

**THE POTENTIAL FOR SHORT
TERM DEPLOYMENT OF CARBON
DIOXIDE UTILISATION
TECHNOLOGY IN THE EUROPEAN
STEEL INDUSTRY**

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Abstract

The following EngD thesis presents research performed by the author on the potential for short term deployment of carbon dioxide utilisation technologies within the context of the European steel industry, in collaboration with Tata Steel Europe. The aim of the project was to identify options for short term utilisation of CO₂ directly from steelmaking process exhausts and then evaluate them in terms of their technical feasibility, CO₂ reduction potential and economic sustainability. An initial review of steel production processes and CDU routes resulted in the selection of two potentially promising processes for further investigation; production of precipitated calcium carbonate (PCC) from steelmaking wastes, and combined biomass production and steelmaking wastewater remediation using microalgae. Each technology was investigated experimentally to determine its technical feasibility, and then via a techno-economic evaluation in order to estimate the scale of potential CO₂ mitigation and economic viability.

Investigations into the technical feasibility of the PCC process were focused on two areas; extraction of calcium from waste material using ammonium chloride, and the carbonation of the resulting calcium rich solution by direct contact with steelmaking exhaust gas. Results from extraction work indicated that calcium can be leached from waste materials with a very high selectivity (>95%) and moderate efficiency (<60%) using ammonium chloride, but that co-leaching of sulfur from feed materials could lead to operational issues when the plant is scaled up. In addition, mineralogical effects of the extraction process on the slag were reported at both a micro and macro scale. The objective of work into the carbonation step was to determine the effect of using flue gas as a source of CO₂ on the product. Trials were undertaken to test the process using flue gases from a steelworks power station; results showed that the production of high purity (>99%) PCC with a suitable morphology to be taken to market is technically feasible

using flue gases directly, although elevated sulfur concentration in the precipitate did reduce purity in some samples.

Technical work on the microalgae process consisted of a series of four cultivation trials, where two microalgae species were cultured in varying wastewater, nutrient and CO₂ concentrations. Results from these trials showed that microalgae could be successfully cultivated in undiluted steelmaking wastewater when supplemented with some additional nutrients (phosphorus), and that elevated levels of CO₂ could potentially boost both growth rate and nitrogen removal. The cultivation process was found to be very effective at removing nitrogen from the wastewater, with removal efficiencies of up to 93.4% observed.

Although both technologies were deemed to be technically feasible, when techno-economic evaluations were performed it became clear that neither technology is likely to be able to achieve significant CO₂ emissions reductions (reduction is limited to less than 1% of typical integrated site emissions). Despite this, economic estimates for a scaled up PCC production process were promising; a moderate payback on capital expenditure of around 5.51 years was estimated under baseline conditions, with a significant additional revenue potential if the process were credited under the European Union Emissions Trading Scheme. In contrast, the microalgae based process was found to be highly uneconomical when using technology which is currently available at a commercial scale, and the CO₂ mitigation potential was determined to be limited by the indirect CO₂ emissions from very high electricity demands as the process is scaled up.

The following thesis contributes knowledge in a number of areas to the field of mineral carbonation; developments regarding the mineralogical effects of calcium extraction from steelmaking slag were published in *Minerals Engineering* (Hall, *et al.*, 2014), the effect of using of steel works flue gas on the product quality during production of precipitated calcium carbonate were presented at the International Conference on

Carbon Dioxide Utilisation 2015 in Singapore, and the associated paper was invited and subsequently has been accepted to Environmental Science and Pollution Research (Springer) pending revision (as of February 2016). In addition, this work contributes a number of findings to the field of microalgal CO₂ utilisation; it presents a realistic portrayal of the techno-economics of deploying an open pond microalgae cultivation and CO₂ sequestration facility adjacent to a steelworks (presented and published in proceedings of the at European Steel Energy and Environment Congress 2014, Middlesbrough) and experimental work assessing the feasibility of cultivating microalgae in steelmaking wastewater (presented and published in proceedings of the European Union Biomass Conference and Exhibition 2014, Hamburg).

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List of Abbreviations

AEL	Advanced Emission Level
APC	Air Pollution Control
BAT	Best Available techniques
BET	Biological Effluent Treatment
BF	Blast Furnace
BFG	Blast Furnace Gas
BOS	Basic Oxygen Steelmaking (also known as the Linz-Donawitz process)
CAPEX	Capital Expenditure
CCA	Climate Change Agreement
CCS	Carbon Capture and Storage
CDU	Carbon Dioxide Utilisation
COD	Chemical Oxygen Demand
COG	Coke Oven Gas
CV	Calorific Value
DAF	Dissolved Air Flootation
DECC	Department of Energy and Climate Change (UK gov)
EAF	Electric Arc Furnace
EDX	Electron Dispersive X-ray spectrometry
EU ETS	European Union Emissions Trading Scheme
FTIR	Fourier Transform Infra-Red spectrometry
GCC	Ground Calcium Carbonate
HMD	Hot Metal Desulfurisation (slag)
HRAP	High Rate Algal Pond
ICP	Inductively Coupled Plasma
JM	Jaworski's Medium
JM-n	Nitrogen deficient Jaworski's Medium
ktpa	kilo-tonnes per annum
MLA	Mineral Liberation Analysis
MS	Mass Spectrometry

Mtpa	Mega-tonnes per annum
NO _x	Combustion derived nitrogen oxides
OD	Optical Density
OES	Optical Emission Spectrometry
OPEX	Operating Expenditure
PBR	Photobioreactor
PCC	Precipitated Calcium Carbonate
SEC	Specific Energy Consumption
SEM	Scanning Electron Microscope
SO _x	Combustion derived sulfur oxides
SS	Secondary Steelmaking (slag)
TN	Total Nitrogen
TOC	Total Organic Carbon
ULCOS	Ultra-Low CO ₂ Steel (EU funded research project)
XRD	X-ray Diffraction spectrometry
XRF	X-Ray Fluorescence spectrometry

Table of Contents

Abstract.....	iii
Acknowledgements.....	vi
List of Abbreviations	vii
1. Introduction	1
1.1 Background	1
1.2 The Engineering Doctorate scheme	2
1.3 Tata Steel company profile	2
1.4 Rational for the project.....	3
1.5 Project Aims and Objectives.....	4
1.6 Thesis structure	5
2. Iron and steel production in a carbon constrained world.....	10
2.1 Background	10
2.2 Integrated steelmaking processes	12
2.3 Climate change policy and emissions trading.....	17
2.4 Limits to energy efficiency	21
2.5 Breakthrough technologies in low CO ₂ steelmaking	23
2.6 Carbon capture and storage (CCS) in the steel industry	25
2.7 CO ₂ utilisation in the steel industry.....	27
2.7.1 International perspective	29
2.7.2 Technology selection criteria	30
2.7.3 Direct CO ₂ use.....	32

2.7.4 Chemical CDU processes.....	33
2.7.5 Biological CDU processes	39
2.7.6 Mineral CDU (Mineral Carbonation) processes	41
2.8 Summary and processes for further research	45
3. Production of high purity precipitated calcium carbonate from steelmaking residues	50
3.1 Indirect carbonation of alkaline industrial residues	50
3.1.1 Acid based routes	53
3.1.2 Ammonium salt based pH swing process	55
3.1.3 Precipitated calcium carbonate	61
3.1.5 Utilisation of calcium extraction residue	64
3.1.5 Residue pre-treatment	65
3.1.5 Summary and research focus	66
3.2 Alkaline residues produced at an integrated steelmaking site	67
3.2.2 Materials selection and preparation	69
3.3 Experimental methods	70
3.3.1 Calcium extraction	70
3.3.2 Carbonation experiments	71
3.3.3 Analysis.....	72
3.3.4 Calculations.....	74
3.4 Calcium extraction.....	76
3.4.1 Preliminary analysis.....	76
3.4.2 Calcium extraction	77

3.4.4 Summary	85
3.5 Effect of steelmaking exhaust gases on the carbonation process and products .	87
3.5.1 Process efficiencies and CO ₂ sequestered	87
3.5.2 Effect of flue gas on the product	90
3.5.3 Precipitate morphology	92
3.5.4 Summary	96
3.6 Chapter summary	97
4. A techno-economic evaluation on the production of precipitated calcium carbonate from steelmaking residues	99
4.1 Introduction.....	99
4.2 Methodology	99
4.2.1 Plant design	100
4.2.2 Mass and Energy balances.....	102
4.2.3 Unit operations	104
4.2.4 Capital costs	106
4.2.5 Direct production costs (OPEX).....	107
4.2.6 Product revenue and other considerations	109
4.2.7 Software.....	109
4.3 Milling optimisation.....	109
4.4 CO ₂ balance.....	112
4.5 Plant economics	114
4.6 Sensitivity analysis.....	117
4.7 Chapter summary	120

5. Combined steelmaking wastewater remediation and CO ₂ utilisation using microalgae	122
5.1 Microalgae growth requirements, cultivation and uses	122
5.1.1 Microalgae growth and limiting factors	123
5.1.2 Large scale cultivation systems.....	128
5.1.3 Products from microalgae	131
5.1.4 Use of microalgae in wastewater treatment	132
5.1.5 Direct flue gas utilisation at steelworks	133
5.2 Wastewater production at an integrated steelmaking site	135
5.2.1 Biological Effluent Treatment (BET) Plant	136
5.2.2 Treatment of BET effluent with microalgae	137
5.3 Materials and Methods	137
5.3.1 Microalgal species, source and maintenance	138
5.3.2 Cultivation trials.....	138
5.3.3 Analyses	142
5.3.4 Calculations.....	142
5.3.5 Statistical analysis	143
5.4 Results and Discussion	143
5.4.1 BET plant effluent composition and variability	143
5.4.2 Trial 1: Toxicology Screen.....	145
5.4.3 Trial 2: N use efficiency.....	148
5.4.3.2 Nitrogen removal	150
5.4.4 Trial 3: <i>S. obliquus</i> N-use efficiency with added PO ₄	153

5.4.5 Trial 4: N-use efficiency with PO ₄ and CO ₂ amendments.....	158
5.4.5.2 Nitrogen removal.....	162
5.5 Chapter summary and conclusions.....	167
6. A techno-economic evaluation of combined microalgae production and wastewater treatment at an integrated steelmaking site.....	169
6.1 Scope and process description	169
6.2 Methodology.....	171
6.2.1 Microalgae cultivation	171
6.2.2 Harvesting.....	172
6.2.3 Anaerobic digestion	173
6.2.4 Nutrient requirements	173
6.2.5 Electricity requirements.....	175
6.2.6 CO ₂ balance	177
6.2.7 Operational expenditure.....	178
6.2.8 Capital expenditure.....	179
6.2.9 Data analysis	181
6.3 Results and discussion	181
6.3.1 Pond design.....	181
6.3.2 CO ₂ balance	183
6.3.3 Plant economics	186
6.3.4 Optimised scenario	189
6.4 Opportunities for improvement.....	190
6.5 Chapter summary	191

7. Technology appraisal, conclusions and recommendations.....	193
7.1 Technology appraisal.....	193
7.1.1 Economical potential.....	193
7.1.2 CO ₂ mitigation potential	195
7.1.3 Impact of reductions in CO ₂ emissions from grid electricity	197
7.1.4 Advances in microalgae biotechnology	198
7.2 Conclusions.....	199
7.2.1 PCC production process.....	200
7.2.2 Combined CO ₂ capture and wastewater treatment using microalgae	201
7.2.3 Overall conclusions.....	202
7.2.5 Recommendations to Tata Steel.....	203
7.2.6 Recommendations for further work	204
References	207
Appendix A: Supplementary data on analysis of PCC.....	238
Appendix B: Culture medium composition.....	241

1. Introduction

1.1 Background

Steel has in many ways come to shape the modern civilisation of today. Its combined strength and formability render it invaluable to a wide range of applications; from construction to engines, power generation to food packaging and white goods to cutlery. Steels versatility, coupled with the projected increasing world demand (Wortler *et al.*, 2013) suggests that steel will continue to be an essential material well into the 21st century. Society is under increasing social, political and environmental pressure to rapidly transition to a low carbon economy due to the effects of human induced climate change, and steel is expected to play a key role in this transition due to its use in many enabling technologies including wind turbines and nuclear power. Paradoxically though, steel itself is highly carbon intensive to produce from raw materials; contributing approximately 6.7% to world carbon dioxide (CO₂) emissions (WSA, 2012). In order for a low carbon economy which uses steel to be realised, steel production itself must be decarbonised; a problem which poses significant challenges.

The following thesis evaluates the role that carbon dioxide utilisation (CDU) technologies can play to reduce CO₂ emissions within the European steel industry. While there is a wide breadth of literature in the area of CO₂ utilisation, the majority of these works are from a purely academic perspective. In contrast, the current thesis is intended to provide a more applied approach. The research focuses on two technologies determined to be the most promising for short term implementation:

- Carbonation of calcium rich steelmaking residues to produce high purity precipitated calcium carbonate.
- Remediation of steelmaking wastewater and biomass production using photosynthetic microalgae.

This chapter is intended to introduce the reader to the engineering doctorate scheme, the industrial partner, and the project including a brief rationale behind the technologies selected for the research. The aims of the thesis are set out and eight objectives are presented. Finally, the thesis structure is outlined and explained and an overview of publications is given.

1.2 The Engineering Doctorate scheme

The project is part of the University of Nottingham's Industrial Doctorate Centre in Efficient Fossil Energy Technologies co-funded by the Engineering and Physical Sciences Research Council (EPSRC) and Tata Steel as an industrial partner. The Engineering Doctorate (EngD) was undertaken over a period of 4 years; the first of which consisted of taught technical, business and social responsibility courses at the university. This was followed by three years of research based in the Environmental Technology department of Tata Steel's Swindon Technology Centre research facility in Rotherham.

1.3 Tata Steel company profile

Tata Steel Group is a large multinational steel producer which was founded in India in 1907 and is a major constituent of the much larger Tata Group. It was the 11th largest global steel producer in 2013, with an output of 25.3 million tonnes of crude steel (WSA, 2014). Tata Steel Europe is the subsidiary which governs the company's European operations, which became part of the group in 2007 following Tata's acquisition of Corus Group. European manufacturing operations consist currently of three integrated sites at Port Talbot (UK), Scunthorpe (UK) and IJmuiden (NL), one electric steelmaking site in Rotherham (UK) and a number of satellite rolling mills located throughout Europe. Total European production capacity is 18 million tonnes per year, over two thirds of the group total (Tata Steel, 2014). The following work is set within the context of Tata Steel's European integrated sites, but is applicable more broadly across the group and to primary steel production in general.

1.4 Rational for the project

The implementation of the European Union emissions trading system (EU ETS) means that emissions of CO₂ from Tata Steel Europe's large manufacturing sites currently incur costs of around £10¹ per tonne of crude steel produced. Although this cost is currently quite low, the traded CO₂ price reached a high in 2008 of around £24.79² (€30 at 2008 exchange rate) per tonne and the nature of the system means it is expected to increase substantially above the current value in the near future. If exposure to this cost in the short term can be reduced through deployment of carbon dioxide utilisation processes, this could provide a commercial advantage. CO₂ mitigation through utilisation is not currently credited through the system, though there is the scope for a change in legislation to include it in Phase VI, which begins in 2021 (Hendriks *et al.*, 2013). In addition to limiting future EU ETS exposure, the deployment of such technology could give further advantages to Tata Steel by satisfying stakeholder demand for increased sustainability and reduced environmental impact.

Carbon dioxide utilisation (CDU) comprises a broad range of technologies which treat CO₂ as a resource that can be used as a feedstock to produce products including fuels, chemicals and polymers. By implementing CDU, not only can emissions be sequestered from industrial sites, but the products can be sold to offset costs and generate additional revenue. In addition, further CO₂ emissions can sometimes be avoided indirectly by reducing demand for mined raw materials.

CDU differs from the more widely known CCS (Carbon Capture and Storage) because the CO₂ is ultimately used to produce a product. As the CO₂ is chemically stabilised in a product, CDU can avoid the public perception issues surrounding underground CO₂ storage which have limited CCS progress in some European countries. However, most

¹ Estimate based on current (Feb 2015) carbon price of approximately £5 per tonne (EEX, 2015) and typical integrated route steelmaking emissions of 2 tonnes of CO₂ per tonne of crude steel (Birat, 2010).

² Using an exchange rate of 1.21 EUR/GBP (December 2008)

CDU processes in development are only able to process pure streams of CO₂ meaning that they are dependent on the successful future implementation of CCS technology to purify CO₂ from exhaust gases, at very high costs. A small number of CDU processes have the potential to treat flue gases directly meaning that they could be deployed on a smaller scale and on a shorter timescale. These technologies will be the focus of this thesis.

1.5 Project Aims and Objectives

The overarching aim of this thesis is;

“To provide Tata Steel with a basis from which they are able to make an informed decision as to whether short term implementation of carbon dioxide utilisation can be technologically feasible and economically sustainable as a means to reduce CO₂ emissions from primary steelmaking processes.”

The following thesis gives a detailed technical analysis and an economic overview of two of the most appropriate short term CO₂ utilisation options for the steel industry; production of high purity precipitated calcium carbonate using calcium rich steelmaking residues as feed stocks, and combined steelmaking wastewater remediation and biomass production process using photosynthetic microalgae. In order to determine applicability of each technology to the industry, consideration is given to integration of CDU into existing steelmaking operations, with the intention for the technologies to be complementary to current processes.

Eight objectives for this thesis are outlined below:

1. To review CDU process routes currently in development in order to determine which are most promising as options to undertake research on (Chapter 2).
2. To determine the potential to use steelmaking wastes as feed stocks for CDU processes, in order to reduce material costs and to add additional value due to avoided disposal or treatment costs (Chapters 2, 3 and 5).

3. To investigate the application of precipitated calcium carbonate manufacture from wastes to residues produced at Tata sites (Chapter 3).
4. To demonstrate the direct use of steelmaking flue gas in production of calcium carbonate from steelmaking residue and to determine the effect of flue gas impurities on the resulting product (Chapter 3).
5. To investigate the application of microalgae cultivation as a combined wastewater treatment and CO₂ utilisation technology to wastewater produced at a Tata site (Chapter 5).
6. To determine the effect of flue gas level CO₂ concentrations on the growth rate and wastewater remediation potential of microalgae (Chapter 5).
7. To perform technical and order of magnitude economic evaluations for each technology (Chapters 4 and 6).
8. To provide recommendations to Tata Steel on which processes, if any, are candidates for further development and future implementation (Chapter 7).

1.6 Thesis structure

The thesis is split into seven chapters in order to guide the reader through the logical flow of the research. The research focuses in detail on the technical and commercial feasibility of the two most promising CDU routes, rather than attempting to consider more options at a higher level. It was felt that this would best suit the aim of providing solutions which are deployable in the short term. The routes chosen for investigation are (a) production of high purity precipitated calcium carbonate from calcium rich steelmaking residues and (b) combined biomass production and remediation of steelmaking wastewater using microalgae. An overview of the thesis structure is presented in Figure 1.1.

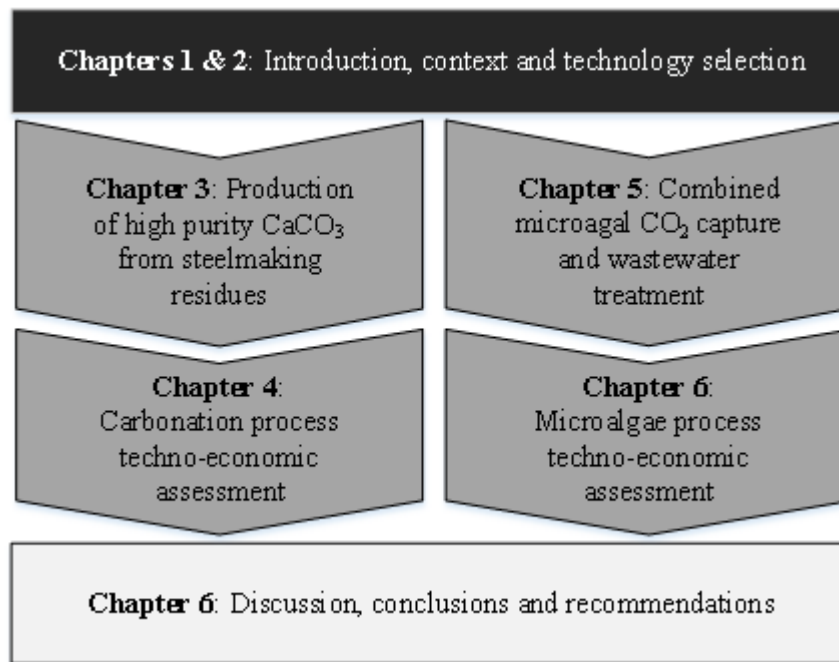


Figure 1.1: Overview of the thesis structure

A more detailed description of the six chapters which follow this introduction is given below;

Chapter 2: The context of the project is set by reviewing current steelmaking processes, the impact of climate change policy on the industry and options available for achieving significant CO₂ reductions. In this context the broad subject of CO₂ utilisation is introduced and discussed. Options for further investigation are refined to those where there is maximum potential for short term deployment and integration into existing plant functions.

Chapter 3: In Chapter 3, the production of precipitated calcium carbonate (PCC) from steelmaking wastes using an ammonium chloride additive is investigated experimentally. Suitable materials produced at integrated steelmaking sites are assessed for availability and samples of residues which are currently treated as wastes are obtained. These materials are characterised for mineralogy and chemistry both before and after extraction of calcium.

Results are then presented from trials which were conducted at a steelmaking site, using steelworks power station flue gas to directly carbonate the leachate. The calcium carbonate (CaCO_3) product is compared to that produced using bottled CO_2 and samples of commercial grade PCC in order to determine the effect of flue gas impurities on the product quality.

Chapter 4: In Chapter 4, a techno-economic model is presented to give a rough evaluation of whether the process has economic and CO_2 mitigation potential. A preliminary design is made on a PCC production plant fed with calcium rich Tata wastes, units are sized and an order of magnitude estimate of capital and operating costs is made.

Chapter 5: In Chapter 5, the area of microalgae biotechnology is reviewed and it is concluded that the most promising option to pursue is the combined CO_2 utilisation and remediation of steelmaking wastewater in high rate algal ponds. A treated steelmaking effluent with a high concentration of the nutrients required to sustain algal growth was identified and sampled, and this forms the basis for subsequent work. Survival trials using *Chlorella vulgaris* are presented as a means to determine the toxicity of the effluent and its suitability as a growth medium. This is followed by multiple growth trials using two algal species, *Scenedesmus obliquus* and *Chlorella vulgaris* in order to determine the relative growth rate, biomass production, wastewater nitrogen remediation and the benefit, if any, of introducing simulated flue gas to the cultures.

