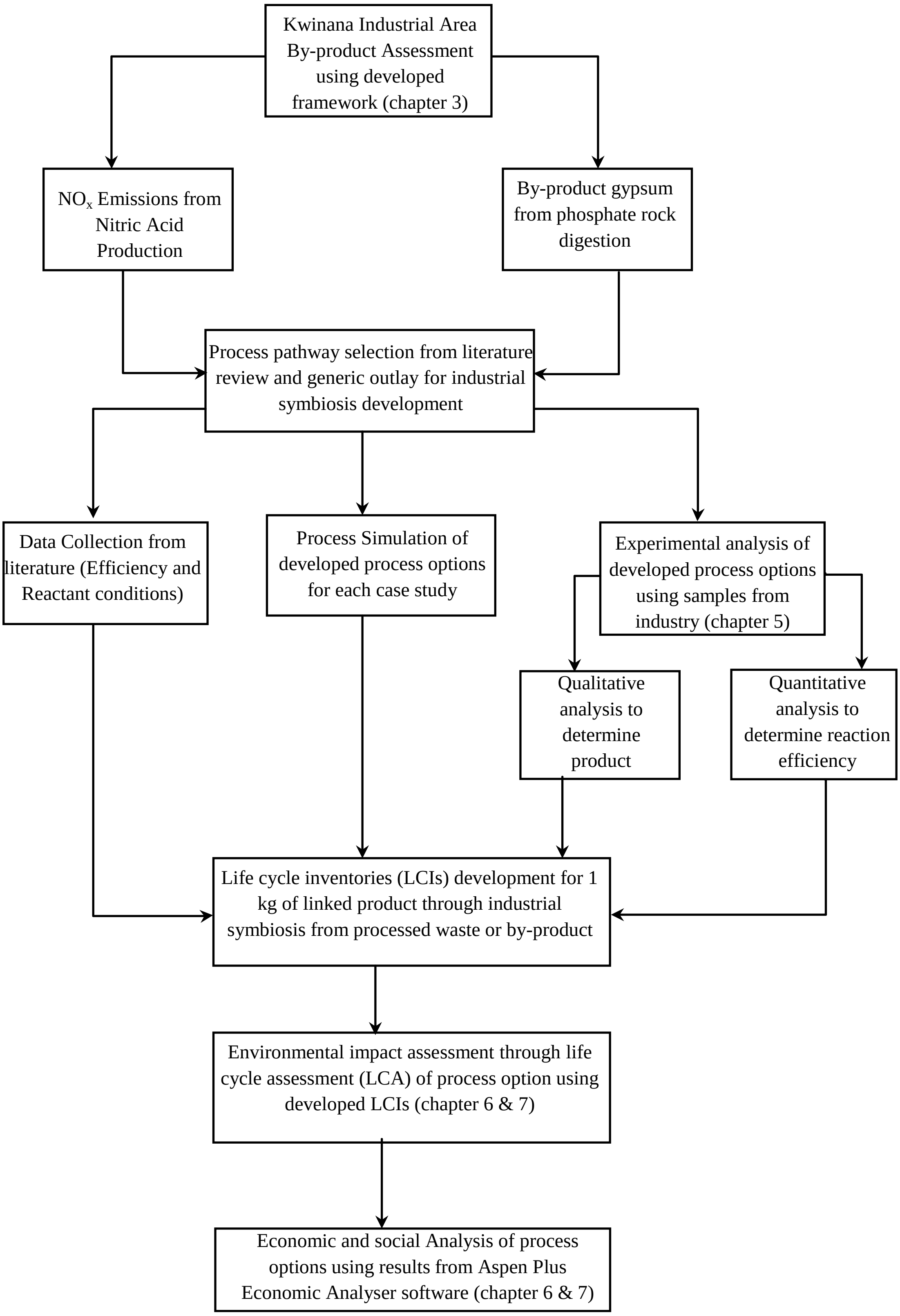

Figure 4.1 Process tree diagram for the research methodology using the developed framework

4.2 Feasibility Studies of Post Processing Methods of Treating the Wastes

Feasibility studies were performed through the aid of the generic industrial symbiotic outlay developed in Figure 3.1. The waste or by-products chemical compositions were determined through reference material such as scholarly journals and chemical encyclopaedias such as Ullmann's Encyclopaedia of Industrial Chemistry and Kirk-Othmer Encyclopaedia of Chemical Technology.

After determination of chemical compositions, the use of suitable absorbents, oxidants or suitable chemical reductants were determined from literature review in order to determine the process pathways that could be chosen for post treatment of the waste or by-products into valuable products. The products were then matched to potential industries through the generic industrial symbiotic outlay to determine possibility of symbiotic or synergy development with surrounding industries in KIA. Thereafter, experimental analysis of the post treatment process options was performed after waste or by-product samples were obtained from the relevant industry used in the case study - fertilizer industry.

4.3 Experimental Design and Analysis of Phosphogypsum Reduction

4.3.1 Experimental Set-up and Design

Experiments of phosphogypsum (PG) reaction with suitable redox reagents were carried out in a batch reactor as shown by the schematic in Figure4.2. Each experiment was run for an hour and the resultant products were of two different phases, a liquid solution and solid product. Separation of the phases was performed through centrifugation at a centrifugal speed of 4900 rpm for 5 minutes.

Phosphogypsum (mainly $CaSO_4$) was the limiting reactant and the amount of redox reagent was calculated from the amount of PG used for reaction. For each experimental run, about 2g PG, corresponding to 0.012 mols of $CaSO_4$ was weighed and placed in the reactor before the addition of 15mL of ultrapure water (with a resistivity of 17.9 MΩ-cmi).

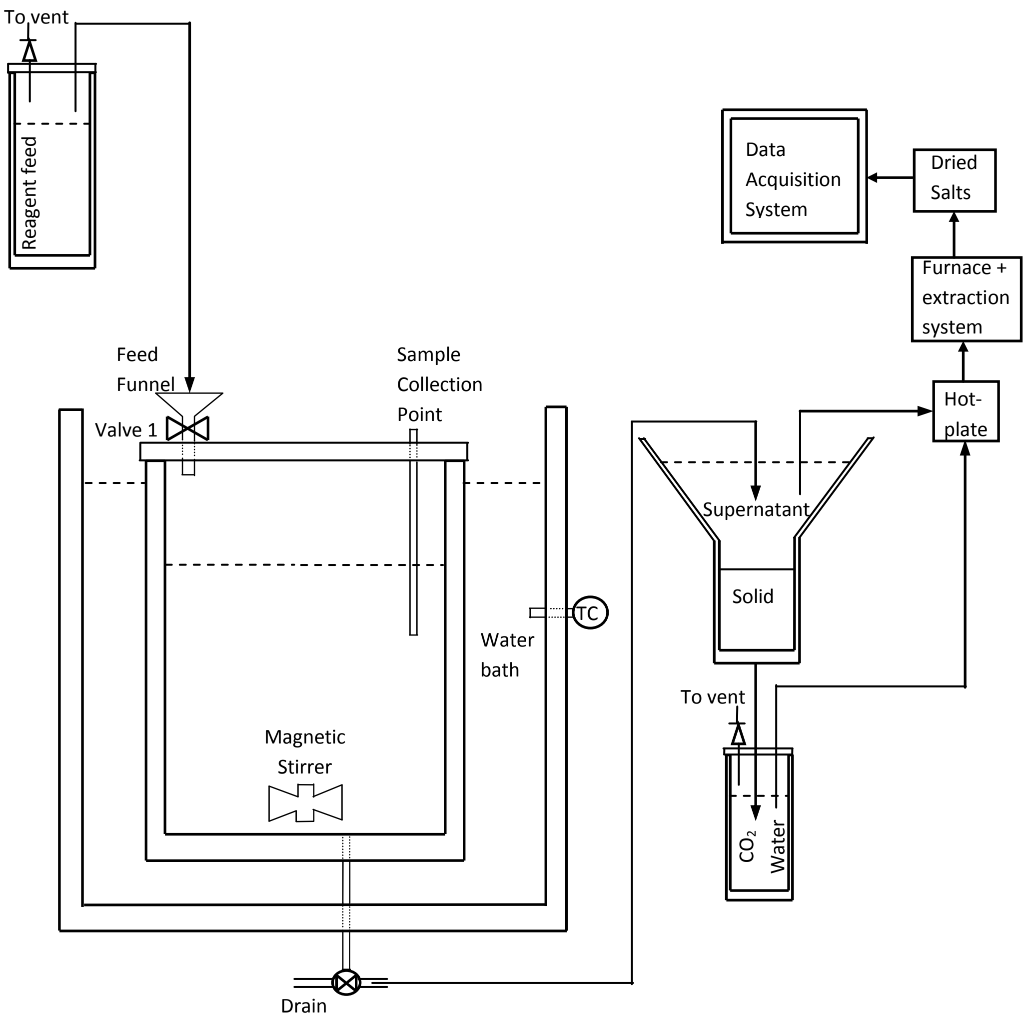

Figure 4.2 Experimental setup for reduction of phosphogypsum through suitable redox reagents

A magnetic stirrer was then used to enhance equal mixture of sample in the ultrapure water before the addition of a predetermined redox reagent. The two main redox reagents utilised in the experiments were sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). Additionally, three variables were selected for experimental analysis of PG reduction with each of the redox reagents. The variables are:

- Mole ratio of redox reagents to PG
- Magnetic stirring speed
- Effect of temperature on reaction efficiency.

(1) Mole ratio of Redox Reagents to Phosphogypsum

In order to determine the optimum reagent to phosphogypsum ratio for complete reaction, the amount of redox reagent was varied so that the ratios from 1:2 to 1:3.5

could be tested. The limiting reactant in all experiments is the $CaSO_4$, which needs to be reduced by the redox reagents. The stoichiometric reactions of each redox reagent with PG were used as the basis for calculation. The different mole ratios and corresponding weights of redox reagents used for experiments on the basis of 0.012 mols or 2g of PG are provided in Table 4.1.

Table 4.1 Molar ratios used for the different redox reagents for phosphogypsum reduction experiments

NaOH Redox Reagent			**Na_2CO_3 Redox Reagent**		
Mole Ratio to PG	**Mols of NaOH to be added**	**Weight in grams**	**Mole Ratio to PG**	**Mols of Na_2CO_3 to be added**	**Weight in grams**
1:2	0.024	0.96	1:1	0.012	1.27
1:2.5	0.03	1.2	1:1.5	0.018	1.91
1:3	0.036	1.44	1:2	0.024	2.54
1:3.5	0.042	1.68	1:2.5	0.03	3.18

(2) Magnetic Stirring Speed

The effect of three different stirring speeds in each experimental run with different redox reagents were investigated in order to establish the optimum conditions for enhancing mixing and reaction extent. The stirring rates used were 300rpm, 500 rpm and 700rpm.

(3) Effect of temperature on reaction efficiency

Temperature affects solubility of reagents and thus could enhance reaction rate. Therefore, the effect of temperature was studied to determine the optimum temperature for reaction. Temperature was considered as a variable because the drying process of products produced from the redox reaction uses heat and this heat could be utilised for enhancing reaction through heat exchange networks. There were four temperatures selected for each redox reagent, i.e. 30 °C, 40°C, 50°C and 60°C. Temperatures below 30°C were not considered as solubility of the reagents investigated (NaOH and Na_2CO_3) and the product formed (Na_2SO_4) reduce with temperature. A thermocouple was used to monitor the temperature so that it did not fluctuate from the set requirements for experimentation.

4.3.2 Analytical Procedure and Instruments

4.3.2.1 Qualitative Analysis

In order to determine the success of reaction, the solid residue remaining after redox reagent was dried on a hot plate at 105°C to evaporate most of the water. The sample was then placed in a furnace at 120°C overnight to effectively dry the compound salts formed. An X-ray diffractometer (XRD) machine was used to analyse the phase identification of sample to determine the major salts or compounds present (greater than or equal to 1% of total composition). Samples were finely ground by mortar and pestle, and then placed on a holder through random orientation for proper identification of phases present. The samples on the holder are compacted through cover with a glass holder and shaking until the sample covers the holder evenly and is flatly compacted before being input into the XDR machine for analysis. The XRD works by bombarding the samples with x-rays that interact with electrons in the sample and are reflected back to detectors to analyse the wavelengths produced that define the composition of samples. Each element or compound crystal structure produces a unique set of wavelengths after interaction with the x-rays, which are used to determine their presence.

The XRD machine used was a D8 Advance (Bruker AXS, Germany) with a copper k alpha radiation source (@40kV & 40 mA) with a lynxEye detector. The XRD parameters used for the phase identification were a 2theta scan range of 7.5-90 degrees, a step size (degree) of 0.015 and time/step of 0.7 seconds. The XRD is a qualitative technique for determining phases present in a sample. Quantitative analysis is also possible with the XRD but its limitation is that it cannot assess compositions of less than 1% of total composition. Nonetheless, the XRD was used as a first step in determining reaction completion through monitoring the raw phosphogypsum and by-product samples compositions from redox reaction.

4.3.2.2 Quantitative Analysis

Quantitative assessment of samples was made through an inductively coupled plasma atomic emission spectrometer (ICP-AES). Samples collected were firstly digested with 70% nitric acid and 32% hydrochloric acid in a ratio of 3:1 respectively according to US EPA Method 3050B. The sample to acid concentration was one-part sample to ten parts acid i.e. 0.1g of sample were digested with 7.5 mL nitric acid and

2.5 mL hydrochloric acid. The samples were left to cold digest overnight and then heated at 90°C ± 5°C for 2 hours.

The digested sample was later diluted by water to a 1% volume solution before being analysed by ICP-AES. The ICP-AES works by ionizing argon gas to form plasma through high radio frequencies. Digested samples were firstly converted into a mist by a nebulizer before being introduced to the chamber containing the inductively coupled plasma. Upon contact with the plasma, the ions present in the sample are excited giving different electromagnetic radiations. Each element produces a unique wavelength from the electromagnetic radiations, which are checked against prepared elemental standard solutions to determine the inorganic elements present and their amount. The benefit of the ICP is that it can pick up trace elements up the part per million ranges (ppm).

4.4 Process Flowsheets Development

Analysis of experimental runs for the phosphogypsum reduction revealed the extent of reaction by comparing the concentration of phosphogypsum sample before redox reaction and the amount of unreacted sample left after reaction. This was aided through elemental concentration analysis by ICP-AES.

The data for NO_x absorption efficiency and reactant conditions of absorbents and oxidants was sourced from scholarly literature, as experimental analysis could not be performed due to constraints in obtaining equipment and logistics of laboratory experimental setup. Collected data was used to calculate the mass input and output of involved chemical species in each reaction from the different process pathway options using the reaction efficiency and molar masses of chemical species. Energy balances were derived from thermodynamic equilibrium relations based on enthalpy of reaction and drying requirements to produce desired product concentrations. Simulation of the process pathways was also conducted through Aspen Plus v8.4 software to verify reaction could take place and that mass and energy balances were justifiable.

Thereafter, process flowsheets were developed detailing the processes involved with the mass and energy requirements of each stage in the different pathway options. Aspen Plus has been used to develop the flowsheets based on the models present and data obtained from laboratory experimentation. It has also been widely used in literature for flowsheet formulation (Gorensek, 2011; Samborskaya *et al.,* 2015; Azad *et al.,* 2016).

4.5 Life Cycle Assessment of Alternative Pathway Options

The life cycle assessment applied throughout the case studies is regarded as a streamlined LCA or SLCA as it takes a cradle to factory gate approach. This means it does not take into account downstream activities including the transportation of the produced fertilizer to wholesalers, retailers, end users and its subsequent use (Biswas, 2014; Todd & Curran 1999).

The following four steps of International Organization for Standardization (ISO) 14040-44 were conducted to carry out the LCA (ISO 2007): (1) goal and scope definition; 2) inventory analysis; 3) impact assessment; and 4) interpretation. The goals of the current LCA studies were to investigate various process pathways for NO_x absorption (case study 1) and phosphogypsum reduction (case study 2) in order to determine the reaction pathways with the least environmental impacts for post treatment of waste and linking the products formed to potential industries for industrial symbiosis development. To this effect, the following indicators from the LCA study were analyzed for each alternative process option or reaction pathway:

a. GHG emissions (i.e. CO_2, N_2O and CH_4) from the production, transportation and use of inputs for the different stages of NO_x conversion into nitrates or nitrites;
b. Eutrophication for the evaluation of the nutrient enrichment level that the inputs and processes might have on water resources, and thus oxygen-level depletion potential in these waters.
c. Solid waste amount from the waste produced from each process, which could otherwise go to landfill.
d. Acidification potential resulting from the release of chemicals (i.e. SO_2, NO_2 and) NH_3 from inputs and processes, which has the potential to form acid rain.

The above indicators were chosen as they quantitatively provide an overall environmental outlook associated with each process, with which comparison can be made on the process option with least environmental impact. The same categories have been found to be the predominant impacts in other studies involving chemical processing (Biswas *et al.*, 2013). Other impact categories including land use, human toxicity, freshwater aquatic toxicity, etc., evaluated from the LCA had negligible results with very small values, and thus were not considered.

The functional units of the case studies analysed were:

- conversion of NO_x into 1 kg of potassium nitrate fertilizer
- reduction of phosphogypsum to: i) sodium sulphate for use in the production of 1 kg of packaging paper, or ii) ammonium sulphate for production of 1 kg of ammonium sulphate fertilizer

The functional units determine the system boundary of the LCAs. There are four stages that were contained in the system boundary in the LCA studies, which are: 1) oxidation; 2) absorption; 3) Drying; and 4) redox reaction. The NO_x conversion into 1 kg of fertilizer incorporated all the identified four stages, while the reduction of phosphogypsum to sodium or ammonium sulphates incorporated the last two stages of drying and redox reaction due to the nature of chemical reactions.

To supplement the LCA, the volume of dilution water needed for each process option was directly calculated from stoichiometry. The amount of required dilution water makes a significant contribution to the process water use.

4.6 Economic and Social Analysis of Alternative Pathway Options

Comparison of economics of the different pathways was made through the Economic Analyser software in Aspen Plus v8.4. This was based on the developed flowsheets for each process option with an absorption rate of 20 kmols/hr) of NO_x ($NO:NO_2$ = 1:1) in case study 1 or a reduction rate of 20 kmols/hr of phosphogypsum in case study 2.

There are many studies found in literature that have used Aspen Economic Analyser for economic analysis (Hunpinyo *et al.*, 2013; Hammer *et al.*, 2013; Jiang & Bhattacharyya, 2017), and they are what provided the motivation of using it. The Aspen Plus v8.4 Economic Analyser is a powerful cost estimation tool that provides detailed economics such as capital expenses (CAPEX), operating expenses (OPEX), scheduling, volume of materials used, etc. based on methods, models, design and cost data found on the Icarus Evaluation Engine. Therefore, a comprehensive set of calculations of all aspects from scheduling, building of instruments, vessels, auxiliary supporting equipment, operating and capital expenses required throughout the lifespan of the project life can be provided through the economic analyser in present value terms. This can then be used to compare the profitability of the different options, the return on their investment, profitability and the labour man hours that will be utilised from construction to the design lifespan of the processes.

The social analysis of the process options will also depend on the results of the Economic Analyser. Aspect such as volume of utilised waste or by-product over the lifespan of project can be calculated. The amount of waste reduced from release into the environment will be used to determine the benefits of avoided chronic long term exposure to KIA surrounding communities. The reduction of residue area and virgin resources from the utilisation of by-products will be used to determine the intergenerational equity that arises from resource conservation and avoided vegetation loss from land use.

4.7 Summary

The chapter covered the methodology employed in utilizing the developed framework to the case studies of NO_x absorption and phosphogypsum (PG) reduction in KIA. The process route options for both case studies were determined through reviewing various processing options undertaken in literature for the conversion of the wastes/ by-products into useful product forms. The experimental procedures employed in investigating the reduction of PG with suitable reducing reagents were subsequently described. Simulation of both case studies was described through the aid of Aspen Plus v8.4, and the mass and energy balances obtained from experimental (PG reduction) and simulation were used for the development of process flow sheets. These would be utilized for life cycle inventories for LCA analysis for environmental impact analysis of the different process routes through Simapro 8.03 software utilizing the Australian LCI database. Finally, the chapter described how the economic (through Aspen Economic Analyser v8.4) and social assessments (benefits from avoided waste to surrounding community) would be carried out for the case studies.

Chapter 4

Chapter 5 Application of Framework to Case Study 1: Nitrogen Oxides Tail Gas Absorption Environmental Aspects

5.1 Introduction

Case study 1 involves nitrogen oxide gases (NO_x) that are released as flue gases from nitric acid production plants. Absorption of these gases with suitable absorbents offers not only a means to reduce their release into the atmosphere but also the creation of valuable by-products that could be utilized for economic opportunities through industrial symbiotic development with neighboring industries. The application of the developed framework has been applied to assess the environmental impacts of several process pathways that involve the conversion of NO_x into potassium nitrate fertilizer using different combination of oxidants and absorbents. This will be assessed by utilization of the Life Cycle Assessment (LCA) tool to evaluate environmental impacts of global warming potential, eutrophication, acidification potential and solid waste generation for each option. The use of calculated dilution water requirement for each pathway has been used to supplement other environmental indicators. Thereafter, comparison of the by-product fertilizer produced from the various pathway options will be compared with conventional fertilizer to assess the by-product fertilizer (best pathway option) that could substitute conventional fertilizer through industrial symbiosis.

The chapter begins with prefeasibility studies performed through the framework to assess the best NO_x control strategy to apply for aiding symbiotic development. This is followed by selection of absorbents and oxidants for evaluating suitable pathways to produce by-product fertilizer before the life cycle inventories for each option are developed and detailed. Analysis of the environmental impacts of each option is then carried out through an LCA analysis to identify further utilization strategies and the environmental performance of by-product discussed with comparison to environmental impacts of conventional fertilizer. This is supplemented with uncertainty analysis through Monte Carlo simulation inbuilt in the LCA software to identify the best pathway option for industrial symbiosis through replacement of the conventional fertilizer. This chapter is reprinted with permission from Mohammed *et al.* (2016), Copyright 2016 Elsevier BV (Appendix 3).

5.2 NO_x –Prefeasibility Studies

There are three main methods that nitrogen oxide emissions can be controlled. They have been detailed in the literature review section of Chapter 2 and are:

- Selective catalytic reduction (SCR)
- Selective non- catalytic reduction (SNCR)
- Direct reduction

The SCR method incorporates the use of special catalysts to breakdown nitrogen oxides to nitrogen and oxygen gases. For tail gas such as nitrogen monoxide (NO), SCR is ideal with very high efficiencies. However, in the case of nitrogen dioxide (NO_2), higher temperatures of more than 400°C are required to effectively reduce them (Yoshikawa *et al.*, 1998). This is the major drawback of SCR as higher tail gas temperatures mean higher energy costs, which can make the process economically unviable. In addition, the capital cost of setting up the SCR technology and cost of catalysts and their regeneration are also highly expensive (Jakubiak & Kordylewski, 2011; Wang *et al.*, 2007).

The SNCR method utilizes reductants to react with the oxygen atoms in nitrogen oxides thereby reducing them to nitrogen gas, water and CO_2 (Zabetta *et al.*, 2005). Hydrocarbons, generally methane, are one of the most widely used reductants for SNCR methods. The use of hydrocarbons is equally effective at lower tail gas temperatures for NO_x reduction as the SCR methods. However, the use of hydrocarbons results in the production of CO_2, a green-house gas. Furthermore, there is additional expense associated with using hydrocarbons. The use of urea and ammonia can replace the use of hydrocarbons to lower costs. However, urea is affected by temperature – lower temperatures affect efficiency, while ammonia has high capital costs for setup (Javed *et al.*, 2007; Nguyen *et al.*, 2008).

The direct reduction method entails the scrubbing of tail gases through a liquid medium to absorb the nitrogen oxides. Water and alkali/alkali earth oxides solutions are the main liquids employed for the absorption. With water usage, the conversion of N_2O into dinitrogen tetroxide (N_2O_4) is necessary for it to be absorbed by water to form nitrous and nitric acids. Nitrous acid decomposes to NO and oxygen and can be recycled for nitric acid production through water spraying. However, the NO and oxygen from nitrous acid recombine to form N_2O. This is the drawback of this method as N_2O_4 can easily change state to N_2O.

The use of alkali/alkali earth metal oxides (caustic solutions) for scrubbing the nitrogen oxides is a suitable alternative to the water scrubbing. The nitrogen oxides react with metal oxides to form water and metal nitrates. The capital cost of using caustic solutions is fairly reasonable and the metal nitrates produced can be sold as by-products, offsetting investment costs and adding income to the process (Wang *et al.*, 2012; Jakubiak & Kordylewski, 2012; Zhang *et al.*, 2008). The efficiencies for NO_x removal are reasonably acceptable (85%-95%) though they are still much lower than those of the SCR and SNCR methods. Higher efficiencies would entail the use of multiple scrubbers, which would increase operational costs of this method.

The SCR and SNCR methods consist of expensive processes, because the process conditions for effectively running them entails the use of higher utilities to maintain desired specifications for the effective reduction of NO_x emissions (Jakubiak & Kordylewski, 2011; Wang *et al.*, 2007). The process conditions are also very sensitive to temperature, which will affect reduction efficiency and thus needs to be carefully controlled. Impurities also have to be controlled to avoid choking the catalysts in SCR methods, or change the process dynamics to produce undesired CO_2 for SNCR methods (Nguyen *et al.*, 2008). Although both SCR and SNCR have high efficiency in reducing NO_x emissions for nitric acid plants, the high operating cost limits their applications.

The NO_x reduction methods using caustic solutions take place at ambient temperatures. Thus, the operating cost is also lower and the process conditions are not as sensitive as the SCR and SNCR methods (Wang *et al.*, 2012; Jakubiak & Kordylewski, 2012). Capital costs for setting up such a process are also cheaper and the relatively high efficiencies (85% - 95%) in reducing NO_x emissions make it more economically viable.

A preliminary sustainability assessment to assess the benefits of using sodium hydroxide as a scrubbing solution (absorbent) of NO_x was performed using the triple bottom analysisor economic, environmental and social benefits. This would result in the production of sodium nitrate as a by-product that can be utilized or sold to other companies.

The results of the assessment are summarized in Table 5.1 where the avoided emissions of NO_x gases are seen to bring improved environmental conditions that result in lower impacts to the surrounding communities and natural environment. The resale value of by-product sodium nitrate adds an additional economic benefit.

Table 5.1 Sustainability assessment of sodium hydroxide use for NO_x absorption

By-product		Nitrogen Oxides
Further use		Sodium nitrate production
Preliminary Sustainability Assessment	**Social**	• Less acidic rain and adverse effects of nitrogen oxides to health from avoided release • Resource conservation • Inter-generational equity
	Economic	• Avoided fines resulting from emissions making savings to company. • Revenue from the sodium nitrate sale
	Environmental	• Less environmental burdens from avoided nitrogen oxides emissions. • Avoided virgin resource use through substitution or blending of ammonium nitrate with sodium nitrate in safety explosives

5.3 NO_x Reduction through Chemical Absorption

A life cycle assessment approach has been conducted to determine the environmental impact of industrial symbiotic relationships that utilize both oxidants and absorbents in converting tail gas NO_x to useful by-products for fertilizer production in a neighbouring industry. A variety of absorbents was considered for the absorption of NO_x based on literature review (Table 2.1). These included sodium carbonate solutions Na_2CO_3, potassium hydroxide (KOH), ammonium hydroxide (NH_4OH), ammonium Carbonate ($(NH_4)_2CO_3$), calcium carbonate ($CaCO_3$), calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH).

Firstly, the justification of the selection of suitable reaction pathways for NO_x absorption and development of related process flow sheets is presented. Secondly, analysis on the use of the by-products formed from NO_x absorption for fertilizer production has been carried out for industrial symbiosis linkage. Thirdly, LCA has been carried out to identify the most environmentally friendly reaction pathway to form industrial symbiosis. Finally, the environmental benefits of the replacement of conventional fertilizer with the by-product based fertilizer produced under industrial symbiotic process have been determined.

Fertilizers play an important role in food production by meeting the growing food demand from the increasingly growing world population. The way fertilizers achieve this is by providing nutrients to enhance soil quality and crop productivity (Bumb & Baanante, 1996; Stewart et al., 2005). Additionally, the use of potassium and phosphorus fertilizers have been found to play a pivotal role in helping nitrogen fixating bacteria in leguminous plant to affix Nitrogen from air to provide it as a nutrient to soils (Bumb & Baanante, 1996). This helps in improving deprived soils of nutrients and increasing crop growth and yield to meet the world food demand. The use of fertilizers and lime also helps to reduce acidity and improving crop yield to above 90% as evidenced in investigation of their application in Peru and Brazil on acidic tropic soils from land cleared from the Amazon for farming (Stewart et al., 2005). The improved productivity not only helps to supply food to meet the demands of the population but also helps in avoiding clearing further land from forests for cultivation (Bumb & Baanante, 1996; Stewart et al., 2005). However, there is a need to increase fertilizer production to maintain the constantly growing demand of food production. Nonetheless, the raw materials for conventional fertilizer like natural gas and phosphate rock are finite resources. Thus, the by-products through the proposed synergy offer an alternative fertilizer production route that avoids using the finite virgin resources and thus aiding to address food security.

5.4 Selection of Process Pathway Options

The selection of pathway options is based on the choice of available absorbents and oxidants for aiding NO_x absorption through reduction oxidation reactions, where NO_x is oxidized to higher soluble oxides and absorbed to form nitrates that are fixated in liquid solution from gaseous form and finally into solid form through drying. The absorbents and oxidants impact process conditions of the pathways, as they determine the amount of water to be used and thus utility requirements. The selection of the choice of absorbents and oxidants was based on literature review findings as presented in Table 2.1.

The use of carbonates as absorbents resulted in the substitution of CO_3^- anions with NO_3^- anions from the absorption. This leads to the production of CO_2 gas as a by-product, which is a greenhouse gas. As a result, additional process requirements for capturing the CO_2 make the utilization of carbonates unsuitable.

Ammonia is produced from the combustion of methane and air at high temperatures with the aid of special catalysts thereby resulting in a considerable CO_2 footprint. Thus, all ammonium related absorbents were neglected in the absorption analysis.

Potassium hydroxide appears to be a useful absorbent for NO_x capture with the formation of potassium nitrate - an important fertilizer and feedstock for the explosives industries. However, the market price of KOH input is higher than resultant potassium nitrate product, making KOH use as an absorbent uneconomical.

Calcium hydroxide and sodium hydroxide are relatively cheap in comparison with KOH. They are commonly used industrial reagents, and readily available in the market. The operation cost savings associated with the use of by-product nitrates/nitrites increase the profit margins. Thus, these absorbents have been considered in this case study for the development of industrial symbiosis.

Kuropka, (2011) highlights that some of the main oxidants that have been widely used for the oxidation of NO and NO_2 are ozone (O_3), hydrogen peroxide (H_2O_2) and sodium hypochlorite (NaClO). They have been selected in the current analysis due to their availability in the market and their effectiveness in NO and NO_2 oxidation.

Therefore, combinations of selected absorbents and oxidants generate the process pathways under study. Table 5.2 summarizes the six possible reaction pathways for creating industrial symbiotic relationship for the current study.

Table 5.2 Different pathway options, based on selection of absorbents and oxidants.

Absorbent	**Options**	**Oxidants**	**By-product**	**End Products**
$Ca(OH)_2$	Option 1.1	Ozone	Calcium Nitrate	Potassium Nitrate and Calcium Sulphate
	Option 1.2	Hydrogen Peroxide		
	Option 1.3	Sodium Hypochlorite		
NaOH	Option 2.1	Ozone	Sodium	Potassium Nitrate and

	Option 2.2	Hydrogen Peroxide	Nitrate	Sodium Sulphate
	Option 2.3	Sodium Hypochlorite		

The associated overall reaction equations for the NO_x absorption and by-product generation for each option are represented below:

Option 1.1, $\mathrm{NO + NO_2 + 2O_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2O_2 + H_2O}$ (5.1)

Option 1.2, $\mathrm{NO + NO_2 + 2H_2O_2 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 3H_2O}$ (5.2)

Option 1.3, $\mathrm{NO + NO_2 + 2NaOCl + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2NaCl + H_2O}$ (5.3)

Option 2.1, $\mathrm{NO + NO_2 + 2O_3 + 2NaOH \rightarrow 2NaNO_3 + 2O_2 + H_2O}$ (5.4)

Option 2.2, $\mathrm{NO + NO_2 + 2H_2O_2 + 2NaOH \rightarrow 2NaNO_3 + 3H_2O}$ (5.5)

Option 2.3, $\mathrm{NO + NO_2 + 2NaOCl + 2NaOH \rightarrow 2NaNO_3 + 2NaCl + H_2O}$ (5.6)

The production of potassium nitrate fertiliser from the resultant nitrate by-products are represented by the following equations:

$$\mathrm{Ca(NO_3)_2 + K_2SO_4 \rightarrow 2KNO_3 + CaSO_4} \qquad (5.7)$$

$$\mathrm{NaNO_3 + K_2SO_4 \rightarrow 2KNO_3 + Na_2SO_4} \qquad (5.8)$$

Pathways can be generalised according to Figure 5.1, which shows the inputs and outputs of each process stage until the final nitrate product that will be utilised for industrial symbiosis/synergy development.

The general process firstly involves oxidation of NO_x into higher nitrogen oxides (NO to NO_2; and mixture of NO and NO_2 to N_2O_5) with the aid of chemical oxidants, for facilitating the absorption in the subsequent stage. After absorption with a suitable absorbent, majority of the nitrogen oxides are chemically converted into metal nitrate by-product based on the absorbent used, and are dried to form a powdered product. The nitrate by-product is then mixed in an ion-exchange bath with potassium sulphate to produce potassium nitrate fertilizer and metal sulphate through a redox reaction. Potassium chloride can be used in place of the sulphate but it is deemed unsuitable due to the production of metal chloride by-product, which has lower demand compared to metal sulphate.

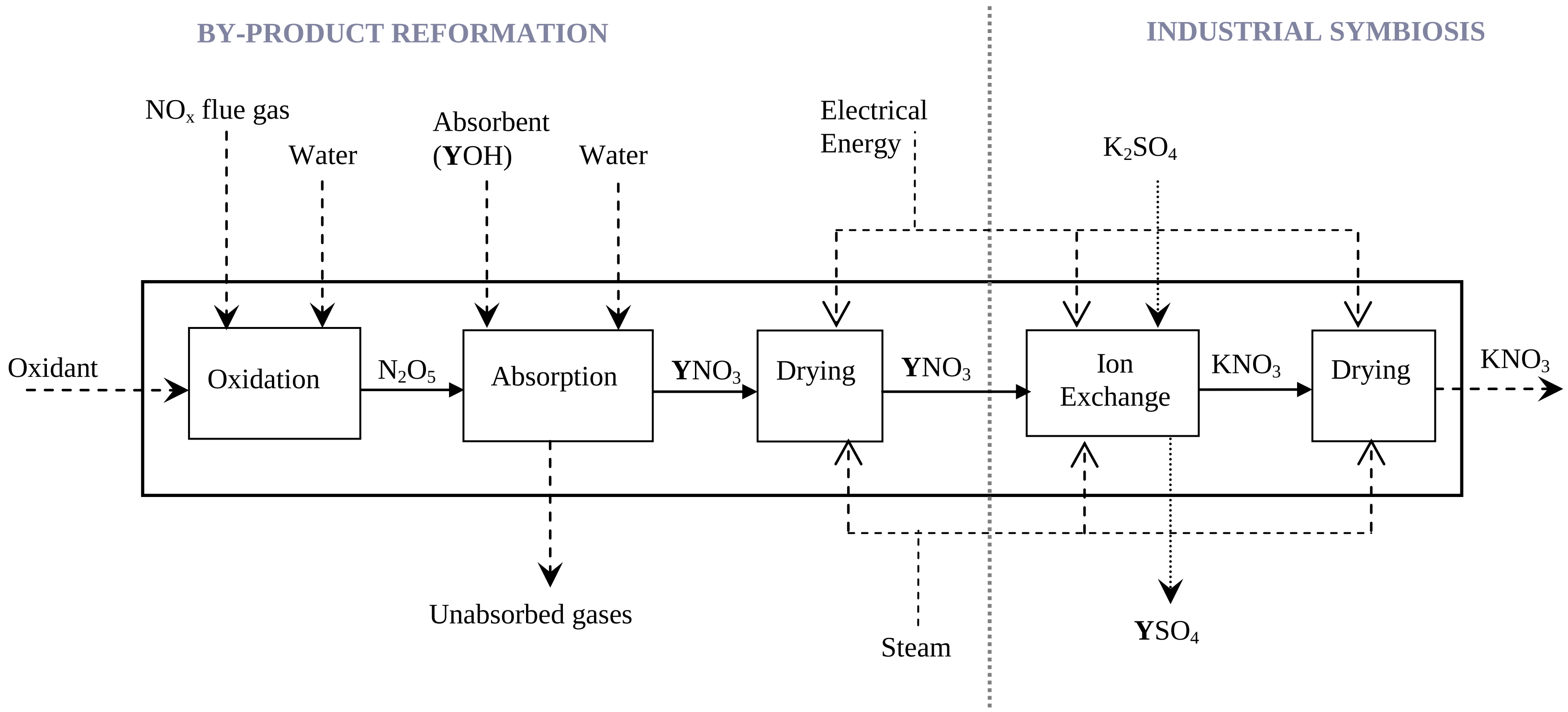

Figure 5.1 General process pathway of NO$_x$ by-product in industrial symbiotic relationship creation.

5.5 Life Cycle Inventory for the Selected Pathways

A life cycle inventory (LCI) for the chemical inputs and outputs of the three stages using various process pathways was developed as shown in Tables 5.3 and 5.4. The LCI includes the amount of chemical reagent and utilities required to produce 1 kg of potassium nitrate fertilizer, as well as the source of chemicals and the distance required for of inputs transportation from vending companies/industries.

The study assumed the absorption efficiency of NO_x to be 90% for each of the various absorbents used based on NO_x removal efficiencies derived from Table 2.1. Figure 5.2 shows the process flow chart of mass and energy balances which was used for developing inventories for 6 different pathways. The mass and energy balances were calculated from stoichiometric balances and thermodynamic properties such as enthalpy of formation of products, heat of reaction, heat capacities of reagents and products. Simulation using Aspen Plus v8.4 software was made to ensure that the reaction in the different pathways could take place and to verify the mass and energy balances.

The source of inputs for the development of the life cycle inventories (Tables 5.3 and 5.4) have been based on their availability from relevant industries within the Kwinana Industrial Area. In instances where the inputs could not be sourced within KIA, regional and national industries were firstly assessed for availability of required inputs before looking at international sources.

The main absorbents used for the case study were calcium hydroxide and sodium hydroxide, common industrial reagents that could be sourced easily from nearby industries at KIA, Cockburn Cement and Coogee Chemicals respectively. Each of the absorbents used determined the final products after NO_x absorption. Sodium nitrate was the resultant product from use of sodium hydroxide (NaOH) as absorbent and calcium nitrate was the final product from utilization of calcium hydroxide ($Ca(OH)_2$) as absorbent.

As previously described in Chapter 2, the main constituents of NO_x from nitric acid production tail gases are NO and NO_2 gases in an equimolar ratio of 1:1. The absorption of these gases with the selected absorbents produces both nitrate and nitrite by-products. In order to eliminate the nitrite by-products, oxidation of the

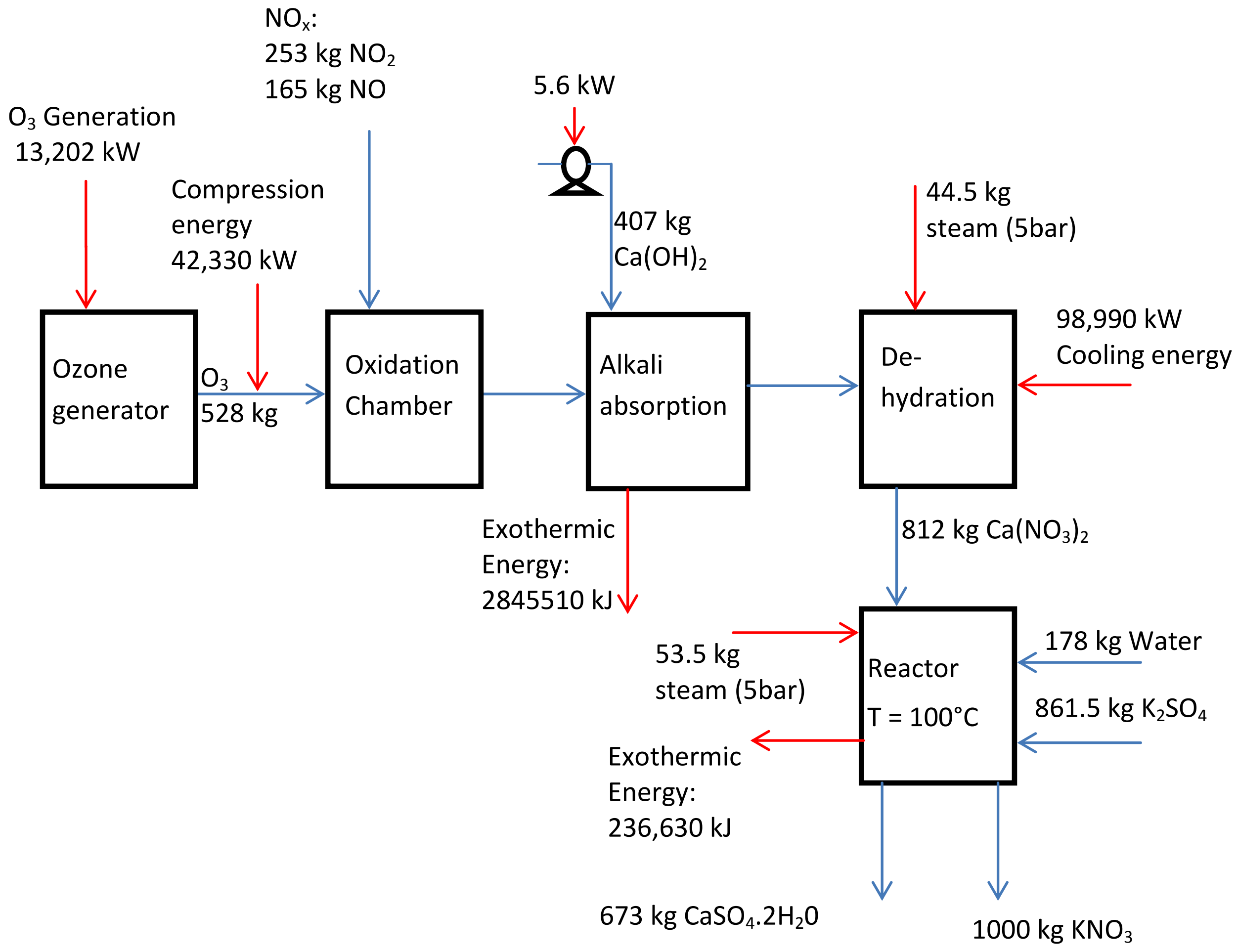

Figure 5.2 Process flow sheet for NO_x absorption with $Ca(OH)_2$ as absorbent and ozone as oxidant

NO_x gases was first carried out before absorption to produce nitrates as the only final products. The three main oxidants used to develop the life cycle inventories and process pathways are ozone, hydrogen peroxide and sodium hypochlorite. Ozone can be produced on site through an ozone generator, sodium hypochlorite could be sourced from Coogee Chemicals and hydrogen peroxide from Solvay Interlox Pty from South Australia.

The selection of the oxidants does not affect the resultant products from the use of NaOH or $Ca(OH)_2$ as absorbent, sodium nitrate and calcium nitrate respectively. However, they offer three alternative pathway options with the use of any of the absorbents. Thus, the arrangement of the life cycle inventories has been made with the use of calcium hydroxide as the main absorbent in Table 5.3 and the three oxidants as various alternatives for the production of calcium nitrate. Table 5.4 on the other hand uses NaOH as the absorbent, with the three oxidants as alternative for the production of sodium nitrate.

The sodium and calcium nitrates produced offer alternative ways for industrial symbiotic development with the production of potassium nitrate through reduction oxidation with suitable potassium salts, potassium sulphate in the current case study. Thus, both absorbents can lead to the absorption of NO_x and the production of products that could serve as inputs, which could be used for potassium nitrate fertilizer production in a neighbouring industry.

Table 5.3 Life Cycle Inventory for 1 kg KNO_3 formation using $Ca(OH)_2$ as absorbent

Inputs	**Amount**	**Unit**	**Location**	**Distance from Kwinana (km)**
NO	165	g/kg	CSBP	0
NO_2	253	g/kg	CSBP	0
Option 1 (Absorption with Calcium Hydroxide)				
Water for dilution of $Ca(OH)_2$ to 1 Mole/Litre solution	5.5	Litre/kg	Water Corporation	0
$Ca(OH)_2$	407	g/kg	Cockburn Cement	14
Process Options (Based on Oxidant Use):				
Option 1.1				
Ozone Oxidation				
Ozone	528	g/kg	On site	0
Electrical energy for ozone generation	13.2	kWh/kg	On site	0
Electrical energy for ozone compression	42.3	kWh/kg	On site	0
Drying				
Steam required for by-product 1 concentration	6.7	kg/kg	On site	0
Electrical energy for by-product 1 crystallisation	1	kWh/kg	On site	0
Option 1.2				
H_2O_2 Oxidation				
H_2O_2 solution (35% w/w)	1.1	Litres/kg	Solvay Interlox Pty	3500
Water for dilution of H_2O_2 to 1 Mole/Litre solution	10	Litres/kg	Water Corporation	0

Inputs	**Amount**	**Unit**	**Location**	**Distance from Kwinana (km)**
Drying				
Steam required for by-product 1 concentration	20.5	kg/kg	On site	0
Electrical energy for by-product 1 crystallisation	1	kWh/kg	On site	0
Option 1.3				
NaClO Oxidation				
NaClO solution (15% w/w)	5.5	Litres/kg	Coogee Chemical	2
Water for dilution of NaClO to 1 Mole/Litre solution	5.5	Litres/kg	Water Corporation	0
Drying				
Steam required for by-product 1 concentration	19	kg/kg	On site	0
Electrical energy for by-product 1 crystallisation	1.2	kWh/kg	On site	0
By-product 1 (from $Ca(OH)_2$ and oxidant use)				
$Ca(NO_3)_2$	812	g/kg	On site	0
Redox Reaction (for all options)				
K_2SO_4	862	g/kg	PotashCorp, Canada	17300
Water	178	g/kg	Water Corporation	0
Steam required for heating	1.4	kg/kg	On site	0
Electrical energy for cooling	0.2	kWh/kg	On site	0
By-product 2 (from Redox reaction)				
$CaSO_4$	673	g/kg	On site	0

Table 5.4 Life Cycle Inventory for 1 kg potassium nitrate by-product formation using NaOH as absorbent

Inputs	**Amount**	**Unit**	**Location**	**Distance from Kwinana (km)**
NO	165	g/kg	CSBP	0
NO_2	253	g/kg	CSBP	0
Option 2 (Absorption with Sodium Hydroxide)				
Water for dilution of NaOH to 1 Mole/Litre solution	11	Litre/kg	Water Corporation	0
NaOH	440	g/kg	Coogee Chemicals	2
Process Options (Based on Oxidant Use):				
Option 2.1				
Ozone Oxidation				
Ozone	528	g/kg	On site	0
Electrical energy for ozone generation	13.2	kWh/kg	On site	0
Electrical energy for ozone compression	42.3	kWh/kg	On site	0
Drying				
Steam required for by-product 1 concentration	13.9	kg/kg	On site	0
Electrical energy for by-product 1 crystallisation	1.2	kWh/kg	On site	0
Option 2.2				
H_2O_2 Oxidation				
H_2O_2 solution (35% w/w)	1.1	Litres/kg	Solvay Interlox Pty	3500
Water for dilution of H_2O_2 to 1 Mole/Litre solution	10	Litres/kg	Water Corporation	0

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
Drying				
Steam required for by-product 1 concentration	27.6	kg/kg	On site	0
Electrical energy for by-product 1 crystallisation	1.2	kWh/kg	On site	0
Option 2.3				
NaClO Oxidation				
NaClO solution (15% w/w)	5.5	Litres/kg	Coogee Chemicals	2
Water for dilution of NaClO to 1 Mole/Litre solution	5.5	Litres/kg	Water Corporation	0
Drying				
Steam required for by-product 1 concentration	27.9	kg.steam/kg	On site	0
Electrical energy for by-product 1 crystallisation	1.3	kWh/kg	On site	0
By-product 1 (from NaOH and oxidant use)				
$NaNO_3$	842	g/kg	On site	0
Redox Reaction (for all options)				
K_2SO_4	862	g/kg	PotashCorp, Canada	17300
Water	178	g/kg	Water Corporation	0
Steam required for heating	3.8	kg/kg	On site	0
Electrical energy for cooling	1.3	kWh/kg	On site	0
By-product 2 (from Redox reaction)				
Na_2SO_4	703	g/kg	On site	0

5.6 Environmental Impacts of Symbiotic Relationships

Table 5.5 shows the water use and key environmental impacts of the analysed process pathways. Overall, Option 1.2 that utilizes $Ca(OH)_2$ as absorbent and H_2O_2 as oxidant offered significantly reduced level of global warming, solid waste, eutrophication and water use compared to the other five options. This is due to the reduced level of GHG emissions associated with H_2O_2 production, which is about 2.1 kg CO_2-e/kg KNO_3. In comparison, the GHG emissions of NaClO and O_3 are about 7.4 kg CO_2-e/kg KNO_3 and 48.4 kg CO_2-e/kg KNO_3 respectively and are the primary reason for them being less favorable oxidants as opposed to H_2O_2. The associated emissions from the production of the chemical oxidants, obtained from the LCA study show that H_2O_2 contributes about 22% of the GHG emissions associated with production of 1 kg of KNO_3. This is in comparison to the contributions from NaClO and O_3, which are about 51% and 93% for production of an equivalent amount a kg of KNO_3. Further discussion and comparison of the environmental impact of each option based on the selected indicators are explained in the subsequent sections. The hotspots are then identified and potential solutions to solve them are provided.

Table 5.5 LCA results summary for combination of absorbents and oxidants for 1 kg KNO_3 production

Process Alternatives	**Water Use (Litres)**	**Global Warming Potential (kgCO_2 equivalent)**	**Acidification Potential (kg SO_2 equivalent)**	**Eutrophication Potential (kg PO_4^- equivalent)**	**Solid waste (kg)**
Option 1.1	5.7	52	0.09	-0.044	0.6
Option 1.2	15.7	9	-0.073	-0.058	0.1
Option 1.3	11.2	15	-0.047	-0.053	0.2
Option 2.1	11.2	58	0.114	-0.039	0.7
Option 2.2	21.2	15	-0.049	-0.053	0.2
Option 2.3	16.7	20	-0.021	-0.048	0.3

5.6.1 Water Use

The amount of water required for dilution purposes for the six process options is represented in Table 5.5. The basis for all the alkali oxides used in this study for the absorption of NO_x is 1M (mole/Litre) of feed. This translates to 1 Litre/kg of water required per 74g and 40g of calcium hydroxide ($Ca(OH)_2$) and sodium hydroxide (NaOH) respectively.

In total, 11 mols of NaOH and 5.5 mols of $Ca(OH)_2$ are utilized in the absorption process according to equations 1 – 6 for 1kg KNO_3 production. The amount of water in NaOH use is thus double the amount required for the $Ca(OH)_2$ use.

The use of oxidants also has an effect on the amount of water used. In the utilization of ozone as oxidant, there is negligible increase in water usage as ozone is supplied and reacts with NO_x in the gaseous state. Water is only used to dilute the alkali oxides' solutions to the desired feed concentration. However, when NaClO and H_2O_2 are used, there is considerable increase in water utilization in the absorption process. This is because of the fact that these oxidants are provided in solution form, with water required to dilute them to concentrations of 1M each.

The resultant effect on the water required by each of these oxidants provision is an additional 11 Litres for both H_2O_2 and NaClO oxidants. However, NaClO and H_2O_2 are sourced from suppliers in solution form at a concentration of 15% and 35% in water on a weight/weight basis respectively. Thus, additional water required for dilution of the oxidants has been worked out to be 5.5 Litres and 10 Litres for NaClO and H_2O_2 use respectively. Water required for the redox reaction constitutes an approximate addition of 0.2 Litres for each absorbent used.

The study has evaluated that the highest water utilization will result from the use of NaOH as the absorbent and H_2O_2 as the oxidant with total feed requirement of about 21.2 Litres of water. The lowest water utilization is from the use of $Ca(OH)_2$ as the absorbent and O_3 as the oxidant, where 5.7 Litres of water are required for absorption.

5.6.2 Global Warming Potential

Global warming potential was estimated in terms of kg CO_2 equivalent (CO_2-e) GHG emissions resulting from the production, transportation and use of energy and chemicals required for each process option.

5.6.2.1 *Implications of Oxidant use*

For Options 1.1 and 2.1, the use of ozone has the highest global warming potential. About 93% and 84% of the total CO_2-e emissions are attributed to use of ozone for the production of KNO_3 from absorption by-products ($Ca(NO_3)_2$ or $NaNO_3$). The other two oxidants also have significant contributions to CO_2-e emissions, with contributions of about 22% and 15% of the total CO_2-e for H_2O_2, and 51% and 36% for NaClO use. These are attributed mainly to the emissions from their production processes based on the findings of the SLCA.

The main reason for ozone's contribution to CO_2-e emissions is the consumption of the electrical energy (i.e. 25kWh per kg of O_3 produced (Stamate *et al.*, 2010)) required during air intake and ionization of oxygen. Thus, options that use ozone as oxidant are more carbon intensive than other reaction pathways.

5.6.2.2 *Effect of the absorbents and drying processes*

The use of different absorbents affects the drying process. Figures 5.3 highlights that 2.5 kg of CO_2-e emissions are produced from processes involving ozone as the oxidant and $Ca(OH)_2$ as absorbent. In contrast, about twice the CO_2-e emissions, amounting to 4.5 kg, were produced from the use of ozone and NaOH. Use of $Ca(OH)_2$ with NaClO and $Ca(OH)_2$ with H_2O_2 as oxidant resulted in 5.8 kg and 6 kg of CO_2-e emissions respectively. When NaOH was used instead of $Ca(OH)_2$, the CO_2-e emissions from the drying stage increased by about 2 kg for combinations of both NaClO and H_2O_2. This can be attributed to the explanation of water use where it was evaluated that 2 mols of NaOH are required to absorb NO_x (1 mole of NO and 1 mole of NO_2) while only 1 mole of $Ca(OH)_2$ is required for the same. Therefore, it can be concluded that the use of higher water volume causes the heating load to be higher due to the mass difference of solution per mole of by-product present.

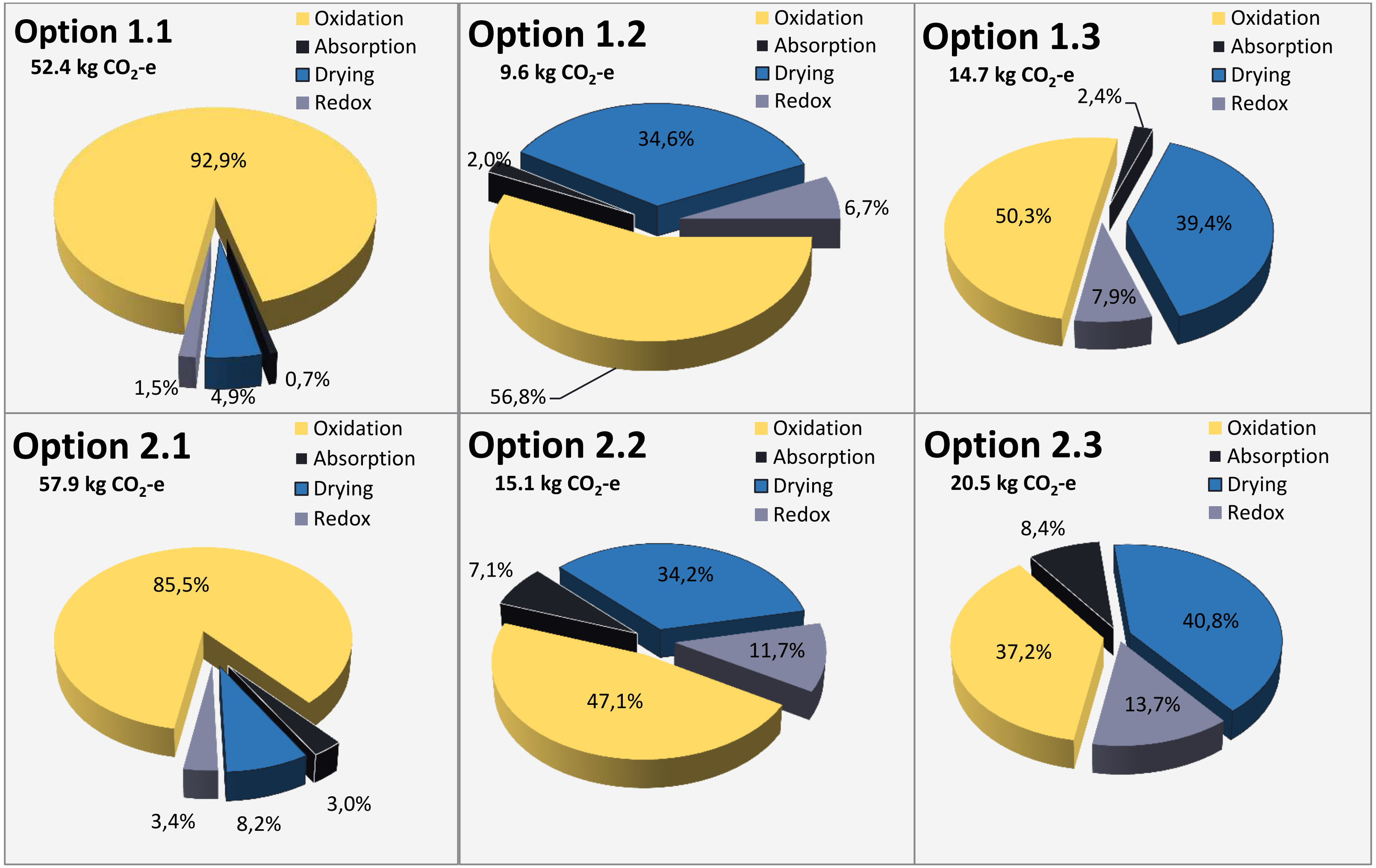

Figure 5.3 Percentage contribution of each stage towards the overall GWP for each process alternative.

The GHG emissions associated with the drying varies distinctively with type of oxidants used. In the case of processes involving ozone as the oxidant, the drying stage constitutes between 5% – 8% of all CO_2-e emissions (Figures 5.4 and 5.6). In contrast, drying contributes about 40% and 53% - 64% of the total CO_2-e emissions for processes utilizing NaClO and H_2O_2 respectively. The reason for this is that both NaClO and H_2O_2 require water for them to be diluted to desired concentrations for effective oxidation; this is in addition to separate water utilized for absorbent dilution to desired concentrations. Coal and gas generated electricity, in WA, is then required for heating the solution containing the by-product in order to concentrate the solutes at high temperature, which depends on the solubility of by-product at different temperature.

Ozone on the other hand does not require water for oxidation and thus only water resulting from absorbent use is heated and evaporated. Thus, it is evident from Figures 5.5 and 5.6 that the processes that contain water (in solution) for both absorbent and oxidant have higher CO_2-e emissions for by-product drying.

5.6.2.3 *Effect of the Redox reaction*

The redox reaction stage also contributed to the CO_2-e emissions for all process options in the current case study. Total emissions from this stage can be seen in Figure 5.5. There are approximately 1kg CO_2-e/kg and 3.1 kg CO_2-e/kg of product for processes using $Ca(OH)_2$ and NaOH respectively. The emission from redox reaction accounts for 2 – 5% of total emissions when ozone is used as an oxidant and for the case of NaClO as oxidant, this figure is raised to between 7 – 15%.

In the redox process, the reactants are mixed in a bath at about 115° C for the exchange of anions to take place. Thus, the heating requirements for the process are high. Additionally, once the reaction is finalized, the separation of soluble nitrate from insoluble sulphate takes place at the same high temperature as the reaction. This is to facilitate concentration of the nitrate brine before it is cooled to form crystals. The cooling and heating energies derived from electrical energy makes the redox reaction to also have significant contribution to global warming impact. Approximately 1.3 kWh and 3.8 kg of steam are used for cooling and heating in the redox reaction per kg KNO_3 when $NaNO_3$ is used in the redox reaction (derived

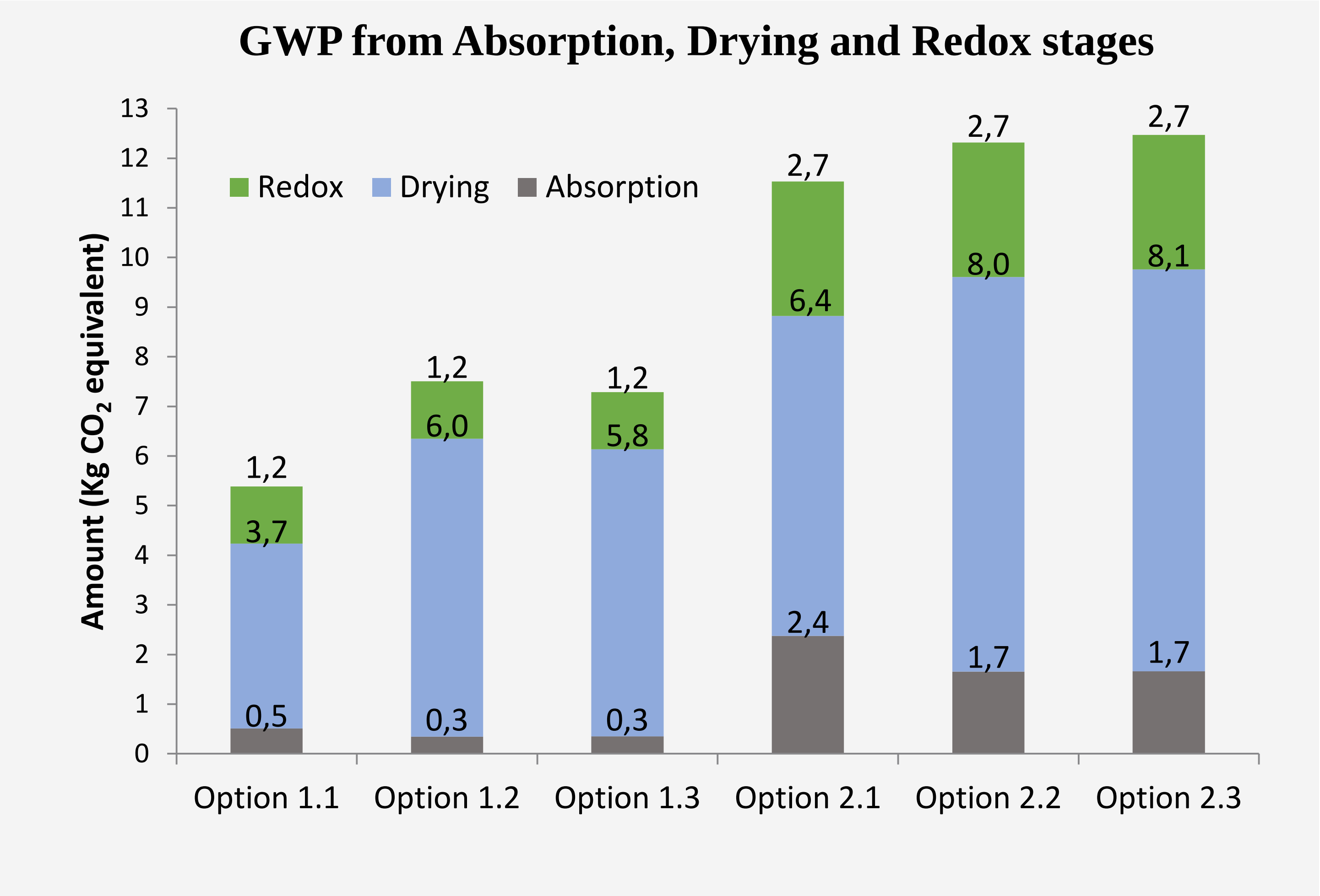

Figure 5.4 Global warming potential (GWP) from absorption, drying and redox stages of each process alternative

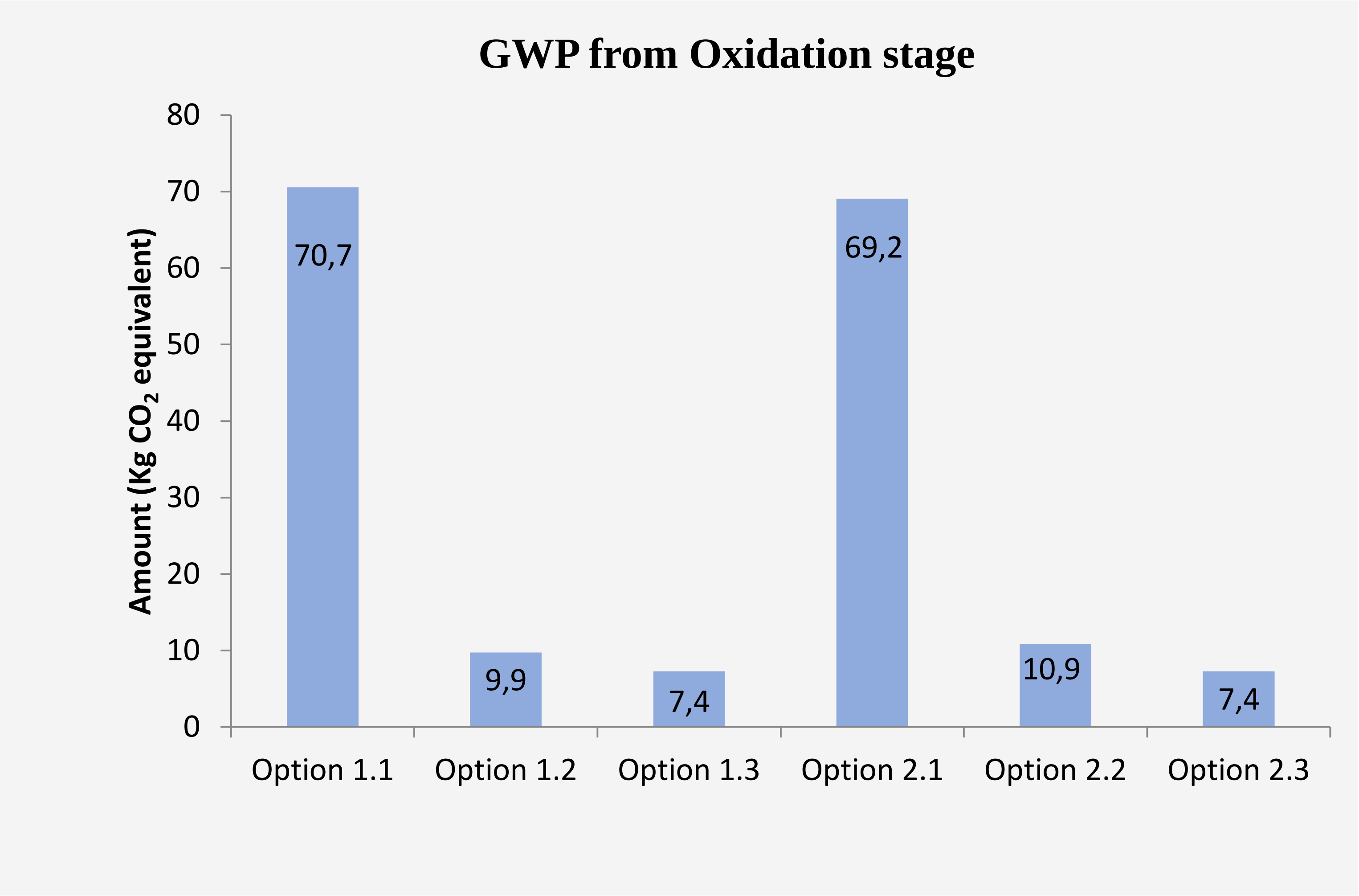

Figure 5.5 Global warming potential (GWP) from the oxidation stage of each process alternative

from NaOH use as absorbent). In contrast, the cooling and heating requirements for the redox reaction are 0.2 kWh and 1.4 kg of steam per kg KNO_3 when $Ca(NO_3)_2$ is used (derived from $Ca(OH)_2$ as absorbent). This is because the by-product calcium sulphate ($CaSO_4$) is insoluble in water making it easy to separate from the KNO_3. $Na_2SO_4$by-product from utilizing $NaNO_3$ is highly soluble in water and therefore makes the redox process have higher cooling and heating requirements as crystallization separation is employed to separate it from KNO_3

The CO_2-e emissions from the redox reaction are much lower than the emissions from the drying stage due to the difference in water utilized in both stages. It is evident from the LCI inventory that in the redox stage, about 178g of water per kg KNO_3 is added to facilitate the ion exchange process. However, the drying stage utilizes 11 Litres or 11 kg water/kg KNO_3 and 5.5 Litres or 5.5 kg water/kg KNO_3 when NaOH and $Ca(OH)_2$ absorbent are used, and an additional 11kg water/kg KNO_3 when either H_2O_2 or NaClO are used as oxidants.

5.6.3 Acidification Potential.

The acidification potential was determined from all the stages and processes that produce acid gases, which have the potential for acid rain formation.

The effects of acidification potential for different stages are similar to the findings from the GWP. The use of higher energy results in a higher acidification value. This is evidenced in Figure 5.6, where ozone use as oxidant leads to the oxidation stage having the highest acidification value of about 88% and 79% of total acidification when used in combination with $Ca(OH)_2$ and NaOH respectively.

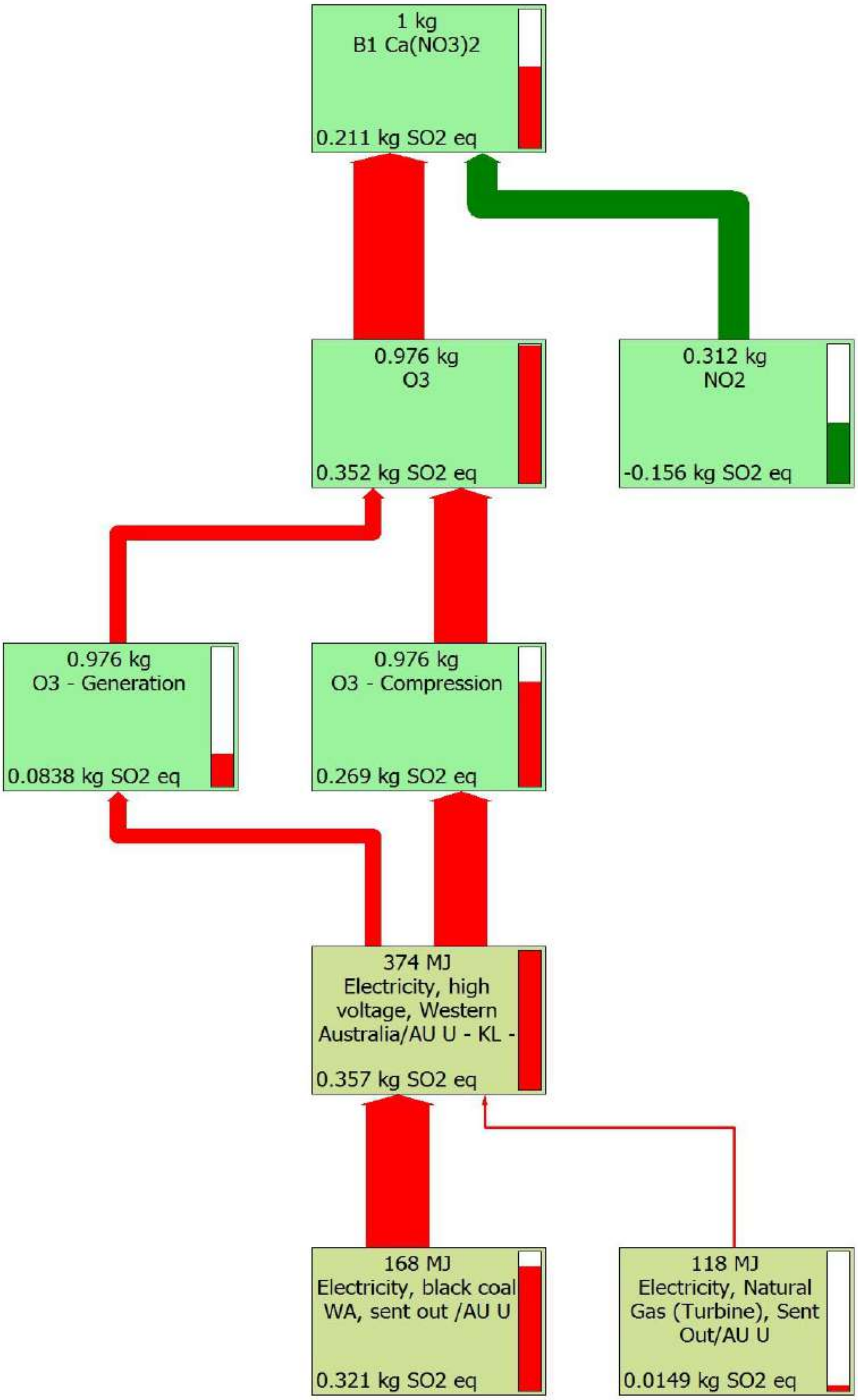

Figure 5.6 Acidification Potential from the utilization of ozone as oxidant and calcium hydroxide as absorbent

Figure 5.7 also shows that the utilization of H_2O_2 as oxidant results in about 22% and 15% of acidification value when used with $Ca(OH)_2$ and NaOH respectively. When NaClO is used instead, the oxidation stage contributes about 49% and 37% of the acidification values with $Ca(OH)_2$ and NaOH respectively. These values are attributed to the production processes for both H_2O_2 and NaClO, where H_2O_2 production has a lower acidification potential compared with NaClO. The values of other stages are also similar to the GWP, where higher water use results in higher electrical energy for the drying and redox stages.

The sequestration of waste NO_x gases to produce fertilizer avoids the gases from being released into the atmosphere (Equation 9). Sequestering of NO_x in the LCA for the production of 1kg KNO_3 leads to a reduction of -0.123 kg PO_4^{-}- equivalent in acidification value for each process pathway. The benefits of sequestration are that only the stages that use ozone as oxidant have significant acidification. This is because the high electrical energy utilized outweighs the benefits of sequestration.

$$Acidification\ = kg\ PO_4\ saved\ from\ NO_x\ sequestration - kg\ PO_4\ from\ electricity\ use \quad (9)$$

On the contrary, the other pathways where ozone is not utilised have negative acidification values, brought from the NO_x sequestration offsetting the acidification values resulting from respective inputs and processes involved. The benefits of sequestration are shown in Figure 5.8.

Option 1.2 that utilises H_2O_2 and $Ca(OH)_2$ is found to have the best acidification value of -0.073 kg SO_2-e. This is again attributed to the production process for H_2O_2, which has lower impacts than NaClO.