Chapter 6: In chapter 6, a techno-economic assessment of is presented, based on the concept of a combined wastewater treatment and CO_2 utilisation plant developed in Chapter 5. A plant design is outlined and basic operating and

capital cost estimates are made. The viability of the plant is then considered based on product (biogas) price competitiveness, CO₂ capture cost and potential capture capacity.

Chapter 7: In order to conclude the thesis, results from the techno-economic works are evaluated side by side, following which conclusions to the thesis are presented and recommendations to Tata Steel and for future work are offered.

The research presented in this thesis has resulted in 3 publications; 1 publications in peer reviewed journals and 2 publications in conference proceedings. A further journal paper is currently in preparation. An outline of each publication is given in Table 1.1.

Table 1.1: Summary of publications resulting from the research presented in this thesis.

Authors	Title	Publication	Theme ¹	Description
C. Hall., D. J. Large., H. M. West., B. Adderley	<i>Calcium leaching from waste steelmaking slag: Significance of leachate chemistry and effects on slag grain mineralogy.</i>	Minerals Engineering 65 (2014); 156 – 162	PCC	The paper presents observations on the chemical and mineralogical composition of waste slag prior to and following calcium extraction in ammonium chloride. In addition, the chemistry of the leachate is examined in the context of potential engineering challenges during scale up of the process.
C. Hall., H.M. West, D. J. Large., B. Adderley	<i>Microalgae at an integrated steelmaking site: Treated cokemaking effluent as a water and nitrogen nutrition source.</i>	Proceedings of the 22 nd European Biomass Conference and Exhibition, 23 rd –26 th June 2014; Hamburg, Germany	MWT	The paper presents results from initial microalgae cultivation and survival growth trials in steel making waste water. Comparisons are drawn between growth rate, biomass production and waste water remediation between cultures in differing dilutions of waste water and specially prepared culture medium.
C. Hall., H.M. West., D. J. Large., B. Adderley	<i>Current and future potential for deployment of a combined microalgae wastewater treatment and carbon capture process at an integrated steel works.</i>	Proceedings of the European Steel Environment and Energy Congress, 15 th – 17 th September 2014; Middlesbrough, UK	MWT	The paper presents a techno-economic study on deployment of a combined microalgal wastewater treatment and CO ₂ utilisation plant at an integrated steelworks.
C. Hall., D.J. Large, B. Adderley., S. Woolass., H. M. West	<i>The impact of flue gas impurities on product quality in the production of precipitated calcium carbonate via indirect carbonation of steelmaking residues</i>	In preparation (Environmental Science & Pollution Research)	PCC	The paper presents results from in situ PCC production trials using steelmaking power station exhaust gases. The purity and morphology of the PCC product obtained from these trials is discussed and compared to that of samples produced from bottled gas and samples which were commercially obtained.

¹ The technology which the paper addresses; precipitated calcium carbonate production (PCC) or microalgal wastewater treatment (MWT)

2. Iron and steel production in a carbon constrained world

In this chapter the context of the project is set by reviewing current steelmaking processes, the impact of climate change policy on the industry, and options available for achieving significant reductions in CO₂ emissions. The case will be made that not only will carbon continue to be used as the reductant in primary steelmaking for the foreseeable future, but also that the potential for future emissions savings from increased energy efficiency are very limited. When these factors are combined, it follows that the only realistic option for reducing emissions in line with global and national targets is downstream management of the CO₂ produced. The economic uncertainties surrounding the application of carbon capture and storage (CCS) to steelmaking will be discussed, and the concept of indirectly and directly using CO₂ from flue gases as a feedstock for chemical and biological processes via carbon dioxide utilisation (CDU) will be explored. Finally, the two most appropriate CDU options for the steel industry will be selected as the basis for further research in Chapters 3, 4 and 5 and 6.

2.1 Background

Since the beginning of industrialisation, carbon dioxide concentrations in the atmosphere have increased by approximately 30% to over 400 ppm from an average in 1760 of around 278 ppm (Dlugokencky and Tans, 2016). Although natural fluctuations in the Earth's temperature are common, it is widely accepted that the recent increase in CO₂ concentrations is a direct result of anthropogenic activities and that this has been responsible for a temperature increase of almost one degree Celsius over the last century. If atmospheric CO₂ concentrations continue to increase it is highly likely that

there will be further rapid temperature increases in the near future. It is anticipated that such rapid increases of temperature will result in sea level rises, retreat of glaciers and an increase in the frequency and intensity of droughts along with increased acidification of the oceans (IPCC, 2013). Such effects would prove devastating to at least some of the human population, and in order to mitigate them there is substantial social and political pressure to make the transition to a low carbon economy.

Within a low carbon economy, steel is likely to keep many of its current applications while at the same time taking on increasing roles in low carbon technologies such as in wind power, next generation nuclear power and electric vehicles. Steel production from raw materials is however highly carbon intensive and must itself be decarbonised.

In order to be able to consider the options for reducing CO₂ emissions from steel production it is essential to understand current production processes. The vast majority of steel is produced via two routes, the blast furnace (BF)/basic oxygen steelmaking (BOS) process and the electric arc furnace (EAF) process. The first is referred to as the primary route because it is currently responsible for the highest volumes, producing steel from raw materials by chemically reducing mined iron oxide ore to metallic iron and accounting for around 70% of the total world steel production. The EAF process is termed secondary steelmaking, is principally used for the recycling of scrap steel into new products and accounts for around 29% of the total world production (WSA, 2015). EAF production uses electricity as an energy source, so decarbonisation of this process can be coupled with decarbonisation of the electricity grid. In contrast, primary route steelmaking uses carbon in the form of coke as a chemical reductant and to supply heat to the furnace.

The need for steel production from raw materials is likely to remain for the long term as steel demand is forecast to increase at least until 2050, and recycling alone cannot meet this increase in demand (Wortler *et al.*, 2013). Huge economies of scale help to

enable producers to maintain competitive prices, while non-carbon based reduction technologies are unlikely to be available at such scales for the foreseeable future due to the high cost of research, development and implementation (Birat *et al.*, 2008a).

Multiple independent processes are required in primary steelmaking and are typically all located on a single site in order to achieve economic benefits from a localised and integrated supply chain. This is referred to as “integrated steelmaking”. The following section demonstrates the complexity of these sites from a carbon management view point by outlining each of the major CO₂ producing processes at an integrated site, quantifying the CO₂ produced at each as a proportion of the total site emissions and examining the composition of the CO₂ containing exhaust.

2.2 Integrated steelmaking processes

Integrated steelmaking sites are very large, consisting of multiple interconnected but independent plants. The main raw materials for producing iron in a blast furnace are coal, iron ore and fluxes such as lime. These are brought to the site by ship, train and road freight and stored in large materials handling areas.

Iron ore is delivered in varying forms; lump, pellet or fines. Lump ore is that which is directly charged to the furnace without pre-treatment. In order to be charged directly, the ore must be within a narrow size range (8 mm-40 mm) (Geerdes, 2009). The nature of milling processes mean that the majority of ore falls below this range and must be agglomerated into larger particle size, either by pelletizing or sintering, depending on material size. Small particles (<0.15 mm) are pressed into pellets, often at the mine site (Geerdes, 2009). Sintering is typically carried out on an integrated site at the sinter plant where fines (0.15 mm – 6 mm) of iron ore, lime and coke are all agglomerated at high temperature into a porous lump type material (Walker, 1986; Geerdes, 2009). The sinter plant is also used to recycle iron, calcium or carbon rich wastes and residues from other processes back into the blast furnace (Walker, 1986; Geerdes, 2009), helping to

maximise materials efficiency and reduce waste. Sintering is typically responsible for 15-20% of total emissions at an integrated site with a typical exhaust composition in the region of 5-10% CO₂, 100-200 ppm SO₂ and 80-170 ppm NO_x (Carpenter, 2012; Tata Steel internal documents and discussion).

The second raw material, coke, is a porous carbon rich solid produced through high temperature (900 - 1200 °C) pyrolysis of suitable “coking” coals in the absence of oxygen. This process drives off the majority of volatile content in the coal, to leave a highly porous, carbon rich material called coke. Coke making is a batch process performed in refractory lined coke oven batteries, of which there can be upwards of 50 at each plant. After the coking process is complete, coke is discharged by a horizontal hydraulic ram into a rail car before being rapidly quenched to prevent combustion (Walker, 1986). Volatile gases released from the coal during coking are collected and processed at a coke oven by products plant, where various components such as naphtha, cyclic hydrocarbons and ammonia/ammonium sulfate are stripped from the gas (Walker, 1986). In the past these components were removed as valuable by products, however more recently the main driver to remove these components is to improve the quality of the resultant coke oven gas (COG) as a fuel. COG is the most energy rich of the works arising gases at an integrated site, with a typical calorific value of 18 MJ/Nm³ in the UK (Whiting, 2011). Following clean-up, a proportion of COG is used mixed with blast furnace gas to provide the required heat for coking, and the remainder is exported for use elsewhere on the site. CO₂ emissions from this combustion at the coke ovens account for 15-20% of the site total, with a typical flue gas composition of 25% CO₂, 200 ppm SO₂ and less than 10 ppm NO_x (Carpenter, 2012; Tata Steel internal documents and discussion).

Lime as both quicklime and calcined dolomite is used as a flux in furnaces including the blast (BF) and steelmaking (BOS) furnaces. Fluxes are used to increase the fluidity

of non-metal impurities in the furnace and promote their transfer from the hot metal into slag which can be easily separated. Calcination of limestone and dolomite is performed at a lime kiln plant. Lime kilns in Europe are typically owned, operated and located independently from the integrated steel mill (IEA, 2012) and so will not be considered in any detail here. Although the calcination process does contribute to the total CO₂ emissions from primary steelmaking, the integrated plant operator has little control over emissions from this process and therefore for the purposes of this study, lime plant emissions have been excluded when calculating the total emissions from site.

The blast furnace reduces iron ore to metallic iron and is the core reactor(s) at an integrated site. It is the largest source of CO₂, accounting for around 70% of the total (Carpenter, 2012). The furnace is a large vertical shaft of circular cross section and comprises five main sections. At the bottom of the shaft is a parallel sided hearth, where liquid metal and slag collect. This is surmounted by an inverted truncated cone known as the bosh. A short vertical section called the barrel connects the bosh to the stack, a truncated upright cone which in turn supports the throat. Iron ore, coke and fluxes together form a solid charge at the throat of the stack and are carried to this point by either conveyor or skip car loading. At the same time, pre-heated oxygen enriched air (the “hot blast”) is blown into the hearth through tuyeres. Combustion of coke immediately in front of the tuyeres generates a large amount of heat which is largely transferred to the burden by the ascending gasses. The gasses, which are rich in CO as they leave the combustion zone, partially reduce the iron oxides present in the iron ore and oxygen is transferred from the ore to the gas. Around 60% of the original oxygen content of the ore is removed in this way, the reduction being completed via reactions with solid carbon in the bosh and hearth. As a reactor, the blast furnace is a counter current heat and mass exchanger that effects heat transfer from gas to solid and mass (oxygen) transfer from solid to gas (Walker, 1986; Geerdes, 2009). The hot gas which leaves at the top of the furnace is cooled, cleaned and used as a low calorific value (CV

= 3-4 MJ/Nm³) (Whiting, 2011) fuel on the works called blast furnace gas (BFG). This means that although the blast furnace is the largest producer of CO₂ on a steelworks, it is not itself a point source of emissions to the atmosphere (IEA, 2012). In addition to being exported to other processes, a significant proportion of BFG is mixed with COG and burned in the blast furnace stoves, which are used to heat the hot blast (Carpenter, 2012). The blast furnace stoves are responsible for around 20% of the total site CO₂ emissions and have both high CO₂ concentrations of around 25% and low acid gas concentrations; 3 ppm NO_x and 35 ppm SO₂ (Carpenter, 2012; Tata Steel internal documents and discussion).

Liquid iron from the blast furnace is upgraded to steel in the basic oxygen steelmaking (BOS) furnace where liquid iron is charged along with some scrap steel and fluxes into a large vessel and blown with high velocity oxygen from above. The oxygen reacts with carbon in the liquid iron, reducing the carbon content to produce steel, while other impurities are dissolved in the fluxes to form a slag called BOS slag. In most modern steel plants, the gas produced in the process is collected and cleaned to be used as another works arising fuel called BOS gas. As gas is collected to be combusted elsewhere, there are usually very low direct CO₂ emissions to atmosphere from the BOS plant. BOS gas can however be flared depending on demand, producing a highly variable and intermittent CO₂ point source (Turkdogan, 1996).

Downstream of the BOS furnace, liquid steel is further refined to the customers' requirements, before being cast into a suitable shape for rolling into products in rolling mills. Rolling mills usually fire a mixture of works arising gases in reheating furnaces in order to heat the steel to a desired temperature before further processing. Exhaust gases from these furnaces are typically in the range of 10% CO₂ and represent only around 5% of total CO₂ emissions from an integrated works (Carpenter, 2012).

Integrated sites have an onsite power plant which burns works arising gases such as BFG, BOS gas and COG to produce steam to drive turbines. These turbines are used for mechanical energy to drive the hot blast to the blast furnace at a turbo blower house, and to produce electricity for use in onsite operations. This plant is typically the largest single point source of CO₂ on the site as it is where much of the gases produced in other processes are fired (Figure 2.1). As a result the power station is responsible for around 40% of the total CO₂ emissions on an integrated site (Carpenter, 2012). As the flue composition is dependent on the fuel(s) being used, it is highly variable. CO₂ concentration in the exhaust can range from 20%-30% (v/v), SO₂ concentrations between 19 ppm and 533 ppm and NO_x concentrations between 2ppm and 300ppm (Carpenter, 2012; Tata Steel internal documents and discussion). Though highly variable, the composition of individual boiler exhausts can be controlled relatively easily by fuel switching; for example to produce a flue with lower SO₂ emissions, the fuel mixture can be modified to reduce the proportion of COG.

In summary, CO₂ emissions from primary steelmaking are highly decentralised, with point sources spread out over multiple plants across a site. Flue gas compositions can vary hugely not only between point sources, but also at each source depending on the works gases being burned, which is in turn dependent on the raw material quality. The significance of this will become apparent in subsequent chapters, where the composition of flue gases will be shown to impact on processes and products when utilised directly.

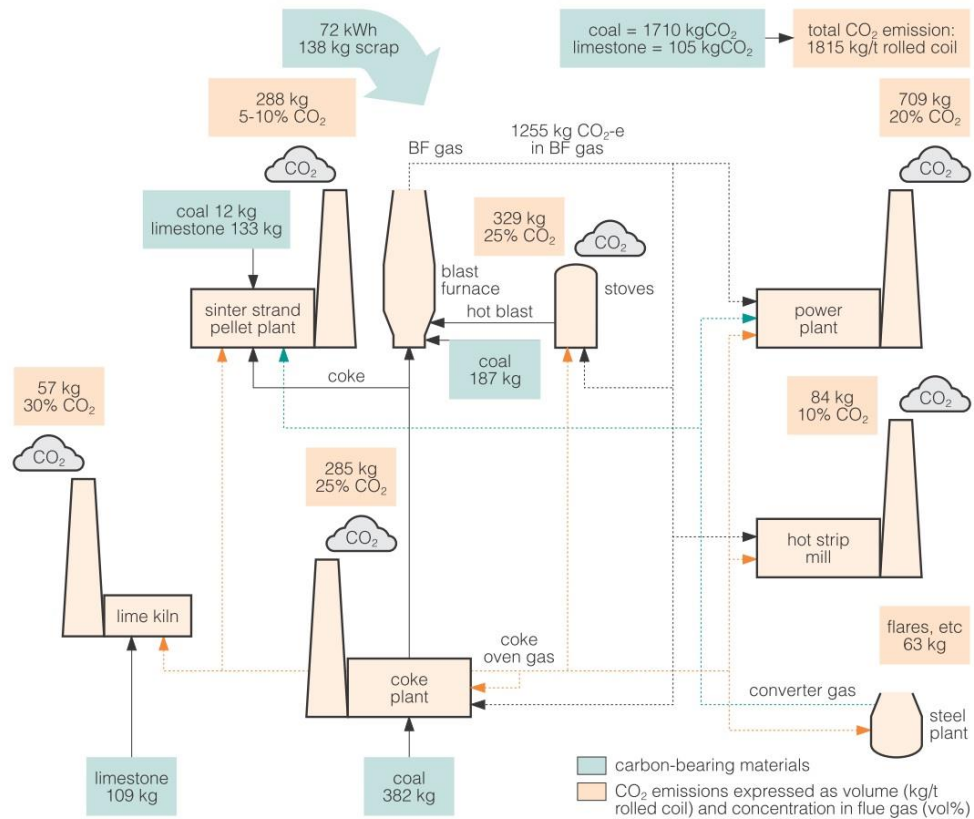


Figure 2.1: Works arising gas flows and CO₂ emissions from a typical integrated steelmaking site (Carpenter, 2012).

2.3 Climate change policy and emissions trading

World efforts to reduce greenhouse gas emissions to the atmosphere have resulted in a number of agreements, targets and laws on international, continental and national scales. An overview of these agreements and policies follows, focused on those in the EU and the UK in order to give the reader an understanding of the current policy frameworks in which Tata Steel Europe operates. The detailed mechanisms of these treaties, targets and trading schemes are extremely complicated and fall out of the scope of this thesis.

The United Nations Framework Convention on Climate Change (UNFCCC) is the primary international treaty on climate change, founded following the United Nations Conference on Environment and Development in Rio de Janeiro, Brazil in 1992. The treaty has been ratified by all United Nation member states with the objective to “stabilize greenhouse gas concentrations in the atmosphere at a level that would prevent

dangerous anthropogenic interference with the climate system" (United Nations, 1992).

The treaty is not itself legally binding, instead providing a framework for negotiating further treaties or “protocols” which can set legally binding limits on emissions (UNFCCC, 2014). The first and only protocol to date is the Kyoto protocol, which binds some of the signatory countries to emission reduction targets relative to 1990 emissions over two commitment periods; the first from 2008 to 2012, and the second began in 2013 and will expire in 2020 (UNFCCC, 2014). The treaty is signed by virtually all UN member states and is ratified by most, with the notable exception of the United States of America. Though signed by most of the world’s nations, legally binding targets are only applicable to some members within a subsection called “Annex I” countries, 37 high CO₂ emitting and industrialised countries including the 15 original European Union nations, Russia, Canada, Australia and Japan (UNFCCC, 2014).

The European Union (EU) has implemented a number of its own policies which are designed to ensure that the Kyoto Protocol commitments are met and to hasten the decarbonisation of European economies. The EU has committed to reducing its emissions to 20% below 1990 levels by 2020, with a further 10% reduction by 2020 offered on the condition that other major emitting countries in both the developed and developing world make similar commitments (EC, 2014a). In addition, future targets of 40% and 80-95% emissions reductions compared to 1990 levels have been proposed for 2030 and 2050 respectively (EC, 2014a).

The main mechanism by which large industrial emitters such as operators of integrated steelmaking sites have been incentivised to reduce emissions in the EU is through the European Union Emissions Trading System (EU ETS). The EU ETS is the largest emissions trading scheme in the world and currently regulates over 11,000 heavy energy using installations in 31 European countries. These installations are collectively responsible for around 45% of the EU’s total CO₂ emissions (Okereke and McDaniels,

2012). The EU ETS operates on a “Cap and Trade” principle; a limit or “cap” is set on the total amount of greenhouse gases which can be emitted by the installations and emitters are allocated allowances. At the end of each year, a company must surrender enough allowances to cover all its emissions, otherwise heavy fines are imposed. Allowances can be sold by those who have an excess to a company which is short of allowances, or can be saved for use in subsequent years, creating a market for allowances, and subsequently a CO₂ price. The cap is reduced over time so that total emissions fall, and the CO₂ price increases. This in turn should result in an increased value to cutting emissions by investing in low carbon technologies (EC, 2014b). The allocated emissions will be reduced to the extent that emissions in 2020 will be 21% lower for these installations than in 2005, and by 2030 it is proposed that they will be 43% lower (EC, 2014b).

Although reaching a peak of around ~£24.79¹ (€30) per tonne of CO₂ in 2008, the CO₂ price has since plummeted and now sits below £8.50 (€10) per tonne (Figure 2.2). The underperformance of the EU ETS market is generally accepted to be a direct result of the recent economic recession which caused an overall decline in industrial output in Europe, causing emissions to drop below the expected level. This difference resulted in the over allocation of emission allowances, contributing to a surplus of allowances which held the carbon price down in the early stages of the system (Perthuis and Trotignon, 2014). In addition to there were instances of large scale fraud which reduced confidence in the system (Perthuis and Trotignon, 2014). The carbon price has remained below all three scenarios projected by DECC (2011) for the period 2012 to 2015. While it was projected that between 2012 and 2015 the carbon price would raise from £6 to £10 per tonne in a low carbon price scenario or from £14 to £17 per tonne in a high

¹ Using an exchange rate of 1.21EUR/GBP (December 2008)

carbon price scenario, the actual price has remained fairly static within this time at almost half of the low price scenario projected value (Figure 2.2).

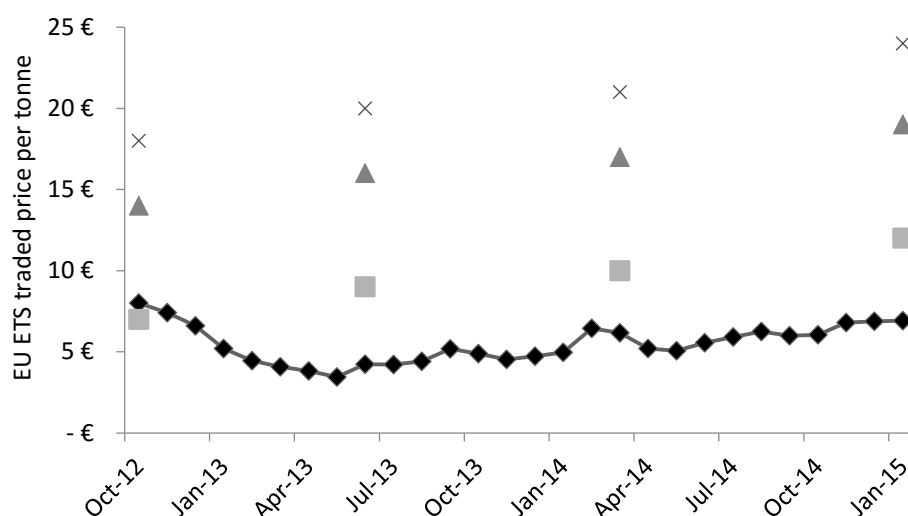


Figure 2.2: EU ETS trading price per tonne of CO₂. Solid black line represents monthly average real trading prices (ECarbix). Un-joined markers represent projected CO₂ price; (□) Low (Δ) Central and (X) High. (Market data modified from European Energy Exchange (EEX, 2015) and projections taken from DECC (2011)).