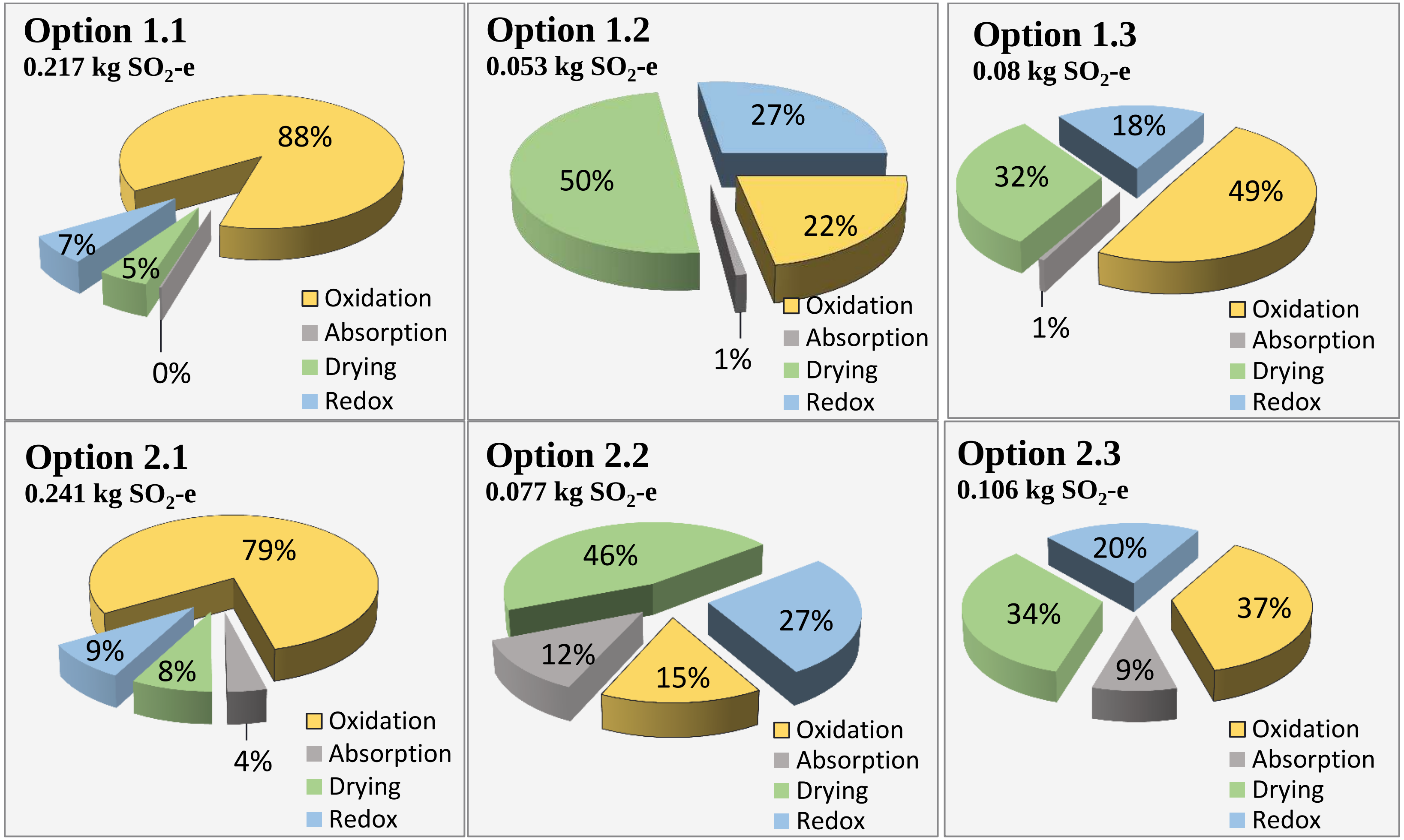

Figure 5.7 Percentage contribution of each stage towards the overall acidification potential for each process alternative.

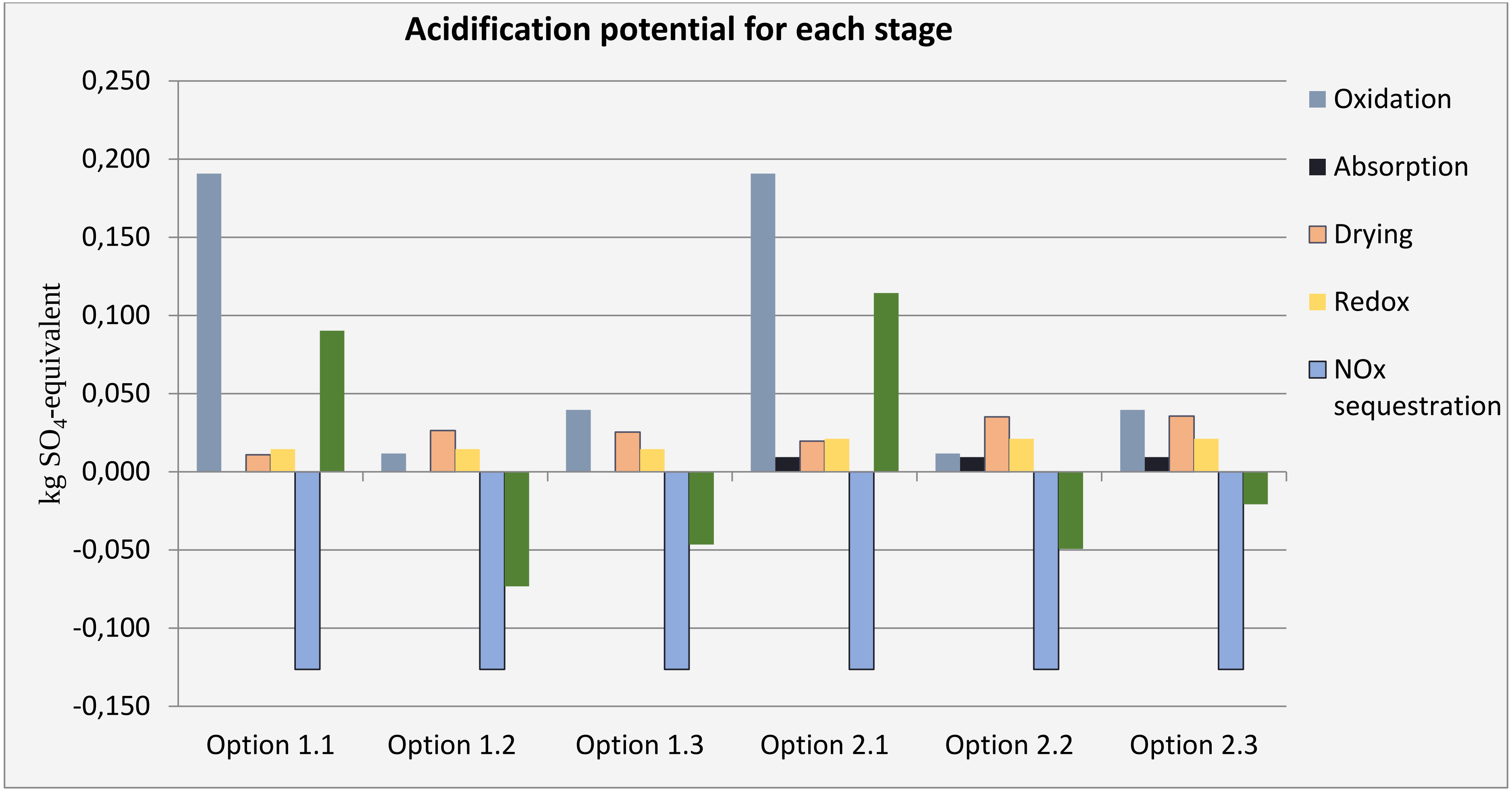

Figure 5.8 Acidification values for all stages taking NO_x sequestration into account

5.6.4 Eutrophication Potential

The impacts of eutrophication from each of the analysed processes result from energy supply. The amount of NO_x derived from oxidation of nitrogen in air and fuels during combustion determines the level of eutrophication. Table 5.6 presents a conclusive message that the higher the energy required for a process, the higher the eutrophication level. The NO_x emissions associated with the combustion of coal and natural gas for electricity might have been responsible for this eutrophication impact.

Table 5.6 Eutrophication values produced from different stages for 1 kg KNO_3 produced (kg PO_4^-- equivalent)

Stages	Option 1.1	Option 1.2	Option 1.3	Option 2.1	Option 2.2	Option 2.3
Oxidation	0.019	0.001	0.006	0.019	0.001	0.006
Absorption	0.000	0.000	0.000	0.001	0.001	0.001
Drying	0.002	0.006	0.006	0.004	0.008	0.008
Redox	0.001	0.001	0.001	0.003	0.003	0.003

The processes that use ozone as the oxidant (Option 1.1 and 2.1) have between 84 - 93% of their energy consumed in the oxidation stage (Figure 5.9). This translates to 14 and 13 times higher eutrophication values compared to the use of other oxidants due to high electricity utilization. The use of NaClO and H_2O_2 has similar eutrophication levels of about 0.006 (with $Ca(OH)_2$) and 0.008 (with NaOH), which is attributed to the heating and cooling energy requirements for drying.

When NO_x sequestration is taken into consideration in the LCA, the effect is that the total NO_x utilized for the production of 1kg KNO_3 results in a 0.066 kg PO_4^--equivalent reduction in eutrophication for each pathway option. Therefore, the overall eutrophication values for all the pathway options is negative as the benefits that arise from sequestering of NO_x outweigh the effect of processes involved. This is represented in Figure 5.8. Option 1.2 is found to have the best eutrophication value of -0.058 kg PO_4^--e, while the lowest values results when ozone is utilized as oxidant. Options 1.1 and 2.1 have eutrophication values of -0.044 and -0.039 kg PO_4^- -e.

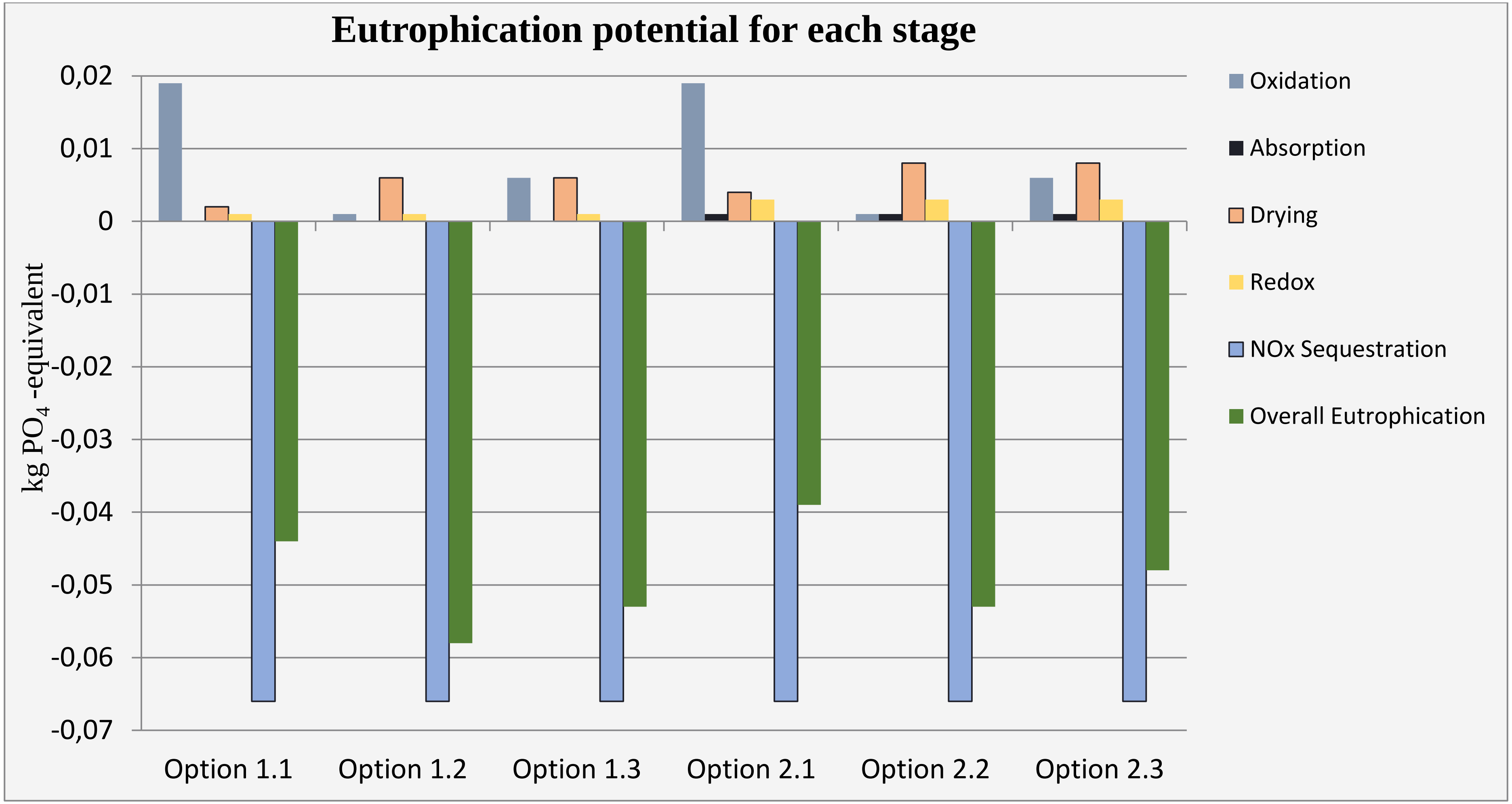

Figure 5.9 Eutrophication values for all stages taking NO_x sequestration into account

5.6.5 Solid Waste

The major source of solid waste is from the residue of fuel combustion. In this study, coal is the primary energy source. The solid waste is mainly from the resultant fly ash after coal combustion for energy generation. Fly ash can be used as a cement replacement in the manufacture of concrete to reduce the impacts of land filling and offset the environmental impacts associated with cement use (Ondova & Estokova, 2014). Thus, its utilization in cement production will help to lower the environmental impacts of solid wastes from the associated energy generation for all the reaction pathways in the current study.

Table 5.7 shows the amount of solid waste produced from different process alternatives. The key highlight is that most of the solid waste results from the production of oxidants used to oxidize NO_x, and follows a similar trend to the results of eutrophication values for other stages. Therefore, it can be concluded that the amount of solid waste generated, like the eutrophication values, is dependent on the consumption of electrical energy. The electrical energy is also linked to the amount of water used as determined under the Global Warming Potential discussion.

Table 5.7 Solid wastes produced from different stages (kg per kg KNO_3 produced)

Stages	Option 1.1	Option 1.2	Option 1.3	Option 2.1	Option 2.2	Option 2.3
Oxidation	0.58	0.06	0.22	0.58	0.06	0.22
Absorption	0.00	0.00	0.00	0.06	0.06	0.06
Drying	0.01	0.01	0.01	0.01	0.01	0.01
Redox	0.00	0.00	0.00	0.02	0.02	0.02

5.7 Hotspots in the Study

Water has been found to be a hotspot in the pathways selection. This is because the amount of water used determined the amount of energy required for separation of by-product salts through crystallization and drying. This is elaborated under the discussion of Global Warming Potential for each case study. A solution to reduce the water demand would be to reduce the concentration of both absorbent and oxidant solutions. However, studies performed on absorption efficiencies have evaluated that increasing the concentration of NaOH absorbent beyond the optimum of 2% weight/volume (w/v) reduced absorption efficiency (Pourmohammadbagher *et al.*, 2011). Kuropka (2011) found similar results to Pourmohammadbagher *et al.* (2011) after investigating the effects of increasing H_2O_2 and NaClO oxidant concentrations with NaOH as absorbent. The optimum H_2O_2 and NaClO concentrations in the study were evaluated to be 2 wt% of the solution and any increase in oxidant concentration had no significant increase in NO_x absorption. There were no conclusive results found for $Ca(OH)_2$ from literature, and it was assumed that $Ca(OH)_2$ would behave similarly due to the chemical similarities to NaOH. Thus, there are little prospects for the reduction of water use through increasing absorbent and oxidant concentrations.

Perth has a growing water crisis due to limited supply of fresh water resources, which poses a problem to the mineral industries in KIA due to competition for this vital resource from increased demand by the rising population growth. In order to alleviate the water shortage, desalination of wastewater has been undertaken to relieve pressure from fresh water resources, which are mostly used to serve domestic water needs for Perth inhabitants. Nonetheless, the use of desalination is carbon intensive meaning that as the demand for water increases both for domestic and industrial use, purification of wastewater from desalination will increase thereby increasing environmental problems due to increased energy use (fossil derived).

Energy use is the other major hotspot for the pathways selection. In the study, the electrical energy used Western Australia’s grid energy mix to represent local industrial symbiotic relationship. This energy mix is dominated by coal and natural gas, resulting in high CO_2-e emissions. However, there is an enormous amount of conventional energy saving and GHG mitigation potential by switching from conventional to environmentally friendlier renewable sources of energy. Dolan and Heath (2012) have reviewed LCA studies of wind power generation and harmonized the results to show that on average 11g CO_2-e are produced for 1 kWh of electricity produced from wind. The current study utilized electricity from the energy grid in Western Australia (WA), where the LCA study has evaluated that about 1.61 kg CO_2-e is produced per kWh generated. Thus, if electrical energy were harnessed from wind power instead of the WA grid, it has been evaluated that about 93% of GHG emissions from ozone production can be avoided, resulting in 86% and 80% overall GHG reduction for pathway Option 1.1 and 1.2 respectively. This has the significance of making pathways with ozone use environmentally friendlier and viable as opposed to the current situation where it is the least environmentally friendly. More importantly, there is a significant potential for electrical energy production from wind power in Western Australia (Biswas *et al.*, 2014).

In other studies, authors try to change fuels used in processes like the replacement of coke used in cement production with bio-fuels (Feiz *et al.*, 2015a; Hashimoto *et al.*, 2010) but none have covered the topic of electricity generation . In the current study, electricity is assumed to be sourced from the grid and no fuels is used in the processes of post-processing the wastes to valuable products.

A forecast energy mix to 2050 of Australia was obtained from Bureau of Resources and Energy Economics (BREE) report ´Australian Energy Projections to 2049-2050´(BREE, November 2014). In the forecast energy mix of Western Australia, overall electricity generation is expected to increase 44% over this period. However, renewable energy (of which wind is about two thirds) is expected to grow 1.8% annually, which translates to double the current generation from wind. Additionally, coal generation is forecast to grow by 1.6% annually. Though the percentage generation of wind will increase to about 7% of total energy generated in the state it is deemed insufficient to reduce environmental implications considerably. Additionally, according to the clean energy council of Australia, Western Australia is one of the states that does not have a renewable energy target set for electricity generation.

5.8 Comparative Environmental Assessment of Conventional and By-product Based Fertilizers in Case Study 1

The process with the highest energy demand is the one that utilizes ozone with NaOH for absorption. This system, as shown in Table 5.5, thus produces the highest amount of solid wastes of 0.7 kg/kg nitrate product. Similarly, the $Ca(OH)_2$ with H_2O_2 is the process that requires the least energy and produces the least solid waste of 0.1 kg per kg of by-product.

The GWP of conventional KNO_3 fertilizer from Simapro 8.03 European LCI database (as Australian LCI database has no impacts of conventional KNO_3) shows that it has equivalent cumulative emissions of 16.8 kg CO_2-e/ kg KNO_3 with the by-product KNO_3 produced from NO_x. In comparison, the CO_2-e emissions for KNO_3 obtained from NO_x absorption in this study are comparable to the conventional KNO_3 from the Eco-invent database for processes that use $Ca(OH)_2$ as absorbent (apart from the use of ozone as oxidant). In fact, when either $Ca(OH)_2$ is used with NaClO (Option 1.3) or when NaOH is used with H_2O_2 (Option 2.2), the cumulative emissions, as evidenced in Table 5.5, are found to be lower than the conventional KNO_3 fertilizer by a margin of about 2 kg CO_2-e/kg KNO_3 (11% GWP reduction). However, the option with the highest amount of reduction in GWP compared with conventional KNO_3 is Option 1.2 ($Ca(OH)_2$ and H_2O_2) with a net cumulative emission of more than 7kg CO_2-e/kg KNO_3 (about 45% GWP reduction).

There is no data obtained from the amount of solid wastes produced by the conventional KNO_3 from the Eco-invent database and therefore comparison cannot be made. In comparison to the eutrophication values, when sequestration of NO_x taken into account, all options have a negative eutrophication value. Options 1.3 and 2.2 are similar with about 4 times less eutrophication than conventional KNO_3, which has a value of 0.012 kg PO_4^-- equivalent. The rest of the options also have negative eutrophication values. Thus, all options are favorable when eutrophication is considered as the environmental indicator. The highest negative value results from Option 1.2 with a value of -0.058 kg PO_4^-- equivalent, which is about 5 times lower than the conventional KNO_3.

The results of acidification are similar to those of eutrophication, as NO_x sequestration offsets any acidification values produced from inputs and processes in each option. All options have a negative value except for Option 1.1 and 2.1 that utilizes ozone as oxidant. In comparison, Options 1.1 and 1.2 have about 2 and 3 times higher acidification values than conventional KNO_3, even after NO_x sequestration. The high electrical energy use in these options outweighs the benefits brought by NO_x sequestration. Option 1.2 has the best acidification potential of -0.073 kg SO_2-e. This value is two times lower than the acidification value of conventional KNO_3, which is 0.042 kg SO_2-e.

Therefore, it can be concluded that the most environmentally friendly pathway for the absorption of NO_x is the utilization of $Ca(OH)_2$ as absorbent and H_2O_2 as oxidant, though consumption of water is high for the option. The percentage savings or loss for utilization of by-product fertilizer compared with conventional (Table 5.8) further support that Option 1.2 as the most environmentally pathway. The benefits of this combination can be seen in the industrial symbiotic relation formed from utilizing the $Ca(NO_3)_2$ by-product for KNO_3 fertilizer production, where the relation offers not only an incentive for cheaper feed resource but also a better environmentally friendly product than conventional KNO_3. Thus, the LCA of multiple reaction pathways has enabled the identification of the best industrial symbiotic relationship that could potentially replace conventional fertilizer in an environmentally manner.

Table 5.8 Savings (negative) or loss percentage of Pathways Compared to Conventional Fertilizer

Impact Category	**Option 1.1**	**Option 1.2**	**Option 1.3**	**Option 2.1**	**Option 2.2**	**Option 2.3**
GWP	210%	-46%	-11%	245%	-11%	19%
Acidification Potential	114%	-274%	-212%	171%	-217%	-150%
Eutrophication	-467%	-583%	-542%	-425%	-542%	-500%

5.8.1 Uncertainty Analysis

The environmental benefits of the replacement of conventional fertilizer with by-product based fertilizer produced under the six reaction pathways have been statistically verified by an uncertainty analysis. The uncertainty analysis incorporating the use of the inbuilt Monte Carlo simulations in Simapro was performed to analyses the difference between the environmental impacts of each option and that of conventional KNO_3fertilizer. This was performed at a 95% confidence interval through a 1000 iteration step where random values within the prescribed probability distribution in the LCA study were generated, in order to see the resultant effect of on the LCA values.

The uncertainty analysis results, shown in Tables 5.9, 5.10 and 5.11, only compared the impacts of global warming potential, acidification and eutrophication as there was no data for solid wastes for conventional KNO_3 in Simapro to compare with.

Water use was determined from stoichiometry and therefore uncertainty analysis is not applicable as the data was established through calculation.

Table 5.9 Uncertainty analysis of global warming potential (kg CO_2-equivalent) due to substitution of conventional KNO_3 with by-product based fertilizer

Global Warming (kg CO_2-equivalent)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	35.40	35.3	3.34	27.6	41
Option 1.2	-7.44	-8.48	2.89	-15	-3.73
Option 1.3	-2.33	-2.44	2.94	2.26	-9.6
Option 2.1	40.89	40.9	3.29	33.5	46.8
Option 2.2	-1.95	-3.15	2.91	-9.27	1.8
Option 2.3	3.52	3.56	2.83	-2.54	8.37

The negative values in the tables indicate the potential savings that result from replacing conventional KNO_3 with the KNO_3 formed from the symbiotic relation. The mean of the Monte Carlo simulations is very similar to the single point values obtained from the net difference between environmental impacts of each option with that of conventional fertilizer for eutrophication, acidification and global warming impacts.

Table 5.10 Uncertainty analysis of acidification potential (kg SO_2 equivalent) due to substitution of conventional KNO_3 with by-product based fertilizer

Acidification (kg SO_2-equivalent)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	0.048	0.047	0.013	0.023	0.071
Option 1.2	-0.116	-0.122	0.01	-0.14	-0.101
Option 1.3	-0.089	-0.09	0.01	-0.108	-0.071
Option 2.1	0.082	0.081	0.016	0.054	0.115
Option 2.2	-0.081	-0.087	0.016	-0.11	-0.051

Option 2.3	-0.053	-0.053	0.015	-0.076	-0.02

The only noticeable difference is in the global warming potential of Options 1.2 and 2.2 (options with H_2O_2 as oxidant). There is no justification to the difference being related to the selected oxidant. However, the differences are about 1kg CO_2-equivalent for each option and this is considered not to have a drastic impact on the uncertainty analysis.

It can be seen from Table 5.9 that the global warming benefits of replacing 1kg of KNO_3 fertilizer with that obtained from Option 1.2 are between 3.73 and 15 kg CO_2-equivalent, with a mean of about 8.5 kg CO_2-equivalent. Results from acidification and eutrophication, Tables 5.10 and 5.11, show a similar outlook with an average reduction of about 0.12 kg SO_2 -equivalent and 0.08 kg PO_4^--equivalent respectively for Option 1.2.

Table 5.11 Uncertainty analysis of eutrophication potential (kg PO_4^--equivalent) due to substitution of conventional KNO_3 with by-product based fertilizer

Eutrophication Potential (kg PO_4^- equivalent)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	-0.056	-0.059	0.004	-0.069	-0.054
Option 1.2	-0.069	-0.075	0.004	-0.082	-0.068
Option 1.3	-0.065	-0.070	0.004	-0.078	-0.064
Option 2.1	-0.051	-0.055	0.005	-0.064	-0.048
Option 2.2	-0.064	-0.07	0.004	-0.079	-0.063
Option 2.3	-0.06	-0.064	0.005	-0.073	-0.057

Thus, within a 95% confidence interval the results of the uncertainty analysis agree with the findings of the LCA that Option 1.2 is the most suitable for the symbiotic relation development.

5.9 Conclusions

Life cycle assessment has been used as a decision making tool for establishing an optimum and environmentally friendly pathway for industrial symbiosis linkage. The symbiotic case employed in the study has been production of fertilizer from by-products derived from absorption of NO_x tail gases.

Analysis of various process pathways using different absorbents and oxidants for NO_x absorption was carried out. Mass and energy balances calculations were used to create inventories for the LCA to determine the environmental impacts of each alternative process option based on 1 kg of KNO_3 fertilizer formed. The use of ozone as the oxidant contributed over 90% of the emissions of the entire process. However, both NaClO and H_2O_2 had considerably higher heating and cooling requirements than ozone due to the amount of water present or added for oxidation purposes. In the case of $Ca(OH)_2$ use, the environmental impacts were lower than NaOH due to a lower mole ratio to reagents being used, which in turn reflected on less water and energy demand compared to NaOH. The result of this study concludes that use of NaOH as absorbent and ozone as oxidant was the least environmentally friendly pathway with 245% and 171% increase in GWP and acidification potential respectively compared to conventional fertilizer, though with a 425% reduction in the eutrophication potential. On the contrary, $Ca(OH)_2$ as the absorbent and H_2O_2 as oxidant gives the least environmental impacts for converting NO_x absorption by-product to fertilizer. This option had overall savings of 46%, 274% and 583% reduction in GWP, acidification potential and eutrophication compared to conventional fertilizer.

Water use and energy have been identified as the hotspots through this LCA. There was no solution to alleviate the impact of water use, but wind electricity was found to be the best mitigation option for reducing the impacts of energy use associated with utilization of the carbon intensive electricity grid of Western Australia.

Chapter 6 Application of Framework to Case Study 2: Phosphogypsum Reduction via Redox Reaction

6.1 Introduction

The application of the framework to Case study 2 incorporates the utilization of solid by-product waste for analyzing the potential for synergy development. Phosphogypsum (PG) that is produced as a by-product from phosphate rock digestion with sulphuric acid for the production of phosphoric acid has been considered for symbiotic application. The environmental impacts associated with the conversion of PG to suitable chemical sulphates for utilization as inventories for other chemical industries have been investigated through the framework. Laboratory experimentation using suitable reagents to reduce the sulphate (SO_4^{-2}) present in PG and form usable products has been carried out and is presented in Section 6.4.

The chapter begins with the selection of suitable reagents for the reduction of PG through reduction-oxidation process (redox reaction). The reagents have been selected to assess the potential of symbiotic relationship development of forming either ammonium sulphate fertilizer by-product or sodium sulphate that can serve as a raw material in the production of packaging paper. After reagents selection and development of life cycle inventories from mass and energy balance calculations, LCA is applied to assess the environmental impacts of different pathway options. The environmental indicators used for this purpose from the LCA are global warming potential, eutrophication potential, water use and solid waste. The indicators have been found to be the predominant impacts in other studies involving chemical processing (Biswas *et al.*, 2013; Mohammed *et al.*, 2015). The results of the LCA are discussed and compared with conventional ammonium sulphate and packaging paper, which were derived from the Simapro 8.03 Australian LCI database. The hotspots are then identified to consider further improvement opportunities. An uncertainty analysis has also been carried out to evaluate as to whether the by-product based reagents can offer environmental benefits while replacing conventional fertilizer or paper feed.

6.2 Phosphogypsum Reduction through Redox Reaction

In order to utilise the sulphur present in PG, various published studies have utilised the double displacement (redox) reaction of PG with group 1 alkali metal salts and ammonia salts (Cardenas-Escudero *et al.*, 2011; Mulopo & Ikhu-Omoregbe, 2012; Zhao *et al.*, 2014).

The selection of process pathways for the reduction of sulphate from PG to form suitable by-products were based on the effectiveness and availability of the chemical reagents. Chemical reagents considered for sulphate reduction of PG were grouped into sodium, potassium and ammonium salts based on findings of literature review as shown in Table 6.1.

The use of potassium hydroxide and carbonate salts offer potential for the reduction of PG and formation of potassium sulphate, however, the price of the reducing salts are higher in comparison to formed potassium sulphate, which can be derived cheaply from abundant natural ores. Economic viability issues of the selection of process pathways thus are the deciding factor. Various studies have investigated the use of the chloride as a cheap potassium resource for sulphate reduction (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 after reaction with PG. The formation of these double salts impedes the redox reaction as the reagents are locked in the double salts (Aagli *et al.*, 2005). This can be overcome through the utilisation of additives such as ammonia and isopropanol that inhibit double salt formation. However, the addition of these additives would incur considerable costs, especially the use of ammonia as it requires at mole ratio of above 4:1 with PG (Abu Eishah *et al.*, 2000). Therefore, the utilisation of potassium salts was not considered for pathway selection.

Table 6.1 Different reagent efficiencies for PG sulphate reduction

Reagent	**Reaction Efficiency**	**Additives and Mole Ratio**	**References**
Sodium Hydroxide (NaOH)	*77%	*Mole ratio of NaOH to Gypsum (1.6:1)	Cardenas-Escudero *et al.*, 2011
Sodium Carbonate (Na_2CO_3)	98.5%	Mole ratio of Na_2CO_3 to Gypsum of 2:1	Mulopo & Ikhu-Omoregbe, 2012.
Potassium Chloride (KCl)	97%	33% ammonia solution at 4.32:1 mole ratio with PG and presence of 7% isopropanol. KCl to Gypsum (1:1mole ratio)	Aagli *et al.*, 2005
	87%	Presence of HCl to KCl (1:1 mole ratio), and KCl to Gypsum (1:0.75 mole ratio)	Abu-Eishah *et al.*, 2000
Potassium Carbonate (K_2CO_3)	100%	Mole ratio of K_2CO_3 to Gypsum (1:1)	Ennaciri *et al.*, 2013

Reagent	Reaction Efficiency	Additives and Mole Ratio	References
Ammonium Carbonate ($(NH_4)_2CO_3$)	97%	Mole ratio of ammonia to Gypsum (2.8:1), and CO_2 (at 0.8 MPa) to Gypsum (1:1)	Zhao *et al.*, 2014

Note:

*Calculated values in Table 6.1 based on Gypsum reduction data obtained from Cardenas-Escudero *et al.*, 2011 paper.

The sodium salts that have the potential of reducing the sulphate from PG are sodium hydroxide and sodium carbonate. Cárdenas-Escudero *et al.* (2011) investigated the efficiency of sodium hydroxide for displacing the sulphate anion from PG and evaluated that 77% reduction of PG to sodium sulphate was made through the use of NaOH as reductant. Romero-Hermida *et al.* (2014) analysed various wastes that constituted sodium hydroxide or other sodium salts on the reaction with calcium sulphate in comparison to pure sodium hydroxide use and established that most waste sodium salts from various industries like the olive oil industry were unsuitable for PG reduction as they constituted chloride anions, which did not reduce the sulphate in PG. However, they used the same parameters for NaOH as Cárdenas-Escudero *et al.* (2011) and found similar results for PG reduction with NaOH. In both the above studies, a mole ratio of 1.6 NaOH: $CaSO_4$ was used instead of a mole ratio of 2:1 based on the stoichiometric balance for chemical reaction (Equation 6.1).

$$\mathrm{CaSO_4}.2H_2O + 2NaOH \rightarrow Ca(OH)_2 + Na_2SO_4 + 2H_2O \quad (6.1)$$

This limited the determination of a suitable NaOH/$CaSO_4$ mole ratio for efficient reduction of $CaSO_4$ to $Ca(OH)_2$. Another limitation for both studies was that there was neither analysis of the most suitable mixing speed nor the temperature for optimum reaction conditions.

The only study on use of sodium carbonate with phosphogypsum reaction found in literature was that of Mulopo and Ikhu-Omoregbe (2012). The results of their investigation showed that sodium carbonate is oxidised to sodium sulphate and PG is reduced to calcium carbonate upon reaction (Equation 6.2) with a high reaction conversion of about 98%.

$$\mathrm{CaSO_4}.2H_2O + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 + 2H_2O \qquad (6.2)$$

Analysis of effects of rotating speed, different molar-ratio of sodium carbonate to PG, reaction time and slurry content (in %) were investigated by Mulopo and Ikhu-Omoregbe (2012) to find the optimum conditions of reaction. Similar to the studies on utilisation of NaOH, the effect of temperature on reaction was not considered. In the current study, consideration of utilising the energy required for crystallising or drying the sodium sulphate by-product through heat exchange was made. This facilitated investigating the most suitable temperature for both sodium salts to determine optimum reaction temperature.

Ammonium chloride and hydroxide reaction with PG form soluble salts, which mean there is a balanced net ionic state for each product ions and thus no chemical reaction takes place. Ammonium carbonate and hydrogen carbonate are the only suitable and common industrial ammonium salts for the reduction of PG. The dissolution of CO_2 into ammonia solution before conversion of PG was investigated by Zhao et al (2014). CO_2 firstly reacts with ammonia solution to form ammonium carbonate before it can react with PG according to the Equations 6.3 and 6.4.

$$\mathrm{CO_2} + 2NH_4OH \rightarrow (NH_4)_2CO_3 + H_2O \qquad (6.3)$$

$$(NH_4)_2CO_3 + CaSO_4.2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O (6.4)$$

Direct utilisation of ammonium hydrogen carbonate was not encountered in literature. Nonetheless, it reacts similarly to ammonium carbonate in reducing PG though with the utilisation of 2 mols of reagent and release of a mole of CO_2 according to stoichiometric balance (Equation 6.5). Thus, it was also considered along with ammonium carbonate as possible pathways for PG redox reaction.

$$2NH_4HCO_3 + CaSO_4.2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + CO_2 + 3H_2O (6.5)$$

6.3 Selection of Process Pathway Options

The four selected possible reaction pathways utilising redox reagents are from the use of sodium and ammonium salts (Table 6.2).

Table 6.2 Different pathway options based on selection of redox reagents

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

Figure 6.1 shows the general description of the selected pathways comprising the inputs and outputs of the different stages from PG reaction with redox reagents to the final products formed through industrial symbiosis/synergy.

The overall process begins with the reduction of the sulphur present in the gypsum through the ion exchange with the aid of suitable redox reagents (sodium and ammonium salts). After separation of the two phases formed through centrifugation, the soluble reagent sulphates formed from redox reaction are dried before they can be

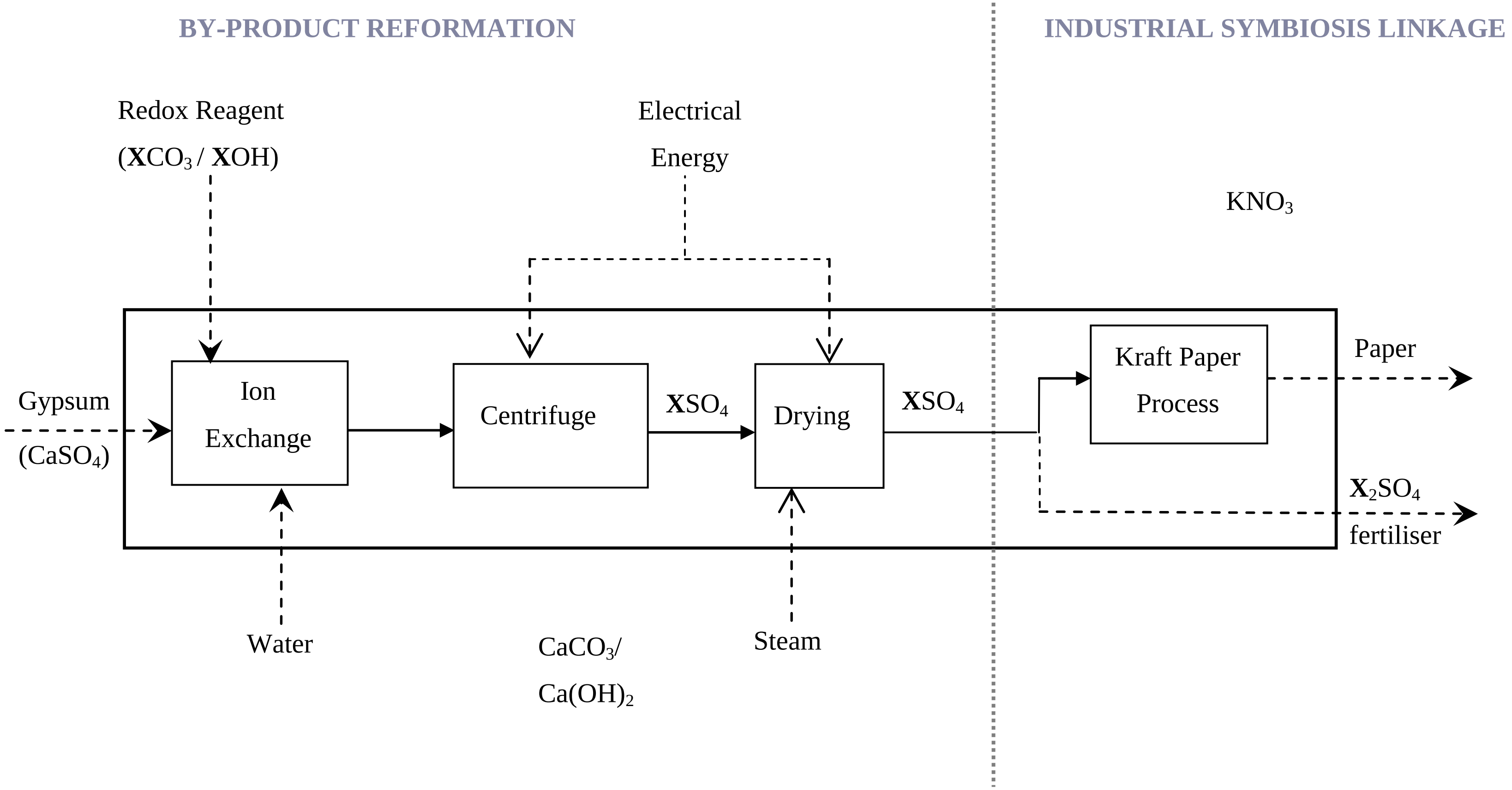

Figure 6.1 General process pathway for PG reduction and industrial symbiotic linkage

utilised for industrial symbiosis. Ammonium sulphate formed from ammonium salts utilisation is crystallised and dried for use as fertiliser.

Sodium sulphate formed from the utilisation of sodium salts for PG 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.

6.4 Experimental Results and Analysis

The results of the experimental analysis on PG reduction with suitable redox reagents are presented in this section. The only reagents that were investigated for the reduction of PG were the sodium based reagents of sodium hydroxide and sodium carbonate. The use of ammonium based reagents (Option 2.1 and 2.2) were not experimentally investigated due to constraints of time and sourcing. The analyses for these options were based on simulations carried out in Aspen Economics with 90% conversion as the basis for the reaction completion.

Generally, the conversion rate of PG using Na_2CO_3 was observed to be higher than reduction with NaOH as per the findings in the ensuing discussion. The primary reason for the higher conversion rates are solely because of the insolubility of the by-product calcium carbonate formed from Na_2CO_3 use that encourages more PG to dissolve into solution thereby increasing the conversion rate. On the contrary, the by-product from NaOH use (calcium hydroxide) is sparingly soluble in water which limits the amount of PG that can come into solution and thus resulting in the lower conversion rates observed in the discussion in the preceding section.

In order to determine the optimal conditions for PG reduction using the sodium based reagents, the effect of mixing speed, mole ratio of reagents to PG and temperature were analysed. Decisions could then be made on whether the optimal conditions evaluated from the analysis improved conversion rate of PG reduction at the expense of higher operating costs due to utility (mixing speed and temperature) or reagents (mole ratio of reagents to PG).

6.4.1 Effect of Operation Variables on NaOH Reduction of PG

The first variable investigated with use of NaOH as a reductant of PG was the effect of different mixing speeds when temperature and number of mols of NaOH used for reaction were held constant at 30°C and 2 mols respectively. Three different mixing speeds of 300 rpm, 400rpm and 500rpm were chosen to study the effect on the percentage conversion of PG to calcium hydroxide and the oxidation of NaOH to sodium sulphate.

The reaction conversion was found to increase from about 88% at 300rpm to approximately 91% at 400rpm, which meant an improvement in the contact area between reactants and thus improved reaction conversion. However, further increase in mixing speed from 400rpm to 500rpm resulted in a decrease in reaction conversion to about 83% as depicted in Figure 6.2. The probable explanation of the reduced conversion could be a lower contact area of reactants that could be brought about by centrifugal effect, where the reaction mixture is separated into phases due to different densities by the increased mixing speed. The phases react wherever they contact or overlap, but the extremities where there is a larger separation between the reactants results in lower contact and thus reduced reaction conversion. The optimum mixing speed was thus selected as 400rpm.

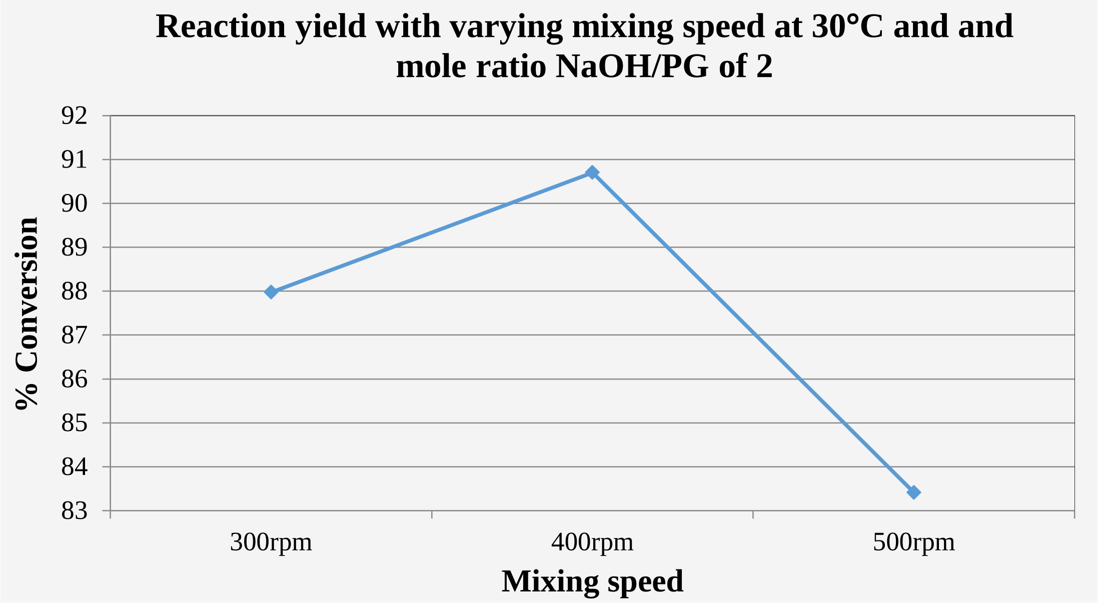

Figure 6.2 Effect of varying mixing speed on reaction conversion with NaOH reagent

The second variable selected for investigation was the effect of the mole ratio between NaOH and PG on the reaction conversion, while temperature and mixing speed were kept constant at 30°C and 400rpm respectively. The stoichiometric balance for complete reaction between the reactants is 2 mols of NaOH for every mole of PG as depicted in Equation 6.1. Thus, the initial mole ratio of NaOH/PG was selected as 2 and was varied subsequently by an additional 0.5 mols.

Results from analysing the effects of different NaOH/PG mole ratio (Figure 6.3) indicate that there is an almost linearly inverse relation with increase in the mole ratio with respect to the reaction conversion. This inverse relation applies as the NaOH/PG mole ratio was increased from 2 to 3, whereby the reaction conversion reduced from approximately 91% to 86%. Further increase in the mole ratio to 3.5 showed there was no additional effect on the reaction conversion as witnessed by the straight horizontal line (86% conversion) in Figure 6.3 as the mole ratio moved from 3 to 3.5.

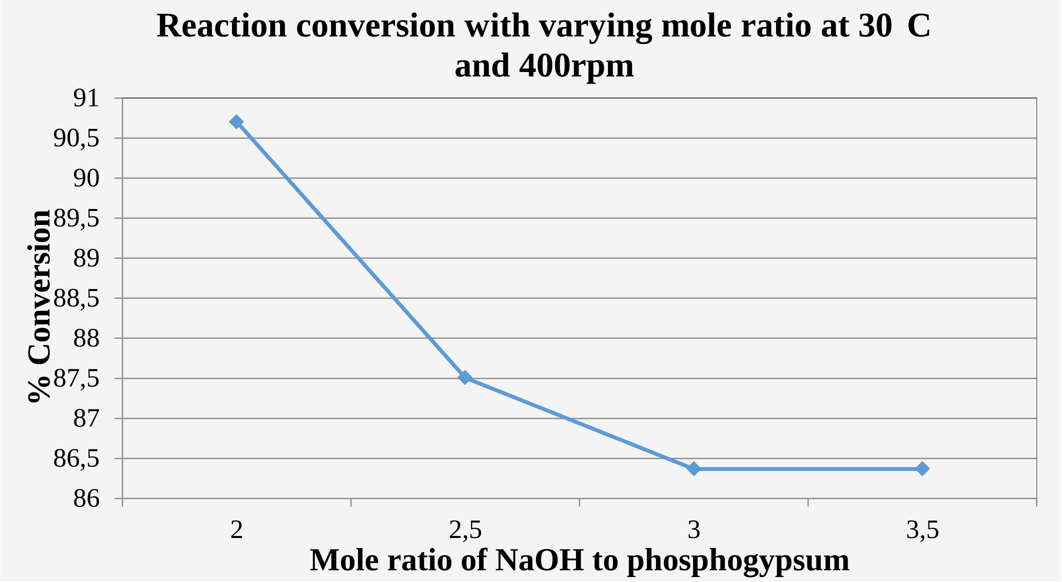

Figure 6.3 Effect of varying mole ratio of NaOH to PG on reaction conversion.

The likely reason why the reaction conversion decreases with the increase in amount of NaOH is because as NaOH concentration increases, it limits the amount of $CaSO_4$ from the partially soluble PG that enters solution. This is enhanced by the increase in the concentration of $Ca(OH)_2$ product in the solvent, which reduces complete reaction due to solvent saturation. Therefore, the most ideal NaOH/PG ratio for ideal reaction is 2, where greater than 90% of PG can be effectively reduced by NaOH solution.

Temperature was the last variable analysed for its effect on the reaction conversion and was varied each time by a step increase of 10°C from 30°C to 60°C with the NaOH/PG mole ratio fixed at 2 and mixing speed maintained at 400rpm. The effect of temperature on reaction rate had an abnormal trend, where increase in temperature from 30°C to 40°C initially reduced conversion rate from about 91% to 84%. However, subsequent increase of temperature from 40°C to 60°C led to an increase in conversion rate from 84% to 89% respectively (Figure 6.4). The anomaly in the reduction of conversion rate as temperature was initially increased from 30°C could be due to the change of state of sodium sulphate from the decahydrate (prevalent below 32°C) to anhydrous. At this point of crystal phase transformation, the solubility of sodium sulphate reduces and the solution becomes supersaturated leading to some of the anhydrous sodium sulphate to crystallise into solid phase. The super saturation caused by the phase change is what reduces the conversion rate of PG with NaOH as the less PG is dissolved into solution.

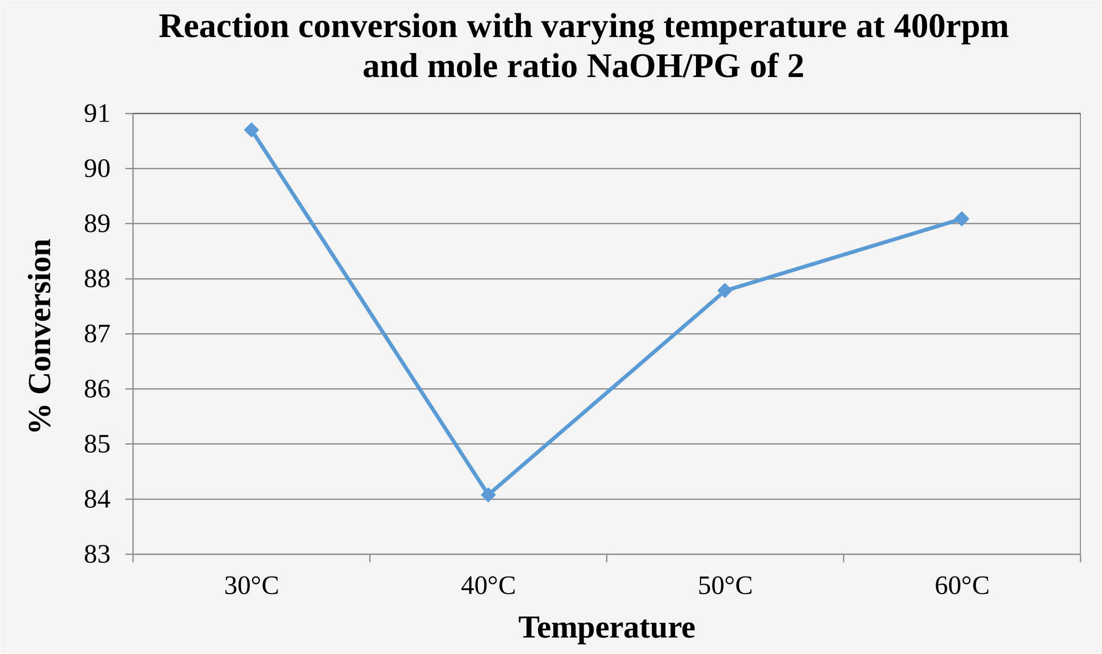

Figure 6.4 Effect of varying temperature on reaction conversion with NaOH reagent.

As temperature is raised further from 40°C to 60°C, more sodium sulphate is crystallised from solution thereby allowing more PG to come into solution and thus increasing the conversion rate. Nonetheless, the temperature with the highest conversion is 30°C where 91% conversion was achieved, meaning an increase in temperature beyond this point (30°C) only increases operational costs at the expense of lower conversion rates.

Therefore, it can be concluded that the ideal conditions for optimised conversion of PG using NaOH are a molar ratio of NaOH/PG of 2, a mixing speed of 400rpm and a temperature of 30°C. At the optimised conditions, about 91% conversion of PG to sodium sulphate is achieved. This conversion is higher than that of Cardenas-Escudero *et al.* (2011) who obtained 77% conversion from the same reaction at room temperature, an unknown magnetic stirring rate and at a mole ratio of 1.6 NaOH: PG. The lower conversion by Cardenas-Escudero *et al.* (2011) is due to a lower mole ratio of NaOH to the limiting reactant (PG).

6.4.2 Effect of Different Variables on Na_2CO_3 Reduction of PG

The same variables analysed for reduction of PG with NaOH were investigated for the reduction of PG using sodium carbonate. The first variable analysed for utilisation of Na_2CO_3 as a PG reducing reagent was the effect of different mixing speeds. Three mixing speeds (300rpm, 500rpm and 700rpm) were tested at constant conditions of Na_2CO_3/PG mole ratio of 1 and 30°C. The conversion rates from each were compared to determine the speed with optimal PG reduction. The results are depicted in Figures 6.5, 6.6, and 6.7.

The main finding for the effect of mixing speed was that the conversion rate reduced almost linearly from approximately 94.9% to 93.9% as the mixing speed was increased from 300rpm to 700rpm (Figure 6.5). The reduction in conversion as the mixing speed was increased is probably due to the centrifugal effect of increased mixing speed. The denser PG is mostly rotated in the lower part of the solution and the Na_2CO_3 mostly on the upper part resulting in a slight reduction in the surface area of contact between the reactants and thus the slight difference in conversion rates. Therefore, the 300rpm speed is deemed the most suitable as it gives a better conversion rate of PG reduction to $Ca(OH)_2$ and utilises less energy compared to the other mixing speeds.

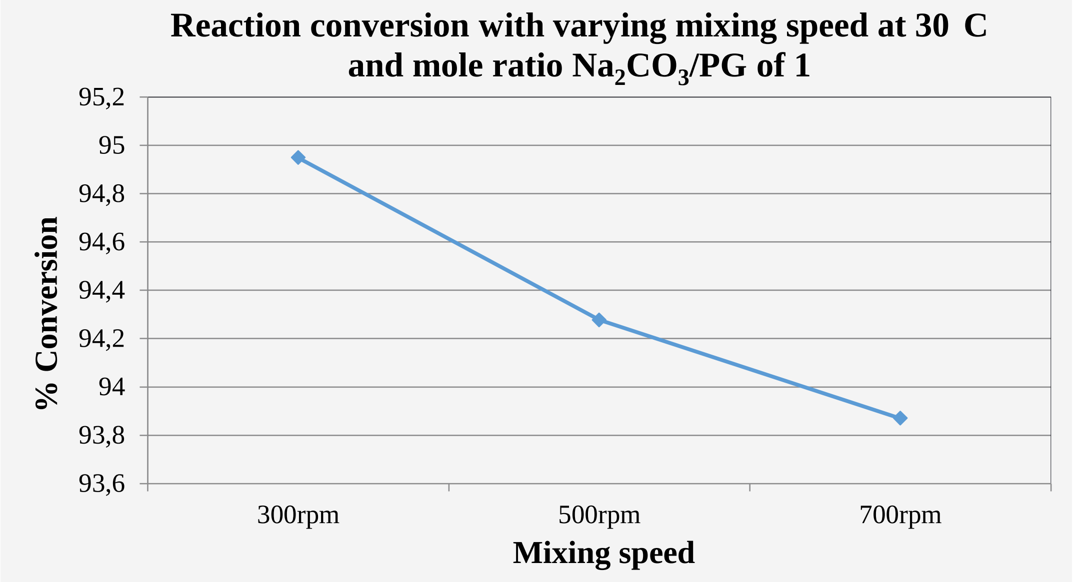

Figure 6.5 Effect of varying mixing speed on reaction conversion with Na_2CO_3 reagent

The second variable under study was the effect of the Na_2CO_3/PG mole ratio on the conversion rate. The Na_2CO_3/PG mole ratio was varied from 1 according to stoichiometry (Equation 6.2) until 2.5 with a step increase of 0.5. The outcomes of varying the mole ratio are summarised in Figure 6.6 where the general trend is the increase in conversion rate with an increase in the Na_2CO_3/PG mole ratio.

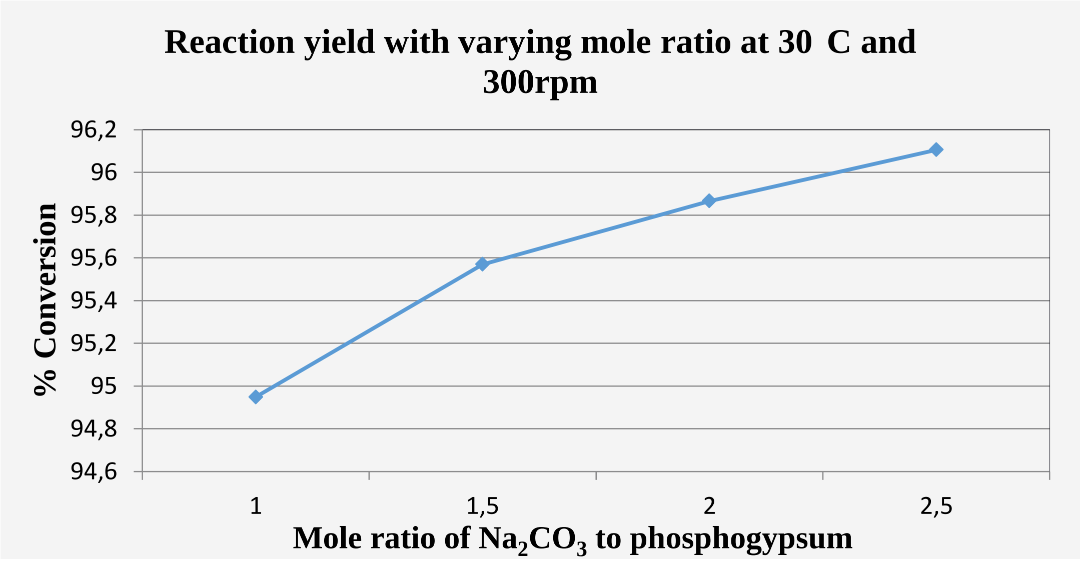

Figure 6.6 Effect of varying mole ratio of Na_2CO_3 to PG on reaction conversion.

The conversion rate improved from about 95% at a mole ratio of 1 to 96.1% when the mole ration was increased to 2.5. However, the highest variance in conversion rate was approximately by only 1%. Therefore, it is not logical to increase the mole ratio from stoichiometry to improve the conversion rate as it only results in higher reagent use, which means more expense. Thus, the optimum mole ratio of Na_2CO_3/PG for PG reduction was selected as 1 (that of stoichiometry).

The last variable analysed was the effect of temperature on PG conversion rate using the optimised conditions of 300rpm mixing speed and Na_2CO_3/PG mole ratio of 1. Increase in temperature from 30°C to 40°C had a negligible increase (0.2%) in reaction conversion (Figure 6.7). However, when the temperature was increased beyond 40°C, the reaction conversion reduced and finally reached to about 91.8% at 60°C. The reduction in conversion with increase in temperature is similar to the explanation of effect of temperature on NaOH reduction of PG. This is because of the change in crystal formation of PG from the decahydrate to anhydrous above 32°C. The change in crystal form lowers the solubility of PG affecting the interaction with Na_2CO_3 resulting in lower conversions of sodium sulphate. Thus, the best temperature for reducing PG with Na_2CO_3 is 30°C.

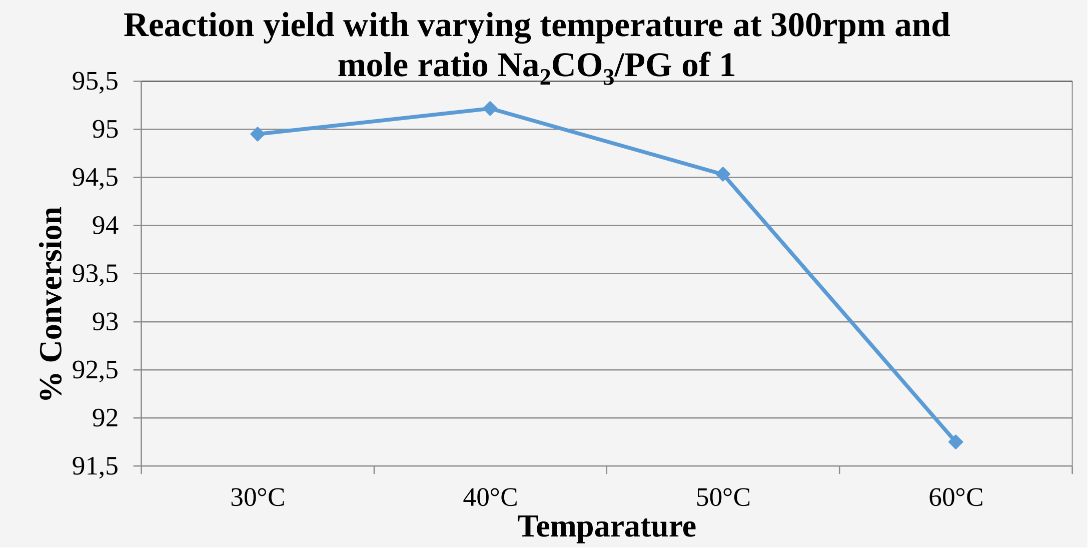

Figure 6.7 Effect of varying temperature on reaction conversion with Na_2CO_3 reagent.

Therefore, it can be concluded that the ideal conditions for optimised conversion of PG using Na_2CO_3 are a molar ratio of Na_2CO_3/PG of 1, a mixing speed of 300rpm and a temperature of 30°C. At the optimised conditions, about 95% conversion of PG to sodium sulphate is achieved.

6.4.3 Effect of Sodium Ions on Conversion Rate

The concentration of sodium in the solid phase ($Ca(OH)_2$ by-product) separated by centrifuging after PG reduction with NaOH was found to vary with the different experimental runs as observed from the ICP results (Figures 6.8). Therefore, further analysis on the possible effect of the sodium ions on the reaction conversion was made for the case study involving NaOH as the reducing reagents. Comparison of the sodium ions to the sulphur ions and the calcium ions detected by ICP was made to ascertain whether there was any relationship between sodium and the other ions.

The presence of sodium ions was evaluated to have a linear correlation with that of sulphur ions for experimental runs involving NaOH. Any increase of sodium causes a corresponding increase in the sulphur ions as seen from the trend of the plots of different experimental runs in Figures 6.8. The justification of this trend is that the sodium and sulphur are from the same salt, in this case sodium sulphate produced from the reduction of PG with NaOH. Analysis of the effects of the sodium ions on calcium ions shows that as the sodium concentration increases, the calcium concentration tends to reduce. This is observed when the peaks of sodium ions rise resulting in the dip in the peaks of calcium ions (Figures 6.8), especially for the variables of 60°C, 3 mols and 500 rpm.

The result of the increase in sodium lowers the total concentration of calcium by-products and increases the sulphur concentration as sodium sulphate accumulates and is considered as part of the by-product. This alludes that the conversion rate to be lower due to higher sulphur ions from the sodium sulphate present. This is because the conversion rate is based on reduced sulphate from PG.

The validation that sodium sulphate ions exist in the products from NaOH use are observed from the 2 theta XRD plots of the analysed solid products from NaOH reduction of PG (Figures 6.9). The XRD plots provide qualitative indication of the presence of sodium sulphate, which results from improper centrifuging of the supernatant solution from the solid residue after reaction completion. It could also result from the crystallisation of the sodium sulphate from the supernatant due to saturation, especially at higher mole ratios of NaOH with respect to PG.

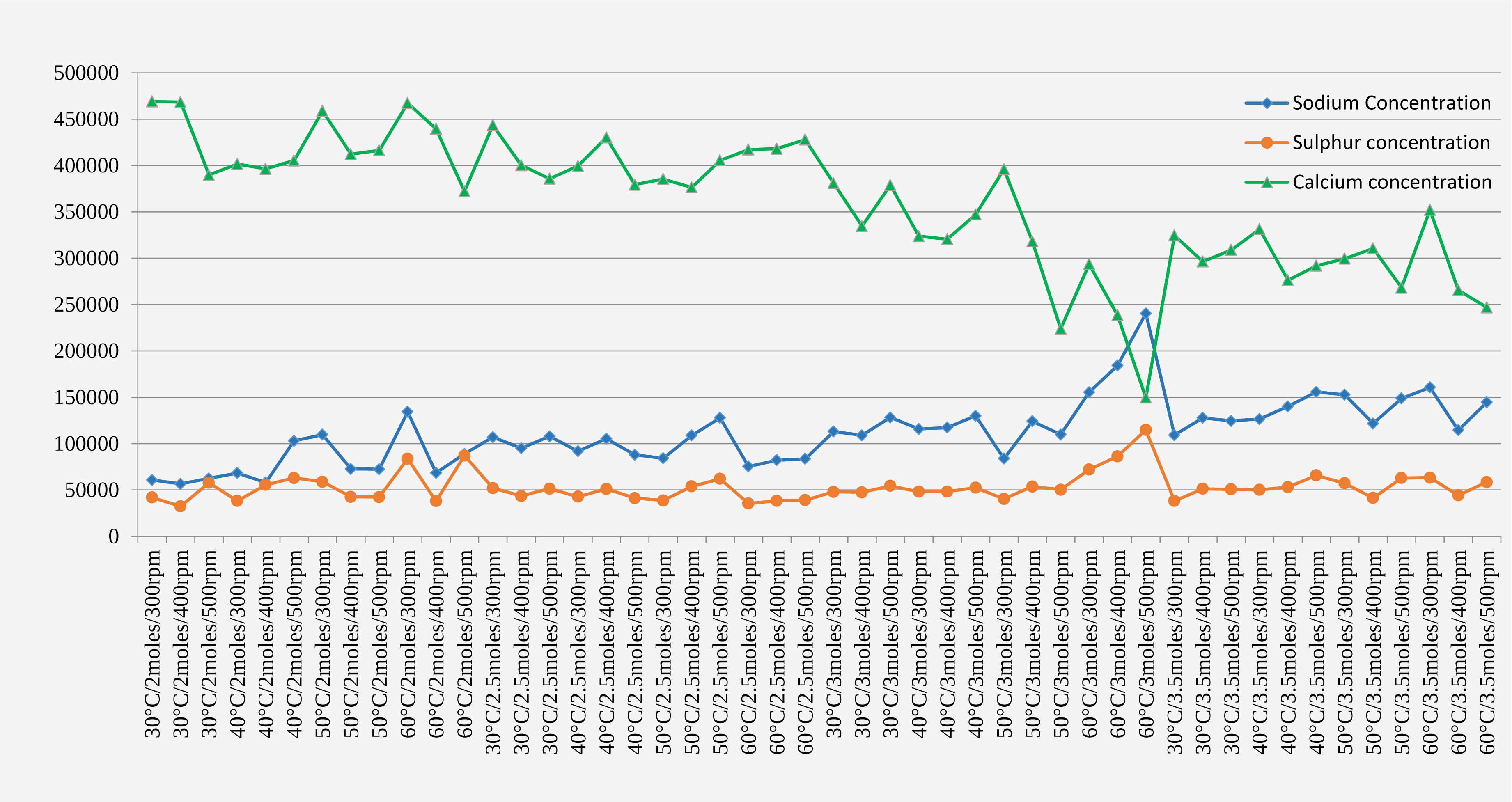

Figure 6.8 ICP results showing the influence of sodium ions on conversion rate using NaOH as reagent

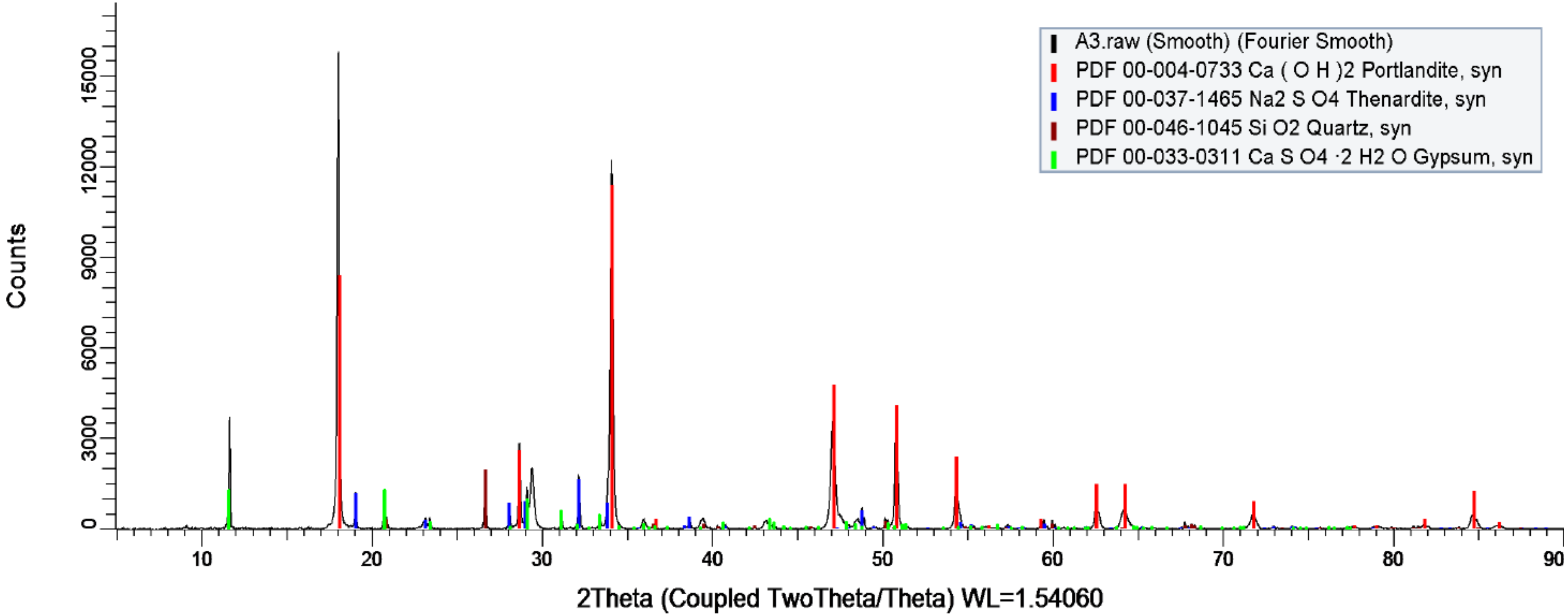

Figure 6.9 XRD qualitative plot of salt compounds after PG reduction with NaOH

6.5 Life Cycle Inventory for the Selected Pathways

The environmental implications of the replacement of virgin packaging paper and chemical fertilizer with the same produced from solid by-product have been determined using an LCA approach as discussed in Chapter 4. The life cycle inventory (LCI) consisting of inputs and outputs of different stages of the symbiotic relationship pathways (Table 6.2) are presented in Tables 6.3 and 6.4. These inventories have been developed for a functional unit of either 1kg packaging paper or 1 kg ammonium sulphate fertiliser, depending on the reagents used.

The study assumed the reduction efficiency of PG by redox reaction for each of the various reducing reagents to be 90%, which is based on findings of laboratory experimentation (section 6.4) and data derived from Table 6.1. Similar to the NO_x absorption case study for fertilizer production in Chapter 5, the source of inputs for the development of the LCIs (Tables 6.3 and 6.4) have been based on their availability from the relevant industries within KIA. 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. The two main reagents used in the case study for the production of 1kg packaging paper (Table 6.3) were NaOH and Na_2CO_3, which could be sourced easily from Coogee Chemicals (at KIA) and Penrice Soda Products (Osborne, South Australia) respectively.

Two moles of NaOH were utilized per mole of PG reduced as opposed to one mole of Na_2CO_3. This is because of the number of sodium ions in Na_2CO_3 are twice that of NaOH and due to sodium having a valence of one, two ions are required in order to reduce the sulphate in PG, which has a valence of 2. The use of NaOH as reagent for PG reduction resulted in the production of sodium sulphate (Na_2SO_4) and calcium oxide (CaO) as the main products. On the contrary, the use of sodium carbonate as reagent formed Na_2SO_4 and calcium carbonate ($CaCO_3$) as products from PG reduction. The Na_2SO_4 could then be used in a neighbouring industry as a source of sodium sulfide (Na_2S) for digesting lignin during paper production. The use of waste $CO_2$from CSBP plant in Option 1.3 was utilized in order to investigate the reduction of environmental impacts associated with production of Na_2SO_4 from NaOH by sequestering the waste CO_2into the $CaCO_3$ after reaction with the CaO by-product formed, thus avoiding its release into the atmosphere. Thus, there were three life cycle inventories (process options) investigated for the production of 1kg packaging paper (Table 6.3) and they are from the use of reagents, including NaOH, NaOH with waste CO_2, and Na_2CO_3.

When the production of ammonium sulphate is considered as main product for use as fertilizer from the PG reduction, two main reagents used were ammonium carbonate ($(NH_4)_2CO_3$) and ammonium hydrogen carbonate ((NH_4HCO_3). Both the reagents could be sourced from Consolidated Chemical Company from Melbourne, Victoria. One mole of $(NH_4)_2CO_3$ (two ions NH_4^-) was utilized for the reduction of one mole of PG and on the contrary, two moles of NH_4HCO_3 (one ion NH_4^-) was utilized per mole of PG reduced. The reason for the difference is attributed to the number of ammonia ions present in each of the reagents, which is similar to the case of sodium ions in reagents used for reducing PG to sodium sulphate. Ammonia has a valence of one, meaning two moles of ammonia are required to reduce the sulphate (valence 2) from PG. The use of both $(NH_4)_2CO_3$ and NH_4HCO_3 as reagents result two process options for the production of ammonium sulphate ($(NH_4)_2SO_4$) as the main product and $CaCO_3$ as the by-product. The $(NH_4)_2SO_4$ product could then be utilized directly as fertilizer or mixed with other salts in a nearby fertilizer company to produce compound fertilizers that have different nutrients.

Table 6.3 Life Cycle Inventory for 1 kg Packaging paper formation using Na_2SO_4 from sodium based redox reagents.

Inputs	**Amount**	**Unit**	**Location**	**Distance from Kwinana (km)**
$CaSO_4$	3.3	g/kg	CSBP	0
Option 1 (Redox reaction with Sodium Reagents)				
Process Options (Based on Reagents Use):				
Option 1.1				
NaOH Reduction-Oxidation				
Water for dilution of NaOH to 1 Mole/Litre solution	0.05	Litre/kg	Water Corporation, Perth	0
NaOH	1	g/kg	Coogee Chemicals, Perth	2
Drying				
Steam required for Na_2SO_4 concentration	0.1	kg/kg	On site	0
Electrical energy for Na_2SO_4 crystallisation	0.002	kWh/kg	On site	0
Option 1.2				
NaOH Reduction-Oxidation with CO_2 Carbonation				
Water for dilution of NaOH to 1 Mole/Litre solution	0.05	Litre/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
Drying				
Steam required for Na_2SO_4 concentration	0.1	kg/kg	On site	0

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
Electrical energy for Na_2SO_4 crystallisation	0.002	kWh/kg	On site	0
Option 1.3				
Na_2CO_3 Reduction-Oxidation				
Water for dilution of Na_2CO_3 to 1 Mole/Litre solution	0.025	Litre/kg	Water Corporation, Perth	0
Na_2CO_3	2.5	g/kg	Penrice Soda Products, Adelaide	2700
Drying				
Steam required for Na_2SO_4 concentration	0.03	kg/kg	On site	0
Electrical energy for Na_2SO_4 crystallisation	0.001	kWh/kg	On site	0
By-product 1 (from NaOH use as redox reagent)				
$Ca(OH)_2$	1.6	g/kg	On site	0
By-product 2 (from CO_2 carbonation or Na_2CO_3 use as redox reagent)				
$CaCO_3$ (from CO_2 carbonation of $Ca(OH)_2$)	2.1	g/kg	On site	0
$CaCO_3$ (from Na_2CO_3 use as redox reagent)	2.2	g/kg	On site	0

Table 6.4 Life Cycle Inventory for 1 kg $(NH_4)_2SO_4$ formation using Ammonium based redox reagents.