Although the over allocation of emissions allocations has meant that so far buying additional allocations has been cheaper than anticipated, the most recent stage in the system “Phase III” is designed to reduce emissions more rapidly by implementing an EU wide emissions cap which is set to reduce by 1.74% per year resulting in an emissions reduction of 21% by 2020 compared with 2005 (DECC, 2014). This should result in a substantial rise in the CO₂ price as demand for allowances begins to outstrip a diminishing supply. CO₂ mitigation achieved through CDU technologies is not currently credited by the scheme; however there is scope for progress to be made toward achieving this prior to implementation of Phase IV in 2021 (Hendriks *et al.*, 2013). Although the EU ETS has underperformed in the first two phases of implementation, it is the authors view that the system can provide a viable incentive for investment in CO₂ reduction technology, and that the removal of the process would be a backward step in

addressing climate change. However, steps must be taken by the European community to push for an international carbon trading system in order to prevent outsourcing emissions to areas which do not have a trading system in place.

The UK has a number of national level policies intended to mitigate the effects of climate change. The UK government set legally binding targets for CO₂ emissions reduction in 2008 through the Climate Change Act. The act mandates that all six greenhouse gases covered by the Kyoto Protocol, including CO₂, must be cut to 80% below 1990 levels by 2050 (Climate Change Act 2008). The Climate Change Levy was introduced in 2001 as a means to incentivise energy efficiency and electricity generation from renewables. The levy applies to fossil fuels and electricity (except that generated from renewable sources) to all sectors except transport and domestic use (UK Government, 2014a). Energy intensive industries including iron and steel are eligible for reduction of up to 90% on the levy price if they sign up to the Climate Change Agreement. This aims to minimise the exposure of heavy energy users to the additional costs of the climate change levy, but requires the industries meet agreed targets for improving energy efficiency (UK Government, 2014b).

In modern integrated steelmaking processes, the opportunities for further energy efficiency savings are limited and will be unable to meet the demand for CO₂ reductions in order to meet the UK targets, or to adequately reduce exposure to the EU ETS. The following section outlines the reasons behind these limitations.

2.4 Limits to energy efficiency

The specific energy consumption (SEC) (the energy consumed per unit of product produced) of primary steel production is highly dependent on a number of factors including the process used and the raw materials available. A general trend is that the SEC of steel production has been decreasing for a number of decades, especially in the developed world. As efficiency is directly related to operating costs and profit margin,

process optimisation has played a key role in keeping steel industries competitive among rising fuel and energy costs. The average SEC of steel production can be as much as twice as high in developing economies such as Russia, China and India than in more developed economies such as the EU or Japan. This lower performance can be explained by a number of factors such as the use of outdated and inefficient processes in Russia and former Soviet states, poor quality ore in China and inferior coal quality in India (ABB, 2011; Bhaktavatsalam, 1995). Despite these local differences, the world average SEC of steel production almost halved in the second half of the 20th century; falling from around 46 GJ/tonne of crude steel (tcs) in 1950 to around 25 GJ/tcs in 1990 (Bhaktavatsalam, 1995). Furthermore, between 1990 and 2008, the SEC in the EU-27 steel industries fell by another 27% (EEA, 2011).

Overall energy efficiency figures for the steel industry by country can be misleading because they often bundle primary and secondary production routes together. Due to the significantly lower energy demand for using the EAF process, and its exclusion from the specific problem being addressed by this work, it is more useful to compare the specific energy consumption to the proportion of EAF production in the country (Figure 2.3) (EEA, 2011). The countries with the highest energy efficiency steel plants are the ones utilising the best available technologies, represented by the red line. The countries utilising these technologies within the EU are the Netherlands, Hungary and Poland. Even when utilising the best available technologies for the primary production route, energy consumption still stands at around 0.32 tonnes of oil equivalent per tonne of steel. In these most advanced plants, the iron reduction technologies operate close to thermodynamic limits, meaning that the current rate of improvements in energy efficiency is unsustainable (Kundac, 2009). As a result of this, although improvements in energy efficiency can contribute towards meeting CO₂ reduction targets and reduce exposure to the EU ETS, they will not be enough to enable the steel industry to operate in the coming years in the EU without significant financial penalties. Instead, is it

argued that a step change in technology is required; either to begin a transition to non-carbon based primary steelmaking, and/or to permanently sequester the CO₂ which is produced.

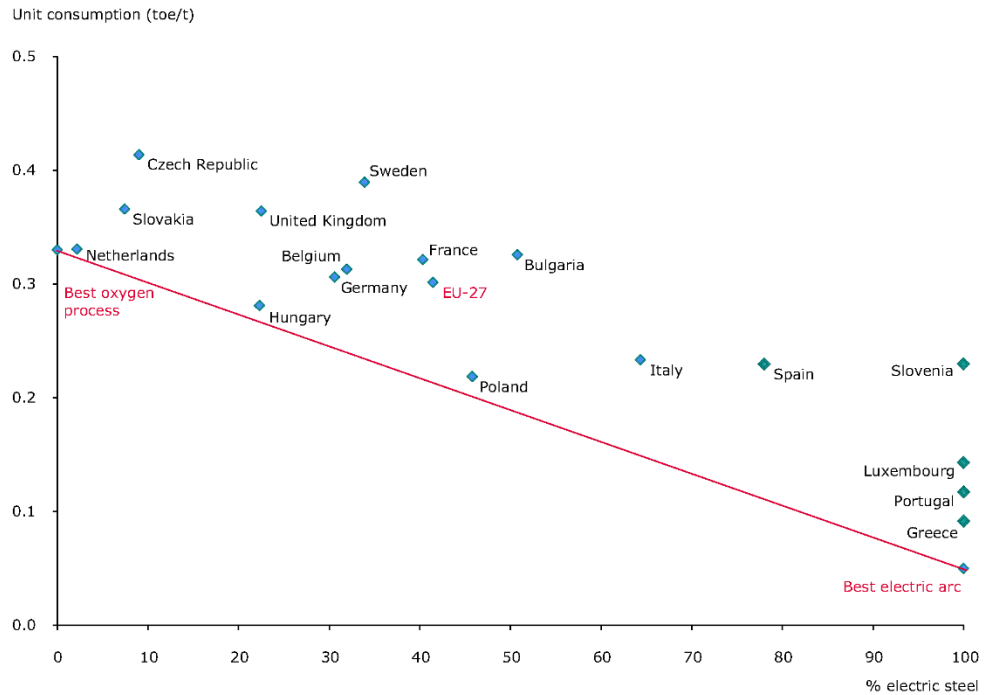


Figure 2.3: EU steel production energy consumption vs proportion electric steel production (toe/t is the tonne of oil equivalent per tonne of crude steel produced) (EEA, 2011).

2.5 Breakthrough technologies in low CO₂ steelmaking

Faced with the challenge outlined above, European steel makers and the European Commission initiated the Ultra-Low CO₂ Steel (ULCOS) research programme. ULCOS is a £62 million European research programme launched in 2004 by a consortium of 48 partners and led by a core group of European steel producers (including Tata Steel) with the aim of developing breakthrough process routes to cut the CO₂ footprint of primary steel production to 50% of the emission levels from current best practice (Birat and Hanrot, 2006; EC, 2012). As the energy efficiency of a modern steel plant is close to thermodynamic limits, the main aim of ULCOS was to identify routes to decoupling energy and CO₂ emissions. In order for the identified technology routes to mature, a timescale for commercialisation was set at 15-20 years (Birat and Hanrot, 2006). The

main output of the programme was the identification and subsequent development of a number of promising process routes for reducing emissions. These are divided into five themes splitting each process route into a family:

- (1) New blast furnace
- (2) New coal based reduction
- (3) New natural gas reduction
- (4) Electrolysis steel production
- (5) Carbon Capture and Storage (CCS) for steelmaking

Of these options only one, electrolysis (4), is not carbon based. Electrolysis reduction is mature in a number of metal producing industries; the production of aluminium and magnesium rely solely on electrolysis for their entire worldwide production. In addition to magnesium and aluminium, a number of other metal industries such as copper and zinc are expanding their electrolysis operations in order to give a more direct ore reduction route (Birat *et al.*, 2008b). In the case of steel, however, the carbon reduction route has become so widespread, efficient and operates so cheaply on such a massive scale that electrolysis based steelmaking would be unable to compete for the foreseeable future. In addition, the process would only be sustainable if carbon lean electricity is available at a very large scale and at competitive prices, and if the price of emitting CO₂ would offset the additional costs of developing and implementing an electrolysis reduction route (Birat *et al.*, 2008b). When the high cost of electricity and the underperformance of the EU ETS are considered, the conclusion must be that while electricity based primary steel production may become an option in the long term, for the foreseeable future iron will be reduced from iron ore chemically using carbon, which in turn will result in the production of CO₂.

Some of the new build next generation carbon based technologies identified by ULCOS do offer opportunities to make significant advances in reducing CO₂ emissions from

primary steelmaking even before CCS is deployed (Birat *et al.*, 2008a), however it is likely that the market penetration of such technologies will be limited for some time as long the capacity from legacy integrated plants remains. In order to achieve significant emission reductions before 2050 it is necessary to find retrofit solutions to decarbonise plants which are currently operating or in development using existing BF/BOS processes (Rootzen and Johnsson, 2013). Whether on new carbon based technologies or retrofitted to integrated plants, some form of CO₂ capture will be required in order to sequester the emissions produced to an extent that will meet European emission targets.

2.6 Carbon capture and storage (CCS) in the steel industry

Carbon capture and storage (CCS) is a term used to describe a number of technologies in various stages of development which aim to capture CO₂ produced during heavy industrial operations, purify and compress the CO₂ so that it is suitable for transportation and then store it by injecting the CO₂ into geological formations. Suitable storage sites are typically identified as either depleted oil and gas reservoirs or deep underground saline aquifers and, for the UK are almost exclusively off shore (Simmonds *et al.*, 2010).

Although carbon capture and storage (CCS) is considered as the most promising way to reduce emissions beyond the scope of energy efficiency, the high cost of the technology combined with market uncertainty and the associated risk of carbon leakage mean that it is unlikely that it will be widely adopted in the near term.

High cost of implementation was cited by the International Energy Agency (IEA) and the United Nations Industrial Development Organisation (UNIDO) as one of the fundamental barriers to deployment of CCS in industrial sectors (IEA and UNIDO, 2011). It is generally accepted that while the actual cost is very industry specific, the capture step will have a higher cost than transport or storage steps (Simmonds *et al.*, 2010). There have been a number of studies which have attempted to determine the capture cost from steelmaking operations. Estimates tend to vary according to which

source on the works the CO₂ is captured from; for blast furnace capture using chemical absorption process based on monoethanol amine (MEA) solvents, the cost has been estimated at £35¹ per tonne (Ho *et al.*, 2011). A study of CO₂ capture from a number of integrated site plants using a variety of capture technologies estimated costs of between £26 and £46² per tonne (Kuramochi *et al.*, 2011). Tsupari *et al.* (2012) estimated that retrofitted MEA based CO₂ capture at an integrated site power plant would cost in the range of £40 to £63³ per tonne. It must also be considered that this price only accounts for the capture process; in addition transport is expected to cost a minimum of around £4 per tonne and storage is expected to cost a minimum of around £8 per tonne if shared, high capacity pipeline infrastructure is available (Simmonds *et al.*, 2010). This means that under the most optimistic capture scenario, CO₂ mitigation from steelmaking via CCS is likely to cost at least £38 per tonne. Using the low scenario estimates for EU ETS traded carbon prices as a guide (though by past observations this now seems rather high), deployment of CCS in the steel industry would not become a viable option until 2031, when the traded CO₂ price is expected to reach £41 per tonne (DECC, 2011). If applied to steelmaking, these costs would have to be passed to the customer in increased prices. In a globalised steel market, and without a globalised carbon trading market, these localised increases in production costs could lead to a loss in competitiveness. This in turn could result in “carbon leakage”, where production is outsourced to an area where CO₂ emission restrictions are not in place (EC, 2014c).

One of the main incentives in Europe for the demonstration of an integrated CCS system at full scale was the UK CCS Commercialisation competition, which made available £1 billion of capital funding to support the design, construction and operation of the UK’s first fully integrated (capture, transport and storage) CCS system. This competition

¹ Originally reported in Australian Dollars (AUD)

² Originally reported in Euros (EUR)

³ Originally reported in Euros (EUR)

prize was scrapped in 2015 (Carrington, 2015), increasing uncertainty in the likelihood of deployment of CCS technology.

Evidence indicates that the pace of development of both ULCOS and CCS technologies have not matched that of EU carbon management policy, and that their deployment is obstructed by huge capital investment requirements (DECC and BIS, 2015). Though these options may become viable as a means to reduce CO₂ emissions from iron and steelmaking in the mid to long term, and are arguably the only solution to substantially reduce emissions from carbon based iron production, there is a need to investigate and evaluate smaller scale options which may be implemented in a shorter timescale. In addition, due to the decentralised nature of CO₂ emissions at an integrated site, complete decarbonisation by carbon capture and storage would require multiple CCS plants at huge capital cost. The deployment of multiple smaller CCS plants would likely result in an increased energy penalty than would be expected for a single plant of the combined capacity due to loss of economies of scale. The impact of emissions being distributed across integrated sites is illustrated in the DECC and BIS roadmap on Carbon reduction in the Iron and steel industry, where it is estimated the technical maximum for CO₂ reduction in the sector is to 60% of current emissions; when only CCS, ULCOS and energy efficiency measures are considered (DECC and BIS, 2015). With the exception of the sintering process, flue gases from integrated sites have relatively high CO₂ concentrations (Section 2.1) meaning that direct utilisation could be an attractive option either immediately or in the longer term to exhausts where CCS deployment is unfeasible.

2.7 CO₂ utilisation in the steel industry

In carbon dioxide utilisation (CDU) processes, rather than injecting CO₂ into the ground for storage, CO₂ is used either directly or converted into products such as fuels, chemicals or biomass. As the CO₂ serves a function or is used to produce a product there

is the potential for CDU processes to generate additional revenue streams for the operator and, at least to some extent, use this to offset the costs of CO₂ mitigation. In addition, due to the wide variety of approaches and material requirements, CDU processes also present a number of opportunities to combine CO₂ reduction with waste reduction and valorisation. This is particularly attractive in industries such as iron and steel which produce a vast array of potentially suitable co-products and waste streams. This section will review CO₂ utilisation processes, with particular focus on their application to integrated steelmaking sites including the potential to utilise steelmaking by-products and wastes with the aim to choose two of the most appropriate technologies for further research. In order to be consistent with the aim of short term implementation, technologies which are deemed to be the most mature in each process route will be reviewed. This means that technologies in relatively early stages of development will not be considered.

Carbon dioxide gas is already used on an industrial scale as a feedstock to produce a variety of products (Table 2.1). The global demand for CO₂ is currently around 200,000,000 tonnes, with the two main uses being the production of urea for use as a fertiliser and as a feedstock for agrochemicals production and production of precipitated calcium carbonate for use as a filler in plastics and paper. Together these account for over 80% of current demand. A further 14% is accounted for by direct technological applications, such as in analytical chemistry and other laboratory uses.

Table 2.1: Current uses for CO₂ as an industrial feedstock, all figures in millions of tonnes (Mt) (Aresta *et al.*, 2013).

Compound	Actual production	CO ₂ used	2016 forecast	CO ₂ needed
<i>Urea</i>	155	114	180	132
<i>Methanol</i>	50	8	60	10
<i>Polycarbonates</i>	4	0.01	5	1
<i>Carbamates</i>	5.3	0	>6	1
<i>Polyurethanes</i>	>8	0	10	0.5
<i>Acrylates</i>	2.5	0	3	1.5
<i>Formic acid</i>	0.6	0	1	0.9
<i>Inorganic carbonates</i>	200	50	250	70
<i>Of which is CaCO₃ (PCC)¹</i>	113.9	-	-	-
<i>Soda Solvay</i>	50	-	-	-
<i>Technological</i>	-	28	-	80
<i>Algae for the production of biodiesel</i>	0.005	0.01	1	2
Total		200		299

2.7.1 International perspective

Interest and investment in development in CDU technology has accelerated internationally in the last 8 or so years, particularly in the USA, Germany and Australia.

¹ This value is misleading as it gives the combined market size for both ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). As GCC is essentially just milled limestone, PCC is the only CO₂ utilising material here, with an annual production rate of only 14 Mtpa in 2011 (Roskill, 2012). For the purpose of this work, the higher value represents the total market size for calcium carbonate fillers which have the potential to be fulfilled entirely by PCC.

In the USA there has been a massive injection of cash into CDU research; \$100 million focused on mineralisation, plastics and fuels production. One promising route that is nearing commercialisation is a company called Calera which is using CO₂ to produce construction materials using calcium carbide waste (Calera, 2016). German investment of over 100 million Euros to fund reuse of CO₂ has enabled construction of the Bayer pilot plant to produce polyurethane foams (discussed in Section 2.7.4.3) from CO₂. The Australian government has invested AU\$40 million into a mineralisation project, aiming to capture CO₂ from a power station and convert it into aggregates and building materials (Styring *et al.*, 2011).

In Iceland, Carbon Recycling International have built and operate a full scale plant to produce methanol from CO₂, the methanol is blended with petroleum for use in vehicles (Carbon Recycling International, 2012).

2.7.2 Technology selection criteria

Carbon dioxide utilisation technology can broadly be split into four process routes;

- **Direct Utilisation:** use of CO₂ as CO₂, without any chemical conversion
- **Biological Utilisation:** conversion of CO₂ through photosynthesis into biomass
- **Chemical Utilisation:** the use of CO₂ as a feedstock to produce an organic product
- **Mineral Utilisation:** the use of CO₂ to produce inorganic mineral carbonates

Many of these process routes can be broken down into a large number of sub-categories each with a wide breadth of literature. A detailed account of each would be extremely long and falls out of the scope of this thesis. Instead, an overview of each route is presented and more detail is provided for the technologies deemed as the most appropriate solutions for deployment at an integrated steelmaking site. Appropriate solutions are defined as those which are able to best address the following challenges:

1. Market capacity and risk of saturation

The capacity of a CDU product market determines how much CO₂ can be converted into a product and sold to generate additional revenue. There is a risk that by deploying new production routes utilising CO₂, the increased production will result in market saturation and cause the value of the product to decrease. If, however, the new route to production can produce a product of the same quality and cost but at a reduced environmental impact, then this process route may be preferred by customers and have the potential to displace current production routes.

2. Conversion energy requirement and source

If energy is required to achieve a CO₂ transformation, then the overall sustainability of this transformation will be closely related to the sustainability of this energy source. For example, if a process is heavily dependent of electrical power to drive the transformation, then this electricity must be supplied from a low carbon source in order to maintain a net reduction of CO₂ emissions.

3. Feedstock materials availability and sustainability

Similarly to energy sources, ensuring the sustainability of co-reactants is critical to maintaining overall process sustainability. In some CDU routes, the feedstock may be available as a waste or by-product from steelmaking processes and by utilising it the waste is valorised alongside CO₂ into a product, compounding the environmental benefit.

4. CO₂ feed quality requirements

In order to be able to utilise CO₂ from steelmaking in the short term without being dependent first on the deployment of CCS, the chosen CDU routes must be able to utilise CO₂ in its diluted and contaminated form directly from a steelmaking process exhaust.

2.7.3 Direct CO₂ use

CO₂ is a valuable industrial gas with a wide range of direct applications including as an inert agent in packaging and welding, use in refrigeration systems, fire extinguishers, water treatment processes, analytical laboratories and horticulture. Many of these applications require a high purity source of CO₂ which is already provided at low cost and in adequate volumes as a by-product from fertiliser production, fermentation, natural gas processing and calcination processes (Mazzotti *et al.*, 2005).

In a supercritical state ($T_c = 304.12\text{ K}$; $P_c = 7.37\text{ MPa}$), CO₂ can also be used as an alternative to liquid organic solvents in a number of applications including in natural product processing (for example coffee decaffeination) and as a solvent medium to conduct chemical reactions. Supercritical CO₂ has a number of advantages over organic solvents including low cost, high availability, high stability, good biocompatibility, low toxicity and low flammability (Galia and Filardo, 2010).

The value of high purity CO₂ for direct use can range from £2 for gaseous to £10 for supercritical per tonne (Global CCS Institute and Parsons Brinckerhoff, 2011).

Direct use of CO₂ does not involve a reaction and therefore there are no concerns over the availability or sustainability of additional reactants, or energy requirements for driving a reaction. However, the market capacity of these direct uses of CO₂ is limited by the small volumes required and the real storage value in such products is questionable. In addition, the purity of CO₂ required is among the highest of any technology, meaning that direct utilisation from exhausts is not possible.

2.7.3.1 Enhanced oil recovery

Enhanced oil recovery (EOR) is the direct use of supercritical CO₂ by injection into oil reservoirs in order to enhance well productivity. EOR is discussed here separately to

the other direct applications above due to the vastly higher capacity to utilise CO₂ and due to the differences in permanence of storage.

EOR is operated at a commercial scale widely in the Permian Basin in the south of the USA, where wells are perfectly suited to EOR (USDOE and NETL, 2010). Here, natural high purity CO₂ sources are used as a gas source; the gas is compressed and cooled to a supercritical state before being injected into the well. At the extraction point, a mixture including oil and CO₂ is recovered and separated. As CO₂ is here a commodity, the most economical solution is to purify the CO₂ recovered from the well and compressed it, mix it with the fresh CO₂ feed and re-inject it into the well (USDOE and NETL, 2010). It has been reported that around 50% of the gas injected returns to the surface with the oil, and as this separated and re-injected, the actual storage value is over 90% (Gale, 2013). This storage is essentially the same as that proposed for CCS and can be considered permanent. In addition, the market in terms of CO₂ capacity could be very large for CO₂ point sources located near to suitable EOR injection sites. Though it can be considered as utilisation which results in permanent storage, it has also been argued that EOR facilitates the burning of additional fossil fuel reserves which would, without EOR, have been uneconomical to extract and thus worsen rather than addresses the issue of climate change. Either way, the deployment of EOR requires a low cost and high purity CO₂ source and thus applying the technology in a steelmaking context is dependent on the implementation of CCS.