Inputs	**Amount**	**Unit**	**Location**	**Distance from Kwinana (km)**
$CaSO_4$	1.27	kg/kg	CSBP, Perth	0
Option 2 (Redox reaction with Ammonium Reagents)				
Process Options (Based on Reagents Use): **Option 2.1** *NH_4HCO_3 Reduction-Oxidation*				
Water for dilution of NH_4HCO_3 to 1 Mole/Litre solution	17	Litre/kg	Water Corporation, Perth	0
NH_4HCO_3	1.33	kg/kg	Consolidated Chemical Company, Adelaide	3500
CO_2 emitted as by-product	0.33	kg/kg	On site	0
Drying				
Steam required for $(NH_4)_2SO_4$ concentration	18.2	kg/kg	On site	0
Electrical energy for $(NH_4)_2SO_4$ crystallisation	0.36	kWh/kg	On site	0
Option 2.2 *$(NH_4)_2CO_3$ Reduction-Oxidation*				
Water for dilution of $(NH_4)_2CO_3$to 1 Mole/Litre	8.6	Litre/kg	Water Corporation, Perth	0

Inputs	Amount	Unit	Location	Distance from Kwinana (km)
solution				
$(NH_4)_2CO_3$	808	g/kg	Consolidated Chemical Company, Adelaide	3500
Drying				
Steam required for $(NH_4)_2SO_4$ concentration	9.3	kg/kg	On site	0
Electrical energy for $(NH_4)_2SO_4$ crystallisation	0.36	kWh/kg	On site	0
By-product 1 (from ammonia redox reagents)				
$CaCO_3$	0.76	kg/kg	On site	0

6.6 Environmental Impact of Pathways

The environmental impacts of the five alternate process pathways through LCA have been summarised in Table 6.5. Option 1.3 that utilizes Na_2CO_3 as redox reagent provided the lowest global warming (1.31 kg CO_2-e), eutrophication (0.0022 kg PO_4-e), acidification (0.0265 kg SO_2-e) and water use (1.33litres) per kg paper product compared to the other four options. This is due to the reduced level of GHG emissions associated with production of Na_2CO_3, which is about 0.06 kg CO_2-e/kg paper. In contrast, the environmental impacts from NaOH production that is used in both Options 1.1 and 1.2 is about 0.104 kg CO_2-e (GWP), 0.0001 kg PO_4-e (EP), 0.0003 kg SO_2-e (AP) and 1.1 litres (water use) per kg paper, thus making its use more unfriendly to the environment. The utilisations of ammonium carbonate in Option 2.1 had similar values of global warming (2.23 kg CO_2-e/kg $(NH_4)_2SO_4$) and acidification (0.0091 kg SO_2-e/kg $(NH_4)_2SO_4$) as Option 1.3from its production process. Therefore, depending on the demand in surrounding industries, any of these options can be used to form industrial symbiotic relations. Further elaboration and comparison of the environmental impacts of each option based on the selected indicators are provided in the subsequent sections. The hotspots are then identified to determine potential environmental mitigation strategies.

Table 6.5 Environmental impacts of PG reduction for 1 kg packaging paper production (3 pathways for Option 1) and 1 kg of $(NH_4)_2SO_4$ production (2 pathways for Option 2).

End Product	**Pathways**	**Water Use (litres)**	**Global Warming Potential (kg CO_2-e)**	**Acidification Potential (kg SO_2-e)**	**Eutrophication Potential (kg PO_4^--e)**	**Solid waste (kg)**
Packaging Paper	Option 1.1	1.54	1.35	0.0267	0.0022	0.2
	Option 1.2	1.54	1.35	0.0266	0.0022	0.2
	Option 1.3	1.33	1.31	0.0265	0.0022	0.2
Fertilizer	Option 2.1	31.46	2.23	0.00909	0.00400	-0.722
	Option 2.2	218.63	3.88	0.01492	0.00436	-0.721

6.6.1 Water Use

The basis for all the reagents used in this study for the reduction-oxidation has been set as 1M (mole/Litre) of feed. This translates to 1 litre/kg of water required per 40g of sodium hydroxide (NaOH), 106g of sodium carbonate (Na_2CO_3), 79 g of ammonium bicarbonate (NH_4HCO_3) and 96g of ammonium carbonate ($(NH_4)_2CO_3$) respectively.

6.6.1.1 Water Use for Production of 1 kg Packaging Paper

The breakdown of the water used in each stage of the three different pathways for the production of packaging paper from PG sulphate reduction is represented in Figure 6.10. The major use of water in producing the sodium sulphate is attributed to the redox stage where PG is reduced with suitable sodium based redox reagents. This is also the stage that contributes more than half the water required for 1 kg of packaging paper. Figure 6.11 highlights that approximately 73% or 0.85 litres of water required for the production of 1 kg packaging paper from each of Options 1.1 and 1.2 are derived from the processes used for the production of NaOH reagent from cradle to gate. In comparison, a considerable percentage of water is used during the production processes of Na_2CO_3 reagent in Option 1.3 (0.7 litres or 83% of the total water requirement for PG reduction in the same option). The other major water use in the production of 1 kg of paper results from the amount of water required for diluting NaOH and Na_2CO_2 in the redox stage to a molarity of 1 before they can be used for reduction of PG. The total water requirements in this stage per kg paper produced are 0.6% (0.01 litres) of total water requirements for Option 1.3, and 1.2% (0.02 litres) for each of Options 1.1 and 1.2.

The main reason for the lower water of dilution requirements for Option 1.3 as opposed to Options 1.1 and 1.2 is because of the amount of the sodium ions present in the reagents. There is twice the amount of sodium in Na_2CO_3 as opposed to NaOH in Options 1.1 and 1.2, which means that the mole ratio required for Na_2CO_3 reaction with PG (1:1) is half the number of moles required for NaOH to react with PG (2:1). Therefore, more water is utilised to dilute NaOH than Na_2CO_3.

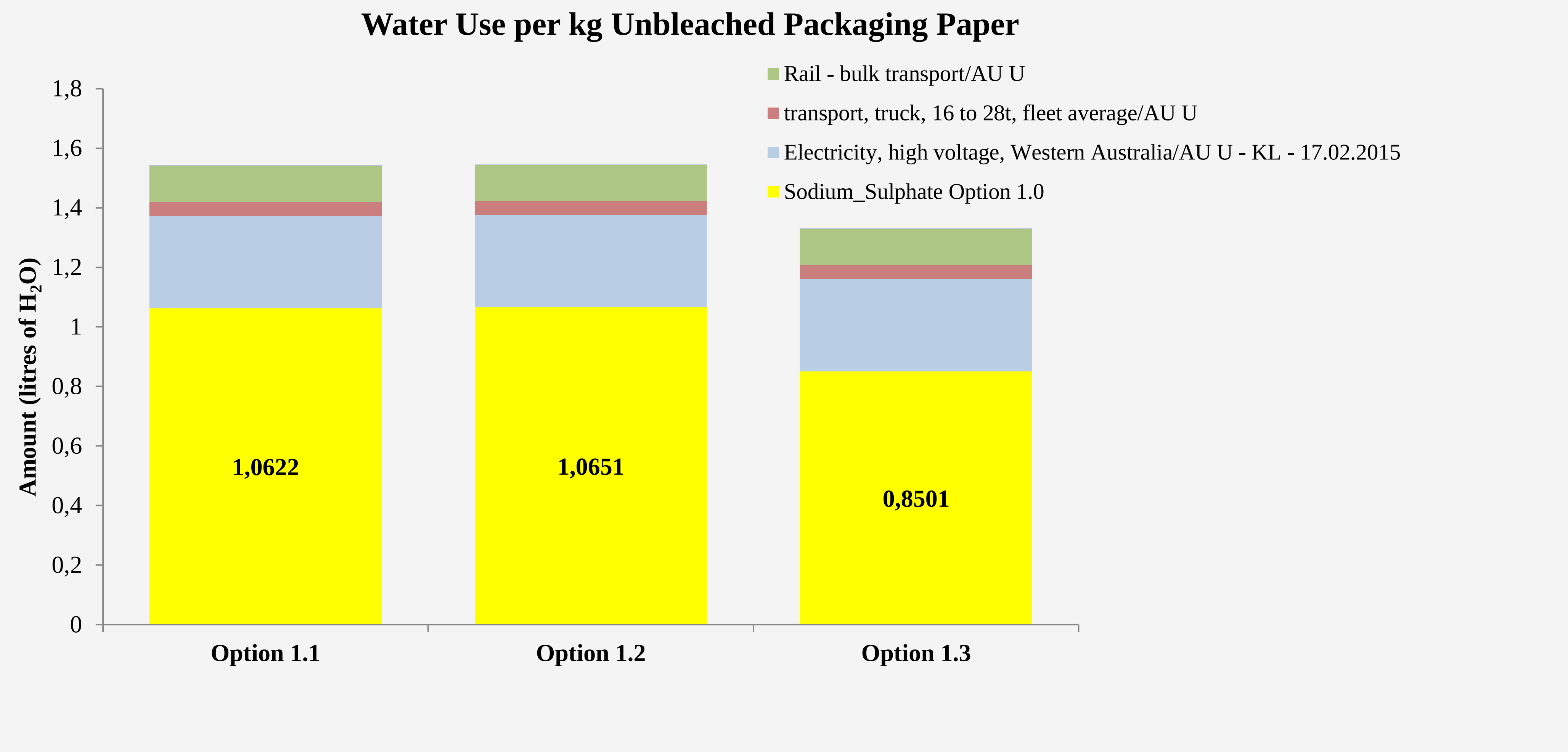

Figure 6.10 Water use breakdown per kg paper (values for only by-product sodium sulphates are represented in the figure)

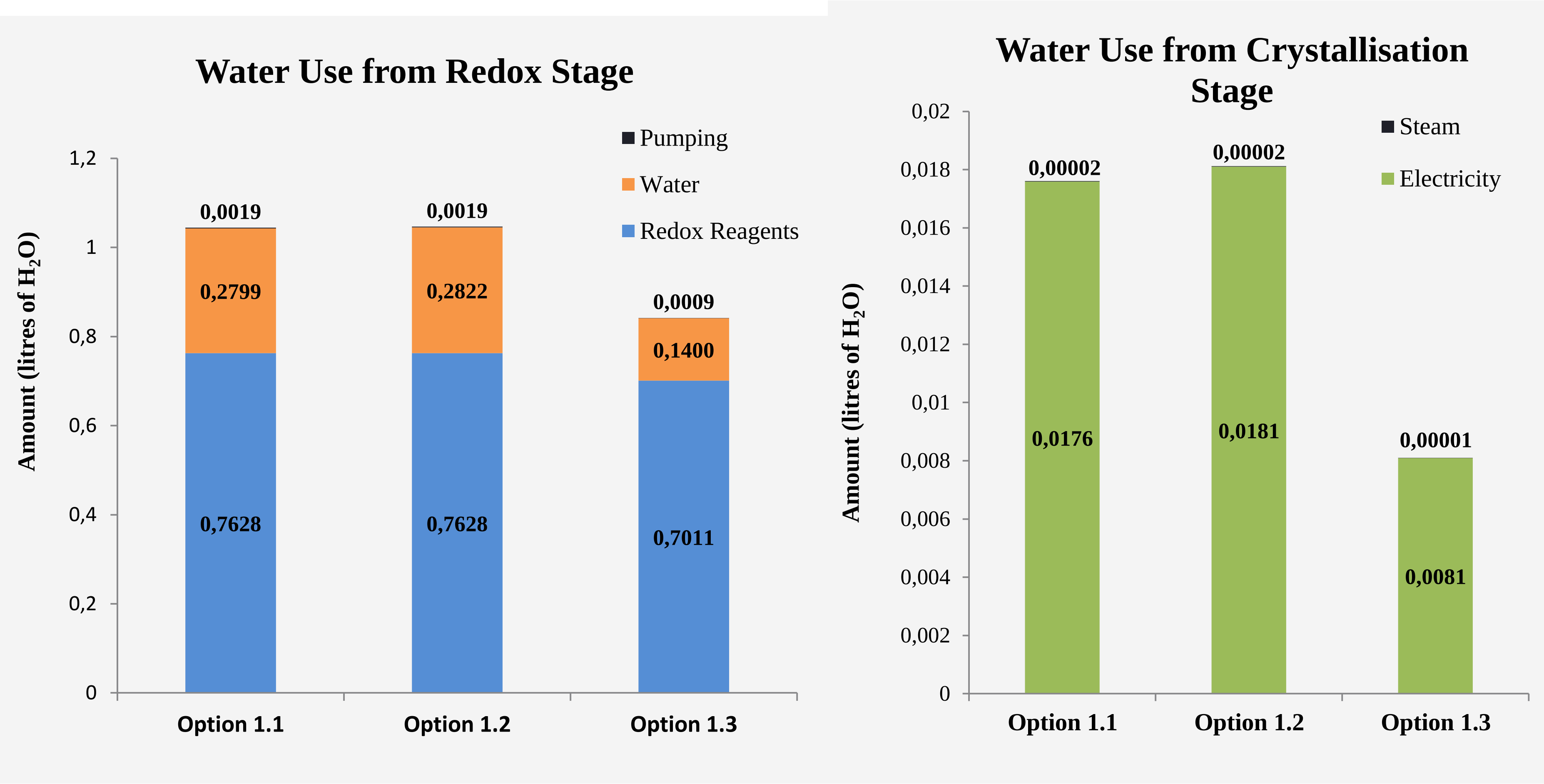

Figure 6.11 Water use from redox and crystallization stages for production of by-product sodium sulphate required for 1 kg of packaging paper

The findings of the study show that the highest water utilisation for 1 kg paper production results from both Options 1.1and 1.2 with about 1.5 litres of water used for each, while water used for Option 1.2 is 1.3 litres. In comparison, the lowest water utilisation is from Option 1.3 with about 0.5 litres of water utilised, which is 30% and 20% lower than water requirement of Option 1.1 and Option 1.2 respectively.

6.6.1.2 Water Use for Production of 1 kg Ammonium Sulphate Fertilizer

The water consumption patterns of Options 2.1 and 2.2 follow the same trend as Options 1.1 to 1.3 (Figure 6.12). The largest percentage contribution of water for 1 kg of ammonium sulphate production is derived from the production processes of reagents in the redox stage, which is about 31.8litres (81%of total water use) and 218.4 litres (95% of total water use) for $(NH_4)_2CO_3$ (Option 2.1) and NH_4HCO_3 (Option 2.2) reagents respectively. Similarly, dilution water for the redox reaction is the other major source of water contributing 5.3 litres or 17% and 10.5 litres or 5% of total water requirements respectively for Options 2.1 and 2.2.

The main reason for the lower water of dilution requirement for Option 2.1 than Option 2.2 is due to the amount of the ammonium ions present in the reagents. There is twice the amount of ammonium in $(NH_4)_2CO_3$ in Option 2.1 compared to NH_4HCO_3 in Option 2.2, meaning the water used to dilute NH_4HCO_3 to the required molarity is twice the amount required to dilute $(NH_4)_2CO_3$ to the same molarity. This is also analogous to the findings in water used for paper production by reduction of PG with twice the amount of water required for NaOH dilution as opposed to dilution of Na_2CO_3.

Overall, the highest water use for the production of ammonium sulphate is attributed to Option 2.2 where 218.6 litres was required per kg $(NH_4)_2SO_4$, while Option 2.1 requires only31.5 litres (i.e. about 86% lower water use than Option 2.2).

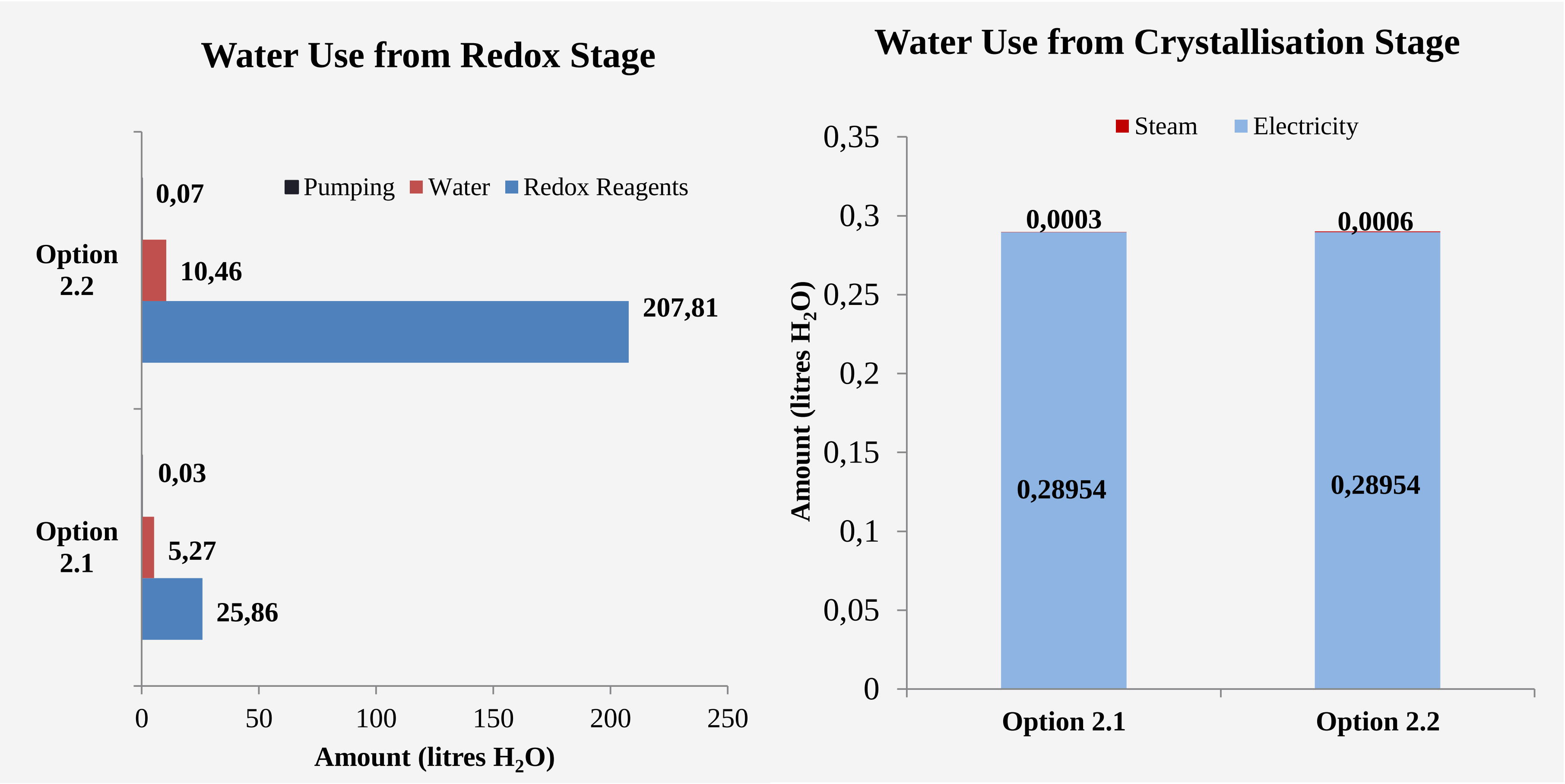

Figure 6.12 Water use from the redox and crystallization stages for production of 1 kg of ammonium sulphate

6.6.1.3 Water Use from the Crystallisation Stage for both Paper and Ammonium Sulphate Production

The crystallisation stage utilises the least water as no additional water is utilised in the production of either sodium sulphate or ammonium sulphate. All the water used in this stage for each of the options (above 99.4%) is derived from water used in the various processes for production of electricity from the WA grid as depicted in Figures 6.11 and 6.12. The heating energy used for drying depends on the amount of water to be removed from the product. The water present in the product is derived from the dilution water added in the redox reaction to the reagents in order to facilitate reaction with PG. The amount of dilution water added to Options 1.1 and 1.2 for paper production is double that of Option 1.3 due to the difference in sodium ions present per mole of sodium salt utilised. As for the production of ammonium sulphate fertiliser, there is twice more water used in Option 2.2 than in Option 2.1 that is attributed to the amount of ammonium ions present in the different ammonium salts utilised as explained in the preceding section. 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. Therefore, energy use also decreases from Options 1.1 to 1.3 and increases from Options 2.1 to 2.2 as the amount of energy used is related to the quantity of water present in the options that needs to be dried. Water produced in the crystallisation stages also depends on the amount of energy used for drying in each of the options, which is depicted by the trend observed in Figure 6.11 (1 kg paper production) and Figure 6.12 (1 kg ammonium sulphate production).

6.6.2 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 that are mostly sourced from fossil fuels. 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 (natural gas, coal and oil) and the rest from renewable energy sources of wind, biomass, landfill gas and solar (Australian LCI database).

6.6.2.1 GWP from the Production of 1 kg Paper

The GWP of by-product sodium sulphate use for the production of 1 kg paper are represented in Figure 6.13. About 16.5g of sodium sulphate are used per kg of packaging paper, representing 1.65% of the total material requirement. However, the GWP do not correspond to the percentage of material used. This is evidenced in Figure 6.13 where the contributions towards overall GWP per kg paper from the use of sodium sulphate derived from PG as feed are 0.1 kg CO_2-e (7.7%) for both Options 1.1 and 1.2, and 0.06 kg CO_2-e (4.6%) for Option 1.3.

The GWP contributions for steam use in the crystallization stage are 0.072 kg CO_2-e (87%) and 0.077 kg CO_2-e (88%) for Options 1.1 and 1.2 respectively. On the contrary, Option 1.3 (0.04 kg CO_2-e or 89%) has nearly half the GWP from steam use for drying than Option 1.1 and 1.2 as depicted from Figure 6.14. 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, the difference is attributed to water use meaning Options 1.1 and 1.2 have twice the amount of steam needed for evaporation and drying of solute products as they have double the water requirement in contrast to Option 1.3.

The reagents use also contributes a significant percentage towards total GWP in the redox stage for the production of 1 kg paper. More than 93% of the GWP from the redox stage are attributed to the production processes of the reagents from cradle to factory gate. Options 1.2 and 1.3 have the least GWP from reagent production of about 0.015 kg CO_2-e as visualized in Figure 6.14. Options 1.1 and 1.2 utilize the same amount of NaOH as reagent; however, Option 1.2 also uses CO_2 for the carbonation of calcium hydroxide by-product formed. The CO_2 use offsets about 0.01 kg CO_2-e of GWP as it acts as a CO_2 sink making Option 1.2 have a slightly lower GWP than Option 1.1.

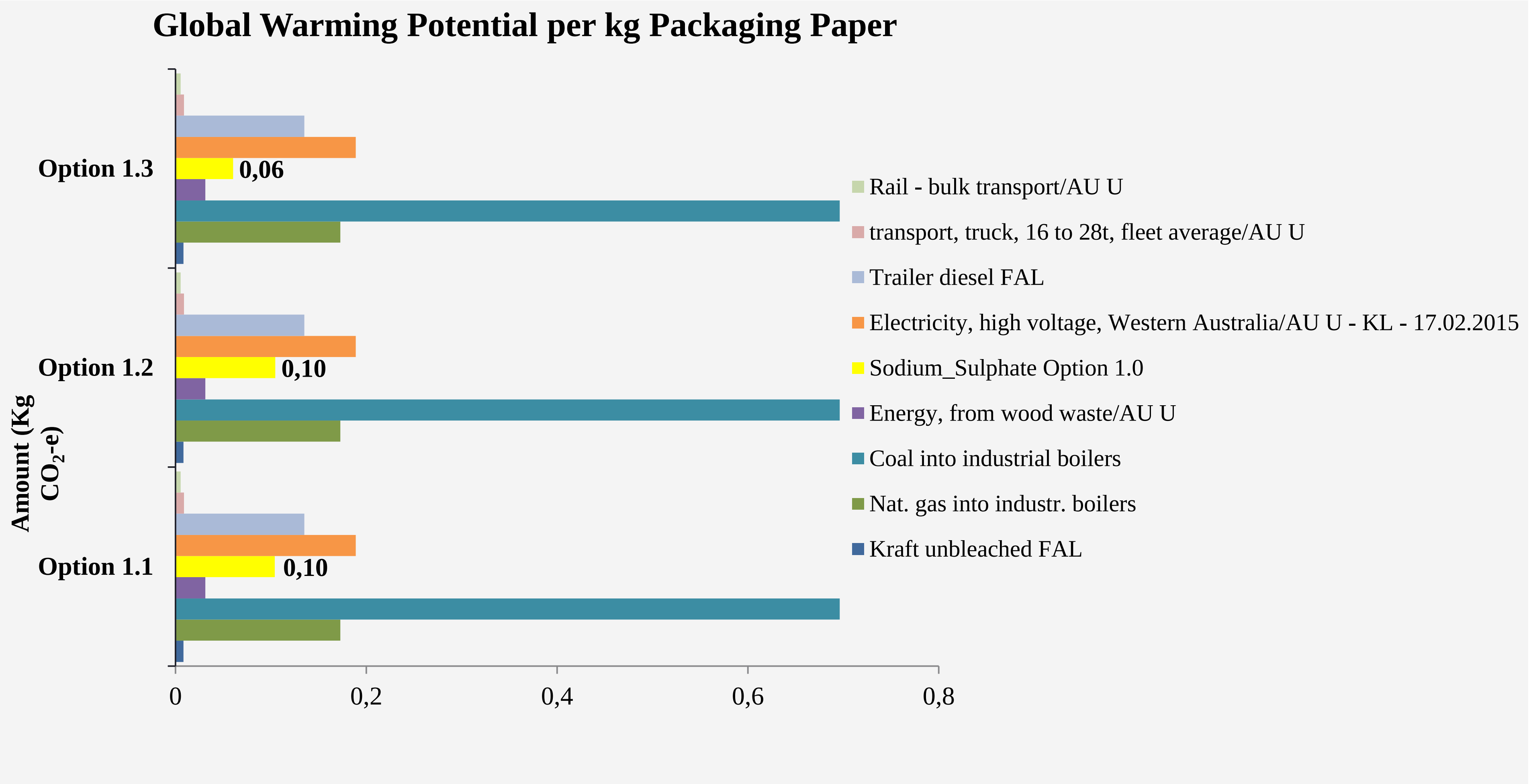

Figure 6.13 Global warming potential per kg packaging paper (values for only by-product sodium sulphates are represented in the figure)

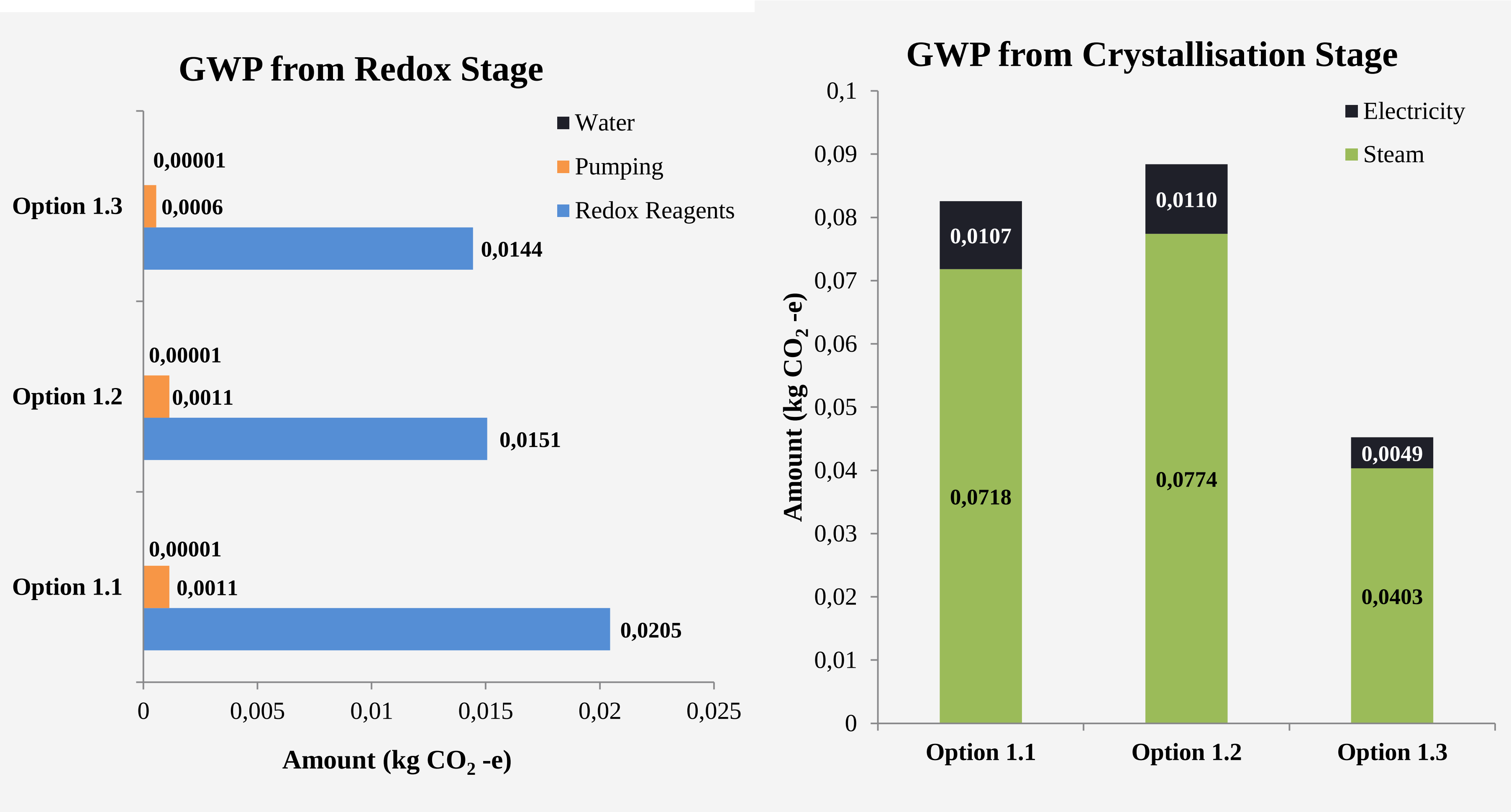

Figure 6.14 GWP from the redox and crystallization stages for sodium sulphate by-products utilized for 1 kg packaging paper

6.6.2.2 GWP from the Production of 1 kg Ammonium Sulphate Fertilizer

The GWP contribution for steam use in the crystallization stage Option 2.2 (2.58 kg CO_2-e) is twice that of the GWP produced from Option 2.1 (1.31 kg CO_2-e) because Option 2.1 utilizes half the amount of steam for drying as opposed to Option 2.2. The difference in steam use arises from the difference in concentration of ammonium ions present in the different options as was explained in section 6.5.1.2 for water use. Option 2.1 utilizes one mole of $(NH_4)_2CO_3$ for reaction with a mole of PG while Option 2.2 utilizes 2 moles of NH_4HCO_3 in order to react with a mole of PG, which means the amount of water present from dilution before reaction with PG is twofold in Option 2.2 than that in Option 2.1. Therefore, steam requirements for drying in Option 2.2 are also double that of Option 2.1 as it has twice the amount of water to be evaporated. 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 CO_2-e GWP from electricity consumption between Options 2.1 and 2.2 (Figure 6.15). 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.

In the redox stage, the highest contribution of GWP arises from the processes involved in reagent production with Options 2.1 and 2.2 having GWP contributions of 0.7 kg CO_2-e (96.2% of total GWP) and 1.1 kg CO_2-e (97.1% of total GWP) respectively as highlighted in Figure 6.15. 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 NH_4HCO_3 moles (or 1.65 times more weight) is required to react with a mole of PG as opposed to $(NH_4)_2CO_3$ (Option 2.1). Thus, the selection of reagents for reduction 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 reduced. Selecting the most environmentally friendly reagent thus helps in lowering environmental impacts associated with process pathways.

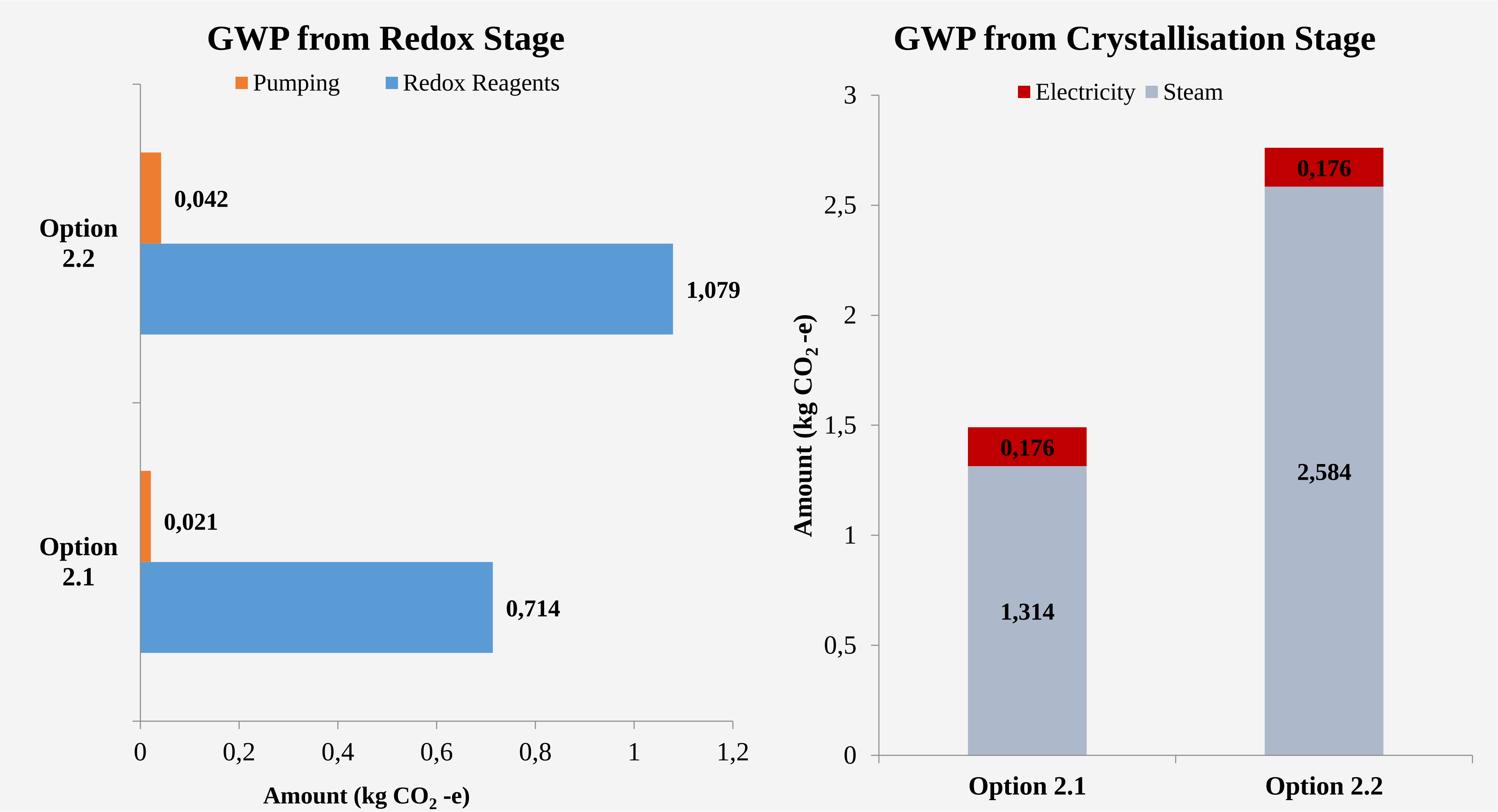

Figure 6.15 GWP from the redox and crystallization stages for production of 1 kg ammonium sulphate

6.6.3 Eutrophication Potential (EP)

The eutrophication values (EP) are mainly associated with energy use and show similarities with GWP in both the redox stage and the crystallisation stage of each option for both paper and ammonium sulphate production. This is evident from the similar trend in the EP of the production of 1 kg of packaging paper in Figure 6.16 and values of the crystallisation stage of all options in Table 6.6, where 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.

Table 6.6 EP from the different Process Options for Na_2SO_4 formed (used in 1 kg paper production)

Eutrophication Potential (EP) from different Process Options					
Stages	*Option 1.1*	*Option 1.2*	*Option 1.3*	*Option 2.1*	*Option 2.2*
Redox	1.23E-05	1.23E-05	4.44E-05	2.42E-03	1.31E-03
Crystallisation	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**

In Figure 6.16, the use of sodium sulphate by-products is shown to contribute about 5% or 0.0001 kg PO_4^- equivalent 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 PO_4^--e and 0.0044kg PO_4^--e respectively (Table 6.6).

The eutrophication impacts from the use of reagents are different (do not follow the same pattern) from GWP as confirmed by Figures 6.17 and 6.18. 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 CO_2 for which phytoplankton can utilise for respiration and food production via photosynthesis during the day (Verspagen *et al.*, 2014). However, increased CO_2 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.