2.7.4 Chemical CDU processes

Chemical CDU processes are defined for this work as processes which involve a chemical reaction to synthesise an organic product using CO₂ as a feedstock. This can be achieved through two types of reaction (Cuellar-Franca and Azapagic, 2015); either CO₂ is used by adding it to other chemicals in insertion reactions with no overall change in oxidation state to produce materials such as polymers or CO₂ is used via reduction

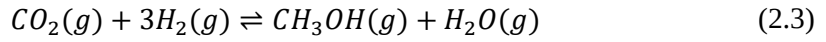
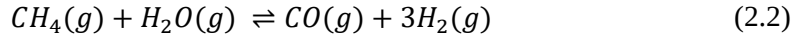
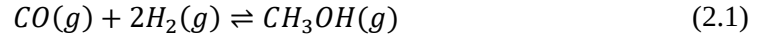
reactions where the O=C=O bonds in CO₂ are broken to produce chemicals such as urea and fuels including methanol and hydrocarbons. Reduction reactions typically require a significant input of energy either as hydrogen, electricity or heat and the use of highly selective catalysts in order to achieve the transformation.

2.7.4.1 Fuels production

CO₂ in exhaust gases is the product of fuel combustion and must be chemically reduced in order to upgrade it back to a higher energy form for reuse. The energy required for this reduction by will always be higher than that gained from the original combustion (assuming the same fuel is synthesised) due to unavoidable losses and therefore CO₂ derived fuels should be considered energy vectors, or energy storage. An often cited advantage of CO₂ derived fuels is that they allow for the use of renewable electricity over capacity to be used indirectly to power road transport and offset the use of fossil derived fuels (Styring *et al.*, 2011; Aresta, 2013). Fuels represent a huge market with an extremely high capacity for CO₂ utilisation. The two most promising options for CO₂ utilisation to produce fuels are both based on hydrogenation; the production of methanol and the production of higher hydrocarbons by Fischer-Tropsch synthesis.

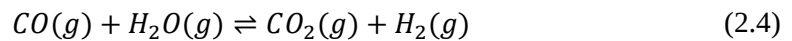
Methanol (CH₃OH) is a C1 chemical and can be regarded as the simplest alcohol. It is used as a fuel in internal combustion engine (Gnanamani *et al.*, 2014) for a number of niche applications and increasingly is blended with petrol for combustion in standard road vehicle engines, or can be used unblended with some engine modifications (Gnanamani *et al.*, 2014). The primary process to produce methanol currently is through a reaction of carbon monoxide (CO) and hydrogen (H₂) over a catalyst of copper, zinc oxide and alumina at elevated temperatures (up to 523 K) and pressures (up to 10 MPa) (Equation 2.1). The CO and H₂ required for this process is typically syngas derived from natural gas (Equation 2.2), which gives an excess of H₂. CO₂ can be injected into the process in order to use this excess H₂ and boost methanol yield (Equation 2.3)

(Chang *et al.*, 1986). This accounts for the current 8 Mt annual demand for CO₂ in methanol production (Table 2.1).



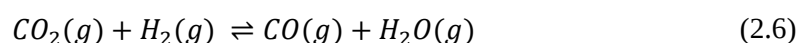
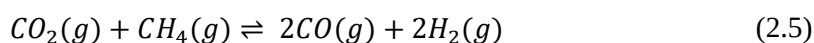
Methanol can be synthesised directly from CO₂ and H₂ (Equation 2.3) under similar conditions and with similar catalysts without the need for any CO to be present, however the methanol yield is substantially lower when compared to the CO route due to the inertness of CO₂ (Gnanamani *et al.*, 2014). In addition to direct use as a fuel, methanol can also be used as a precursor for production of higher hydrocarbons via methanol to gasoline reactions (Gnanamani *et al.*, 2014).

Fischer-Tropsch synthesis is an industrially established process to produce a range of linear hydrocarbon products from syngas consisting of CO and H₂, typically derived from coal or natural gas. The process operates at elevated temperatures (423-573 K) and pressures (>1 MPa) and in the presence of a transition metal catalyst, typically iron or cobalt based (Gnanamani *et al.*, 2014). In syngas produced from coal the high carbon content results in a high CO to H₂ molar ratio, whereas Fischer-Tropsch reactions require a low CO to H₂ molar ratio. This ratio can be modified by using some of the CO to reduce H₂O into H₂ and CO₂ in a reversible reaction called the water gas shift reaction (WGS) (Equation 2.4) (Gnanamani *et al.*, 2014).



It has been demonstrated in various works that it is possible to use CO₂-H₂ mixtures directly in Fischer-Tropsch-type processes (Dorner *et al.*, 2010), however this promotes

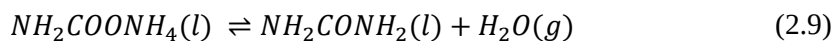
a methanation reaction and the product is typically composed of predominately methane. In addition, it is likely that the high complexity of the required catalysts would render scale up unfeasible (Styring *et al.*, 2011). Instead, the favoured approach is to first reduce CO₂ to CO. This can be achieved via a number of reactions (Styring *et al.*, 2011) including; methane reformation (Equation 2.5), the reverse water gas shift reaction (Equation 2.6) and carbon gasification (Equation 2.7).



2.7.4.2 Urea production

Urea (CO(NH₂)₂) and related molecules have wide ranging uses, predominantly in and as a fertiliser but also in other agrochemicals, petrochemicals and pharmaceuticals (Aresta, 2010). Urea is also currently used to a limited extent in dioxin emission control in the sintering process at Tata Steel's integrated sites. Synthesis of urea uses CO₂ and NH₃ as raw materials and is currently the highest consumer of CO₂ in the world, with a demand of around 114 Mt in 2013 (Table 2.1; Aresta *et al.*, 2013). Manufacture involves two reactions; in the first ammonia reacts exothermically with carbon dioxide to produce ammonium carbonate (Equation 2.4). In the second reaction ammonium carbonate is decomposed in an endothermic reaction to produce water and urea (Equation 2.5). A number of specific synthesis processes exist for urea production, all operating at elevated temperatures (453-483 K) and pressures (14-25 MPa), using compressed CO₂ and liquid ammonia as feeds (UNIDO and IFDC, 1998).





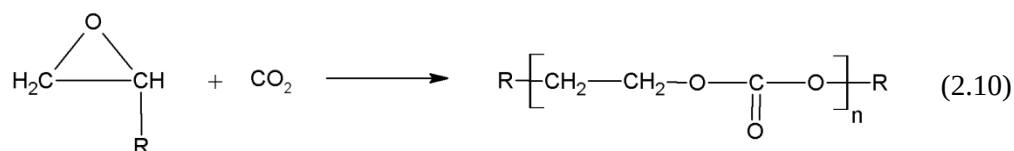
On integrated steelmaking sites, coke oven by-product plants often produce a product called ammonia liquor (see section 2.1). At Tata Steel UK sites, the capacity for liquor production outstrips demand for the product and a significant proportion of ammonia vapour is incinerated. It could be possible to use this excess liquor as source of ammonia for urea production; however the liquor is of a poor purity with a high degree of contamination (see concentrated ammonia liquor analysis in Chapter 4) and would require upgrading in order to be suitable for use. The question of product sustainability must also be considered seriously in the case of urea production. The true climate mitigation value of utilising CO₂ in urea production could well be negative due to the resulting formation of nitrous oxide (N₂O) with use of urea as a fertiliser. N₂O is a greenhouse gas with a global warming potential which is 289 times that of CO₂ (Forster, 2007).

2.7.4.3 Polymers production

The third chemical CDU route with some immediate potential for commercialisation is the production of polymers that, to varying extents, can replace traditionally petroleum derived feedstocks with CO₂. Polymers which can be produced via CDU fall under the category of copolymers, defined as polymers that are derived from more than one monomer (Ring *et al.*, 1985), in contrast to homopolymers which contain a single repeating molecule. Two of the most promising developments in CO₂ utilisation to copolymers are the production of polycarbonates and the production of polyurethanes.

Polycarbonates have highly variable compositions and a wide range of applications due to their ability to be easily moulded and thermoformed, alongside properties such high durability, electrical insulation and heat resistance. The principle applications are in electronic components and construction materials; overall the polycarbonate market is worth around £9.8 billion annually, which equates to a total capacity of around 1.8 Mt

CO_2 year⁻¹ (Huang and Tan, 2014). A promising approach to produce polycarbonates utilising CO_2 that has received recent attention (Taherimehr and Pescarmona, 2014) was first reported by Inoue *et al.* (1969). The polycarbonate is produced via a reaction between epoxide and CO_2 (Equation 2.9).



Polyurethanes are also a broad class of polymers with a wide variety of uses; polyurethanes are used, among other things, in insulation and sealant foams, adhesives, tyres and synthetic fibres. Polyurethane production requires two primary raw materials; isocyanates and polyols. Isocyanates used in polyurethane manufacture must have two or more isocyanate groups ($\text{R}-\text{N}=\text{C}=\text{O}$) per molecule and are typically aromatic, for example methylene diphenyl diisocyanate (Figure 2.4).

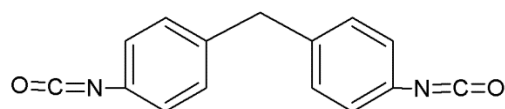
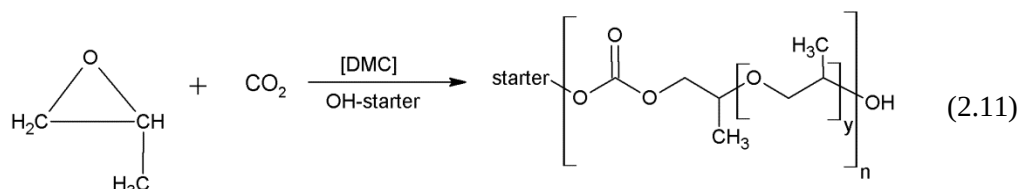


Figure 2.4: Diphenyl diisocyanate (MDI), a common isocyanate used in the manufacture of polyurethanes

Polyols are the second raw material required for polyurethane manufacture and are defined in polymer science as alcohols with multiple hydroxyl functional groups. Polyols vary hugely in molecular weight and structure, with these variables altering the properties of the resulting polymer. The polymer manufacturer Bayer has developed a commercially viable process to produce a polyol called polyether carbonate polyol using CO_2 and propylene oxide for use in the production of foams (Equation 2.10), using a double-metal cyanide (DMC) catalyst and a multifunctional alcohol starter (eg.

glycerol) (Haider *et al.*, 2008). Bayer leads a consortium to develop this proprietary technology, called “DREAM”, to produce CO₂ derived polyols at a commercial scale; €15 million has been invested to commission a production facility to produce 5000 tonnes of polyols per year and this is expected to be operational by 2016 (Bayer, 2014).



Although there have been significant recent advancements in the development of polycarbonates and polyurethanes which contain CO₂, the market size is small when compared to other CDU products. Furthermore, as CO₂ derived polymers contain CO₂ as only a small portion by mass, the actual capacity to use CO₂ in these processes is very low indeed.

2.7.5 Biological CDU processes

Carbon dioxide has a critical function in biology as a feedstock for photosynthesis and creating the foundation for most life on earth. Photosynthesis is a complex biochemical process which chemically reduces CO₂ and water using light energy from the sun, to build organic molecules and release oxygen. Photosynthesis can be engineered to utilise relatively high concentrations of CO₂ (compared to atmospheric) by managing and optimising cultures of single celled organisms such as microalgae. Under optimum conditions microalgae have been reported to exhibit exceptionally high growth rates, producing lipids from 15 to 300 times the rate of terrestrial oil crops (Dahiya, 2015). In addition microalgae do not require fertile soil and so can be cultivated in areas where terrestrial crops cannot, leading to claims that microalgae can avoid the “food vs fuel” debate associated with other biofuels (Singh *et al.*, 2011).

Besides CO₂, microalgae growth requires two macronutrients, nitrogen (typically as either NO₃⁺ or NH₄⁺) and phosphorus (as PO₄³⁻) and a range of other micronutrients (for example, Fe, Se, Mn, K, Na) which are required in only trace quantities. Nitrogen and phosphates can be readily bought as fertiliser, however they, and particularly nitrogen based fertilisers, are produced with significant CO₂ emissions and so this must be accounted for when the process lifecycle emissions are considered (Rogers *et al.*, 2014). In addition to environmental considerations, the requirement of large quantities of fertiliser is cited in a number of techno-economic and life cycle studies as being a financial barrier to commercial deployment of the technology (Beal *et al.*, 2015; Dassey *et al.*, 2014). One way to avoid these barriers and increase the sustainability of microalgae cultivation is by combining CO₂ utilisation/biofuels production with wastewater treatment. Nitrates/ammonia and phosphates in wastewater are considered to be pollutants as they cause eutrophication of waterways (Blackburn, 2004), and use of these nutrients as fertiliser to produce algae can simultaneously remediate the wastewater and reduce the environmental and cost burden of bought in nutrients. As microalgae can be highly effective in rapidly depleting these nutrients, large scale cultures are used commercially in niche applications as a form of tertiary wastewater treatment (Borowitzka, 2005).

Steelworks produce a wastewater that contains nitrogen in the form of ammonia from the Biological Effluent Treatment (BET) Plant. This plant treats highly contaminated wastewater produced as a result of the coke oven gas clean-up processes, before discharging a treated effluent still containing some ammonia. The coke oven gas clean-up process also produces either concentrated ammonia liquor or ammonium sulfate as a by-product, which also has potential to be used as a fertiliser for algal cultivation. The discharge consent (the concentration of a pollutant that is licenced to be released to the environment) for ammonium from the BET wastewater stream is regularly revised in order to improve the environmental performance of the steel plant; in the EU, advanced

emission levels (AEL) are set according the best available technology for reducing a specific pollutant under a system referred to as BAT-AEL (Remus *et al.*, 2013; EC, 2001). Tertiary treatment of this wastewater using microalgae may offer an opportunity to combine meeting future pollution limits with CO₂ utilisation. In fact, evidence suggests that the rate of wastewater nitrogen removal by microalgae can be accelerated when elevated levels of CO₂ are introduced to the culture (Lizzul *et al.*, 2014). There have been a number of studies which demonstrate that microalgae can tolerate the impurities present in raw combustion exhaust gases (Kastánek *et al.*, 2010; Doucha *et al.*, 2005); including from a UK integrated steel plant power station (Zimmerman *et al.*, 2011) and from coke oven exhausts (Chiu *et al.*, 2011; Li *et al.*, 2011).

The main product under consideration for production from microalgal biomass and by far the one with the largest market is biofuel. Microalgae can be cultured to have a very high lipid fraction and the simplest route to produce biofuel from microalgae is by exploiting this; extraction of lipids from dry microalgal biomass, followed by a transesterification of the oils to yield fatty acid esters that are suitable as a fuel in diesel engines. However, the energy intensive nature of drying the high moisture biomass poses a serious challenge (Grima *et al.*, 2003; Lardon *et al.*, 2009) and for this reason there is increasing work on wet conversion technologies to either avoid this step, or to make the most of residual by-products. These include anaerobic digestion to produce biogas (Ward *et al.*, 2014), and hydrothermal processes to produce a synthetic crude oil (Ross *et al.*, 2010).

2.7.6 Mineral CDU (Mineral Carbonation) processes

Production of mineral carbonates can be achieved by reacting carbon dioxide with alkali metal oxides. These reactions occur naturally, primarily as silicate weathering through hydrolysis; acidic water reacts with silicates containing alkali earth metals (Velbel, 1993). This acidic water is formed when CO₂ dissolves in water to form carbonic acid

(H_2CO_3) and because silicate weathering reactions consume this carbonic acid, CO_2 is removed from the atmosphere. Although spontaneous, these reactions naturally occur over geological timescales and must be accelerated by orders of magnitude in order to have any commercial applicability. There has been significant research interest in recent years in developing these carbonation reactions into accelerated, commercially viable processes to produce products of either high purity inorganic carbonates or low purity synthetic rock type carbonate-silicate minerals. Such processes are commonly referred to in the literature as “Mineral Carbonation”. As carbon in mineral carbonates is at a lower energy level than CO_2 , the reactions are both spontaneous and exothermic (Sanna *et al.*, 2014). This means that not only is no energy input required in order to achieve the transformation reactions; they actually produce energy in the form of heat.

Suitable raw materials must be alkali in nature, have low solubility as carbonates and be relatively abundant. Chemically, alkaline (Na, K, etc), alkaline earth metals (Ca, Mg, etc) and a number of transition metals (for example, Zn, Fe and Co) are suitable for carbonation (Huijen and Comans, 2003). However, the Group 1 carbonates are readily water soluble rendering them unsuitable. The transition metals can be carbonated but are generally too rare or expensive to be candidates at any significant scale. This leaves alkaline earth metals, the most abundant of which are magnesium and calcium which each make up approximately 2 mol% of the Earth’s crust each and are bound primarily in silicates and carbonates (Goff and Lackner, 1998). In addition to naturally occurring materials, a variety of synthetic industrial residues have been shown to be suitable for carbonation. A ceramic calcium rich material called slag is produced as a by-product from numerous processes at integrated steelmaking sites, with a significant proportion landfilled as waste (see Section 2.1). Slags typically have calcium concentrations ranging from ~30% to ~50% by mass making them highly suited to carbonation processes. In addition, it has been demonstrated that slag materials can be more readily

carbonated than their mineral counterparts, and under less demanding process conditions (Mazzotti *et al.*, 2005; Huijen and Comans, 2006).

2.7.6.1 Processes and products

Calcium containing wastes can be carbonated to produce two different types of products each via a different process route (Figure 2.5). In the first (Figure 2.5a), finely milled calcium rich waste is carbonated in a single step to produce a product which is a mixture of carbonate, unreacted calcium and other unreacted material. This is called the “direct” route and the carbonated product can be agglomerated to form an aggregate type material for construction use. The market value of such a material is dependent on its application and physical properties but as an example, weathered steel (BOS) slag for use as a general aggregate had an average sale price in the US of ~£3.20¹ per tonne (\$5.22) in 2012 (Oss, 2014). The market capacity for aggregates is huge and currently consists of mostly mined rock, the displacement of which could give additional CO₂ savings due to avoided emissions.

In the second route (Figure 2.5b), finely milled waste is carbonated in two or more steps. These can be split into a first step where calcium is extracted from the waste into solution using a solvent, and a second where the solution is carbonated after it is separated from unreacted residue. Further steps can include filtering of the unreacted residue and separation of the carbonate product. During the carbonation step, calcium carbonate (CaCO₃) precipitates and is separated for sale as a product. The nature of this process means that it is more complicated and costly to implement, but a high purity precipitated calcium carbonate (PCC) product can be produced. PCC is used as a filler in industrial processes such as in the production of paper, plastics and paints and had a market value in 2012 of around £73 per tonne (Eloneva *et al.*, 2012). The global market for PCC is just over 113Mt annually, equating to a capacity of around 50Mt CO₂ (Aresta

¹ Using an exchange rate of \$1.63/GBP (December 2012)

et al., 2013, see Table 2.1). If total PCC production capacity increases due to adoption of new processes utilising slag and CO₂, there is the risk that this could saturate the market and cause a fall in value and therefore revenue potential from the PCC produced. There may however be an opportunity to capitalise on the improved environmental credentials and sustainability (Mattila *et al.*, 2014) of PCC produced via the new route over the traditional route from mined limestone in order to gain a market share and maintain a sale price, if a product of equal quality can be produced.

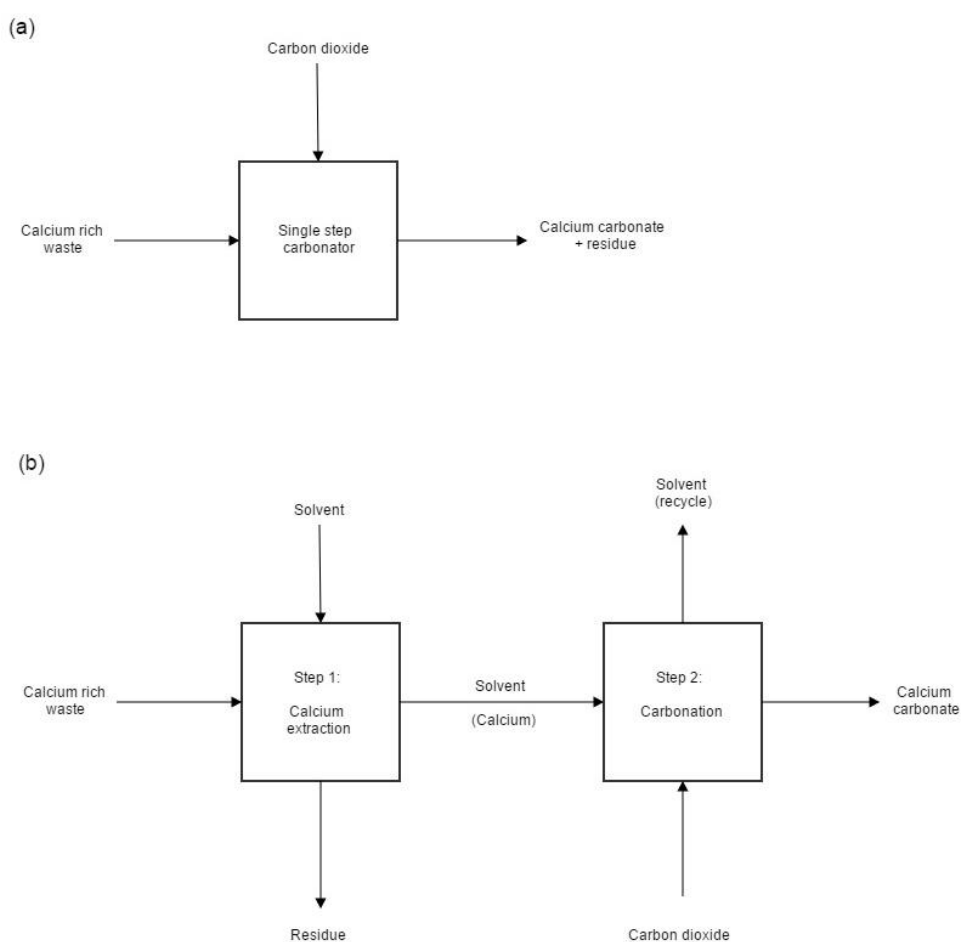


Figure 2.5: Carbonation process routes; (a) direct carbonation to produce mixed carbonate and unreacted residue with potential use as aggregate and (b) indirect carbonation to produce a high purity precipitated calcium carbonate for use as a filler in paper, paint or plastics.