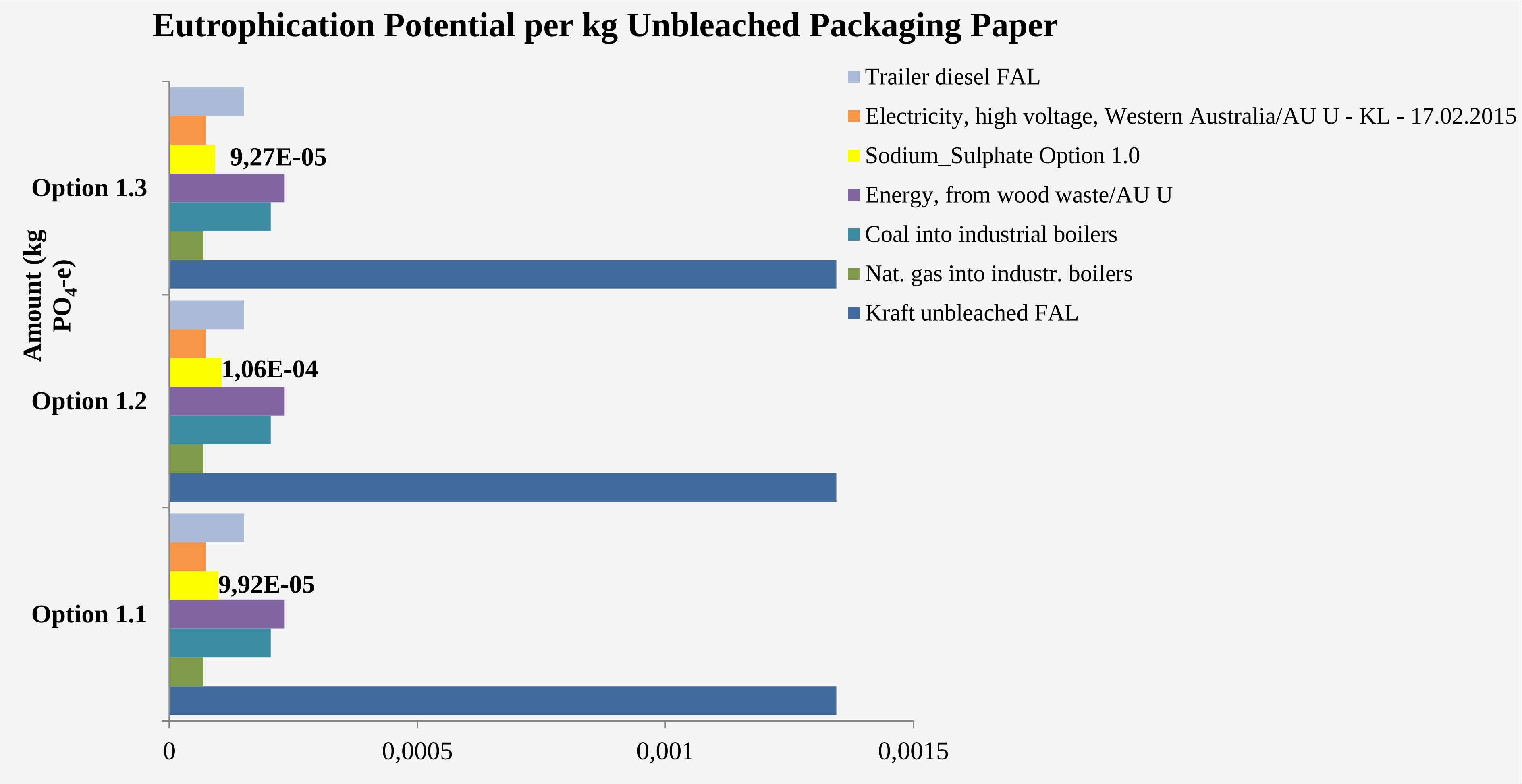

Figure 6.16 Eutrophication potential per kg packaging paper (values for only by-product sodium sulphates are represented in the figure)

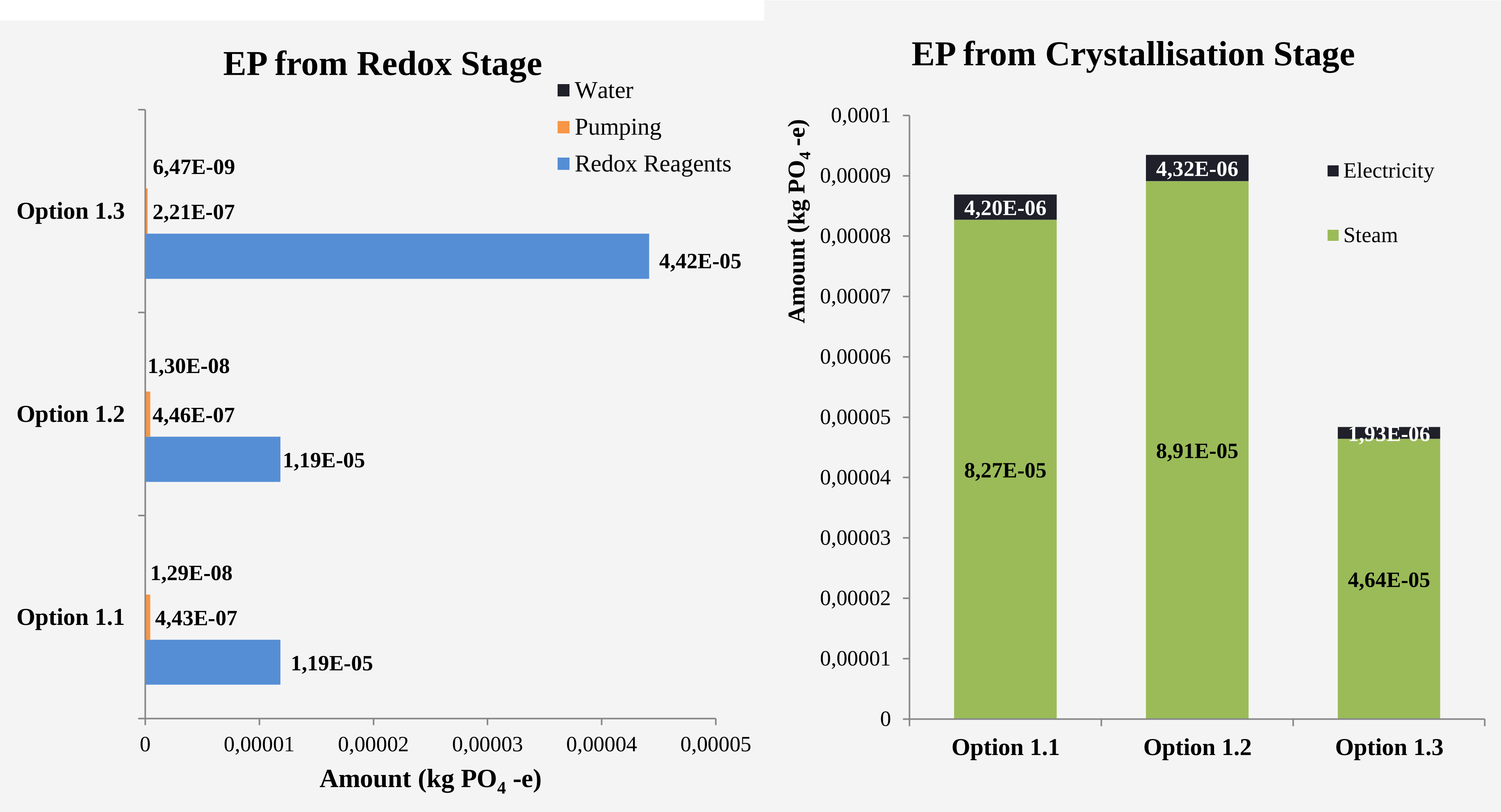

Figure 6.17 EP from the redox and crystallization stages for sodium sulphate by-products utilized for 1 kg packaging paper

Increase in phosphate and nitrogen nutrients also enhances phytoplankton growth. Nitrogen can be provided in the form of dissolved ammonium ions from sources such as agricultural surface run off from fertiliser use (Beman *et al.*, 2005). Thus, the ammonium reagents can also have potential effects towards eutrophication. The use of the latter contributes one mole of carbonate ions while the former two moles and both provide 2 moles of ammonium ions. In the current study, two moles of ammonium bicarbonate and one mole of ammonium carbonate were used as redox reagents per mole gypsum reduced. Nevertheless, there is no explanation to why ammonium bicarbonate has lower eutrophication potential than ammonium carbonate, but could be attributed to other inputs in the production process in addition to energy use contributions.

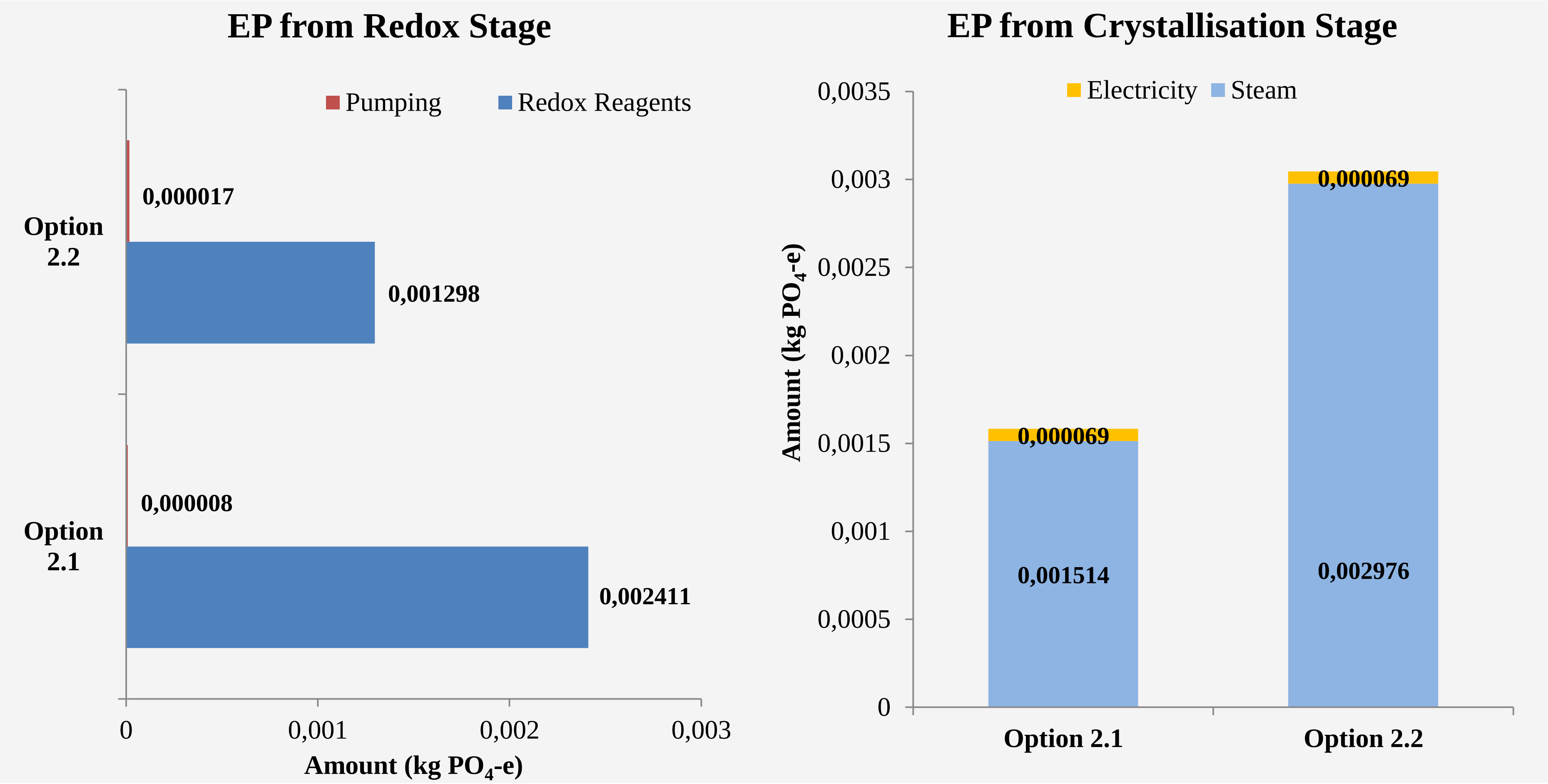

Figure 6.18 EP from the redox and crystallization stages for production of 1 kg ammonium sulphate

6.6.4 Solid Waste

As previously mentioned in Chapter 5, the major source of solid waste is from fuel combustion residue generated in the power plant. The Australian LCI database shows that the WA energy mix is dominated by coal (~43.5%) and natural gas (~49.7%). In addition to electricity, natural gas is used for the production of steam (thermal reactor) for the heating utilities used in the case study. Thus, the primary sources of solid waste result from fly ash produced from the mentioned energy sources combustion for energy generation. Ondova and Estokova (2014) have shown that the impacts of fly ash can offset some of the environmental impacts of cement production and use. This utilisation of fly ash (solid wastes) such as a constituent in concrete production can form additional industrial symbiotic network from energy generation plants, which can reduce or offset the impacts of landfilling. However, utilisation of fly ash to offset landfilling impacts is not within the scope of the current study as they are generated through the WA electricity grid, and only the impacts of electricity that is sourced as input is accounted for in the case study.

Overall, the utilisation of by-product sodium sulphates for the production of 1kg paper has been found to reduce solid waste associated with paper as illustrated in Figure 6.19, where the average amount of solid waste generated from Options 1.1, 1.2 and 1.3 is 0.01 kg each per kg of paper. This mostly stems from the use of the gypsum in the redox stage as depicted in Figure 6.20 for sodium based options. Figure 6.21 also shows that ammonium based options reduce the total solid waste of Options 2.1 and 2.2 such that on average there is a net negative production of solid waste produced per kg of $(NH_4)_2SO_4$ fertiliser produced. This is because gypsum utilisation to form symbiotic linkages offsets its accumulation as tailings or in residue dams.

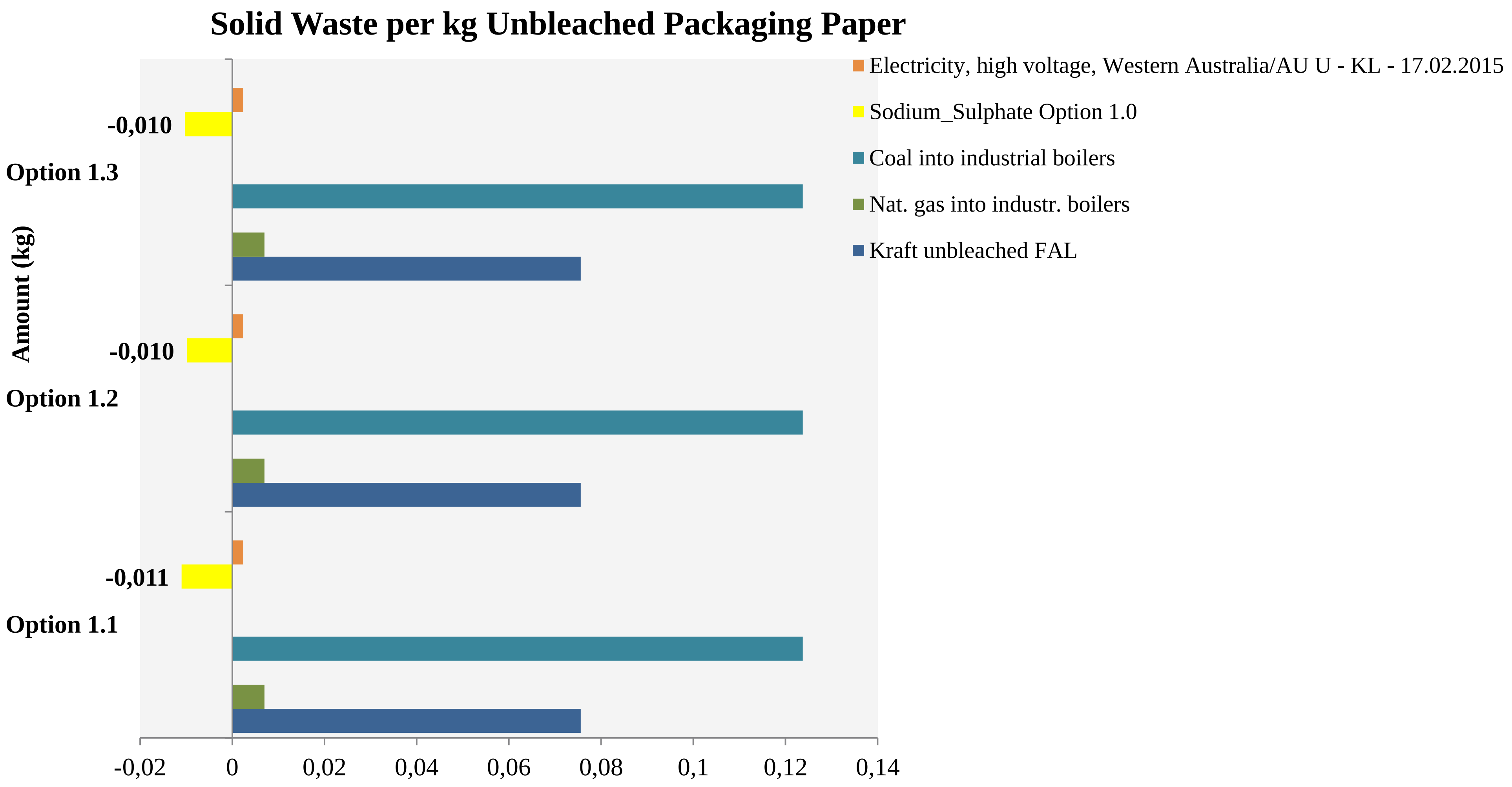

Figure 6.19 Solid Wastes per kg packaging paper (values for only by-product sodium sulphates are represented in the figure)

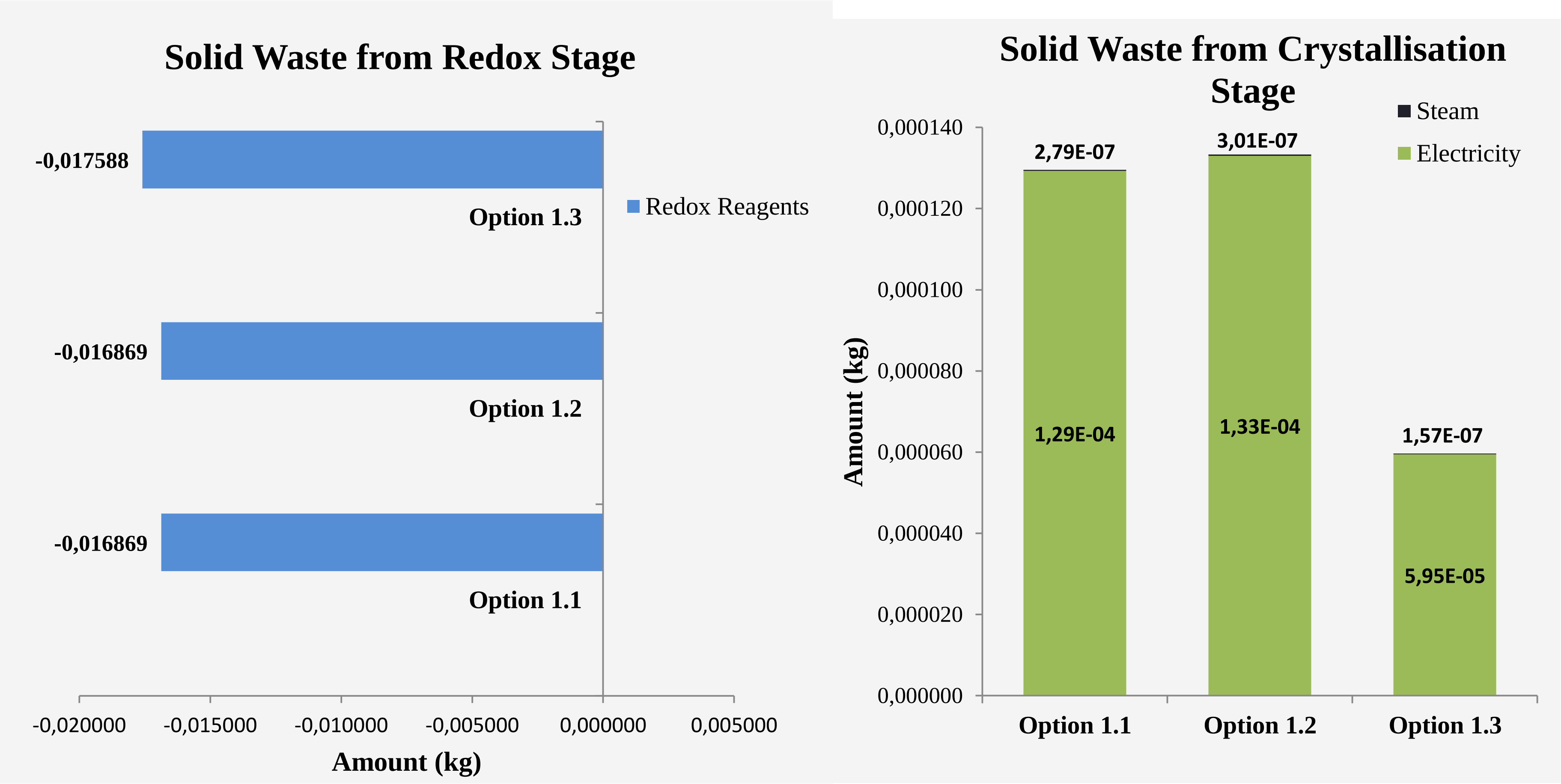

Figure 6.20 Solid Waste from redox and crystallization stages for sodium sulphate by-products utilized for 1 kg packaging paper

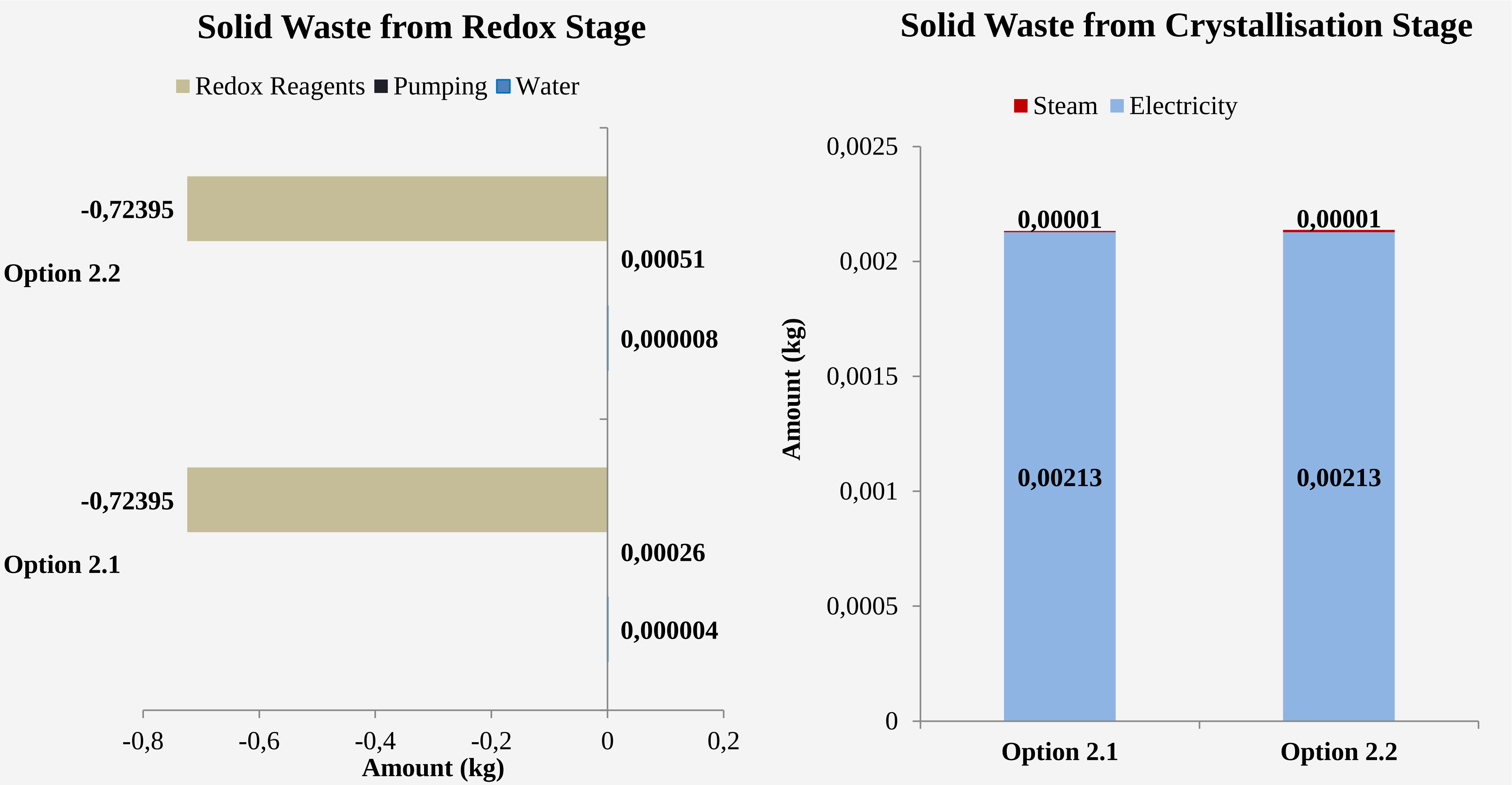

Figure 6.21 Solid Waste from the redox and crystallization stages for production of 1 kg ammonium sulphate

Table 6.7 shows the amount of solid waste produced from different process alternatives. The key highlight is that most of the solid waste in all options results from electricity use in the crystallisation stage, which is approximately 90% of total solid waste from Options 1.1, 1.2, 1.3 and 2.1, and about 80% for Option 2.2. The other major source of solid waste is from the electricity used in pumping of reagents and water in the redox stage, which contributes approximately 10%, 9%, 10%, 11% and 19% from the total solid waste from Options 1.1, 1.2, 1.3, 2.1 and 2.2 respectively. This is again attributed to electricity use for pumping.

Table 6.7 Solid waste from different process options for Na_2SO_4 and $(NH_4)_2SO_4$ production

Solid Waste from the different Process Options					
Redox Stage	*Option 1.1*	*Option 1.2*	*Option 1.3*	*Option 2.1*	*Option 2.2*
Pumping	0.000014	0.000014	0,000007	0.000257	0.000509
Water	0.000000	0,000000	0.000000	0.000004	0.000008
Redox Reagents	-0.016869	-0.016869	-0.017588	-0.723952	-0.723952
Crystallisation Stage	*Option 1.1*	*Option 1.2*	*Option 1.3*	*Option 2.1*	*Option 2.2*
Electricity	0.000129	0.000133	0.000059	0.002127	0.002127
Steam	0.000000	0.000000	0.000000	0.000005	0.000010
Total	**-0.016725**	**-0.016722**	**-0.017522**	**-0.721559**	**-0.721297**

6.7 Hotspots in the Study

Although the LCI and processes are different to the symbiotic relationship from NO_x absorption studies in Chapter 5, both the NO_x absorption and PG reduction have the same hotspots. Water use for dilution is the first major hotspot as it determines the energy requirements used later in the drying stage. The reduction in water use by increasing concentration of reactants is not feasible for NaOH as described in studies by Pourmohammadbagher *et al.* (2011) and Kuropka (2011) for NO_x absorption due to reduction in reaction efficiency. The use of NaOH in the current case study, though differs from NO_x absorption, is assumed to be analogous as the reaction medium (water) is similar. Mulopo and Ikhu-Omoregbe (2012) also describe the optimum conditions for Na_2CO_3 reaction with gypsum as being 5% slurry, which corresponds to 0.5 Molarity of Na_2CO_3 use. The use of higher slurry rates had lower gypsum reduction due to reaction efficiency reduction. Thus, the variation in water use does not seem to improve the situation on water requirements per kg basis of products produced.

Followed by dilution water, heating energy use for the drying of ammonium sulphate and sodium sulphate by-products is the second major hotspot. The utilisation of steam derived from natural gas combustion for heating contributes the highest source of GWP and eutrophication based on results in Figures 6.14, 6.15, 6.17 and 6.18. The contribution of steam towards overall GWP is approximately 69%, 74%, 67%, 59% and 67% of the by-products before industrial symbiosis (paper and $(NH_4)_2SO_4$ production) for Options 1.1, 1.2, 1.3, 2.1 and 2.2 respectively. The contribution of steam for heating towards eutrophication show a similar trend with about 83%, 84%, 50%, 38% and 68% in order of the options mentioned above. This finding ties well with results from Case Study 1 in Chapter 5 since electricity appears to be the main reason for all impacts discussed. Biswas *et al*. (2014) have determined that the generation of electricity from wind could be an option to mitigate GWP impacts from fossil generation in WA. Dolan and Heath (2012) have reviewed LCA studies of wind power generation and harmonized the results to show that on average 11g CO_2-e are produced for 1 kWh of electricity produced from wind. The current study utilized electricity from the electricity grid in Western Australia (WA), where the LCA study has evaluated that about 1.61 kg CO_2-e is produced per kWh generated. This has the potential of reducing overall GWP for both Options 1.3 and 2.1 by 9%, improving their competitiveness, as they will have slightly higher GWP and eutrophication than conventional fertiliser and paper respectively.

The selection of reagents also affects overall impacts. This is evidenced by EP contribution from reagents for Options 1.3 and 2.1 being 48% and 60% of total EP respectively. The contributions of reagents towards overall GWP for the same options are 4% and 32% respectively. These values are attributed to the production of Na_2CO_3 being environmentally friendlier (i.e. lower energy required) than production of $(NH_4)_2CO_3$. The GWP of the required of ammonium carbonate and ammonium hydrogen carbonate inputs (from their production) in Options 2.1 and 2.2 are already higher than conventional ammonium sulphate. This is even before their utilisation in the redox reaction based on the findings of the LCA (Australian LCI database). This is likewise for Options 1.1 and 1.2, where sodium hydroxide that is used as reagent has higher GWP than conventional sodium sulphate. However, these are the most ideal reagents for reduction of sulphate in PG and the SLCA highlights the contribution of their impacts towards overall environmental impacts analysed in the case study.

6.8 Comparative Environmental Assessment of Conventional and By-product Based Fertilizer and Paper in Case Study 2

The process that utilises sodium hydroxide (Option 1.1) as the redox reagent has the highest energy demand. Table 6.5 shows that this option pathway has a GWP of 1.35 kg CO_2 -e/kg paper. On the contrary, the process that utilises sodium carbonate (Option 1.3) as reagent has the least energy demand and has a GWP of 1.31 kg CO_2 -e /kg paper.

The GWP, EP and water use for conventional paper from the Simapro 8.03 Australian LCI database is 1.25 kg CO_2-e, 0.0021 kg PO_4^--e and 0.6 litres respectively. In comparison, the contributions of Option 1.3 towards GWP, EP and water use are 1.31 kg CO_2-e, 0.0022 kg PO_4^--e and 1.3 litres, which is 5% higher GWP, 5% higher EP and 117% higher water use than conventional paper. 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 redox reagent and thus contributes the highest GWP of 3.9 kg CO_2-e per kg fertiliser. 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 CO_2-e per kg paper produced.

The findings of the ammonium sulphate fertiliser production from Simapro 8.03 Australian LCI database shows that the impacts of conventional ammonium sulphate are 0.48 kg CO_2-e, 0.00073 kg PO_4-e and 1.9 litres for GWP, EP and water use respectively. Option 2.2 that uses NH_4HCO_3 as reagent has a higher difference of analysed environmental impacts with conventional $(NH_4)_2SO_4$. The GWP, water use and eutrophication difference are about 3.6 kg CO_2-e, 217 litres and 0.0034 kg PO_4^--e. These values for GWP, water use and eutrophication are about 85%, 608% and

11% greater than the difference between conventional $(NH_4)_2SO_4$ and $(NH_4)_2SO_4$ from Option 2.1 for same impacts respectively. The differences between Option 2.1 and conventional fertiliser is that by-product paper from Option 2.1 has 2kg CO_2-e (or 409%) and 0.004 kg PO_4^-e (or 841%) higher GWP and EP respectively than conventional paper. This makes Option 2.1 less environmentally friendly and unsuitable for industrial symbiosis development.

Thus, the LCA of multiple reaction pathways for PG reduction has shown that pathways for the reduction of PG to ammonium sulphate (Options 2.1 and 2.2) are not suitable for replacing conventional fertiliser due to considerably higher environmental impacts. The most ideal way to reduce PG is through reduction with sodium carbonate for production of sodium sulphate (Option 1.3), which is the best sodium based option for forming industrial symbiotic relation for use as a raw material in paper production. Uncertainty analysis of the difference in inputs between conventional and by-product paper and fertiliser has been assessed in the subsequent section to elaborate the difference between impacts of both.

6.8.1 Uncertainty Analysis

The environmental benefits of the replacement of conventional ammonium sulphate fertiliser with by-product based fertilizer (Options 2.1 and 2.2) and conventional paper with paper produced with by-product sodium sulphate (Options 1.1, 1.2 and 1.3) have been statistically verified by conducting an uncertainty analysis. The uncertainty analysis incorporating the use of the Monte Carlo Simulations built in Simapro was used to carry out the uncertainty analysis in order to determine the difference between the environmental impacts of each option with that of conventional $(NH_4)_2SO_4$ fertiliser or paper. This was performed at a 95% confidence interval through a 1000 iterations where random values within the prescribed probability distribution in the LCA study were generated, in order to study the resultant effect of on the LCA results. The uncertainty analysis results, shown in Tables 6.8, 6.9, 6.10 and 6.11 compared the environmental impacts of water use, global warming potential, eutrophication and solid wastes.

Table 6.8 Uncertainty analysis of GWP due to substitution of conventional $(NH_4)_2SO_4$ and paper with by-product derived equivalents

Global Warming (kg CO_2-equivalent)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	0.068	0.068	0.002	0.066	0.072
Option 1.2	0.061	0.061	0.001	0.059	0.064
Option 1.3	0.035	0.035	0.001	0.033	0.039
Option 2.1	1.937	1.955	0.145	1.719	2.271
Option 2.2	3.601	3.612	0.170	3.290	3.969

The mean of the Monte Carlo simulations is very similar to the single point values obtained from the net difference between environmental impacts of each option with that of conventional fertiliser and paper for global warming, water use, eutrophication and solid waste impacts.

Table 6.9 Uncertainty analysis of water use (liters H_2O) due to substitution of conventional $(NH_4)_2SO_4$ and paper with by-product derived equivalents

Water Use (litres H_2O)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	0.69	0.70	0.10	0.52	0.92
Option 1.2	0.62	0.63	0.09	0.47	0.84
Option 1.3	0.50	0.50	0.05	0.41	0.60
Option 2.1	30.11	30.62	4.94	22.10	41.66
Option 2.2	215.99	217.01	18.38	183.58	255.62

It can be seen from Table 6.8 that the global warming effects of replacing 1kg of $(NH_4)_2SO_4$ fertiliser with that obtained from Option 2.1 are between 1.72 and 2.27 kg CO_2-equivalent higher, with a mean of about 1.96 kg CO_2-equivalent. Results from water use and eutrophication (Tables 6.9 and 6.10) show a similar trend to the findings from GWP, with an average increase of 30.6 litres and 0.0036 kg PO_4^- equivalent respectively for option 2.1. The high water use is the main reason for Option 2.1having higher environmental impacts than the conventional fertiliser. There standard deviation attributed to Options 2.1 and 2.2 for water use is much higher than the other options. The wider data points of these Options (2.1 and 2.2) as depicted from the lower and upper 95% confidence limits of the Monte Carlo simulations (Table 6.9), leads to many data points to be further from the mean. There is no justification to explain why this happens, but it could be due to the high water use from the production processes of the ammonium reagents.

Table 6.10 Uncertainty analysis of EP (kg PO_4^- equivalent) due to substitution of conventional $(NH_4)_2SO_4$ and paper with by-product derived equivalents

Eutrophication Potential (kg PO_4^- equivalent)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	0.000064	0.000065	0.000012	0.000045	0.000093
Option 1.2	0.000061	0.000062	0.000012	0.000043	0.000087
Option 1.3	0.000053	0.000054	0.000010	0.000039	0.000078
Option 2.1	0.003436	0.003576	0.000912	0.002243	0.005735
Option 2.2	0.003863	0.003967	0.000974	0.002514	0.006164

Table 6.8 illustrates that for the utilisation of the by-product sodium sulphate options as raw material for the production of packaging paper, Option 1.3 has about 0.04 kg CO_2-e higher GWP than conventional paper. The water use and EP of the same option are 0.5 litres and 0.000054 kg PO_4^--e higher than conventional paper respectively as evidenced in Tables 6.9 and 6.10. On the contrary, Table 6.8 shows that Options 1.1 and 1.2 have 94% and 74% higher CO_2-e than Option 1.3 for GWP

impacts. Their water use highlighted in Table 6.9 is also 40% and 26% higher than Option 1.3 respectively. Both Options 1.1 and 1.2 use NaOH as the redox reagent. However, the difference in eutrophication between them is due to the benefits from Option 1.2 sequestering CO_2 in the redox reaction to produce paper and $CaCO_3$, thus lowering the eutrophication scores slightly in comparison to Option 1.1 that produces paper and $Ca(OH)_2$.

Within a 95% confidence interval, the results of the uncertainty analysis agree with the findings of the LCA that Option 1.3 is better than the sodium based options (Options 1.1 and 1.3) and also all ammonium based options for industrial symbiotic relation development. The low difference in environmental impacts though attributed to the fact that sodium sulphate use is about 1.65% of the total raw material requirement, still justifies its potential for industrial symbiotic development.

Table 6.11 Uncertainty analysis of solid waste (kg) due to substitution of conventional $(NH_4)_2SO_4$ and paper with by-product derived equivalents

Solid Waste (kg)					
Options	**Single Point Value**	**Mean of Monte Carlo Runs**	**Standard Deviation**	**Lower 95% Confidence Limit**	**Upper 95% Confidence Limit**
Option 1.1	-0.0109	-0.0109	0.0001	-0.0110	-0.0106
Option 1.2	-0.0097	-0.0097	0.0001	-0.0098	-0.0095
Option 1.3	-0.0103	-0.0102	0.00003	-0.0103	-0.0102
Option 2.1	-0.7220	-0.7216	0.0017	-0.7236	-0.7174
Option 2.2	-0.7215	-0.7210	0.0019	-0.7234	-0.7161

The negative values in Table 6.11 indicate the potential savings resulting from replacing conventional $(NH_4)_2SO_4$ with by-product $(NH_4)_2SO_4$, and also conventional paper with that derived from utilising by-product sodium sulphate formed from the symbiotic relation. The values are derived mostly from the utilisation of gypsum, which reduces virgin material and waste that would otherwise occupy land in form of residue areas. The gypsum use reduces the overall solid waste impacts from by-product $(NH_4)_2SO_4$ and paper derived from by-product sodium sulphate options.

6.9 Conclusions

Analysis of different process options for the reduction of phosphogypsum have been carried out through the use of the framework where life cycle assessment has been used to ascertain the most environmentally friendly pathway for industrial symbiosis linkage. Five different pathways were selected for the reduction of sulphate from phosphogypsum through suitable reagents. Two pathway options used ammonium based reagents in order to assess the environmental impacts of producing 1kg of ammonium sulphate. The other three pathway options used sodium based reagents and were used to assess environmental impacts of producing 1 kg of packaging paper using the by-product sodium sulphate formed as a raw material. Laboratory experimentation from section 6.4 aided in calculating mass and energy balance calculations based on extent of reaction. Where experimentation was not done, the calculations were made through data obtained from literature to develop the inventories for LCA analysis. Environmental impacts from the LCA results were compared with conventional ammonium sulphate fertilizer and conventional packaging paper to determine the potential for industrial synergy development.

Solid wastes generated for all options were found to be negative as the use of phosphogypsum offset any solid waste produced from energy generation from the processes. The environmental impacts associated with use of ammonium based reagents, ammonium carbonate (Option 2.1) and ammonium hydrogen carbonate (Option 2.2), from the LCA have shown that neither is suitable for forming industrial linkage. This is because of the difference in impacts between conventional fertilizer and the by-product fertilizer. Option 2.1 had better environmental impacts compared to Option 2.2, however, it produces 2kg CO_2-e more or 4 times greater GWP than conventional fertiliser per kg of by-product formed. The sodium based options had slightly higher impacts when used as a feed material for producing packaging paper as opposed to conventional paper. However, the difference between conventional paper and the sodium based options was not significant, especially for Option 1.3 that had the lowest difference between impacts to conventional paper. The GWP, EP and water use per kg basis of paper produced for Option 1.3 were 1.31 kg CO_2-

e(5%), 0.0022 kg PO_4^--e (5%)and 1.3 litres (117%) higher than conventional paper, respectively. Though the water use is high, 82% of it is attributed to the processes involved in producing the reagent before reduction of PG. Therefore, the result of this study concludes that use of sodium carbonate as redox reagent (Option 1.3) gives the least environmental impacts for producing sodium sulphate from PG reduction and its use as feed in the production of paper.

The hotspots through the LCA have been identified to be from fossil fuel powered energy generation in WA and wind electricity was found to be the best mitigation option that can reduce the GWP of Options 1.3 and 2.1 by 9%. Water is the other hotspot but there is no possible mitigation strategy as reduction in water use lowers the reaction conversion and by-product output, which reduces the competitiveness of all options.

In the subsequent chapter, presentation of economic analysis performed through the aid of Aspen Plus software for the environmentally friendly options (Options 1.3 and 2.1) is discussed to ascertain whether these options are economically viable.

Chapter 7 Socio-economic Assessment of Symbiotic Relationships

7.1 Introduction

This chapter covers the socio-economic analysis for the two case studies in order to determine the cost-effectiveness and social benefits of the symbiotic relationships discussed in Chapters 5 and 6. The outcomes of this analysis are then used to supplement the environmental findings from previous chapters to determine the most sustainable process option for industrial symbiosis offering triple bottom line or economic, environmental and social benefits.

7.2 Economic Analysis of the Two Case Studies

The environmental impacts are one of the factors considered for symbiosis development in the analysed case studies. However, they are not the only critical criteria that can be used to determine the suitability of industrial symbiosis. This is because economic considerations are also crucial too and are a litmus of determining whether setting up relevant decomposing industries for symbiotic development are attractive to potential investors based on financial returns.

The main factors that affect the economic viability are the capital and operational costs. A high capital cost leads to a longer payback period meaning returns can only be obtained much later in the future. In contrast, lower capital costs result in a faster payback, meaning the benefits to investors are realised much earlier. Operational costs also play a role in determining economic viability as they reduce the proceeds from sales revenue. Thus, higher operational expenses lead to lower revenue generated and leads to a smaller profit margin, meaning delayed recoupment of investment. The factors that affects operational costs are different feed size, utility requirement and labour involved. All these vary with different processes and plant scale/ size. In the economic analysis undertaken for the current case studies, the same inputs and outputs considered for LCA analysis in Chapters 5 and 6 are used so as to maintain consistency in order to have a non-biased comparison between environmental performance and economic viability.

Economic analysis was conducted through the Aspen Plus Economic Analyser v8.4. Simulations were first run on the different process options in Aspen Plus v8.4 after inputting the results from either laboratory experimentation (Phosphogypsum reduction) or literature (NO_x absorption) and setting production rate per hour in order to determine the overall mass and energy balances. These are same results that were utilised in developing the LCI in Chapters 5 and 6. The unit prices of the utilities, raw materials and products were also inputs and used after successful simulation by activating the Aspen Economic Analyser in order to determine the economic viability of the different processing options using a discounted cash flow rate of 10% or discounted factor of 0.909.

The plant operating period for each option was set as 20 years, with 4 weeks per annum left for plant maintenance by the Aspen Economics Analyser leaving a total number of 48 operating weeks or 8064 operating hours per year. The operating costs utilised in the discounted cash flow analysis calculation are presented in Table 7.1. Maintenance costs were determined by Aspen Economics based on historical data collected from plants of similar size.

Table 7.1 Operating cost parameters

Operating Items	**Costs**	**Source**
Operating Charges	25% of operating labour costs	Aspen Plus v8.4
Plant Overhead	50% of operating labour and maintenance costs	Aspen Plus v8.4
General and Administration Expenses	8% of subtotal operating costs	Aspen Plus v8.4
Electricity	0.051$ per kWh	AEMO, 2015

In order to cater for inflation, various costs were increased annually by a different percentage rate as outlined in Table 7.2. These annual increments were all based on default settings in the Aspen Economic Analyser v8.4, which are similar to how Australian industries cater for inflation.

Table 7.2 Annual incremental/escalation costs to offset inflation

Items	Percent/year
Project Capital Escalation	5
Products Escalation	5
Raw Material Escalation	3.5
Operating and Maintenance Labour Escalation	3
Utilities Escalation	3

The selling price of by-products produced from the potential decomposing facilities for all options analysed in the economic analysis were varied until they had an NPV value of double the capital investment or 5% average profit per annum on the capital value. This was performed to make the options analysed profitable and attractive to prospective investors. Thereafter, the evaluated selling prices of by-products per ton (when the NPV is double the capital investment) were compared with similar conventional products in the market to verify if they could be economically competitive.

7.2.1 Economic Analysis of Process Options in the NO_x Absorption Case Study

The options analysed for economic viability from the NO_x absorption case study are Options 1.2, and 2.2 as these options produce by-products that have overall lower impacts than similar conventional products as evidenced in Table 5.9. Options 1.2 and 2.2 use H_2O_2 as oxidants. However, Option 1.2 utilises $Ca(OH)_2$ as absorbent to produce calcium nitrate while Option 2.2 utilises NaOH as absorbent instead of $Ca(OH)_2$ to produce sodium nitrate. The calcium and sodium nitrates are then utilised through industrial symbiosis to produce potassium nitrate fertiliser by redox reaction with potassium sulphate. However, the latter process for the production of potassium nitrate is envisioned to occur in neighbouring industries after industrial symbiosis linkage. Thus, the boundary of the economic analysis undertaken is up to the production of calcium and sodium nitrate by-products through potential decomposing industries.

The economic analysis evaluated the total operating costs involved in the production of a fixed product capacity per annum and the associated capital costs of setting up the plants. The results for the analysed pathway options are summarised in Table 7.3, which provides the breakdown of capital cost to be incurred, the raw material costs, operating cost (labour maintenance and administration expenses) and utility costs.

In order to make comparison with the price of conventional products, a scenario where the NPV of the lifespan of the proposed industry equalled double the value of capital investment (average of 5% profit on investment per year). This was done in order to evaluate the selling price per unit amount of product at which capital costs were recouped and an equivalent profit over the lifespan of industry was returned. This price was set in order to make the industrial plant attractive to investors, and the selling price per ton by-product determined could then be compared to the price of an equivalent conventional product amount.

The breakdown of the capital costs, sales and operating costs for the two process options analysed are summarised in Table 7.3. The labour costs are similar as the number of operators and supervisors are the same. The unit selling price ($ per ton) of Option 1.2 and 1.3 are $402.93 and $477.68 respectively.

Table 7.3 Economic analysis of by-product cost for NO_x absorption case study

Pathway Options	**Units**	**Option 1.2**	**Option 2.2**
Total Project Capital Cost	USD	3.77E+06	3.78E+06
Total Operating Expenses	USD/Year	1.06E+07	1.29E+07
Total Raw Materials Cost	USD/Year	8.57E+06	1.073E+07
Evaluated By-product Sale Price (With 5% returns on capital investment per year)	USD/ton	402.93	477.68
Plant Capacity	tons/Year	39501	38184
Conventional product price	USD/ton	240	400

At the analysed scenario (5% profit average return on the capital investment per year), the price of by-product calcium nitrate ($Ca(NO_3)_2$) from Option 1.2 is 67.9% higher than that of conventional $Ca(NO_3)_2$, while that of by-product sodium nitrate ($NaNO_3$) from Option 2.2 is 14.9% higher than the price of conventional $NaNO_3$. This is due to the price of both conventional $Ca(NO_3)_2$ and $NaNO_3$ having a low value of $240/ton and $400/ton respectively. The primary reason for the high cost of by-products is due to the price of raw materials ($Ca(OH)_2$/ NaOH absorbent and

H_2O_2 oxidant), which contributes 81% and 83% of the total operating costs for Options 1.2 and 2.2 respectively.

Therefore, the selling price of calcium nitrate by-product at the considered scenario (an average investment return of 5% profit per year) appears to be not viable as it is almost double the price of conventional calcium nitrate. The cost of sodium nitrate by-product at the same considered scenario appears to be marginally higher (15%) than conventional sodium nitrate and may be considered economically viable.

7.2.1.1 Sensitivity Analysis on Options in the NO_x Absorption Case Study

A sensitivity analysis on different plant capacities was evaluated to determine whether the selling price of by-product nitrates produced could be lowered by increasing production. The different by-product nitrate prices were then matched with the price of conventional nitrate products for comparison on competitiveness. Scale of production was increased by increasing the capacities of two different plants to attain the economic viability for both Options 1.2 and 2.2. Their initial capacities have been doubled and then quadrupled to increase the output while reducing the operating price (Tables 7.4 and 7.5).

Table 7.4 Economic analysis results of varying the plant capacity for Option 1.2

Pathway Options	**Units**	**Option 1.2 (Normal Compacity)**	**Option 1.2 (Double Capacity)**	**Option 1.2 (Quadruple Capacity)**
Total Project Capital Cost	USD	3.77E+06	4.66E+06	6.62E+06
Total Operating Expenses	USD/Year	1.06E+07	1.99E+07	3.85E+07
Total Raw Materials Cost	USD/Year	8.57E+06	1.71E+07	3.43E+07
Evaluated By-product Sales Price (With 5% returns on capital investment per year)	USD/ton	402.93	367.95	350.73
Life Cycle Cost (LCC)	USD/ton	158.14	144.65	139.18
Payback Period	Years	14.55	15.85	16.71
Plant Capacity	tons /Year	39501	79001	158002
Conventional product price	USD/ton	240		

The sensitivity analysis has been conducted by varying the production output of Option 1.2 (Table 7.4), which clearly shows the selling price of by-product $Ca(NO_3)_2$

per ton decreases by 13% (i.e. from $402.93/ton to $350.73/ton) as the plant capacity is increased by 400% (i.e. from 39501 to 158002 tons/year). This is because the life cycle costs (LCC) decreases due to the economies of scale where higher production (i.e. denominator of the unit cost) reduces overall cost. However, the price after doubling capacity and quadrupling capacity are still 53.3% and 46.1% higher than the price of conventional $Ca(NO_3)_2$ ($240/ton). Whilst price decreases, the payback period increases due to capacity expansion of these plants. The payback period increases from 14.55 years (analysed capacity) to 15.85 years for doubling the capacity and to 16.71 years when capacity is quadrupled. The price of raw material again is the main factor behind the higher price per ton as it increases to 86% of total operating expenses when the plant capacity is doubled and to 89% after the plant capacity has been quadrupled.

Table 7.5 Economic analysis results of varying the plant capacity for option 1.2

Pathway Options	**Units**	**Option 2.2 (Normal Compacity)**	**Option 2.2 (Double Capacity)**	**Option 2.2 (Quadruple Capacity)**
Total Project Capital Cost	USD	3.74E+06	4.86E+06	6.80E+06
Total Operating Expenses	USD/Year	1.29E+07	2.46E+07	4.78E+07
Total Raw Materials Cost	USD/Year	1.07E+07	2.15E+07	4.29E+07
Evaluated By-product Sales Price (With 5% returns on capital investment per year)	USD/ton	477.68	443.66	426.23
Life Cycle Cost (LCC)	USD/ton	195.34	184.17	178.40
Payback Period	Years	15.23	16.34	17.19
Plant Capacity	tons /Year	38185	76369	152738
Conventional product price	USD/ton	400		

Similar to the sensitivity analysis results of varying production capacity for Option 1.2, the price per ton of by-product decreases with increase in production capacity (Table 7.5) from $477.68/ton for 38185 tons/year of capacity to $426.33/ton for152738 tons/year of capacity. The LCC is reduced from $195.34/ton at 38185 tons/year capacity to $178.40 for quadrupling the capacity. However, the improved prices are still 10.9% and 6.6% than conventional nitrate when the plant capacity is doubled and quadrupled respectively. Additionally, the trend in the payback period of Option 2.2 follows that of Option 1.2 where it increases from 15.23 years (38185 tons/year capacity) to 17.19 years as the capacity is increased fourfold. This is because the raw material contribution towards total operating expenses increases from 83% to 87.5% when capacity is doubled and to 89% when the capacity is quadrupled.

Any further increase in capacity for both Options 1.2 and 2.2 is foreseen to reduce the by-products $Ca(NO_3)_2$ and $NaNO_3$ price per ton respectively, but has to be warranted by demand in the market. All the costs increased with increased plant production capacity, with the highest increase attributed to raw material cost. The higher raw material costs result in the payback period being pushed towards the end of the lifespan of the proposed plants for each option. The only way to make these options economically viable is by reducing the cost of raw materials but this is not feasible as their prices are controlled by world market dynamics such as demand and supply.

Therefore, the effect of varying capacity is not viable in making the proposed decomposing plant economic as the payback period is delayed and the costs compared to conventional nitrate products ($Ca(NO_3)_2$ and $NaNO_3$) are still higher.

7.2.1.2 Sensitivity Analysis on the Use of Carbon tax

The use of carbon tax as an economic instrument was considered to visualise the benefits of reduced environmental impacts from the considered options. It was evaluated for Option 1.2 that the imposition of a $15 tax per ton CO_2 emitted from GWP impacts would be sufficient to reduce the price of by-product calcium nitrate to that of conventional nitrate (match the same price, $240/ton) while returning 5% profit per year. This is due to the huge savings of 7.44 tonnes CO_2 from reduced GWP per ton of KNO_3 produced from by-product calcium nitrate as opposed to an equivalent ton of conventional KNO_3 (i.e. 16.8 ton CO_2/ton). A similar study on the application of AU$ 25-50 carbon tax showed that it could enhance economic viability of power generation from energy recovered from Kwinana industries flue gases (van Beers & Biswas, 2008). On the contrary, the minimal carbon tax required for Option 2.2 to offset the higher price of by-product sodium nitrate compared to conventional $NaNO_3$ nitrate (while returning 5% profit per year) is $28 tax per ton CO_2 emitted. The reason for Option 2.2 requiring a higher carbon tax is due to the lower environmental savings from reduced GWP, which is only 1.95 tons lower CO_2 per ton of by-product sodium nitrate than an equivalent ton of conventional $NaNO_3$.

Thus, with the application of a carbon tax of $15 and $28 for Options 1.2 and 2.2 respectively, both these options can achieve economic viability while lowering environmental impacts. The selling price of by-product and conventional products will then be equal, which will enhance the by-product KNO_3 fertiliser use for industrial symbiosis. However, a higher carbon tax than those determined above if enacted will make by-product nitrate cheaper than conventional KNO_3.

As discussed in the previous sensitivity analysis (Section 7.2.1.1), the high price of raw materials in both Options 1.2 and 2.2 is because of the high prices associated with oxidant use (H_2O_2 in this case). Nonetheless, though the oxidant has primarily been utilised to produce nitrate (NO_3^-) products, there is still potential for absorption of the NO_x gases using the same absorbents investigated in the case study albeit without the expensive oxidants. The difference is that the products will be in the form of nitrites (NO_2^-), which has analogous use to the nitrate products arising from the oxidant. The formation of nitrite is produced from Equation 7.1, which requires an equimolar ratio of NO/NO_2 for production of only nitrite (Hüpen & Kenig, 2005)

$$NO + NO_2 + 2OH^- \rightarrow 2NO_2 + H_2O \tag{7.1}$$

Pradhan and Joshi (2000) and Patwardhan *et al.* (2002) have verified the potential of sodium nitrite formation through their investigation of NO_x absorption with sodium hydroxide in a plate column by comparing the mathematical model they developed with results from experimental work carried out in a pilot plant. The main factors the authors evaluated that affected selectivity of sodium nitrite formation was temperature and NO/NO_2 ratio. Temperatures between 50-70°Cwere found to impede nitrate formation and favour nitrite formation. A higher than 8 NO/NO_2 ratio enhanced selectivity of nitrite formation to 99% and even at an equimolar ratio of NO/NO_2, the selectivity of nitrite was relatively good at 94%. Thus, the conclusion that the nitrate route is not favourable provides opportunities to focus on production of nitrites because they eliminate the use of expensive oxidant and have similar sales value to the nitrates. The elimination of oxidants use also reduces the environmental impacts associated with their use (elaborated in Chapter 5), which means the production of nitrites offers not only an economical option of absorbing NO but a more environmentally favourable option through NO sequestration than converting them to nitrates. However, the scope of the current research only evaluated the nitrate route and nitrite formation was not considered due to time limitation.

7.2.2 Economic Analysis of Options in the Phosphogypsum Reduction Case Study

The process options from the PG case study analysed for economic viability were Options 1.1, 1.2 and 1.3. These options produced by-product sodium sulphate (Na_2SO_4) that had slightly higher environmental impacts (up to 0.065 kg CO_2 higher GWP) for production of 1 kg by-product paper (Table 6.5). Options 1.1 and 1.2 both utilise the use of NaOH as the reducing agent for reduction of PG to produce Na_2SO_4 and calcium hydroxide ($Ca(OH)_2$) as by-products. However, Option 1.2 incorporates the use of waste CO_2 for carbonation of the formed $Ca(OH)_2$ to calcium carbonate ($CaCO_3$) in order to lower the environmental impacts from NaOH use. Option 1.3 utilises sodium carbonate as the reducing agent of PG in order to produce Na_2SO_4 and $CaCO_3$ as by-products. The resulting Na_2SO_4 in all options mentioned is envisioned to be utilised for the production of packaging paper through industrial symbiosis links with neighbouring industries. Similar to the economic analysis of Case Study 1 (NO_x absorption), the processes for the production of paper is not considered in the system boundary for economic analysis. Instead, the production of by-product Na_2SO_4 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.

Table 7.6 presents the economic results for the process option analysed, where the selling price ($/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 Na_2SO_4 for Options 1.1, 1.2 and 1.3 were 57.1%, 76.7% and 79.9% higher than conventional Na_2SO_4 ($90/ton) respectively.

Table 7.6 Economic analysis of by-product cost for phosphogypsum case study

Pathway Options	**Units**	**Option 1.1**	**Option 1.2**	**Option 1.3**
Total Project Capital Cost	USD	6,46E+06	7,33E+06	3.28E+06
Total Operating Expenses	USD/Year	1.07E+07	1.08E+07	9,13E+06
Total Raw Materials Cost	USD/Year	8.58E+06	8.58E+06	7.24E+06
Evaluated By-product Sale Price (With 5% returns on capital investment per year)	USD/ton	**223,02**	**238,78**	**161.87**
Plant Capacity	tons/Year	25027	33222	49581
Conventional product price	USD/ton	**90**		

The main reason for the higher selling price of by-product Na_2SO_4 from all options is due to the high price of raw materials that increased the by-product price from these options 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 compared to Option 1.3 that uses cheaper Na_2CO_3.

7.2.2.1 Sensitivity Analysis for Options 1.1, 1.2 and 1.3

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. This was to determine as to 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 7.7 show that economies of scale lowers the overall price of Option 1.1from \$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.

Table 7.7 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)**
Total Project Capital Cost	USD	1,18E+07	1,92E+07	9,46E+06	1,28E+07	5,06E+06	6,84E+06
Total Operating Expenses	USD/Year	1,99E+07	3,85E+07	2,01E+07	3,88E+07	1,70E+07	3,26E+07
Total Raw Materials Cost	USD/Year	1,72E+07	3,43E+07	1,72E+07	3,43E+07	1,45E+07	2,89E+07
Evaluated By-product Sales Price (With 5% returns on capital investment per year)	USD/ton	208,63	197,90	213,73	200,10	147,48	139,14
Life Cycle Cost (LCC)	USD/ton	236.62	227.12	177.90	169.76	96.78	92.40
Plant Capacity	tons/Year	50054	100108	66444	132887	99161	198322
Conventional product price	USD/ton	90					

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

7.3 Social Analysis

The social implications of the options analysed under the economic analysis for PG reduction with $Na_2CO_3$and NO_x reduction with $Ca(OH)_2$ and H_2O_2 are presented in this section. These social factors are the benefits that these plants would bring to the surrounding people. 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). The indicators have also been applied on research work of similar by-products performed previously in Kwinana (Biswas & Cooling, 2013).

1 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. These can be both technical and non-technical based roles that are required for the normal operation of the plants

2 Intergenerational Social Equity –the substitution of a ton of virgin resource with a ton by-product produced from the proposed decomposing plants through industrial symbiosis(in the current thesis) that aids in conserving resources for the future generations.

3. Avoided Land Use – the benefits brought from utilising the waste or by-product, especially the reduced land area per square metre for stockpiling the waste PG per ton by-product produced.

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

7.3.1 Employment Opportunity

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

The construction phase of the plants also presents numerous opportunities for employment as both skilled and semi-skilled sets are required. Direct jobs resulting from construction include various engineering roles required for supervising the construction and commissioning of the plant. Contractors engaged in excavation, fabrication of plant equipment, plant setup, building of support facilities such as pipes and roads are the other beneficiaries of direct jobs from construction. There are also many indirect jobs resulting from construction and are linked to the supply chain of resources used in construction. The incomes of the skilled jobs have been calculated by Aspen Economic Analyser v8.4 to be $58,440 and $102,270 for an operator and supervisor respectively per year. This is more than sufficient to meet all their basic needs and also have some savings. Thus, there is a considerable benefit brought to the surrounding localities from the 9 skilled jobs created per ton by-product produced to replace conventional products through industrial symbiosis in the considered case studies.

7.3.2 Intergenerational Equity

The absorption of waste NO_x gases from nitric acid flue gas through H_2O_2 oxidation and $Ca(OH)_2$ absorption is expected to avoid the release of 418 kg of NO_x gases per ton KNO_3 formed through industrial symbiosis. The absorbed waste NO_x would otherwise be released into the atmosphere and affect the environment, property and lives through formation of acid rain and ozone depletion (van Zelm *et al.*, 2007). Van Zelm *et al.* (2008) evaluated that 1 kg emission of NO_x effects on human health from urban sources could reduce the life of a person by 3.9×10^{-8} years based on an 8-hour release of the 1 kg NO_x concentration. Thus, the production of a ton of by-product KNO_3 could help avoid the decrease of 1.63×10^{-5} years of life. Additionally, the utilisation of the waste NO_x per kg KNO_3 formation is expected to avoid the utilisation of about 11 kmols of HNO_3 that would be used as the nitrate source for oxidising potassium carbonate or potassium sulphate to KNO_3 (based on 90% oxidation efficiency). This can help to avoid the production of the required HNO_3 through its replacement with the absorbed NO_x, avoiding the energy and resources utilised in its production and thus associated environmental impacts.

Nevertheless, about 153.2 Giga Joules (GJs) of embodied energy per ton KNO_3 produced is required, which is about 54% higher energy required than the production of an equivalent ton of conventional KNO_3. Nonetheless, the benefits that arise from the utilisation of absorbed NO_x (e.g. 6 tons lower CO_2 per ton KNO_3 and negative acidification potential) outweigh the higher embodied energy required compared to conventional KNO_3.

On the other hand, the proposed plant for the reduction of PG with Na_2CO_3 is anticipated to reduce or preserve the exploitation of natural sodium sulphate ores by 2.2 kg per ton of paper produced. The preserved ores are envisaged to save it for future generations and enhance sustainability by utilising the waste gypsum.

However, the embodied energy required for the reduction of PG is expected to be about 62.5GJs per ton of sodium sulphate produced. This is 607% more embodied energy required than would have been used to produce sodium sulphate via the Manheim process (10.3 GJs) (Simapro 8.03 Australian LCI). This was due to the intensive energy used for production of pure Na_2CO_3 used as reagent as opposed to the Manheim process, where Na_2SO_4 is produced as a by-product from hydrochloric acid production resulting in a smaller environmental allocation. Most of the embodied energy used in the reduction of PG is utilised in the production process of the Na_2CO_3 reagent (24.6%) and the remainder is from the steam generation using natural gas (68.4%). The Manheim process has been used as reference as there was no data on embodied energy derived sodium sulphate produced from natural ore.

7.3.3 Avoided Land Use

The recycling of PG is expected to reduce approximately 12000 m^2 of land used for stockpiling of PG based on the average plant operation of Option 1.1 that processes about 25,000 tons of PG annually (or about 0.4 m^2 per ton PG recycled). This result was based on the assumption that stockpiling is made up to a metre in height and was calculated from the density of PG, 2.32 g/cm^3 (dividing density by metre height to get area). The reutilisation of PG for use as input by a surrounding industry through industrial symbiosis is thus expected to save land that would actually be used for stockpiling PG. The benefits of the avoided land use are that it could be reutilised for other economic benefits such as expansion of the industrial plant or be sold for revenue generation. Additionally, there is a considerable reduction of contamination of underground water sources or land from leaching of the PG constituents that is another benefit from the avoided land use.

7.4 Conclusions

The economic analysis evaluated that none of the process options for NO_x absorption were economically profitable. The primary reason for the high cost of by-products is due to the price of raw materials, which contributes 81% and 83% of the total operating costs for Options 1.2 and 2.2 respectively. This resulted in the price of by-product calcium nitrate ($Ca(NO_3)_2$) from Option 1.2 to be 67.9% higher than that of conventional $Ca(NO_3)_2$, while that of by-product sodium nitrate ($NaNO_3$) from Option 2.2 was 14.9% higher than the price of conventional $NaNO_3$.

The results of sensitivity analysis of varying the production capacity reduced overall price per ton of nitrates. However, the price after doubling capacity and quadrupling capacity were still 53.3% and 46.1% higher than the price of conventional $Ca(NO_3)_2$ ($240/ton). This is because the raw material contribution towards total operating expenses increases from 83% to 87.5% when capacity is doubled and to 89% when capacity is quadrupled. However, the application of policy instrument in terms of carbon tax could help achieve the economic viability of these environmentally friendly options. The sensitivity analysis of introducing a carbon tax of $15 per ton CO_2 emitted for Option 1.2 and $28 tax per ton CO_2 emitted for Option 2.2 would be sufficient to match the prices of by-product nitrates to those of conventional one. This will make the by-product nitrate lucrative because they will be competitive pricewise with conventional nitrates while having lower environmental impacts.

Similar to the NO_x absorption case study, the high cost of ammonia and NaOH reagents for PG reduction offsets the gains from sales of produced ammonium sulphate and sodium sulphate products respectively. The price of the by-product Na_2SO_4 for Options 1.1, 1.2 and 1.3 were determined to be 57.1%, 76.7% and 79.9% higher than conventional Na_2SO_4 ($90/ton) respectively. The application of a sensitivity analysis of varying production capacity reduced the selling price per ton of by-product Na_2SO_4 ($/ton) to $197.90 (from $223.02), $200.10 (from $238.78) and $139.14 (from $161.87) for Options 1.1, 1.2 and 1.3 respectively when production capacity is quadrupled. Nonetheless, the price of by-product Na_2SO_4 even after quadrupling plant capacity for Options 1.1, 1.2 and 1.3 were still 219.9%, 222.3% and 154.6% higher than conventional Na_2SO_4 as raw materials price increased to 89% of total operating costs for all options.

The social benefits that result from setting up either a decomposing plant using Na_2CO_3 as reagent for the reduction of PG or a plant for the absorption of NO_x flue gases with H_2O_2 oxidant and $Ca(OH)_3$ absorbent are employment opportunities for 6 operational workers and 3 supervisors for every single day of operation. The absorption of waste NO_x gases from nitric acid flue gas through H_2O_2 oxidation and $Ca(OH)_2$ absorption is also expected to avoid the release of 418 kg of NO_x gases per ton KNO_3 formed through industrial symbiosis. Nevertheless, about 153.2 Giga Joules (GJs) of embodied energy per ton KNO_3 produced is required, which is about 54% higher energy required than the production of an equivalent ton of conventional KNO_3. The PG reduction with Na_2CO_3 as reagent is anticipated to reduce the exploitation of natural sodium sulphate ores by 2.2 kg per ton of paper produced. However, the embodied energy required for the reduction of PG is expected to be about 62.5 GJs per ton of sodium sulphate produced or 6 times that of sodium sulphate via the Manheim process energy (10.3 GJs). Additionally, about 0.4 m^2 reduction in land use per ton of PG decomposed is expected to be realised in addition to resource conservation for future generation from avoided exploitation of virgin sodium sulphate ores.

Overall, it can be concluded that the most sustainable option from an environmental, economic and social perspective is that of the absorption of NO_x gases with H_2O_2 as oxidant and absorption with $Ca(OH)_2$. This is after the introduction of a $15 tax per ton CO_2 emitted that makes the price of the by-product calcium nitrate competitive with conventional nitrate while having lower environmental impacts.

Chapter 8 Conclusions and Recommendations

8.1 Conclusions from the Research

This thesis has developed a sustainability assessment framework for the evaluation and implementation of symbiotic linkage of wastes or by-products as a feedstock to surrounding industries (Mohammed *et al.*, 2013a and 2013b). The framework comprised of technical, environmental, economic and social aspects that aided in identification of various post processing options for converting waste to useful forms for the neighbouring industries in a sustainable manner. As part of the assessment process, optimisation through experimental and simulation analysis, green process design for environmental comparison of the different processing options analysed through LCA, and finally economic and social assessment through suitable indicators have been conducted.

Nitrogen oxides flue gas and phosphogypsum from the Kwinana Industrial Area were used as case studies for the application of the framework. Accordingly, two synergies have been considered depending on the characteristics of by-products, which are as follows:

1. Gaseous by-product synergy - production of potassium nitrate fertilizer from products derived from NO_x absorption, and
2. Solid by-product synergy - production of either ammonium sulphate fertilizer or paper from products from PG reduction

Feasibility studies for the considered synergies were performed through the aid of the generic industrial symbiotic outlay developed in Figure 3.1. The waste or by-products chemical compositions were determined through refereed literature such as scholarly journals and chemical encyclopaedias such as Ullmann's Encyclopaedia of Industrial Chemistry and Kirk-Othmer Encyclopaedia of Chemical Technology.

After determination of chemical compositions, the use of suitable absorbents, oxidants or suitable chemical reductants were determined from literature review in order to determine the process pathways that could be chosen for post treatment of the waste or by-products into valuable products. The products were then matched to potential industries through the generic industrial symbiotic outlay to determine possibility of symbiotic or synergy development with surrounding industries in KIA.

Thereafter, experimental analysis of the post treatment process options was performed after waste or by-product samples were obtained from the relevant industry used in the case study - fertilizer industry. Experimental results and simulation using Aspen Plus v8.4 software to verify experimental results were then used to develop the mass and energy balances. Where experimental work could not be applied, the use of collected data from literature was utilised to develop the mass and energy balances.

Once the technical feasibility of these synergies have been experimentally tested in the laboratory and through simulation modeling, life cycle assessment using the identified mass and energy balances were used to find the most environmentally friendly pathway for industrial symbiosis linkage.

Economic Analysis and social implications of processing options were then carried out to compare the life cycle costing and social benefits of each of the most environmentally options identified in order to determine the most optimum option for industrial symbiosis development from environmental, economic and social perspectives.

8.2 Gaseous by-product Synergy (Absorption of NO_x gases)

Analysis of various process pathways using different absorbents and oxidants for NO_x absorption was carried out based on 1 kg of KNO_3 fertilizer formed from industrial symbiosis. Options that utilised ozone as oxidant had over 90% of the emissions of their entire process attributed to the production processes of ozone production. However, the use of both NaClO and H_2O_2oxidants had considerably higher heating and cooling requirements than ozone due to the amount of dilution water added for oxidation purposes. The use of $Ca(OH)_2$ as absorbent had lower environmental impacts due to a lower mole ratio per mole of NO_x absorbed, resulting in less water and energy demand compared to NaOH use as absorbent. The least environmentally friendly pathway used NaOH as absorbent and ozone as oxidant that resulted in a 245% and 171% increase in GWP and acidification potential respectively compared with conventional KNO_3 fertilizer. On the contrary, the most environmentally friendly pathway that used $Ca(OH)_2$ as the absorbent and H_2O_2 as oxidant had 46%, 274% and 583% lower GWP, acidification potential and eutrophication potential respectively compared to conventional KNO_3 fertilizer (Mohammad *et al.,* 2016).

Economic analysis of the environmentally options (Options 1.2 and 2.2) evaluated that none of them were economically profitable. This was mostly due to the high cost of oxidants used in NO_x absorption that increased the raw materials cost as a percentage of total operating expenses to 81% and 83% for Options 1.2 and 2.2 respectively. These high costs lead to 67.9% and 14.9% higher prices per ton of by-product Ca $(NO_3)_2$ (Option 1.2) and by-product $NaNO_3$ (Option 2.2) in comparison to conventional nitrate products.

A sensitivity analysis on varying the production capacities was made to determine whether higher economies of scale could improve the economics and lead to lower by-product nitrates price ($/ton). The varied capacities analysed were double and quadruple the initial production capacities of Options 1.1 (i.e. 39501 tons/year) and 1.2 (i.e. 38184 tons/year). Overall, the price of by-product $Ca(NO_3)_2$/ton reduced from $402.93 to $350.73 (15% reduction) while that of $NaNO_3$/ton reduced from $477.68 to $426.23 (10.8% reduction) after the plant capacity was increased fourfold. However, the reduced by-product prices were still 10.9% ($Ca(NO_3)_2$) and 6.6% ($NaNO_3$) higher than that of conventional nitrate products. This again was attributed to the price of raw materials that offset the gains brought from higher product output and sales.

A second sensitivity analysis on the application of a carbon tax (per ton CO_2 emitted) as an economic instrument was incorporated into the analysis to determine the benefits that could be brought from the lower GHG emissions of by-product nitrates compared to conventional nitrates. It was evaluated that a $15 and $28 carbon tax per ton of CO_2 emitted for Options 1.2 and 2.2 respectively could make both these options economically viable. This is because this carbon pricing scheme could make both by-product nitrates price ($/ton) equal those of conventional nitrates, while also returning an average of 5% profit per annum on the capital invested over the lifetime (20 years) of the respective decomposing plants. The value of by-product and conventional products will then be equal and will not affect the KNO_3 fertiliser price after industrial symbiosis, unless a higher carbon tax than those determined are enacted. Option 2.2 requires a higher carbon tax due to lower environmental savings from reduced GWP (1.95 tons lower CO_2 per ton by-product $NaNO_3$) than Option 1.2 (7.44 tonnes lower CO_2 per ton by-product $Ca(NO_3)_2$) in comparison to respective conventional nitrate products. Thus, both options can be made economically viable with the introduction of a carbon tax, which will also result in lower environmental impacts from avoided production of conventional nitrate products.

The social benefits that result from setting up a plant for the absorption of NO_x flue gases are employment creation for 6 operational workers and 3 supervisors for every single day of operation. The absorption of waste NO_x gases from nitric acid flue gas through H_2O_2 oxidation and $Ca(OH)_2$ absorption is also expected to avoid the release of 418 kg of NO_x gases per ton KNO_3 formed through industrial symbiosis. Nevertheless, about 153.2 Giga Joules (GJs) of embodied energy per ton KNO_3 produced is required, which is about 54% higher embodied energy required than the production of an equivalent ton of conventional KNO_3. This means that embodied energy is not conserved but more is required for the production of by-product KNO_3.

8.3 Solid by-product Synergy (Reduction of Phosphogypsum)

Analysis of different process options for the reduction of phosphogypsum were carried out on the basis of 1 kg of paper or 1 kg of ammonium sulphate fertiliser. Laboratory experimentation of NaOH as reagent showed that the optimum conditions for reducing PG with a 91% reaction yield were a molar ratio of NaOH/PG of 2, a mixing speed of 400rpm and a temperature of 30°C. The optimum conditions for use of Na_2CO_3 as reagent were a molar ratio of Na_2CO_3/PG of 1, a mixing speed of 300rpm and a temperature of 30°C that resulted in a 95% reaction yield.

The LCA results of these reaction pathways showed that solid wastes generated for all options were offset from the utilisation of waste PG. The environmental impacts associated with use of $(NH_4)_2CO_3$were 1.96 kg CO_2-e (GWP), 30.6 litres (water use) and 0.0036 kg PO_4^--e (EP) higher than conventional $(NH_4)_2SO_4$ fertiliser. The use of NH_4HCO_3 was the least environmentally option with 3.61 kg CO_2-e (GWP), 27 litres (water use) and 0.004 kg PO_4^--e (EP) higher than conventional $(NH_4)_2SO_4$ fertiliser. The findings from LCA prove that both $(NH_4)_2CO_3$ and NH_4HCO_3 are not suitable for forming industrial linkage. This is because of the difference in impacts between conventional fertilizer and the ammonium sulphate fertilizer formed. The sodium based options had slightly higher impacts when used as a feed material for producing packaging paper as opposed to conventional paper without their use. Na_2CO_3 use as reagent (Option 1.3) had the lowest difference between impacts to conventional paper and was considered for industrial symbiosis. The GWP, EP and water use for by-product paper produced from Option 1.3 were 0.06kg CO_2-e, 0.0001 kg PO_4^--e and 0.85 litres higher than 1 kg of conventional paper, which is 5%, 4% and 177% higher respectively. Though the water use is high, 82% of it is attributed to the processes involved in producing the reagent before reduction of PG. Therefore, the result of this study concludes that the use of sodium carbonate as redox reagent gives the least environmental impacts for producing sodium sulphate from PG reduction and its use as feed in the production of paper.

Water use and electricity consumption have been identified as the hotspots through this LCA. There was no solution to alleviate the impact of water use, but wind electricity was found to be the best mitigation option for reducing the impacts of energy use associated with utilization of the carbon intensive electricity grid of Western Australia.