Many mineral carbonation processes are expected to be able to utilise CO₂ directly from flue gases (Sanna *et al.*, 2014). The main effect of the CO₂ concentration fed to the reactor is on the residence time required in order to complete the reaction. There is also the risk that impurities in flue gases will contaminate the product. Theoretically this should not be an issue in low purity products destined for use as aggregate, but may impact the quality and value higher purity products such as PCC produced via the indirect route. The real world effect of flue gas impurities on carbonation processes and products is poorly understood; Sanna *et al.* (2014) identified this area as a key knowledge gap in their Royal Society of Chemistry review on mineral carbonation technologies.

Neither of the two carbonation routes is, at this stage, clearly more appropriate than the other. The direct route is inherently simpler as it involves fewer steps, no additional chemicals and the product market is large; however the value is low, limiting revenue and payback potential. The indirect route, although more complex and as a result more expensive to implement and operate, produces a high purity product with a considerably higher value than that from the direct process. However, calcium depleted residue must be disposed of and the market is smaller.

An aqueous direct carbonation process is currently commercially operated for carbonation of municipal solid waste incineration ash by a company called Carbon8 (Gunning *et al.*, 2013). The process produces an aggregate product that is up to 10% CO₂ by mass and can be utilised directly as an aggregate, or is used to manufacture construction blocks. It was decided that this was a potentially promising approach and should be taken forward. A decision was made by Tata Steel that the best approach to achieve this was for this work to be performed externally, and so it was decided that direct carbonation processed would therefore not be investigated in detail in this thesis.

2.8 Summary and processes for further research

In this chapter, the context of the thesis has been set by exploring the challenges being faced in decarbonising the production of steel from raw materials. The concept of integrated steelmaking has been introduced and the integral processes outlined, including the gas compositions of the main exhaust on a typical European site. The impact of emission reduction targets and emission trading schemes on steelmaking is discussed, highlighting the pressure to decarbonise the industry. Inherent limitations on further emissions savings from energy efficiency measures and the high likelihood that steelmaking will use carbon as a chemical reductant for decades to come mean that the only option for significant emissions reduction is downstream management of CO₂. Carbon capture and storage (CCS) technology is a promising option for achieving this, but is unlikely to be economical until at least the 2030s. Carbon dioxide utilisation (CDU) technology may present a shorter term opportunity to mitigate some emissions by transforming CO₂ into useful products including fuels, chemicals and minerals. In addition, some CDU routes may be able to utilise steelmaking waste as a feedstock, thereby adding further value to the processes. The purpose of the current thesis is to evaluate the most suitable of these routes to an integrated steelmaking site.

In the previous section, a wide range of CDU process routes were reviewed in terms of their applicability to the steel industry. Here, a summary is provided and two technology routes are chosen for further research. The processes were evaluated according to the criteria set out at the beginning of Section 2.5 (Table 2.2).

CO₂ can be utilised directly in a number of applications, including in food processing, drinks carbonation and as a solvent for chemical processes (in a supercritical state). These applications do not require transformation energy or additional reactants as the CO₂ remains unreacted, however these processes require a very high purity stream of CO₂ and are therefore reliant on CCS before they can be deployed. Furthermore, the market capacity of these processes is low, meaning that the capacity for CO₂ is low.

Enhanced oil recovery does offer a much larger and more permanent option for direct use, but also is dependent on a pure CO₂ stream being available.

The use of CO₂ as a chemical feedstock has a high potential capacity, with fuel being arguably the largest market of any CDU product, and there is some scope for using steelworks wastes and by-products for the production of urea. However, the technologies which fall under this category virtually all require a pure stream of CO₂ either to avoid poisoning of catalysts by flue gas impurities (Aresta, 2010), due to the compression requirements or to ensure a high purity product. This means that deployment of chemical based CDU processes in the steel industry is first dependent on the deployment of CCS. In addition, many chemical CDU processes require large amounts of hydrogen as a reactant meaning that economical yet sustainable sources must be developed in order to produce an environmentally viable product; a substantial challenge in itself. The production of urea using steelworks waste ammonia as a feedstock and the potential use of this urea in air pollution control measures at the steel plant is a potentially promising CDU route, but the risk of producing a more potent greenhouse gas, nitrous oxide, combined with the requirement for high purity streams of both NH₃ and CO₂ mean that it will not be considered for short term implementation.

Conversion of CO₂ into inorganic carbonates is a promising option with two potential markets for products produced via two processes; aggregates and building materials via the direct carbonation route and high purity precipitated calcium carbonate (PCC) produced via the indirect route. The direct route is relatively simple, involving only a single reaction step, but produces a relatively low value product. In contrast, the indirect route is more complex, with multiple reaction steps but producing a product considerably higher in value. There is a net gain in energy from the transformation reactions and the market capacity is large and moderate for aggregates and PCC respectively. The availability of suitable feedstock materials on a steelworks and the

current classification of some of these materials as wastes means that there is the potential to add additional value through waste reduction and upgrading. Finally, carbonation processes are not limited to using high purity CO₂ and can utilise CO₂ directly from exhaust gases. A decision by Tata Steel to outsource work on the direct carbonation route to a company currently operating a commercially viable process means that in this work only indirect carbonation processes will be considered as candidates for further research.

Biological CO₂ utilisation can be achieved through photosynthesis by organisms such as microalgae. As photosynthesis is driven by energy from the sun, this is the source of the transformation energy and is sustainable. An engineered approach to microalgae cultivation offers a potential opportunity to combine direct utilisation of CO₂ from steel plant exhausts with remediation of polluting nitrogen compounds from steelmaking wastewater to produce liquid or gaseous fuels for which there is a very large market. The suitability of treated coke oven wastewater effluent to microalgal culture, the remediation benefits and the actual extent to which CO₂ can be sustainably utilised in such a process are all areas which require more investigation before any conclusions can be drawn.

Table 2.2: Summary of utilisation routes and associated products evaluated to the parameters outlined at the beginning of this section.

Route and product	Evaluation parameter			
	1. Feed sustainability	2. Potential capacity ¹	3. Conversion energy source	4. Use of flue gas directly
Direct CDU				
<i>Food and Drinks</i>	N/A	Small	N/A	No
<i>Solvents</i>	N/A	Small	N/A	No
<i>EOR</i>	N/A	Large	N/A	No
Chemical CDU				
<i>Fuels</i>	Sustainable source of H ₂ required	Large	Electrical / Heat / H ₂	No
<i>Urea</i>	Steelworks ammonia by-products	Medium	Heat and compression	No
<i>Polymers</i>	Precursors required	Small	Electrical / Heat / H ₂	No
Biological CDU				
<i>Microalgae</i>	Use of steelworks wastewater and ammonia/ammonium sulfate by-products	Large	Solar (Photosynthesis)	Yes
Mineral CDU				
<i>Direct Carbonation</i>	Residues produced at steelworks site	Large	Net conversion energy gain	Yes
<i>Precipitated calcium carbonate (PCC)</i>	Residues produced at steelworks site	Medium	Net conversion energy gain	Yes (in principle) ²

¹ Potential capacity defined here as Large (>300 Mt year⁻¹ CO₂), Medium (50-300 Mt year⁻¹ CO₂) or Small (<50 Mt year⁻¹ CO₂) and based on current and projected market sizes for products given by Huang and Tan (2014), Sanna *et al.* (2014) and Aresta *et al.* (2013).

² The ability to directly use CO₂ from flue gas in PCC production is assumed in a number of works but the effects on the process and product quality have yet to be demonstrated experimentally. This is identified as a knowledge gap in a RSC review of mineral carbonation technologies (Sanna *et al.*, 2014).

3. Production of high purity precipitated calcium carbonate from steelmaking residues

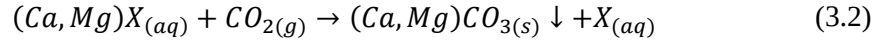
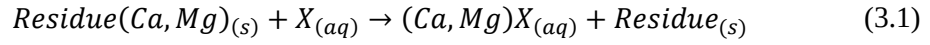
Indirect carbonation of alkaline residues was identified in Chapter 2 as a potentially promising approach to utilising CO₂ at an integrated steelmaking site. This chapter reviews the current state of the art in indirect carbonation processes and examines the technical feasibility of the most promising route when applied to residues and flue gas produced at Tata Steel sites. Materials are chosen, experimental methods are detailed and results are discussed for the two major reaction steps in the chosen process.

3.1 Indirect carbonation of alkaline industrial residues

The carbonation of calcium rich industrial residues has a number of advantages over using virgin mined materials; (a) the materials are available on the site where CO₂ is produced, removing the cost and CO₂ released during transport of materials; (b) they often have a lower chemical stability than virgin raw materials and so react more readily with CO₂ or are extracted into solution more readily (Huijen and Comans, 2006; 2003); (c) cost benefits can be achieved by reducing the mass of material sent to landfill; and (d) there can be the potential for reclassification of hazardous waste following treatment via carbonation (Sanna *et al.*, 2014).

Indirect carbonation processes can be defined as those which involve multiple processing stages to give a high purity product. In the first step the reactive component is extracted into solution (Equation 3.1; X denotes extractive additive), then after being

separated from the solid residue, the solution is reacted with carbon dioxide to precipitate a high purity carbonate product (Equation 3.2).



The simplest indirect carbonation processes involve the leaching of reactive components from feed materials using water and then carbonation of this calcium or magnesium burdened aqueous solution. In a process described by Stolaroff *et al.* (2005), large concrete basins are loaded with milled slag material which is then sprayed with water from a height of around 10m (Figure 3.1). The solution travels through the slag bed and is collected in a wet well before being recirculated and sprayed back onto the slag heap. The recycled solution, rich in $\text{Ca}(\text{OH})_2$ reacts with CO_2 present in the air as is sprayed back onto the heap and precipitates CaCO_3 as the leachate flows back through.

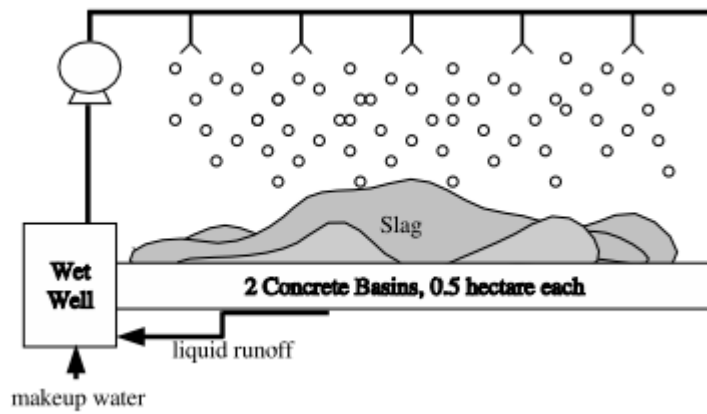


Figure 3.1: Passive water based carbonation process described by Stolaroff *et al.* (2005)

Though potentially economically viable and relatively simple, the process described by Stolaroff *et al.* (2005) blurs the line somewhat between natural and accelerated carbonation, meaning that it could be difficult to quantify the amount of CO_2 sequestered and thus would be unlikely to be credited under emissions trading schemes.

In addition, the nature of the product as a mixture of carbonates and unreacted residue means that it does not fall strictly under the umbrella of “indirect carbonation” as defined above. A similar but more appropriate approach could be to take the leachate formed from basins such as the ones described above, or from a steelworks landfill drainage system, and react this aqueous solution with CO₂ from process exhausts.

The author did investigate the possibility of carbonating leachate from a slag stockpile and landfill site at an integrated works in the UK, but analysis of the leachate indicated that a majority of the calcium present was as CaCO₃ already, and that the remaining unreacted calcium was present in relatively low concentrations (<200 mg L⁻¹; from internal Tata Steel data). Furthermore, an open system would be susceptible to seasonal fluctuations in rainfall, resulting in a highly variable leachate composition.

Katsuyama *et al.* (2005) proposed a pressure swing process to produce high purity PCC from waste concrete; in the first step, a cement paste is contacted with high pressure (0.9-3MPa) CO₂, extracting calcium and the high pressure preventing CaCO₃ precipitation. The aqueous solution containing calcium and dissolved carbon dioxide was then separated from the solid residue before being transferred to a second reactor where the pressure was reduced, resulting in CaCO₃ precipitation. CaCO₃ with a purity of 98% was achieved, and the PCC production cost was estimated at £74.42¹² (\$136) per tonne when the plant is scaled. A significant proportion of this cost is derived from the chemical CO₂ capture plant, as the process requires a high purity stream of CO₂ to operate. The requirement of CCS means that the process falls out of the scope of this work.

In order to extract calcium to a greater extent without requiring a pure stream of CO₂, including from mineral bound phases; a chemical additive is required.

¹² Using an average 2005 exchange rate of 1.82 GBP/USD

3.1.1 Acid based routes

There have been a number of publications presenting calcium extraction from calcium silicates using a variety of additives including HNO_3 , HCl , H_2SO_4 and acetic acid (Newall *et al.*, 2000; Doucet *et al.*, 2010; Eloneva *et al.*, 2008; Eloneva, 2010; Kakizawa *et al.*, 2001) all of which are able to achieve extraction efficiencies of above 80% as they aggressively attack calcium silicates.

It is worth noting that sulfate based additives are unlikely to be effective for indirect carbonation processes due to the low solubility of calcium sulfate (CaSO_4); a significant proportion of extracted calcium is likely to precipitate as CaSO_4 within the extraction reactor. Though this CaSO_4 can subsequently re-dissolve and react with CO_2 to form CaCO_3 , this must occur within the same reactor and therefore it is not possible to produce a high purity product. This was observed by Dri *et al.* (2013) when attempting to use ammonium bisulfate (NH_4HSO_4) to extract calcium from BOS slag and recycled concrete aggregate and it is likely that this is also the reason for the poor performance of H_2SO_4 when used to extract calcium from BOS slag in work by Eloneva (2010).

A hydrochloric acid (HCl) based process was proposed by Newall *et al.* (2000) and investigated in modelling work by Teir *et al.* (2005). In this process, calcium silicates (from wollastonite) are dissolved in aqueous HCl to form calcium chloride, which is then converted to calcium hydroxide using $\text{Mg}(\text{OH})\text{Cl}$. The $\text{Ca}(\text{OH})_2$ is then carbonated in a gas-solid reaction to form high purity CaCO_3 , and the HCl is regenerated from MgCl_2 (Figure 3.2). It was concluded by Teir *et al.* (2005) that the energy demand of the HCl regeneration step would be so high that the process would almost certainly produce more CO_2 than it sequestered (assuming grid sourced electricity), even with heat integration between reactors.

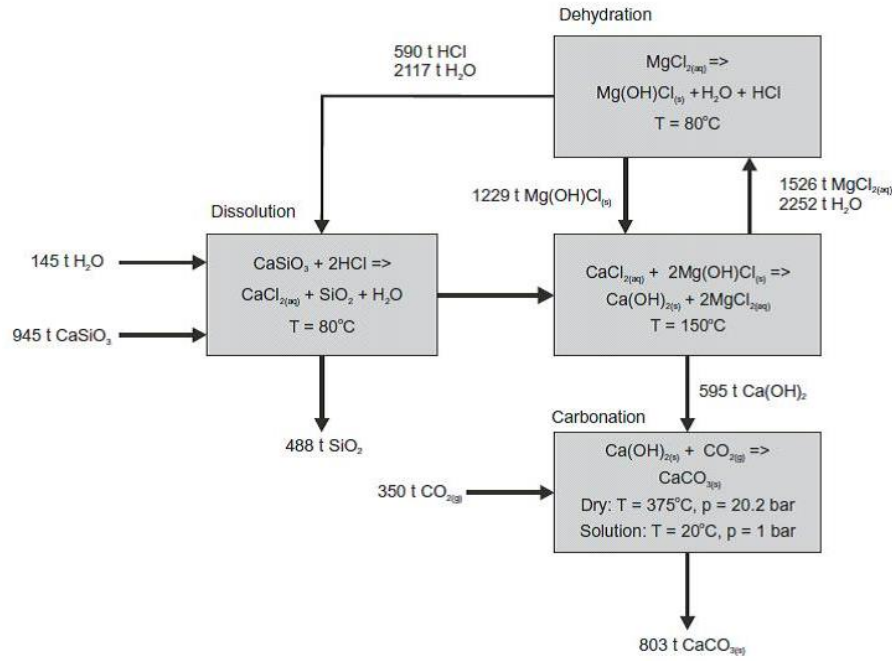
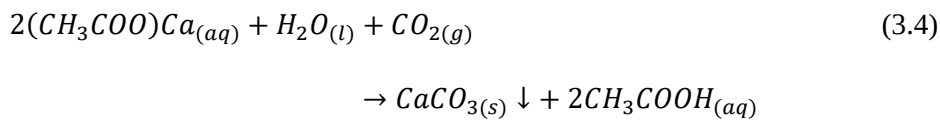
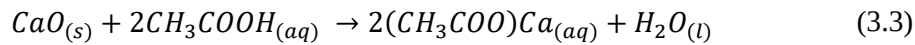


Figure 3.2: The proposed indirect carbonation process using hydrochloric acid (Newall *et al.*, 2000; Teir *et al.*, 2005).

Kakizawa *et al.* (2001) proposed using acetic acid to selectively extract calcium from calcium silicates contained in wallostonite (Equations 3.3 and 3.4). Calculations by Kakizawa *et al.* (2001) estimated that the process would operate at a parasitic energy demand of around 20.4% if operated at a 100MW power station and would cost around £139¹³ (\$200) per tonne of carbon sequestered.



The acetic acid route was investigated in detail by researchers in Finland; firstly by Sebastian Teir (Teir *et al.*, 2005; 2007) before being studied extensively by Sanni Eloneva (Eloneva *et al.*, 2008; Eloneva, 2010) for use with steel slag as a feedstock

¹³ Based on an average 2001 Exchange rate of 1.44 GBP/USD

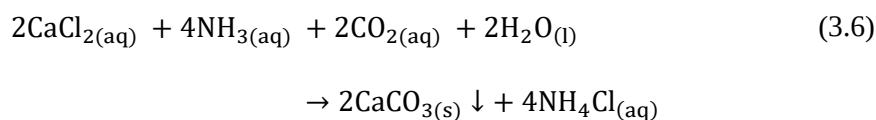
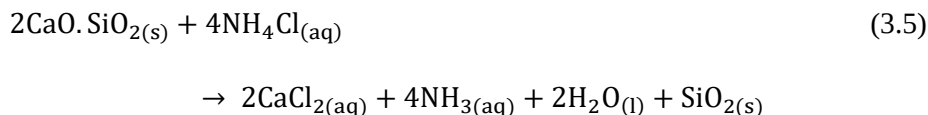
material. It was found that only a very low carbonation efficiency (proportion of calcium extracted into solution that is precipitated as CaCO_3) can be achieved in the process as it is described by Kakizawa *et al.* (2001) (Eloneva *et al.*, 2008). This is due to a combination of factors; firstly CO_2 has a low solubility under acidic conditions and cannot form high concentration solutions. Secondly, CaCO_3 has a high solubility under acidic conditions, limiting precipitation of any CaCO_3 formed. A base such as NaOH must therefore be added to increase the pH to above 5.7 (from calculations by Kodoma *et al.*, 2008). It was concluded by Eloneva (2010) that precipitation rates without base addition were inadequate, and that the volume of NaOH that would be required for pH adjustment renders the process unviable at a commercial scale. It would require 2.25 tonnes of NaOH per tonne of CO_2 captured, at a PCC production cost of around £1292 (€1990) per tonne, compared to the current market value of around £76 per tonne in 2012 (Eloneva *et al.*, 2012).

A large quantity of base addition in order to adjust the pH is a characteristic requirement of all acid based routes. Due to the high energy and economic costs of additive regeneration, it is unlikely that any acid based route would currently be feasible to operate at a commercial scale.

3.1.2 Ammonium salt based pH swing process

Ammonium salts (NH_4Cl or NH_4NO_3) were first proposed by Yogo *et al.* (2005) as an additive which, although is less efficient at leaching calcium than stronger acid based routes, undergoes a pH “swing” meaning that no pH adjustment is required in the carbonation stage and this results in the additive being recyclable. The additive behaves like a weak acid (pH = 4-5; Kodoma *et al.*, 2008) during the extraction step (Equation 3.5), where ammonia is formed, swinging the pH to alkaline (pH = 9-10; Kodoma *et al.*, 2008) as the extraction reaction reaches equilibrium. In the carbonation step, the alkaline nature of the solution both enhances the solubility of CO_2 and reduces CaCO_3

solubility, forcing calcium carbonate precipitation. As the carbonation reaction progresses, the salt reforms (Equation 3.6) and the pH decreases. This means that not only is no additional base required to shift the pH for carbonation, the additive is regenerated spontaneously and can be recycled back through the process.



Kodoma *et al.* (2008) examined the process thermodynamically and experimentally before conducting a brief feasibility study on production of PCC from BOS slag. Thermodynamically, it was discovered that the extraction (Equation 3.5) and carbonation (Equation 3.6) reactions are both spontaneous ($\Delta G = -9.0\text{kJ mol}^{-1}$ and -124kJ mol^{-1} respectively) and exothermic ($\Delta H = -35.1\text{kJ mol}^{-1}$ and -161kJ mol^{-1} respectively), calculated at 80°C for both reactions (Kodoma *et al.*, 2008). Experiments were carried out using three additives for comparison; NH_4Cl , HCl and CH_3COOH . Calcium was extracted from BOS slag using each and the resulting liquor was contacted with CO_2 in an attempt to produce precipitated calcium carbonate. Extraction results indicate that using NH_4Cl as an additive results in a higher selectivity toward calcium compared with both acetic acid and HCl (99.6% using NH_4Cl , compared to 90.2% using acetic acid and 88.0% using HCl), but at a lower extraction efficiency of 59.5% compared to 81.7% and 91.0% using acetic and hydrochloric acid respectively.

The effect of different process parameters on the extraction reactions have been studied widely (Kodoma *et al.*, 2008; Eloneva, 2010; Eloneva *et al.*, 2011; 2012); including the effect of feed particle size, solid to liquid ratio, temperature and additive concentration. Extraction efficiency was determined to be highly dependent on both the particle size

in the feed and the solid to liquid ratio. Extraction efficiency was double at around 61% when the smallest particle slag fraction ($<125\ \mu\text{m}$) was used, compared to the same material milled to $500\ \mu\text{m} - 1000\ \mu\text{m}$. In addition, equilibrium is reached for the extraction reaction much more rapidly when the smaller particle size sample is used (Figure 3.3) (Eloneva *et al.*, 2012). Similar observations were made on the effect of particle size on both the extent and speed of reaction in the work by Kodoma *et al.* (2008). These observations are explained by the mass transfer limitations which occur when the particle surface area to volume ratio decreases as particle size increases. The solid to liquid ratio also has a significant impact on the extraction efficiency (Figure 3.4); the higher the solid loading per litre of solvent, the lower the overall extraction efficiency. At a solid loading of $600\ \text{g L}^{-1}$, extraction is under 20%, compared to around 55% at $20\ \text{g L}^{-1}$ (Eloneva *et al.*, 2012). This has implications in the design of a scaled up process, where a compromise between extraction efficiency and acceptable reactor size must be made.

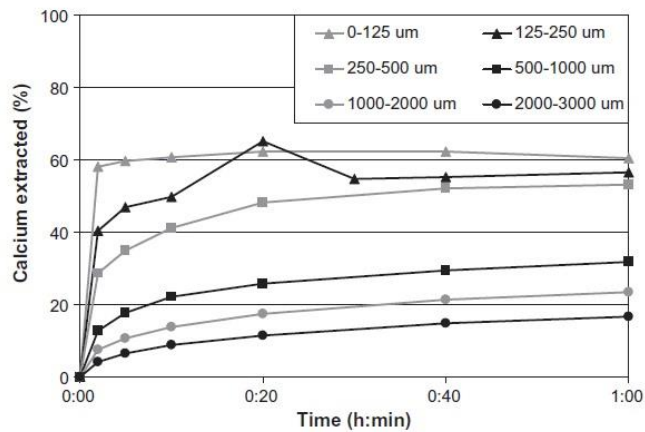


Figure 3.3: The effect of particle size on the efficiency of calcium extraction from BOS slag using ammonium nitrate (Eloneva *et al.*, 2012).

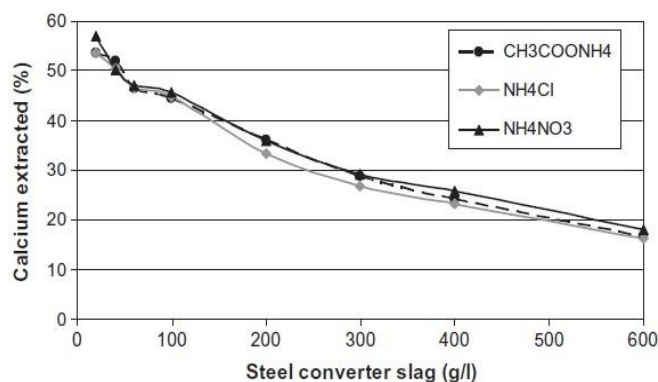


Figure 3.4: The effect of solid to liquid ratio on the efficiency of extracting calcium from BOS slag using ammonium chloride, ammonium nitrate and ammonium acetate (2M) (Eloneva *et al.*, 2012).

The effect of temperature was found by Kodama *et al.* (2008) to have a stronger effect on the extraction reaction at larger particle sizes; at 80 °C, the extraction extent was around 10% higher than at 40 °C for particle sizes between 750 µm and 1000 µm (1M NH₄Cl, 1 hour), however the effect of temperature rapidly diminished as particle size was reduced. Said *et al.* (2013) investigated the effect of additive concentration (NH₄Cl, NH₄NO₃ and CH₃COONH₄) on the extraction reaction and found that increased concentration generally led to higher extraction efficiency; extraction extent was increased by around 10% for each additive between concentrations of 0.5M and 2M (S/L= 20 g L⁻¹, 1 hour).

In the work by Kodama *et al.* (2008), when extraction liquors (NH₄Cl, HCl and CH₃COOH) were contacted with CO₂ (13%CO₂:87% N₂ at 17 cm³ min⁻¹, 40 mL of liquor, 1 hour duration) the only one to produce precipitate was the liquor produced using NH₄Cl; production and precipitation of CaCO₃ in the leachates produced using HCl and CH₃COOH were assumed to be inhibited due to the high pH. A maximum efficiency of around 80% was achieved in the carbonation reaction, and this was effected negatively by temperature; indicating that the reaction is favoured at temperatures below 60 °C. Thermodynamic calculations indicate that the reaction extent should theoretically reach 100% (Kodoma *et al.*, 2008), suggesting that very high

carbonation efficiency could be achieved if process conditions are optimised. Kodoma *et al.* (2008) expressed concern over the possibility of ammonia vapour being leaked to atmosphere due to entrainment in outflowing gases from the carbonation reactor and the possible environmental and cost implications of this. To prevent this, a stripper column was included in their process design and feasibility study. The extent to which ammonia losses are likely to occur was investigated experimentally by Eloneva *et al.* (2011), who concluded that the losses observed at a laboratory scale were insignificant, accounting for only around 0.35% to 0.83% of the total ammonia in the solvent. As temperature appears to have a negligible effect on the carbonation reaction below 60 °C, and lower temperatures should reduce the entrainment of NH₃ in the gas out stream, it is proposed that the carbonation reactor should be designed to operate at ambient temperature (10 - 25 °C).

The calcium carbonate precipitates produced from the ammonium salt process generally are of a high purity; up to 98% was reported by Kodoma *et al.* (2008), while Eloneva (2010) reported 99.86% (based on detectable impurities of 0.14%). Precipitate of a slight lower purity (up to 95±2%) was reported by Sun *et al.* (2011); with impurities consisting predominantly of iron, sulfur and magnesium. The reason for this difference is not given, but similar impurity levels were observed by Eloneva *et al.* (2011) before the precipitate washing step (whether or not the precipitate was washed in the study by Sun *et al.* (2011) is unclear).

Kinetics modelling by Mattila *et al.* (2012) examined the sensitivity of the process to changes in parameters such as temperature, particle size, additive concentration and slag chemistry in the extraction step and CO₂ flow rate, bubble size, mixing rate and ammonia concentration in the carbonation reaction. Results on the extraction step confirmed earlier work which had indicated that temperature had little effect, and that particle size and slag chemistry are the most significant variables affecting the reaction.

In the carbonation step, it was found that the CO₂ flow rate and the ammonia concentration both strongly affected the CaCO₃ precipitation rate. Gas bubble size also had a strong effect on precipitation rate due to increased surface area for gas/liquid mass transfer. It was concluded that a residence time in the carbonation reactor of 30 minutes is sufficient to give a high yield of PCC and that multiple subsequent extraction steps could increase the overall extraction efficiency.

Mattila and Zevenhoven (2014) published a study on the design of a continuous process setup; where the process was scaled to a sub-pilot scale (total volume 70L). A number of process parameters were tested again in the scaled up, continuous process and results showed that the process could be optimised to produce PCC of varying morphologies (vaterite and calcite).

A preliminary economic and technical feasibility assessment of the process was undertaken by Eloneva *et al.* (2012). Results from this work showed that the new PCC production process had economic potential, and that it could potentially result in significant CO₂ savings even when indirect emissions from milling and transportation were taken into account. It was estimated that 1 tonne of CO₂ could be captured and converted to 2.3 tonnes of PCC from 4.7 tonnes of feed material. In addition, if the product were to displace conventionally produced PCC, this could reduce CO₂ emissions even further due to the additional emissions avoided. In a preliminary economic assessment undertaken in the paper by Kodoma *et al.* (2008), the estimated power demand of the process was claimed to be lower than that required for amine based post combustion capture at 300 kWh per tonne of CO₂ sequestered, when the slag was milled to a particle size of 440 µm for a plant treating 147 tonnes of BOS slag per hour.

A more detailed technical and environmental appraisal was carried out in the form of a lifecycle assessment by Mattila *et al.* (2014). This work concluded that PCC produced through the process is likely to be environmentally sustainable, resulting in a net

reduction of CO₂ emissions. The new production route was again found to be more environmentally benign than the current PCC production routes in operation due to reduction in natural resource mining and consumption (primarily limestone) and lower overall energy demand. However, it is important to note that the sustainability of the process was found to be highly sensitive to additional process requirements such as the post-treatment of extracted residues and purification of the PCC product. The study assumed that the carbonation reactor is fed directly by flue gas (post desulfurisation) as a source of CO₂, and as the sustainability of the process appears to be highly sensitive to any additional process demands, it is likely that if a CCS unit were required to provide pure CO₂, that this would damage the sustainability considerably.

The technical feasibility of using flue gas is currently unknown as the effects of low concentrations of acid gases (NO and SO₂) that are inevitably present in real world flue gas on the process and product quality has not been investigated.

3.1.3 Precipitated calcium carbonate

Precipitated grade calcium carbonate is used in manufacturing processes where there is the requirement for high purity and fine particle size that cannot be met by the cheaper ground calcium carbonate (GCC) product produced by milling of limestone. The worldwide market for PCC is around 114 Mt per year (Aresta *et al.*, 2013) serving a variety of applications including;

- Food and pharmaceuticals, for example as the base material of pills
- High performance adhesives where the fine particle size gives improved flow characteristics and give reinforcement
- Paints, PCC is used as an extender and to increase the opacity of the paint
- Paper, where it is used as a filler, a surface finish and to increase the paper brightness

- Plastics, where PCC is used as filler and for reinforcement to increase the strength of the product.

Purity requirements are dependent on the application. Two standards exist which define the requirements for PCC for use in paints and pigments; In the ISO standard, the CaCO_3 purity requirement is set at 98% (BS EN ISO 3262-6:1998 (BSI, 1998)), while the ATSM international standard stipulates that CaCO_3 purity must be a minimum of 96.5% ((D1199-86 (ATSM, 2986))).

The required particle size for PCC is again dependent on application but is typically very small; BS EN ISO 3262-6:1998 stipulates that less than 1 wt% should be retained in a 45 μm mesh sieve. The ATSM international standard specification for calcium carbonate pigments (D1199-86) (ATSM, 1986) specifies six grades of calcium carbonate pigments based on particle size (applicable for both PCC and GCC unless specified);

- Grade I:** **Fine Paint** – less than 0.05% retained on a 45 μm mesh sieve
- Grade II:** **Coarse Paint** – less than 0.5% retained on a 45 μm mesh sieve
- Grade III:** **Filler** – less than 25% retained on a 45 μm mesh sieve
- Grade IV:** **Putty Powder** – less than 30% retained on a 75 μm mesh sieve
- Grade V:** **Superfine (GCC)** – major fraction less than 5 μm , weight median particle size of approximately 1 μm .
- Grade VI:** **Ultrafine (PCC)** – major fraction less than 2 μm , weight median particle size of approximately 0.05 μm

In addition to purity and particle size, the morphology of PCC is also of importance to the customer, for example in paper production rhombohedral calcite is the favourable crystal shape due to good optical properties and good retention in paper sheets (Mattila and Zevenhoven, 2014). It is important to understand crystallisation mechanisms in order to provide a high quality and consistent product. Calcium carbonate crystallises

as three polymorphs; calcite, aragonite and vaterite, depending on reaction conditions (temperature, pH, calcium and carbonate concentration) (Cizer *et al.*, 2012). Calcite is the most stable phase at room temperature and is typically rhombohedral in structure. The other two phases are metastable; aragonite, with a needle like structure and vaterite, consisting of polycrystalline spheres. Vaterite formation typically occurs under carbonate supersaturation conditions and will stabilise to calcite when left in an aqueous environment via a solvent mediated dissolution and re-precipitation mechanism (Fernandez-Diaz *et al.*, 2010). This solvent mediated transformation appears to be dependent on supersaturation ratio rather than environmental conditions (Cardew and Davey, 1985; Spanos and Koutsukos, 1998); at high supersaturation ratios the transformation is inhibited by the slow dissolution of vaterite. In addition, this process can be inhibited by the vaterite stabilising effect of a high sulfate concentration in the solvent (Fernandez-Diaz *et al.*, 2010).

Mineralogy and morphology of calcium carbonate precipitates produced from alkaline industrial residues, via the ammonium salt route, have been reported in a number of studies. Kodoma *et al.* (2008) reported changes in mineralogy as carbonation reaction temperature was altered. Lower temperatures (40 - 60 °C) favoured calcite formation, and at higher temperatures (80 - 90 °C), some aragonite formation was observed. Sun *et al.* (2011) reported a calcite precipitate with some MgCO_3 , Al_2O_3 and FeO impurities. Other studies report calcite only (Eloneva *et al.*, 2011; Said *et al.*, 2013). Mattila and Zevenhoven (2014) observed calcite in the carbonation reactor, and vaterite in the PCC settler in a sub-pilot continuous process setup. Vaterite was formed as the primary phase when the process was investigated using waste cements (Jo *et al.*, 2014), and was observed under high gas flow rate combined with high CO_2 concentration when oil shale ash was used as a calcium source (Velts *et al.*, 2011).

3.1.5 Utilisation of calcium extraction residue

The residue produced as part of the calcium extraction step during indirect carbonation processes presents a major barrier to the sustainability of the process. If the feedstock for carbonation is diverted from a current use, the finely milled residue produced following the extraction reaction is unlikely to be suitable in the previous application, and, unless an alternative utilisation route is developed the residue is likely to be treated as a waste. If BOS slag is taken as an example, currently this material is widely used in the construction industry as an aggregate. If it were diverted from this use for use in an indirect carbonation process, and only around 60% of the available calcium is extracted, around 76% of the original slag mass would remain as residue (based on a BOS slag CaO concentration of 40%). If this residue were to be landfilled, it would pose a serious environmental issue, present a significant additional operating cost (from additional landfill taxes) and more than likely render the process unviable.

Chiang *et al.* (2012) attempted to address this problem by converting post calcium extraction blast furnace slag residues produced from the acetic acid process to porous zeolitic materials via a hydrothermal process. Zeolite materials were successfully produced from the residues when calcium was extracted to a high extent, however, when high calcium concentrations remained in the residue the formation of undesirable calcium containing phases with poor microporosity such as tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (3-x)\text{SiO}_2 \cdot 2x\text{H}_2\text{O}$, $0 \leq x \leq 3$) was observed.

Although there are ongoing efforts to address the residue issue, currently the only way that indirect carbonation processes can be viable is if only materials currently treated as wastes are used as feedstocks. By only treating waste materials the carbonation process will reduce the total mass sent to landfill and this could have economic benefits due to avoided landfill taxes.

3.1.5 Residue pre-treatment

There is evidence that the extent of calcium extraction can be increased by residue pre-treatments other than reduction of particle size through milling, however it is so far unclear whether these could be economical to deploy on an industrial scale. Santos *et al.* (2013) investigated the effect of using ultrasound in a direct carbonation process using different types of stainless steel slag as feeds. They found that introducing ultrasound to the carbonation reaction could increase the extent of carbonation by up to 19% compared to only mechanical stirring. Said *et al.* (2015) investigated the use of ultrasound during the extraction step in the ammonium salt based PCC production process. Results indicate that the use of ultrasound in the extraction process could increase the calcium extraction efficiency considerably; extraction efficiency increased by 31% when the smallest particle size was used (from 65% to 96% for 50-74 μm), and by 20% when the large particle size (from 18% to 38% for 500-1000 μm) was used. Though these results appear to be very promising, there are a number of challenges before the technology can be scaled. Most importantly the electricity demands for producing the sonication must be reduced, or derived from renewable sources; Santos *et al.* (2013) calculated that the electricity associated CO₂ emissions from their sonication test facility were likely to be orders of magnitude in excess of the amount of CO₂ actually captured in the slag, although it should be noted that it was a proof of concept study and conditions were not optimised. Said *et al.* (2015) did not publish figures for electricity demand from their sonication experiments but they are likely to be similar in magnitude. Said *et al.* (2015) also reported that the temperature increase was significantly higher in sonicated samples due to the absorption of acoustic energy, meaning that a higher cooling load would be required if the process is scaled.

Thermal treatment has been used to enhance the reactivity of naturally occurring magnesium bearing materials such as serpentine (Dlugogorski and Balucan, 2014) but

this approach is not appropriate in the case of steel slags as they can be considered to already have undergone a similar treatment at their formation in the furnace.

3.1.5 Summary and research focus

One indirect carbonation route stands out as a prime candidate for further investigation. The ammonium salt based pH swing process is the only process that does not require the expensive addition of a base and can recycle additives without regeneration to produce a very high purity product. Preliminary feasibility work has indicated that not only can the process result in net sequestration of CO₂ emissions, but also offer an alternative, cost effective and more environmentally sustainable PCC production route when compared to those currently operated commercially. The process is however still in the research phase and there are gaps in the knowledge base that must be addressed before it can be taken to the next stage of development. The most prominent of these in our case are: (1) the suitability of the process to the residues produced at Tata Steel sites; (2) the effect of using real flue gas on the process and product; (3) whether the process is likely to be technically and economically sustainable. The purpose of this chapter is to attempt to address research questions (1) and (2), while (3) will be addressed in Chapter 4. The following sections give a detailed account of materials selection (Section 3.2), experimental methods (Section 3.3), results and discussion from extraction experiments (Section 3.4) and results and discussion from carbonation trials directly using steelworks flue gas as a source of CO₂ (Section 3.5).

3.2 Alkaline residues produced at an integrated steelmaking site

A number of calcium rich residues are produced from various processes on an integrated steelmaking site. Many of these residues are currently sold as by-products to a number of industries such as construction and agriculture and thus can be an important source of additional revenue for the steelmaker. Some residues cannot be sold as by-products and are therefore categorised as wastes; wastes are sent to landfill, incurring a cost to the site. This chapter will focus on upgrading and adding value to these waste materials, rather than diverting already utilised by-products.

The residue produced in the highest volumes at an integrated site is blast furnace (BF) slag, at a rate of 0.275 tonnes per tonne of crude steel (WSA, 2014). BF slag is typically fully utilised, with a large proportion processed by rapid quenching and granulation to produce granulated blast furnace slag. This product is valued highly as an additive in Portland cement, and as such is an important source of additional revenue for steelmaking companies (Hiltunen, 2004).

The residue produced in the second highest volumes is basic oxygen steelmaking (BOS) slag from the basic oxygen steelmaking (Linz-Donawitz) process (see Section 2.1) at a rate of 0.125 tonnes per tonne of steel (WSA, 2014). Worldwide, around 85% of BOS slag is currently sold and utilised as road and construction aggregate and as a soil conditioner (Hiltunen, 2004), however the remainder does not meet the required hydraulic specifications and thus cannot be used for these purposes. Some of the remaining slag can be recycled into the blast furnace at some sites to reduce raw materials costs; however this is limited by its high P_2O_5 concentration (Dziarmagowski, 2005). Waste BOS slag is sent to landfill, which can be costly and cause environmental damage through the leaching of metals such as chromium and vanadium (Navarro *et al.*, 2010). BOS slag typically has a calcium oxide content of up to 50% (EC, 2001),

including a significant proportion of free lime, making it ideally suited to carbonation processes.

Prior to steelmaking in the BOS furnace, hot metal from the blast furnace usually undergoes a desulphurisation process to promote the transfer of sulfur from the liquid iron into a slag layer. This process produces another residue called hot metal desulphurisation (HMD) slag. This slag is 55-75% metal, the majority of which is recovered in the metal recovery plant. Following metal recovery, the slag has a chemical composition that is typically considered unsuitable for utilisation and so it is sent to landfill. HMD slag is typically produced at a rate of 0.009 to 0.018 tonnes per tonne of crude steel and is an average of 27% CaO in Europe (EC, 2001).

Following the BOS process, liquid steel undergoes a number of other processes referred to as secondary steelmaking or ladle metallurgy in order to further refine the steel as required by the customer. These processes also produce slag, which following production is processed to remove the metallic fraction for recycling. The metal extraction process removes around 33% of the secondary slag by mass, with the remainder being sent to landfill. Secondary steelmaking slag production rates vary considerably according to steel grades being produced and the specific process in use, but as a rough guide it is produced at a rate of around 0.064 to 0.15 tonnes per tonne of finished steel¹⁴ and has a chemical composition similar to that of BOS slag.

Another source of calcium rich residue is dust collected from air pollution control systems. While typically on a steel plant this dust is rich in iron oxides and carbon rather than calcium, some plants, for example sintering, are beginning to inject calcium containing powders into the exhaust gases in order to improve environmental performance (Remus *et al.*, 2013). In these exhaust streams, the dust collected from the

¹⁴ Data for a specific UK plant from internal Tata steel documents

bag filter can be upwards of 40% calcium, meaning they may be suitable for carbonation processes. This dust is classed as hazardous waste and must be stabilised before disposal, at a high cost.

3.2.2 Materials selection and preparation

Four samples of residues currently treated as wastes were received and are the basis for experimental work in this chapter; three types of slag from an integrated steelmaking site in the UK in addition to a sample of a calcium rich air pollution control dust from an integrated site in the Netherlands. These are outlined below with their respective abbreviations which are used throughout the thesis:

- **Basic Oxygen Steelmaking** (BOS) debris, the portion of slag produced in the basic oxygen steelmaking (BOS) furnace which is rejected for use as an aggregate; landfilled on site as inert waste
- **Secondary Steelmaking** (SS) slag; landfilled on site as inert waste
- **Hot Metal Desulfurisation** (HMD) slag; landfilled on site as inert waste
- **Air Pollution Control** (APC) dust, collected from bag filters as part of the clean-up of sintering off gas; this is a hazardous waste that must be stabilised at a high cost prior to disposal

Samples were dried in an oven at 80 °C for 2 hours to remove residual moisture and then each slag sample was reduced separately in a Retsch jaw breaker (Hann, Germany) to a maximum of 6mm. This was followed by final comminution in a vibratory disk mill in order to achieve a fine particle size. The milled samples were then sieved into 3 size fractions; <150 µm, 150-500 µm and >500 µm and stored separately in sealed containers until further use. The APC sample, received as a very fine powder, was dried using the same procedure as the slag samples and was then stored in a sealed container until further use.

3.3 Experimental methods

This section details the experimental methods used in order to provide the reader with the knowledge required to repeat the experiments. Each instrument used is described with the manufacturers name and model number. A detailed account of instrument operation is not given as this would be beyond the scope of this thesis, and is publically available from the respective manufacturers.