Economic analysis evaluated that none of the process options for PG reduction were economically profitable. This was due to the high cost of oxidants used in NO_x absorption, and the high cost of ammonia reagents and NaOH reagents for PG reduction that offset gains from sales of products formed. The price of the by-product Na_2SO_4 for Options 1.1, 1.2 and 1.3 were determined to be 57.1%, 76.7% and 79.9% higher than conventional Na_2SO_4 ($90/ton) respectively. Varying production capacity through sensitivity analysis reduced the selling price per ton of by-product Na_2SO_4 ($/ton) to $197.90 (from $223.02), $200.10 (from $238.78) and $139.14 (from

$161.87) for Options 1.1, 1.2 and 1.3 respectively when production capacity is quadrupled. However, the price of by-product Na_2SO_4 for Options 1.1, 1.2 and 1.3 were still 219.9%, 222.3% and 154.6% higher than conventional Na_2SO_4 as raw materials price increased to 89% of total operating costs for all options. The introduction of carbon tax is not possible to enhance the viability of PG reduction as the GWP produced from by-product paper is more than that of conventional paper.

The social benefits from setting up a decomposing plant using Na_2CO_3 as reagent are similar to the employment opportunities created for the absorption of NO_x with Na_2CO_3, i.e. 6 operational workers and 3 supervisors per ton by-product Na_2SO_4 produced. The reduction of PG with Na_2CO_3 as reagent is also anticipated to reduce the exploitation of natural sodium sulphate ores by 2.2 kg per ton of paper produced and reduce the land use required for PG waste stockpiling. About 0.4 m^2 reduction in land use per ton of PG decomposed is expected to be realised in addition to resource conservation for future generation from avoided exploitation of virgin sodium sulphate ores. However, the embodied energy required for the PG reduction is expected to be about 62.5 GJs per ton of sodium sulphate produced or 6 times more embodied energy than that of sodium sulphate via the Manheim process energy (10.3 GJs). There was no data obtained from sodium sulphate derived from natural ore, therefore the Manheim process was used as reference.

8.4 Recommendations for Future Work

Based on the findings from the research undertaken, the following are the recommendations for enhancing the framework for future research

1. Conduct a case study on the absorption of NO_x waste gases with absorbents that produce only nitrite products. The current study on use of oxidants to produce only nitrates was not feasible due to cost of oxidants. Nitrite products have analogous uses to nitrates and the omission of oxidants could render different process options to be profitable.
2. Collaborate with industry so that they can provide input to enhance the technical practicability of developing new synergies. This can be from the inclusion of parameters to analyse as variables, production rate to justify practicability, constituents of specific waste or by-product, etc. The collaboration will also

fulfil the last parts of the framework where relevant industries can provide feedback on analysis done up to the economic viability to improve the process and then decide as to whether a pilot plant can be commissioned for industrial scale analysis.

3. Conduct a detailed life cycle assessment with a comprehensive dataset once collaboration with industry is realised to enhance the practicability of developing new synergies.
4. Collaborate with other universities that have specialised laboratories for conducting experimental analysis on sensitive by-products such as NO_x gases absorption (a limitation in the current thesis). This is to compare the findings with literature and analyse any improvement opportunities like use of better absorbents, improvement in absorption rates and by-product preparation.
5. Conduct case studies on other potential by-products that could be utilised for industrial symbiosis linkage that were initially identified in the research but not considered as case studies. These are calcium chloride waste produced from a titanium dioxide pigment plant (via the chloride route) and use of pet-coke by-product from catalytic cracking in an oil refinery.
6. Conduct case studies on the evaluation of utility synergy (i.e. waste heat recovery and waste effluent recovery) through the aid of pinch analysis to improve the usefulness of the current framework.

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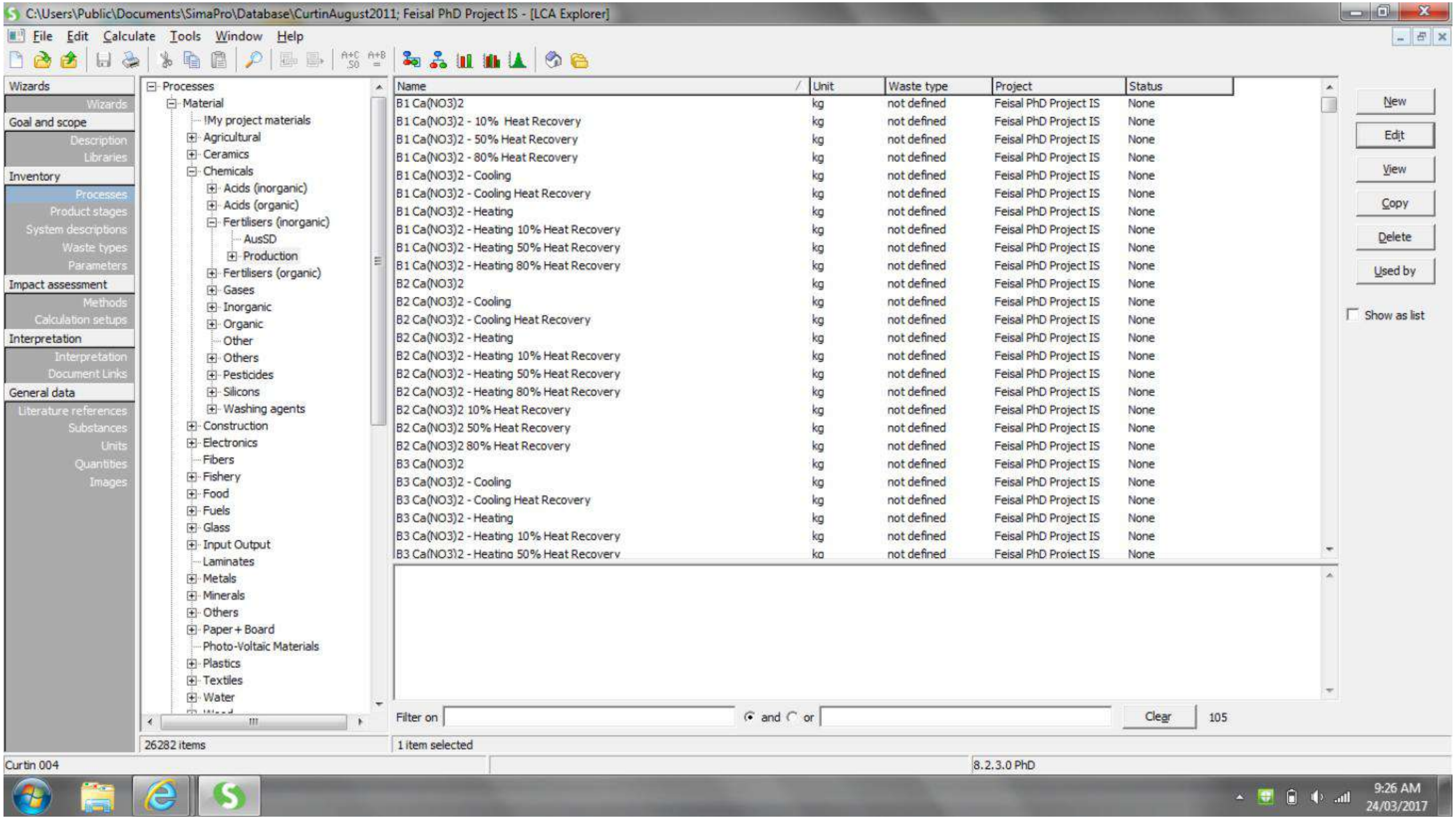
Appendix IV

LCA Emissions Sample Calculation Using Simapro

The screenshots in the subsequent pages show how databases using different inputs and utilities like steam, electricity or chemicals were developed in Simapro in order to obtain the life cycle environmental impact factors of converting waste NO_x gases into either $NaNO_3$ or $Ca(NO_3)_2$ by-products for use in producing potassium nitrate (KNO_3) fertilizer. The first screenshot highlights some of the developed databases for assessing environmental impacts of paper production from the waste NO_x. The next screenshots show how specific individual databases of the three different process routes for producing $NaNO_3$ or $Ca(NO_3)_2$ by-products were created. This is by firstly determining the amount of these by-products that are utilized for 1 ton of KNO_3 production (811.8 kg $Ca(NO_3)_2$ or 841.58 kg of $NaNO_3$ as entered in the input boxes highlighted in blue). Thereafter, all the required inputs and utilities used for producing the above mentioned amounts of either $NaNO_3$ or $Ca(NO_3)_2$ are entered in the input boxes under the `Known inputs from nature (materials)` or `Known inputs from technosphere (electricity/heat)` from the Australian LCI inventory database. The specific inputs or utility values are obtained from Tables 5.3 and 5.4 that were derived from the mass and energy balances calculations from laboratory and simulation analyses. These databases are then linked to the specific databases (analysed process routes) created for producing a ton of KNO_3. Then the environmental impacts are obtained by running LCA analysis using damage assessment in Simapro that pulls all the related environmental impacts from the different created databases of 1 ton KNO_3 from the associated Australian LCI inventory database.



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Name	Unit	Waste type	Project	Status
B1 Ca(NO3)2	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - 10% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - 50% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - 80% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - Cooling	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - Cooling Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - Heating	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - Heating 10% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - Heating 50% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B1 Ca(NO3)2 - Heating 80% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 - Cooling	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 - Cooling Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 - Heating	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 - Heating 10% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 - Heating 50% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 - Heating 80% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 10% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 50% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B2 Ca(NO3)2 80% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B3 Ca(NO3)2	kg	not defined	Feisal PhD Project IS	None
B3 Ca(NO3)2 - Cooling	kg	not defined	Feisal PhD Project IS	None
B3 Ca(NO3)2 - Cooling Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B3 Ca(NO3)2 - Heating	kg	not defined	Feisal PhD Project IS	None
B3 Ca(NO3)2 - Heating 10% Heat Recovery	kg	not defined	Feisal PhD Project IS	None
B3 Ca(NO3)2 - Heating 50% Heat Recovery	kg	not defined	Feisal PhD Project IS	None

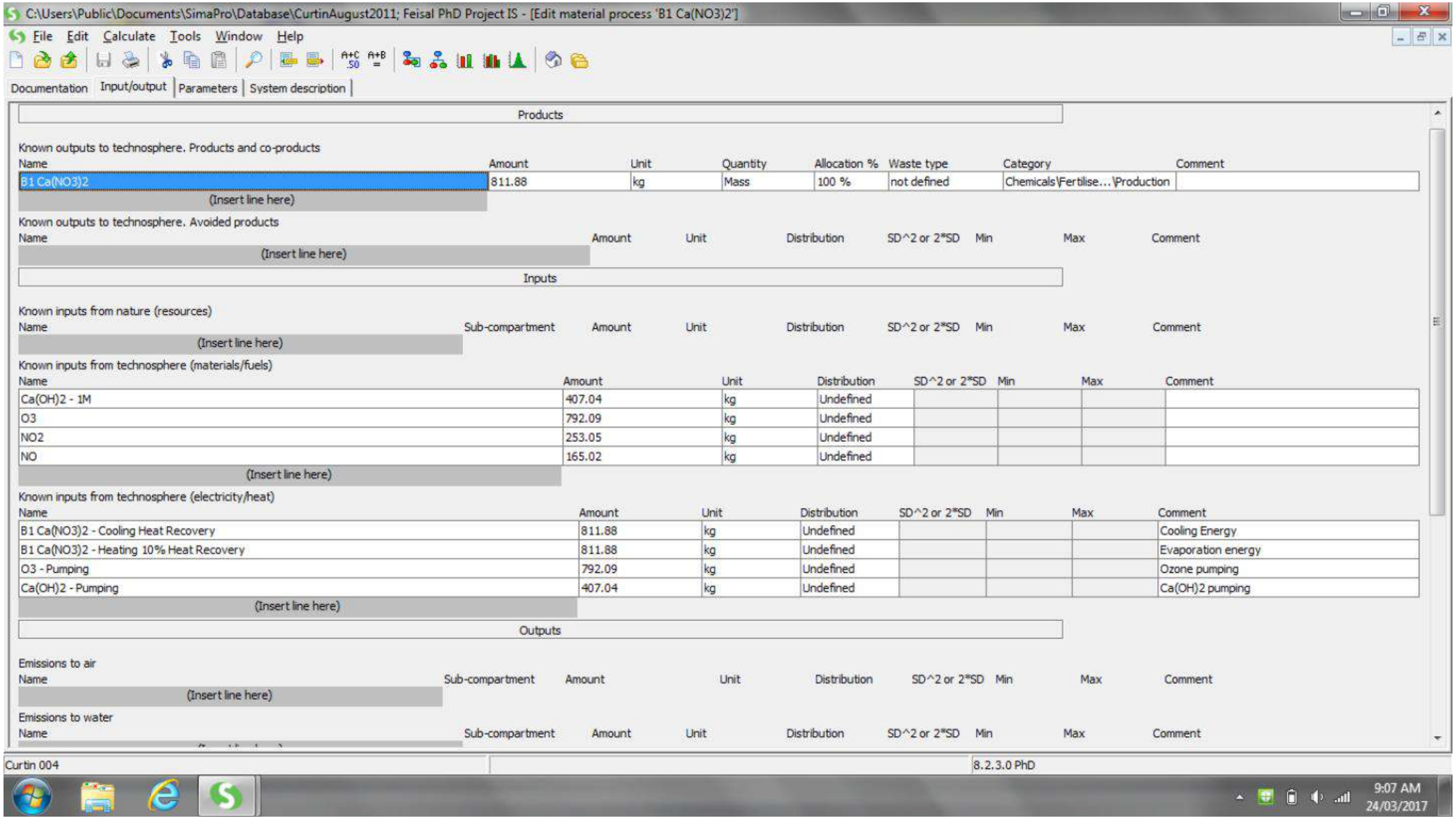
105

26282 items

1 item selected

Curtin 004

8.2.3.0 PhD



Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
B1 Ca(NO3)2	811.88	kg	Mass	100 %	not defined	Chemicals\Fertilise...\Production	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)							

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
Ca(OH)2 - 1M	407.04	kg	Undefined				
O3	792.09	kg	Undefined				
NO2	253.05	kg	Undefined				
NO	165.02	kg	Undefined				
(Insert line here)							

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
B1 Ca(NO3)2 - Cooling Heat Recovery	811.88	kg	Undefined				Cooling Energy
B1 Ca(NO3)2 - Heating 10% Heat Recovery	811.88	kg	Undefined				Evaporation energy
O3 - Pumping	792.09	kg	Undefined				Ozone pumping
Ca(OH)2 - Pumping	407.04	kg	Undefined				Ca(OH)2 pumping
(Insert line here)							

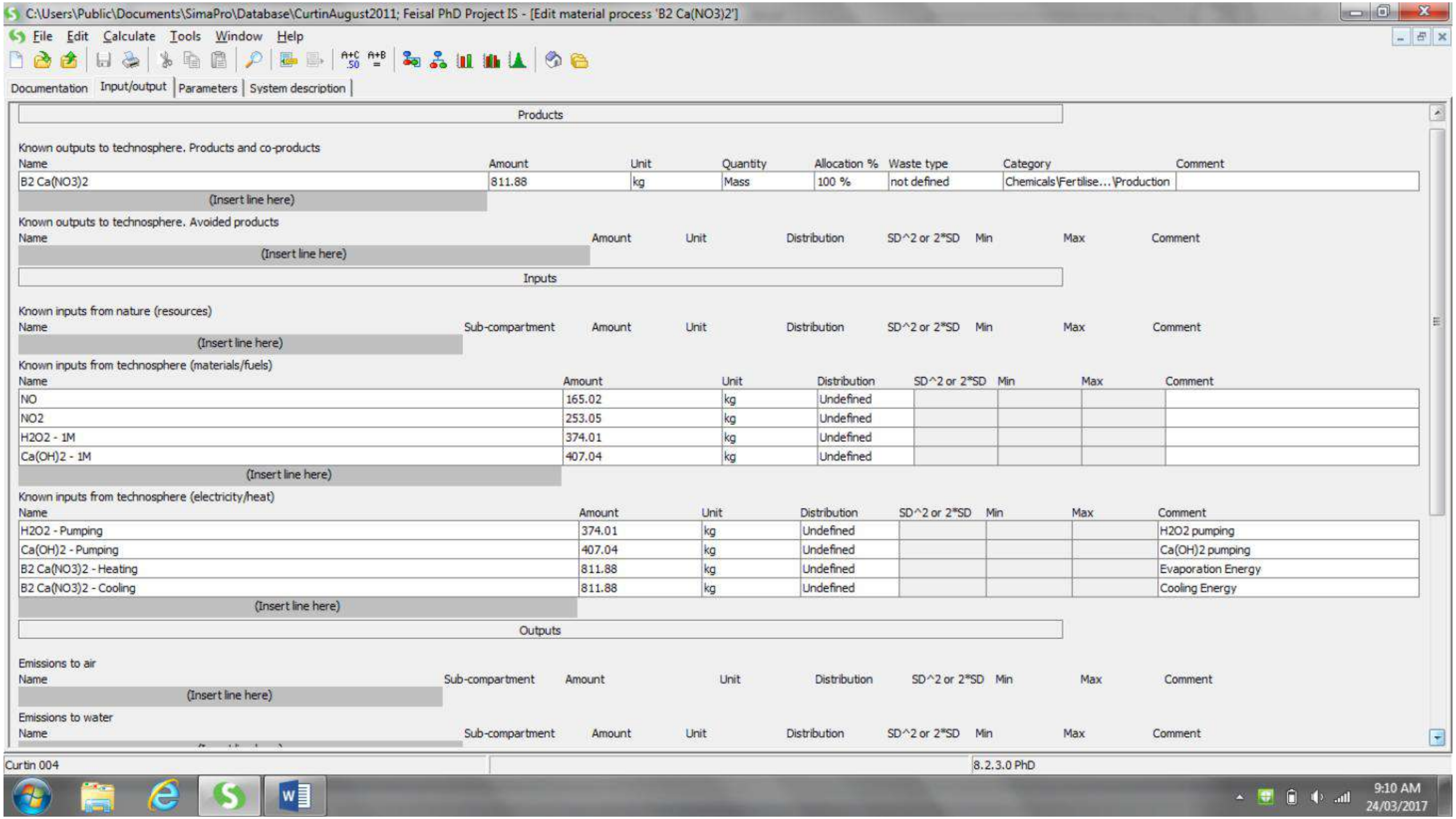
Outputs

Emissions to air

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Emissions to water

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment



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Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
B2 Ca(NO3)2	811.88	kg	Mass	100 %	not defined	Chemicals\Fertilise...\Production	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)							

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
NO	165.02	kg	Undefined				
NO2	253.05	kg	Undefined				
H2O2 - 1M	374.01	kg	Undefined				
Ca(OH)2 - 1M	407.04	kg	Undefined				
(Insert line here)							

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
H2O2 - Pumping	374.01	kg	Undefined				H2O2 pumping
Ca(OH)2 - Pumping	407.04	kg	Undefined				Ca(OH)2 pumping
B2 Ca(NO3)2 - Heating	811.88	kg	Undefined				Evaporation Energy
B2 Ca(NO3)2 - Cooling	811.88	kg	Undefined				Cooling Energy
(Insert line here)							

Outputs

Emissions to air

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

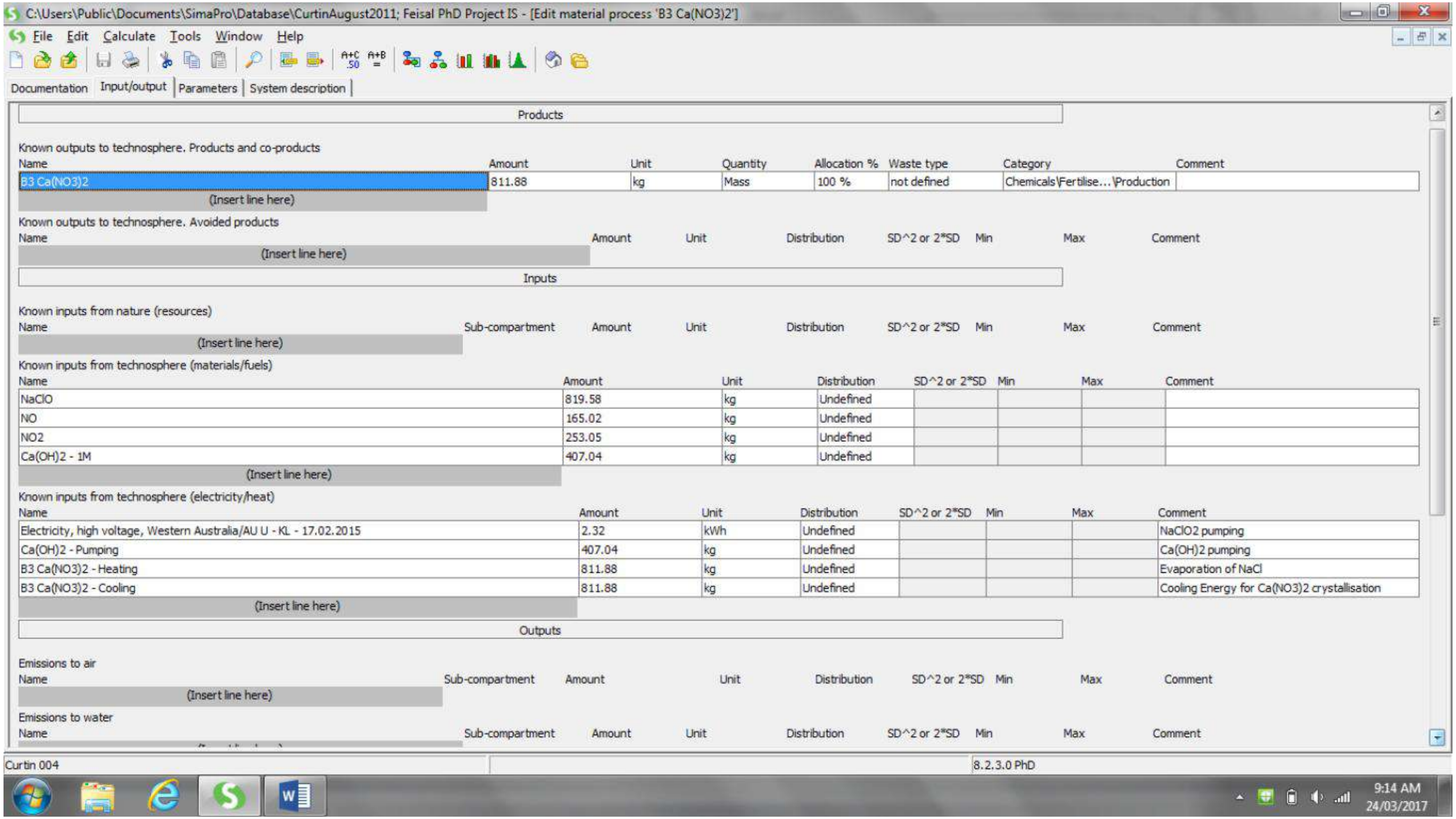
Emissions to water

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment

Curtin 004

8.2.3.0 PhD

9:10 AM
24/03/2017



Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
B3 Ca(NO3)2	811.88	kg	Mass	100 %	not defined	Chemicals\Fertilise...\Production	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)							

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
NaClO	819.58	kg	Undefined				
NO	165.02	kg	Undefined				
NO2	253.05	kg	Undefined				
Ca(OH)2 - 1M	407.04	kg	Undefined				
(Insert line here)							

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
Electricity, high voltage, Western Australia/AU U - KL - 17.02.2015	2.32	kWh	Undefined				NaClO2 pumping
Ca(OH)2 - Pumping	407.04	kg	Undefined				Ca(OH)2 pumping
B3 Ca(NO3)2 - Heating	811.88	kg	Undefined				Evaporation of NaCl
B3 Ca(NO3)2 - Cooling	811.88	kg	Undefined				Cooling Energy for Ca(NO3)2 crystallisation
(Insert line here)							

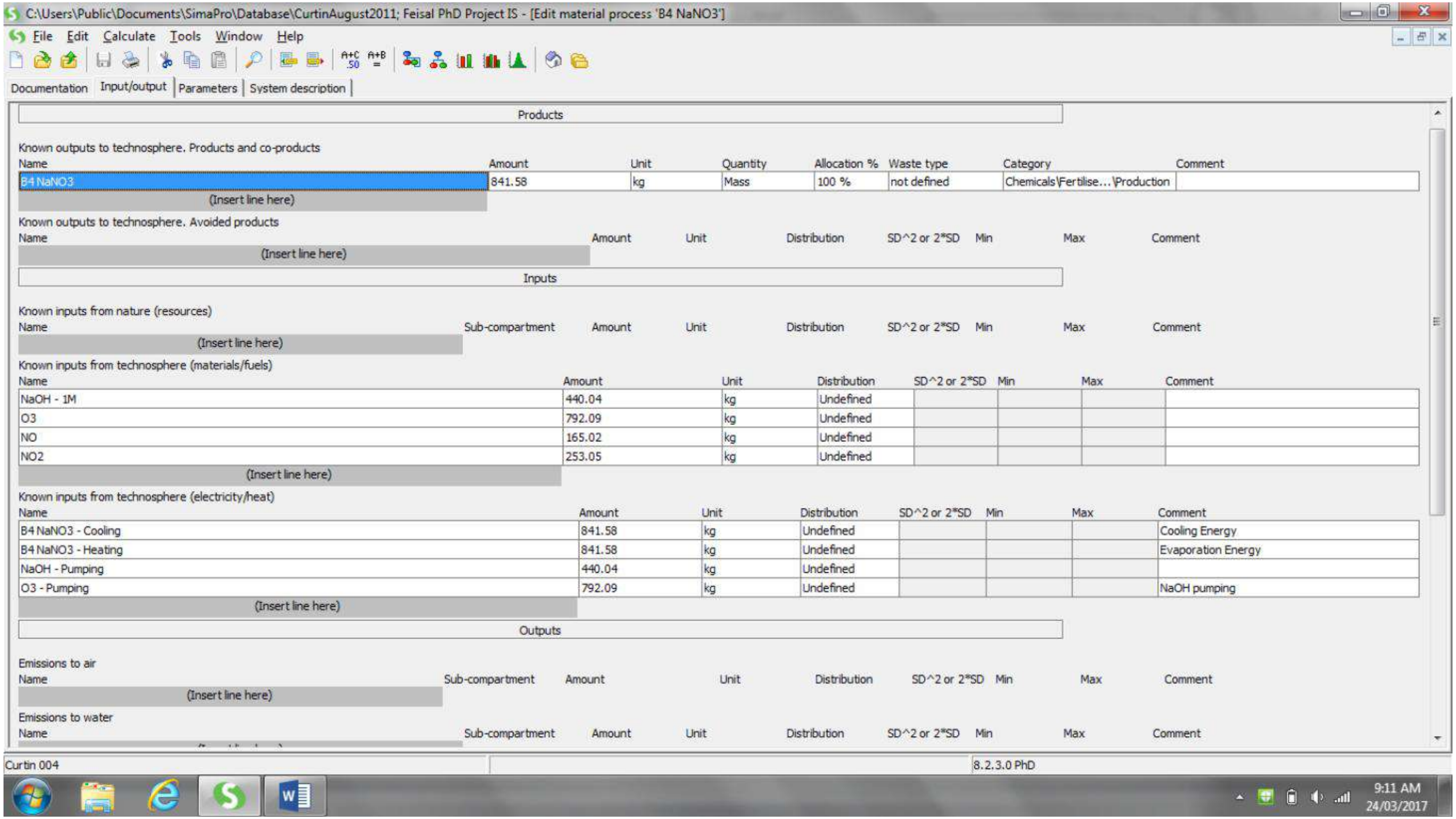
Outputs

Emissions to air

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Emissions to water

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment



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Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
B4 NaNO3	841.58	kg	Mass	100 %	not defined	Chemicals\Fertilise...\Production	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)							

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
NaOH - 1M	440.04	kg	Undefined				
O3	792.09	kg	Undefined				
NO	165.02	kg	Undefined				
NO2	253.05	kg	Undefined				
(Insert line here)							

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
B4 NaNO3 - Cooling	841.58	kg	Undefined				Cooling Energy
B4 NaNO3 - Heating	841.58	kg	Undefined				Evaporation Energy
NaOH - Pumping	440.04	kg	Undefined				
O3 - Pumping	792.09	kg	Undefined				NaOH pumping
(Insert line here)							

Outputs

Emissions to air

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Emissions to water

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment

Curtin 004

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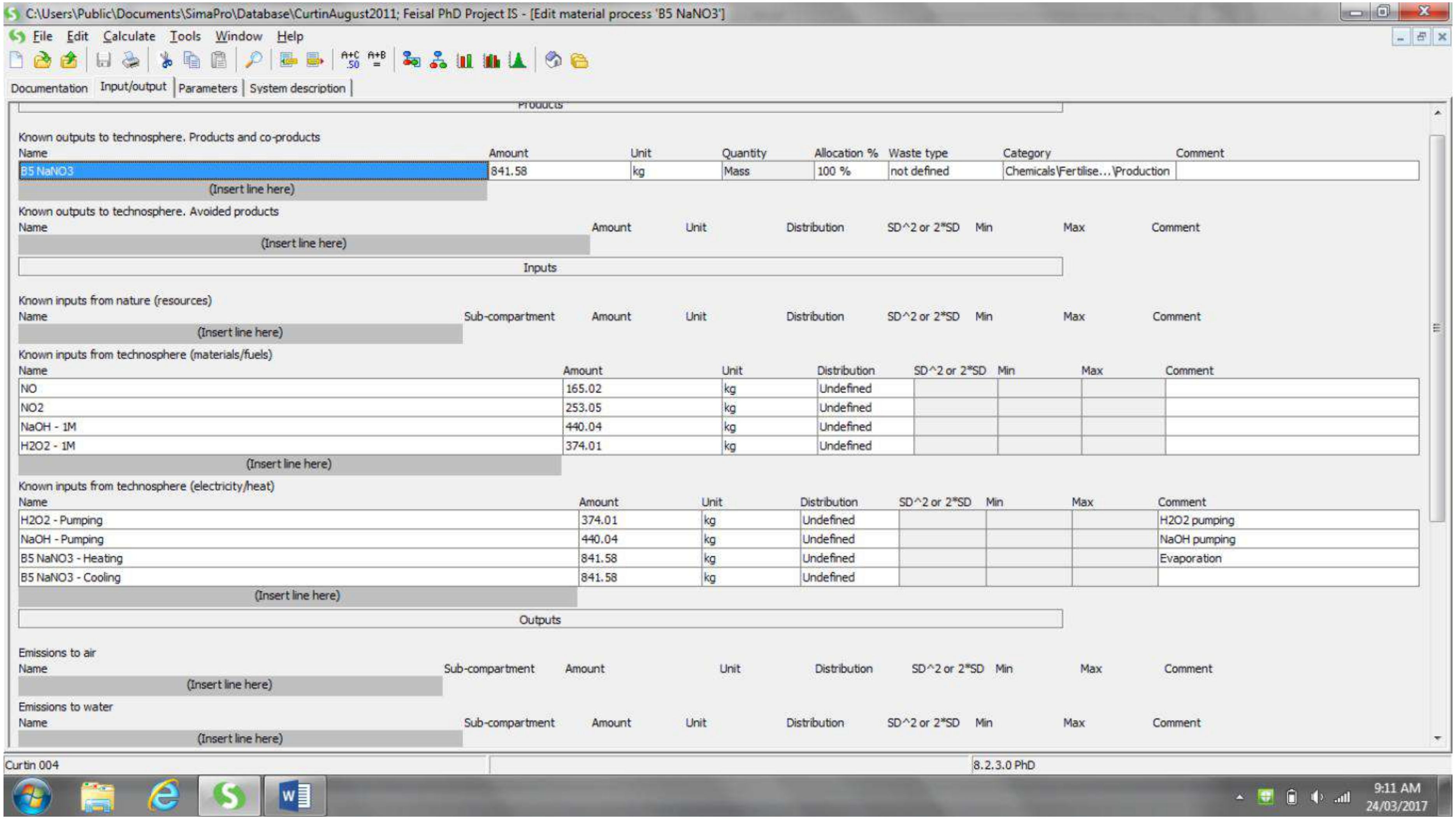


Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
B5 NaNO3	841.58	kg	Mass	100 %	not defined	Chemicals\Fertilise…\Production	

(Insert line here)

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment

(Insert line here)

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment

(Insert line here)

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
NO	165.02	kg	Undefined				
NO2	253.05	kg	Undefined				
NaOH - 1M	440.04	kg	Undefined				
H2O2 - 1M	374.01	kg	Undefined				

(Insert line here)

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
H2O2 - Pumping	374.01	kg	Undefined				H2O2 pumping
NaOH - Pumping	440.04	kg	Undefined				NaOH pumping
B5 NaNO3 - Heating	841.58	kg	Undefined				Evaporation
B5 NaNO3 - Cooling	841.58	kg	Undefined				

(Insert line here)

Emissions to air

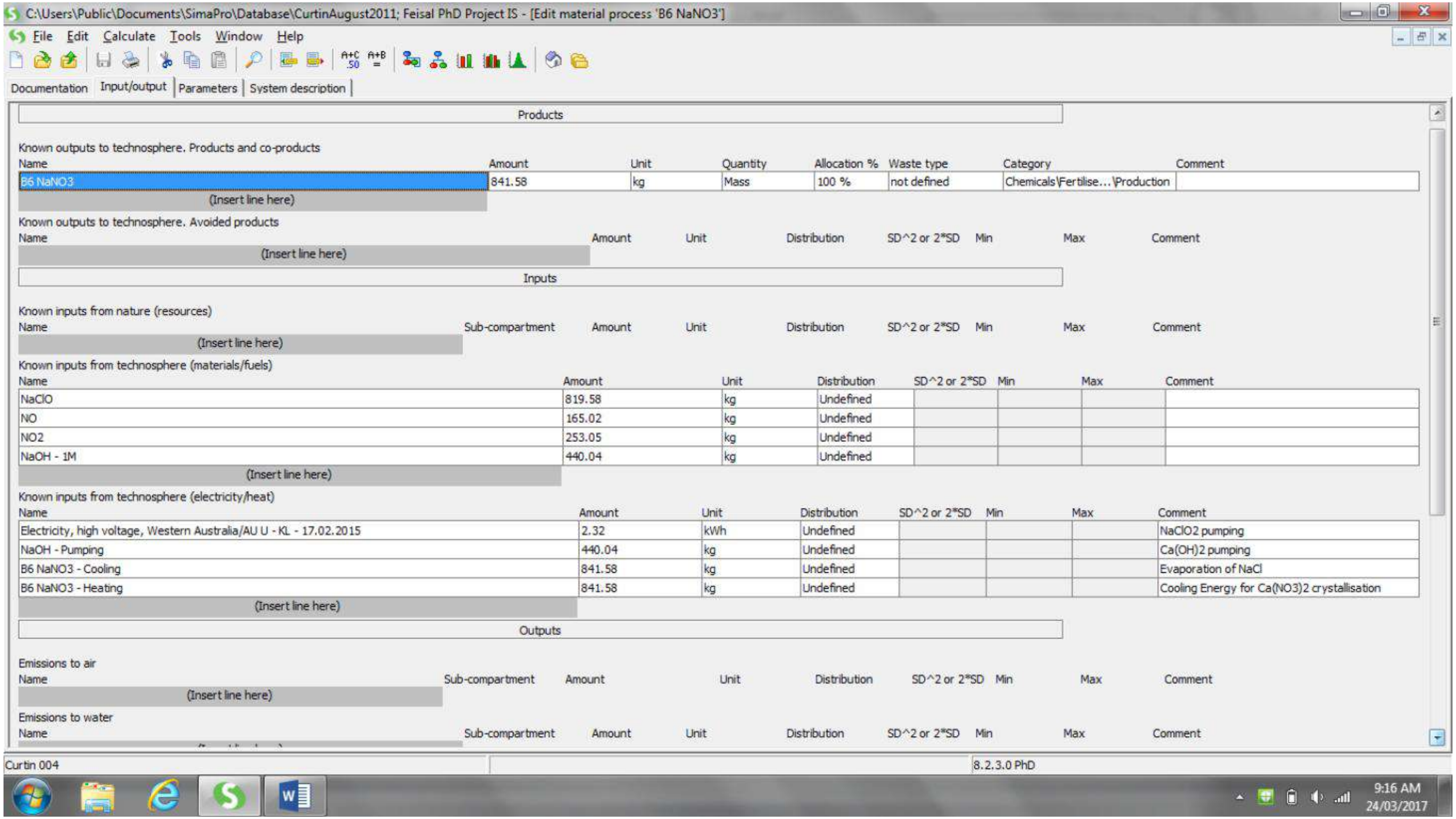
Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment

(Insert line here)

Emissions to water

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment

(Insert line here)



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Products

Known outputs to technosphere. Products and co-products

Name	Amount	Unit	Quantity	Allocation %	Waste type	Category	Comment
B6 NaNO3	841.58	kg	Mass	100 %	not defined	Chemicals\Fertilise...\Production	
(Insert line here)							

Known outputs to technosphere. Avoided products

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)							

Inputs

Known inputs from nature (resources)

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Known inputs from technosphere (materials/fuels)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
NaClO	819.58	kg	Undefined				
NO	165.02	kg	Undefined				
NO2	253.05	kg	Undefined				
NaOH - 1M	440.04	kg	Undefined				
(Insert line here)							

Known inputs from technosphere (electricity/heat)

Name	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
Electricity, high voltage, Western Australia/AU U - KL - 17.02.2015	2.32	kWh	Undefined				NaClO2 pumping
NaOH - Pumping	440.04	kg	Undefined				Ca(OH)2 pumping
B6 NaNO3 - Cooling	841.58	kg	Undefined				Evaporation of NaCl
B6 NaNO3 - Heating	841.58	kg	Undefined				Cooling Energy for Ca(NO3)2 crystallisation
(Insert line here)							

Outputs

Emissions to air

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment
(Insert line here)								

Emissions to water

Name	Sub-compartment	Amount	Unit	Distribution	SD^2 or 2*SD	Min	Max	Comment