3.3.1 Calcium extraction

For selective leaching of calcium, 50 g (± 0.05 g) of slag was mixed with 500 mL (± 0.2 mL) 2M ammonium chloride (analytical grade, VWR) and stirred with a magnetic stirrer at 600 rpm for time periods of both 1 and 2 hours. Each sample was filtered immediately following extraction through Whatman 540 grade (8 μ m) filter paper before being dried overnight in a fume cupboard. Mass loss was determined by weighing the residue. This procedure was carried out on the APC sample in addition to <150 μ m and 150-500 μ m size fractions of each slag type in triplicate in order that a mean mass lost could be taken. The extraction liquor was stored in sealed containers until further use.

Previous works on the process have investigated the effects of variables such as temperature, residence time and solid to liquid ratio on the extraction of calcium from BOS slag using ammonium chloride (Eloneva, 2010; Eloneva *et al.*, 2012; Kodoma *et al.*, 2008; Sun *et al.*, 2011). A maximum extraction time of two hours was chosen to ensure steady state as previous works have shown calcium concentration in solution stabilises for particle sizes <1000 μ m within one hour (Kodoma *et al.*, 2008; Eloneva *et al.*, 2012). 100 g/L solid to liquid ratio was chosen as this has been shown to be a good compromise in efficiency to allow for a reasonable reactor size (Eloneva *et al.*, 2012; Sun *et al.*, 2011). Temperature was not controlled as it has been previously

demonstrated that temperature has minimal impact on the extraction reaction (Matilla *et al.*, 2012; Eloneva *et al.*, 2011).

3.3.2 Carbonation experiments

Carbonation experiments were undertaken in two phases. In the first phase, experiments were performed in a laboratory using bottled gas. In the second phase, carbonation experiments were performed at a steelworks power station, where flue gas was used as a source of CO₂ by extracting it through the sample. Extraction experiments were repeated to give a calcium rich liquor for carbonation. Extractions were performed on APC and the <150 µm slag samples for a 1 hour duration. The same sample was used in both lab and plant based trials. To achieve this, liquor was split into three before trials were conducted; 200 mL for lab based experiments, 200 mL for plant based experiments and the remaining 100 mL for analysis.

Carbonation experiments were performed in the laboratory using a cylinder mixture of 18% CO₂ 82% N₂ (BOC, certified) in order to simulate the composition of flue gas, and give comparative results to the real flue gas based experiments. 200 mL of extraction liquor was measured and poured into a carbonation vessel in an ice bath, an impinger was inserted and gas flow was set to 2 L min⁻¹. After a carbonation period of 40 minutes, the solution was immediately filtered and the resulting liquor stored for analysis. The solids were washed thoroughly to remove residual NH₄Cl, before being dried at 180 °C for 2 hours. The sample was then weighed and stored for analysis. This procedure was repeated for each carbonation liquor produced.

Carbonation experiments were repeated on a steel plant in order to determine any effects of real world steelmaking gas on the process and product. Flue gas was extracted from the primary flue ducting at a steelworks power station burning blast furnace gas (BFG), and used as a source of CO₂ for carbonation. Gas extraction was carried out in accordance with US Environmental Protection Agency (EPA) Method 5 (US EPA,

2000). Gas was extracted from the flue through a heated filter to remove particulates, and then fed directly into the calcium extracted NH_4Cl solution at a gas flow of approximately 2 L min^{-1} . An online FTIR (Gaset DX4000) was used to measure and record the composition (CO_2 , SO_2) of the flue gas prior to use, and after passing through the carbonation reactor (Figure 3.5). In this trail, for practical reasons precipitates were not filtered from the carbonation liquor until the day following carbonation experiments.

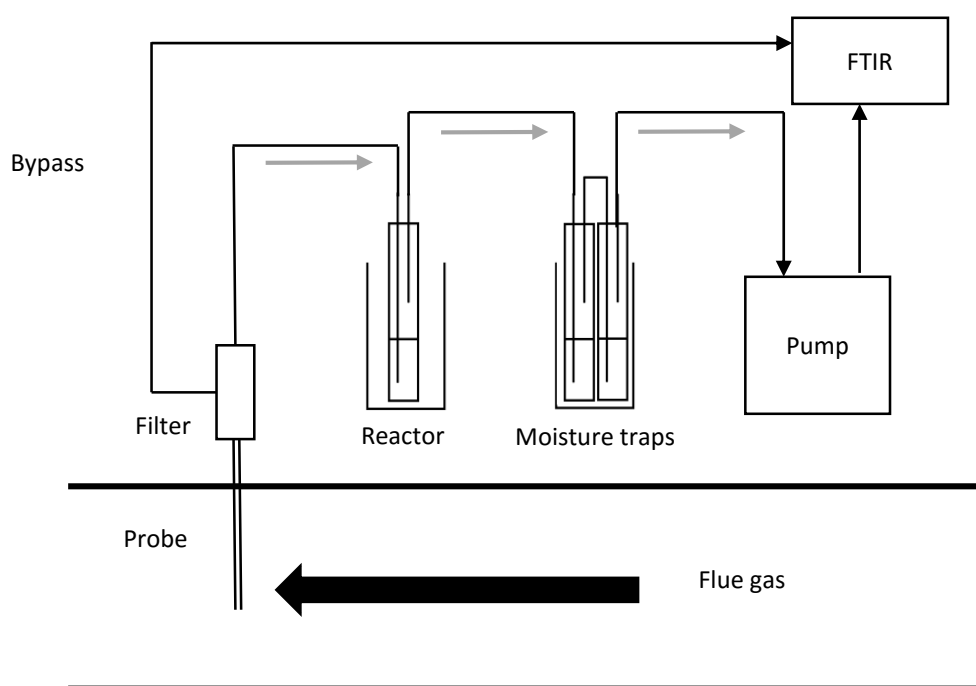


Figure 3.5: Flue gas extraction and carbonation setup. The flue gas is from a boiler burning blast furnace gas at a steelworks power station. Gas samples were pulled from the ducting, through a heated particulate filter. Gas was then passed through the carbonation reactor and two moisture traps before passing through the manual stack sample train (MST) pump and into the FTIR for composition analysis. A second outlet from the particulate filter (bypass) was used to measure gas composition following and prior to use in the reaction.

3.3.3 Analysis

3.3.3.1 Solids

Wavelength dispersive X-Ray Fluorescence spectrometry (XRF) (Brunker S8 Tiger) was used to analyse solids for metal oxides composition. Untreated residues, slag samples following extraction and calcium carbonate precipitates were all analysed by XRF. The instrument was calibrated using synthetic fused beads and this calibration

was verified using certified reference materials. In addition to metals, sulfur concentration in the residues and precipitates were measured using a Leco CS444 combustion analyser, also calibrated using certified reference materials.

A FEI Quanta 600 Scanning Electron Microscope (SEM) was used coupled with Electron Dispersive X-ray Spectroscopy (EDX) to analyse the grain structure and mineralogy of the 150 μm – 500 μm size fraction slag samples pre and post extraction. The very fine particle size of the APC residue meant that it was not possible to get any meaningful data from this sample. Slag samples were set in an epoxy resin before being polished and mounted on a rectangular frame in XBSE mode with a resolution of 1024x800. Operating voltage was set at 25 =kV and magnification at 200x. EDX line scans were used to give a compositional profile across particle cross sections for treated samples.

Mineral Liberation Analysis (MLA) software (version 2.9) was used to give an automated and quantitative analysis of the whole surface area of the loaded sample. Mineralogy of the slags was found to be very complex, with over 30 phases identified for each sample. In order to interpret the data, similar phases were grouped together then weight percentages of each element were determined by EDX spectra and then entered into a database where the mineralogy data was quantified.

Calcium carbonate precipitates were gold coated and imaged at 4000x magnification using a scanning electron microscope (SEM) (FEI Quanta 600). Qualitative X-ray diffraction spectrometry (XRD) (Hiltonbrooks DG3) was used to identify crystalline structures in the calcium carbonate precipitates. Commercial grade PCC (SOLVAY, SOCAL E2 Ph. Eur) was analysed alongside precipitates produced experimentally for comparison and to give an indication of market suitability.

3.3.3.2 Leachate

Leachate composition following extraction and following carbonation were determined by either inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer 3300DV) or inductively coupled plasma mass spectrometry (ICP-MS) (Thermo Scientific, X-series) (the ICP method is indicated alongside results). Samples of leachate were diluted and analysed in argon for Ca, Mg, Fe, and S. ICP analyses were performed in triplicate, with means reported and errors representing standard error of the mean.

After standing for 8 weeks, precipitate formation was observed in the leachate from all three slag types but not in the APC residue. Leachate from each slag was shaken to re-suspend solids and then filtered under vacuum to determine suspended solids in accordance with BS EN 872:2005. The filter cake was analysed for composition by Electron Dispersive X-ray Spectroscopy (EDX) (FEI Quanta 600, low vacuum, 25 kW, spot size 6.5).

3.3.4 Calculations

The selectivity of the NH_4Cl solvent towards calcium was determined using Equation 3.7, where S_{Ca} is the selectivity of the solvent toward calcium, C_{Ca-ICP} is the calcium concentration in the leachate determined by ICP-OES and ΣC_{i-ICP} is the sum of all detected element concentrations.

$$S_{Ca} = \frac{C_{Ca-ICP}}{\Sigma C_{i-ICP}} \quad (3.7)$$

Calcium extraction efficiency ($\eta_{\text{extraction}}$) was determined by converting calcium oxide concentration in the residue (Table 3.1, Section 3.4) to elemental calcium (Equation 3.8), multiplying this by the sample size used for extraction experiments to determine total calcium concentration in the sample and using this to compare to calcium concentration in the leachate (Equation 3.9).

$$[Ca]_{residue} \left(\frac{g}{100g} \right) = [CaO]_{residue}(\%) * \left(\frac{MW_{Ca}}{MW_{CaO}} \right) * 100g \quad (3.8)$$

$$\eta_{extraction}(\%) = \left(\frac{[Ca]_{leachate} \left(\frac{g}{L} \right)}{[Ca]_{residue} \left(\frac{g}{100g} \right)} \right) * 100 \quad (3.9)$$

Carbonation efficiency ($\eta_{carbonation}$) was calculated and is defined as;

$$\eta_{carbonation}(\%) = \left(\frac{[Ca]_{carbonation}}{[Ca]_{extraction}} \right) * 100 \quad (3.10)$$

Where $[Ca]_{extraction}$ and $[Ca]_{carbonation}$ are calcium concentration in the liquor following extraction and carbonation respectively.

Total CO₂ captured ($g \text{ kg}_{feed}^{-1}$) was calculated using Equation 3.11:

$$CO_2 \text{ captured}(g \text{ kg}_{feed}^{-1}) = \Delta[Ca]_{carbonation} * \frac{MW_{CO_2}}{MW_{Ca}} * \frac{1000}{R_c} * P \quad (3.11)$$

Where $\Delta[Ca]_{carbonation}$ is the difference in calcium concentration before and after the carbonation reaction ($g \text{ L}^{-1}$), MW_{CO_2} and MW_{Ca} are relative molecular weights of CO₂ and calcium respectively, R_c is the concentration of residue used in experiments ($g \text{ L}^{-1}$) and P is the purity of the precipitate (as CaCO₃).

3.4 Calcium extraction

In this section, the extraction of calcium using an ammonium chloride additive from four Tata Steel residue samples is investigated experimentally. The selectivity of the additive to calcium is determined, and the significance of the leachate chemistry is discussed with regard to the possibility of fouling issues arising due to precipitate formation. For slag samples, the effect of calcium extraction on the mineralogy of both the whole sample and individual grains is examined using SEM in conjunction with EDX.

3.4.1 Preliminary analysis

In order to ensure the suitability of the sampled materials to precipitated calcium carbonate production, they were analysed for composition. Analysis indicates that all residue samples contain significant calcium oxide, as expected (Table 3.1). The highest CaO concentration was found to be APC (41.7%), followed by SS (34.1%), BOS (30.4%) and finally HMD (25.9%). The three slag types share a similar chemical composition in addition to calcium, predominantly consisting of FeO (16.9%-23.0%), SiO₂ (10.8%-12.5%), MgO (5.0%-15%) and Al₂O₃ (2.8%-7.9%), with some MnO and P₂O₅ also present in smaller concentrations. As could be expected due to its purpose, sulfur concentration in HMD slag is higher than that in BOS or SS slags by a factor of approximately 5 (0.09 in SS compared to 0.44 in HMD). The chemistry of the APC residue is different to that of the slag samples; characterised by low silica (1.1%) and MgO (0.7%), relatively low FeO (7.8%), but much higher sulfur (8.0%) and potassium (2%). In addition, the composition for APC from analysis is less complete than that for the slags, with a substantial proportion of mass unaccounted for. Following communication with engineers at the plant which was the source of this residue, it was concluded that the major missing components were carbon (up to 10%) and chlorine/chloride (up to 5%). These components are consistent with what would be expected in a combustion exhaust.

The similar chemical composition of HMD and SS slags to BOS slag indicates that they should react with ammonium salts similarly to the BOS slag used in other work (Kodama *et al.*, 2008; Eloneva *et al.*, 2012, 2011; Matilla *et al.*, 2012; Sun *et al.*, 2011; Said *et al.*, 2013) and therefore should produce a calcium rich leachate suitable for carbonation to produce PCC. The calcium rich nature of the APC residue indicates that it could be suitable, however, the likelihood and extent of co-leaching of other components is unknown due to differences in chemistry and must be investigated experimentally.

Table 3.1: Chemical composition of each steelmaking residue from XRF and combustion analysis (components with concentration >1%)

Component	Composition (wt%)			
	BOS	SS	HMD	APC
FeO	16.9	23.0	16.7	7.80
CaO	30.4	34.1	25.9	41.7
SiO ₂	12.5	11.8	10.8	1.10
MnO	3.00	3.70	2.60	0.13
Al ₂ O ₃	7.90	4.60	2.80	0.42
MgO	15.0	9.00	5.00	0.70
K ₂ O	-	-	-	2.0
P ₂ O ₅	1.20	1.50	0.81	0.03
S	0.08	0.09	0.44	8.00

3.4.2 Calcium extraction

Mass loss following extraction (Figure 3.6) indicates that the slag samples are all leached of mass to a similar extent, losing around 10% (10 g L⁻¹) of total mass during extraction. A higher value for mass loss is observed in the APC sample, but is not due to an increase in extracted calcium; calcium concentration for APC leachate is only 9.6 g L⁻¹ (Table 3.2), compared to 19.24 g mass lost per litre during extraction (Figure 3.6). Some of this additional mass loss can be attributed to the co-leaching of potassium and sulfur; a high concentration of both was detected in the leachate (K = 1.735 g L⁻¹ and S

= 0.897 mg L⁻¹), however this still does not account for all the mass lost. It is proposed that the remaining mass was lost from chlorine present in the sample; however it is not possible to verify this due to the presence of chlorine compounds in the ammonium chloride solvent. The discrepancy between the mass lost and detected elements for APC indicates that the selectivity of the solvent towards calcium (S_{Ca}) (Table 3.2) is unreliable; with the true value likely to be around 50%. In the slag samples, the mass lost during extraction is generally in agreement with the calcium present in the leachate, indicating that the high selectivity of the solvent to calcium is accurate for these samples. Selectivity ranged from 0.946 in HMD (<150 μ m) to 0.973 in SS (150 μ m – 500 μ m). Selectivity reported here is slightly lower than the 99% selectivity for BOS slag reported by Kodoma *et al.* (2008), although this can be explained either due to the additional analysis of sulfur in this work, or simply due to differing slag chemistry.

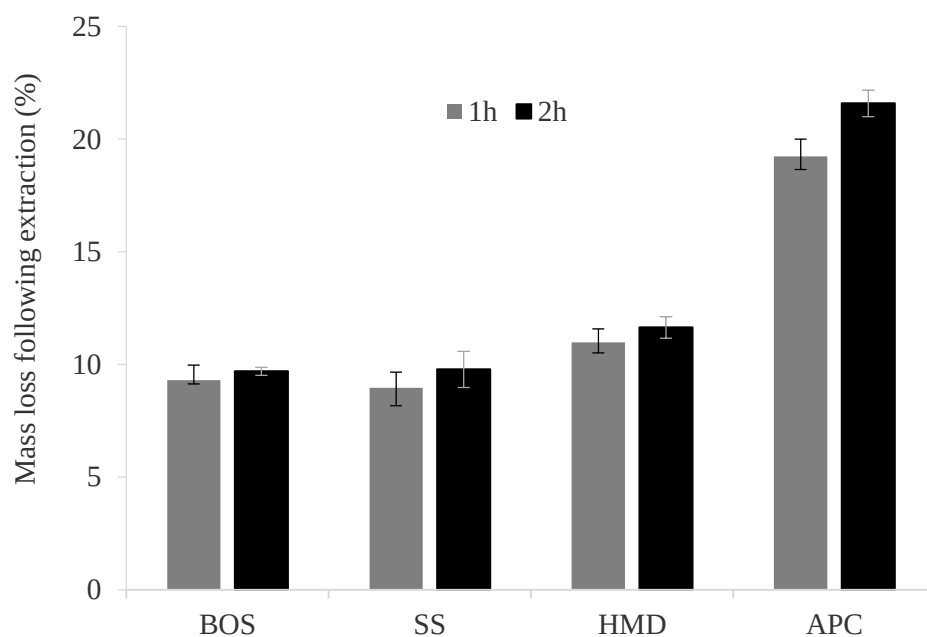


Figure 3.6: Mass loss from APC and small size fraction (<150 μ m) slag samples following extraction in 2M ammonium chloride for residence times of 1 and 2 hours. Data labels give figures for 1 hour extractions.

Efficiency of calcium extraction ranged from 17% from SS (150 μ m – 500 μ m) to 60% from HMD (<150 μ m) and is highly dependent on particle size; efficiency reduces by

between 41% (BOS) and 50% (SS) when the larger particle size (150 μm – 500 μm) is used for extractions. It is clear from Figure 3.6 and Table 3.2 that particle size has a much greater effect on the extent to which calcium is extracted than the one hour difference in reaction duration, indicating that the reaction approaches equilibrium within the first hour. Extraction efficiency values reported here are considerably higher than the value of 6% reported at a similar particle size, residence time and solid to liquid ratio (100 g/L), but lower NH_4Cl concentration (1M) by Said *et al.* (2013).

Table 3.2: Leachate composition, the selectivity of extraction to calcium and the calcium extraction efficiency for all samples at a reaction time of 60 minutes (ICP OES).

Slag type	Size fraction (μm)	Average Concentration (mg/L)						Selectivity (S_{Ca})	Efficiency ($\eta_{\text{extraction}}$)
		Ca	S	Mg	K	V	Fe		
BOS	150-500	5012.1	109.9	37.0	-	0.9	-	0.972	23%
SS	150-500	4212.2	92.0	23.9	-	1.0	-	0.973	17%
HMD	150-500	6241.8	204.8	27.7	-	0.9	-	0.964	34%
BOS	<150	8457.6	197.1	75.1	-	5.5	-	0.969	39%
SS	<150	8369.0	180.7	57.6	-	2.9	-	0.972	34%
HMD	<150	11189.9	607.3	28.2	-	3.6	-	0.946	60%
APC	-	9630.0	897.0	46.0	1735.2	-	-	0.782 ¹⁵	32%

The low concentration of magnesium in the leachate (Table 3.2), when compared to its abundance in the slag (Table 3.1, Section 3.2) suggests that it is relatively unreactive with ammonium chloride, in agreement with previous extraction studies (Sun *et al.*, 2011; Kodama *et al.*, 2008). In contrast, the concentration of sulfur in the leachate is high, accounting for the second highest concentration element leached from the all three slag samples (Table 3.2). Leaching of sulfur is more dependent on particle size than calcium; while calcium concentrations for HMD leachate are approximately double when the particle size is reduced, the sulfur concentration more than triples for the same reduction in particle size (Table 3.2). The increase in sulfur leaching from HMD explains the reduction in solvent selectivity for this sample. The highest sulfur

¹⁵ See the text for clarification of this value.

concentration in the leachate is observed in leachate produced from the APC sample, at almost 0.9 g L^{-1} . Such high levels of sulfur in the leachate for these samples is likely to result in at least some extent of sulfate precipitation, and especially when the solvent has been recycled through multiple cycles; after only one extraction pass, the sulfur concentration in the leachate is approaching the CaSO_4 solubility limit of 2 g L^{-1} (Gangolli, 1999). When considering recycling of the solvent, unreacted calcium, sulfur and other dissolved solids accumulation in the leachate could lead to operational difficulties due to solids build up from precipitation in pipework and reactors. Furthermore, significant precipitation of calcium as anything other than carbonates would reduce the CO_2 mitigation capacity and may degrade the purity of the PCC product.

Precipitates were observed in slag sample leachates after standing for 8 weeks. Precipitates from BOS, SS and HMD extractions were measured as $23.6 \pm 1 \text{ mg L}^{-1}$, $30.1 \pm 1 \text{ mg L}^{-1}$ and $17.8 \pm 1 \text{ mg L}^{-1}$ respectively. SEM-EDX analysis of precipitate formed in BOS leachate identifies the chemistry as predominantly silica (23.3%), with manganese (13.6%) and calcium (7.69%) present.

3.4.3 Effect of calcium extraction on slag mineralogy

Mineral Liberation Analysis (MLA) using EDX data across the whole sample surface was used to give an overall mineralogical composition for all three steel slags pre and post extraction. The complexity of slag mineralogy is illustrated for the BOS sample in Figure 3.8, where a SEM image of the BOS slag sample ($150 \text{ }\mu\text{m}$ - $500 \text{ }\mu\text{m}$) is presented alongside the associated colour coded MLA mineral mosaic and a key containing percentage composition data.

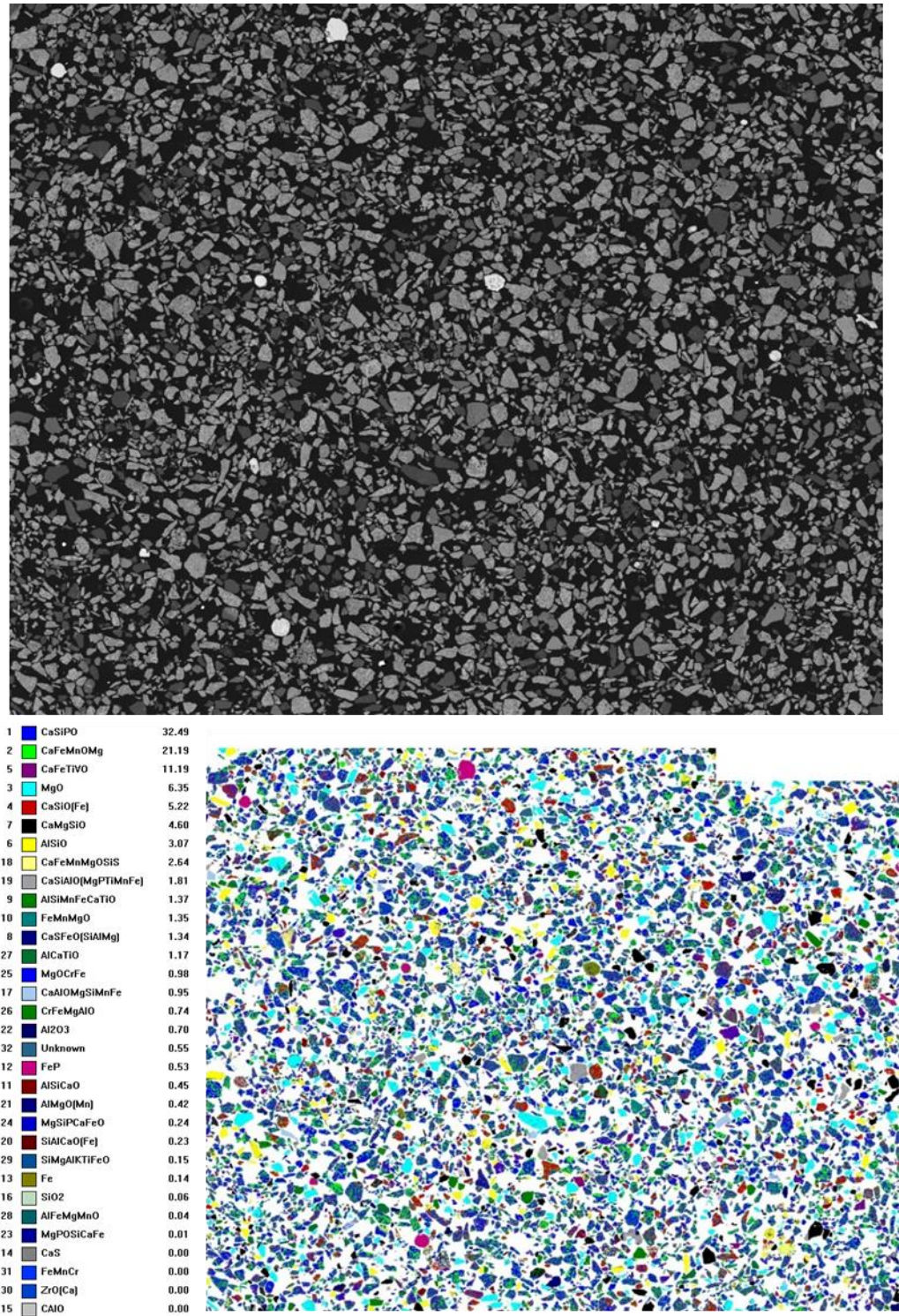


Figure 3.8: Example SEM image (top) and MLA mosaic (bottom right) with accompanying key of minerals (bottom right) for BOS slag sample (150 μm - 500 μm), produced from multiple separate images at 200x magnification. Similar phases were grouped and known mass fractions from XRF were input in order to determine phase chemistry.

The main mineral phases were found to be calcium silicates (dominated by dicalcium silicate (Ca_2SiO_4)) in all three untreated slags, followed by a complex mixture of calcium/magnesium-wuestite (CaFeMnMgO) type phases and calcium ferrates, predominantly srebrodolskite ($\text{Ca}_2\text{Fe}_2\text{O}_5(\text{Ti}, \text{V})$). This composition is similar to that reported in previous studies by Zomeren *et al.* (2011), and is shown in full in Table 3.3, where it is compared to composition following calcium extraction. Free lime (CaO) is reported in the literature as being a major reactive component of the three slags in this study accounting for 1.6-5.4% by mass in BOS slag (Zomeren, 2011). In the samples used for this work, free lime is always found as part of the complex (CaFeMnMgO) group of phases, where it remains unreacted in BOS slag (Table 3.3). The “other” category represents minor phases which were identified by EDX, but cannot be easily grouped with any of the major phases. These phases include free silica (SiO_2) with traces of calcium present in treated samples, free iron and iron oxide (Fe/FeO) present in all samples and calcium sulfide (CaS) in HMD. Following leaching in NH_4Cl in BOS slag, the proportion of calcium silicate, srebrodolskite and CaMgSiO phases are all reduced, indicating that calcium is leached from a number of phases, but not from the free lime containing wuestite type phase. In the case of SS and HMD slags, calcium is leached predominantly from free lime present in the mixed oxide magnesio wustite phase, but also significantly from silicates (11-12% reduction). Evidence of silicate reactivity can be observed in elevated levels of free silica post treatment (Figure 3.9). Elevated levels of alumina and silica (Table 3.3, Figure 3.9) in the residues of BOS and SS following extraction means that they may be suited to hydrothermal zeolite production as described by Chiang *et al.* (2014). However, residual calcium concentrations are at such concentrations (>20%, Table 3.4) that formation of undesirable phases with poor microporosity such as tobermorite ($\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot (3-x)\text{SiO}_2 \cdot 2x\text{H}_2\text{O}$, $0 \leq x \leq 3$) is likely unless calcium extraction efficiency can be improved (Sugano, 2005).

Table 3.3: Mineral composition determined via SEM/EDX and processed using Mineral Liberation Analysis software. Three slag types are shown, pre and post treatment with 2M NH₄Cl for 2 hours. “Other” represents multiple phases which could not be grouped with others.

Mineral phase	BOS			SS			HMD		
	Raw	Treated	% change	Raw	Treated	% change	Raw	Treated	% change
CaSiO(P)	29.10	20.27	-30%	38.94	34.62	-11%	33.68	29.70	-12%
CaFeMnOMg	31.77	32.88	+3%	40.09	32.63	-19%	37.42	28.84	-23%
Ca ₂ Fe ₂ O ₅ (Ti,V)	12.03	10.21	-15%	15.12	18.29	+21%	17.66	20.86	+18%
CaMgSiO	4.90	2.28	-53%	1.96	7.68	+292%	7.37	10.50	+43%
Al ₂ O ₃	7.12	9.84	+38%	1.19	3.46	+191%	2.33	1.33	-43%
MgO	7.69	6.28	-18%	1.92	1.67	-13%	1.55	1.97	+28%
Other	7.37	18.25	-	0.78	1.65	-	0.00	6.79	-

Table 3.4: Slag (150 µm-500 µm) chemical composition following calcium extraction in ammonium chloride (XRF data).

	Component (%)								
	FeO	CaO	SiO ₂	MnO	Al ₂ O ₃	MgO	P ₂ O ₅	Cr ₂ O ₃	S
BOS	18.7	21.1	14.3	3.3	9	16	1.3	0.55	0.07
SS	27	25.2	13.5	4.2	4.7	9	1.7	0.87	0.07
HMD	23	22.2	17.5	3.8	4.7	8	1.2	0.17	0.31

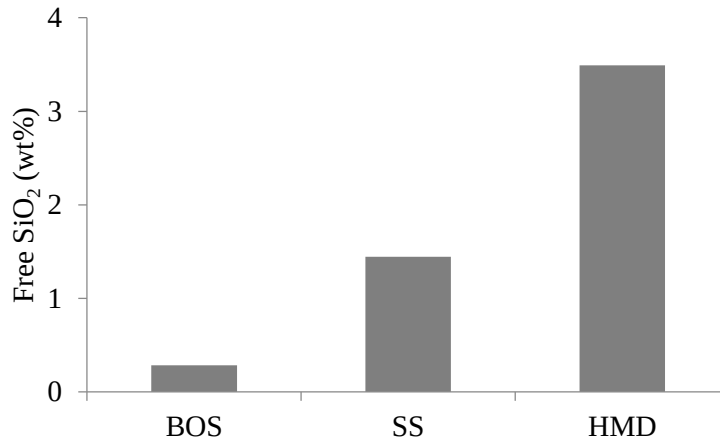


Figure 3.9: Weight % free SiO₂ following extraction in NH₄Cl

Petrographic analysis of the slag post extraction using SEM reveals distinct leached rims around individual grains of Ca₂SiO₄ from each of the three slag samples (Figure 3.10). EDX line scans illustrate the extent of the diffusive loss of calcium. Typical minimum rim widths around free Ca₂SiO₄ particles are in the region of 3 to 5 microns for <150 µm samples treated for 2 hours. The rims display fracturing and this is interpreted as evidence of a volume decrease in the leached silica rich rims. Indications are that rather than forming a silica rich barrier to the inner core, the outer surface is flawed and cracks allow for leaching to continue deeper into the particle. An outermost zone of calcium enrichment in treated BOS slag is unexpected and suggests that as the reaction proceeds this phase has reached saturation and may limit the maximum amount of calcium that can be extracted at this particle size and solid to liquid ratio.

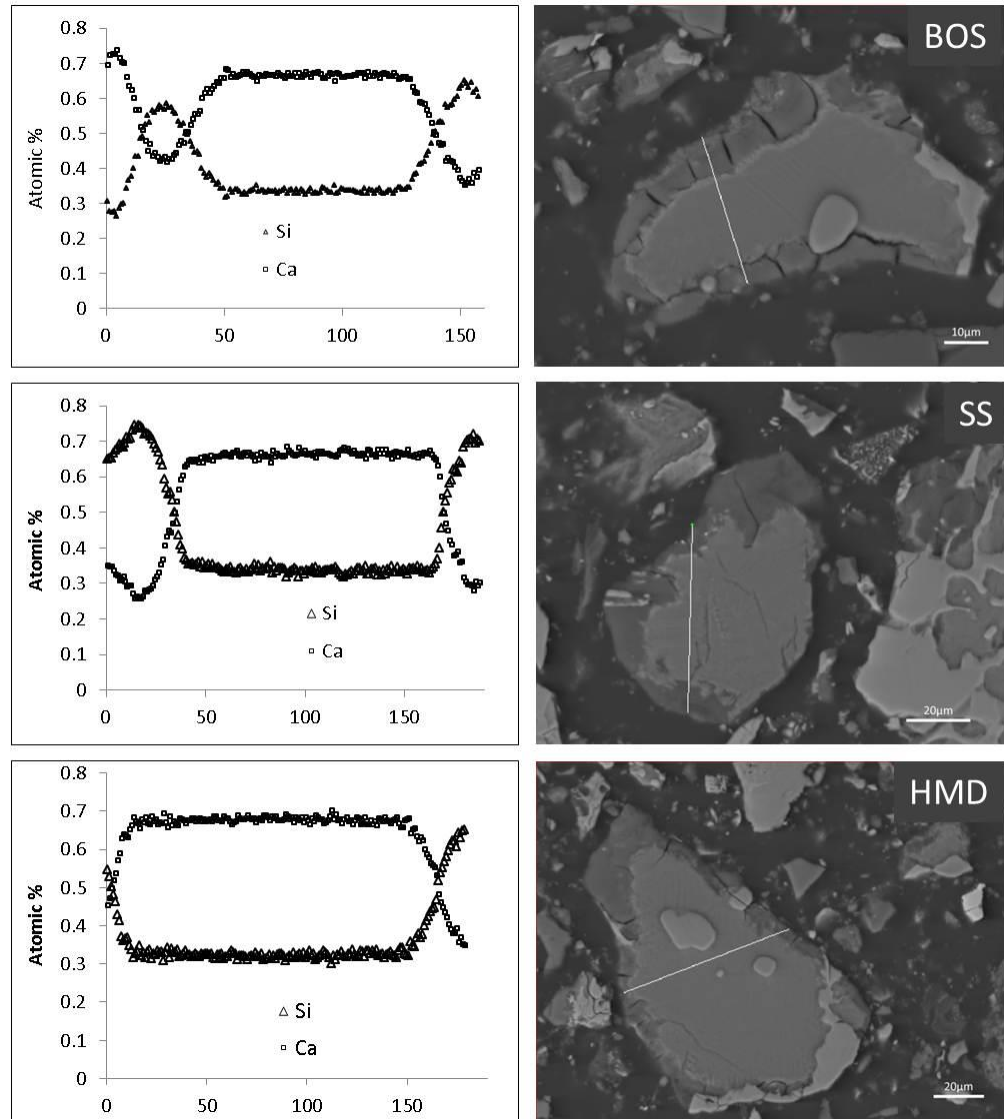


Figure 3.10: SEM images of dicalcium silicate particle cross sections following treatment with NH_4Cl . White lines indicate data points (1-150+) taken during EDX line scan (supporting chart x axis). Supporting charts give compositional Ca/Si atomic ratio across the profile of the particle.

3.4.4 Summary

Calcium was efficiently and selectively extracted from all three steelmaking slag samples, indicating that they are suitable for use in the process. Ammonium chloride acts as a very selective additive for dissolving calcium from the slag which is currently sent to landfill, with selectivity ranging between 0.946 and 0.973. The lowest selectivity towards calcium for slags was observed in hot metal desulphurisation (HMD) slag and can be attributed to the higher levels of sulfur in this slag being co-leached alongside

calcium. The higher concentration of sulfur in the leachate ($>600 \text{ mg L}^{-1}$) helps to explain the increase in mean mass loss during the extraction experiments for HMD slag. Sulfur was also detected in the leachate of other slag types at lower but still significant concentrations. The leaching of sulfur is more highly dependent on particle size than calcium; while calcium concentrations for HMD leachate double when the particle size is reduced, the sulfur content more than triples for the same reduction in particle size. A much lower selectivity was calculated in the case of the APC residue, due in part because of significant co-leaching of both sulfur and potassium. A portion of the mass lost during leaching is unaccounted for; it is suspected to be from chlorine present in the residue, but cannot be verified due to the nature of the solvent.

Observations of silica, manganese and calcium precipitate formation in the leachate raise concerns over the potential for solid deposits to cause fouling in process equipment when the process is scaled. The formation of solid precipitates could be increased due to calcium sulfate formation if sulphur concentrations approach saturation in the recycled leachate.

Mineralogy of the slag samples both pre and post leaching in ammonium chloride was determined using SEM/EDX coupled with MLA software and results show that the most reactive phases are dicalcium silicate and CaMgSiO in BOS slag and both free lime mixed in magnesio-wustite type phases and dicalcium silicate in SS and HMD slags. Although there are differences in phase reactivity, this did not significantly affect calcium extraction efficiency. Ca_2SiO_4 reactivity is supported by the presence of free silica in the treated residue and the presence of silica rich rims surrounding treated particles. Fractures in these silicon rich rims indicate that volume reduction occurs during treatment and this could reduce the shielding effect of the rim to the unreacted core of the particle, however calcium enrichment on the outermost parts of the rims

suggests localised saturation of the solution and may limit the total calcium which can be extracted at this particle size and solid to liquid ratio.

3.5 Effect of steelmaking exhaust gases on the carbonation process and products

A crucial design parameter which remains unaddressed in the ammonium salt based PCC production process is the effect of using real variable and impure, flue gas on the process and on the product quality. Very few works have accessed the effect of real world flue gas impurities on carbonation processes and products (Sanna *et al.*, 2014). This section attempts to address this by demonstrating the direct use of steelworks power station flue gas as a source of CO₂ for indirect carbonation of the four Tata Steel residues and considering the effect of impurities on the market suitability of the resulting precipitates. Although performed specifically on the ammonium salt process, the results have wider implications within the field of indirect carbonation.

3.5.1 Process efficiencies and CO₂ sequestered

Precipitated calcium carbonate was successfully produced from all waste samples using both bottled gas and steelworks power station flue gas. Efficiency of carbonation ($\eta_{\text{carbonation}}$) was generally higher in precipitates formed using bottled gas; this was highest from BOS (79%) followed by those from HMD (78%), SS (77%) and APC (62%) (Table 3.5). Efficiency in flue gas treated samples was generally lower; highest from SS (72%), followed by BOS (70%) and HMD (66%). Flue gas treated samples showed a higher average $\eta_{\text{carbonation}}$ value for precipitates produced from APC (64%), although this difference is not significant.

Chapter 3: Production of high purity PCC from steelmaking residues

The amount of CO₂ captured by the process ranged from 71 g (HMD) to 49 g (SS) for each kg of feed material in bottled gas treated samples and from 66 g (APC) to 46 g (SS) for each kg of feed material in samples treated with flue gas.

Table 3.5: Extraction and carbonation efficiency (η), calcium [Ca] and sulphur [S] concentration and specific CO₂ capture capacity in the liquor pre and post carbonation in both trials. Samples are split following extraction, meaning that the same extraction sample is used for both lab and flue gas carbonation experiments for each repetition of each material.

Residue	Gas source	[Ca] Extraction (mg L ⁻¹) (ICP-MS)	[Ca] Carbonation (mg L ⁻¹) (ICP-MS)	η carbonation	[S] Extraction (mg L ⁻¹) (ICP-MS)	[S] Carbonation (ICP-MS)	CO ₂ captured (g kg _{feed} ⁻¹)
BOS	Lab	7022 ± 213	1488 ± 105	79%	33 ± 1	22 ± 2	60.3
	Flue		2595 ± 211	70%		35 ± 3	48.1
HMD	Lab	8377 ± 381	1822 ± 96	78%	284 ± 23	229 ± 14	71.9
	Flue		2823 ± 211	66%		224 ± 20	59.7
SS	Lab	5867 ± 116	1354 ± 82	77%	15 ± 1	11 ± 1	49.2
	Flue		1613 ± 126	72%		27 ± 6	46.5
APC	Lab	9633 ± 179	3430 ± 498	64%	897 ± 11	765 ± 8	66.4
	Flue		3625 ± 385	62%		720 ± 9	64.6

3.5.2 Effect of flue gas on the product

Gas composition data from the steelworks trial (Figure 3.11) indicates that CO₂ concentration in the flue was high, at around 28% v/v. This is due to the CO/CO₂ rich blast furnace gas being used as a fuel. Sulfur dioxide measurements (Figure 3.11) indicate relatively low concentration (50 ppm) in the flue, but this is almost completely stripped (to <5 ppm) when the gas is passed through the carbonation reactor, meaning that an accumulation of sulfur must be occurring in the carbonation liquor and/or the precipitate. This is confirmed in analysis of the liquor chemistry, where sulfur accumulation is observed in BOS and SS liquors post carbonation with flue gas, but not when bottled gas is used. Accumulation also occurs in the HMD liquor, but is offset by an increase in sulfur concentration in the precipitate (Table 3.6).

When the chemistry of commercially obtained PCC is compared to precipitates produced from slag (Table 3.6), CaCO₃ purity is comparable in samples prepared using bottled gas (>99%). CaCO₃ purity in bottled gas experiments is highest in precipitates produced from HMD slag (99.7%), followed by BOS (99.2%) and SS (99.2%). Product purity was observed to be lower in precipitates from APC produced via both bottled and flue gas (94.7%-94.4%). In all precipitates produced from slag using flue gas there is an increase in sulfur concentration (Table 3.6), while unexpectedly in the precipitate from APC residue the sulfur concentration reduces by around half when produced using flue gas. Degradation of precipitate purity is observed by up to 2% for high compared to those produced from bottle gas, however this appears to be only in precipitates produced from high sulfur feed materials (HMD and APC). CaCO₃ purity in samples produced using flue gas was highest in precipitates produced from SS (99.3%), followed by BOS (98.8%), HMD (97.7%) and finally APC (97.4%).

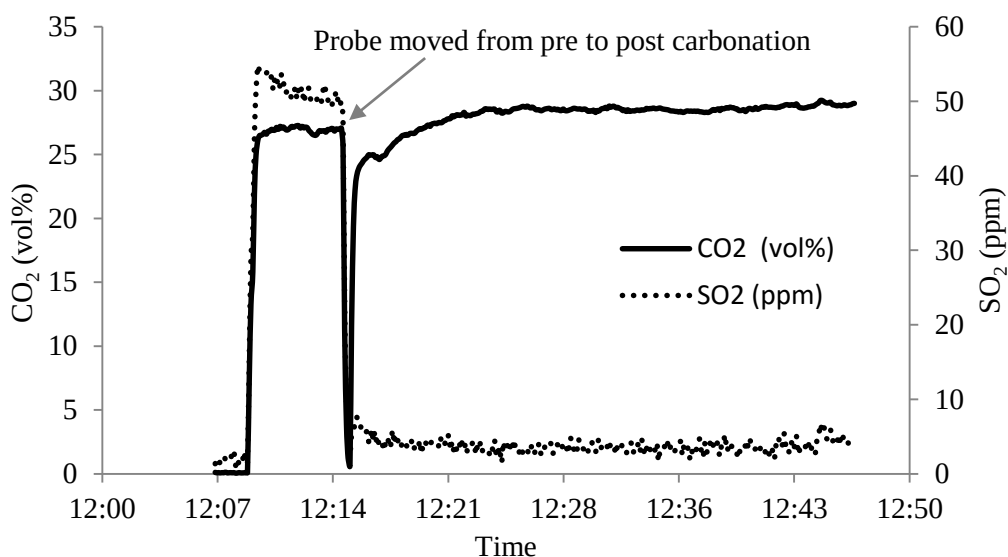


Figure 3.11: Example gas composition (CO₂ and SO₂) data from flue gas carbonation trail (BOS). At the beginning of carbonation (12:07), FTIR (Gaset DX4000) was measuring flue gas directly, before it was swapped (12:14) to measure post carbonation composition.

Table 3.6: Precipitate composition and purity. CaCO₃ concentration was calculated assuming all CaO measured is present as carbonate.

Residue	Gas source	CaO (%)	S (%)	MgO (%)	CaCO ₃ (%)
PCC	-	55.7	0.010	0.43	99.3
BOS	Lab	55.6	0.011	0.10	99.2
	Flue	55.4	0.140	0.09	98.8
HMD	Lab	55.9	0.052	0.10	99.7
	Flue	54.8	0.310	0.09	97.7
SS	Lab	55.6	0.006	0.12	99.2
	Flue	55.7	0.130	0.10	99.3
APC	Lab	54.8	0.490	0.09	97.7
	Flue	54.6	0.280	0.11	97.4

Further evidence of the presence of CaCO₃ is presented in thermogravimetric analysis (TGA) of the precipitates. An example differential thermogravimetric curve (performed in N₂) of the precipitate produced from HMD slag is presented in Figure 3.12. Peaks indicate the temperature at which peak mass loss occurs, and for all samples there is one major peak at between 700 - 800 °C. Mass loss within this temperature range is characteristic of the calcination process where CaCO₃ is thermally degraded to CaO and CO₂. Mass lost in each sample was calculated to be 44±0.5%, the molar mass ration of

CO₂ to CaO in CaCO₃. TGA profiles for the other samples can be found in Appendix A.

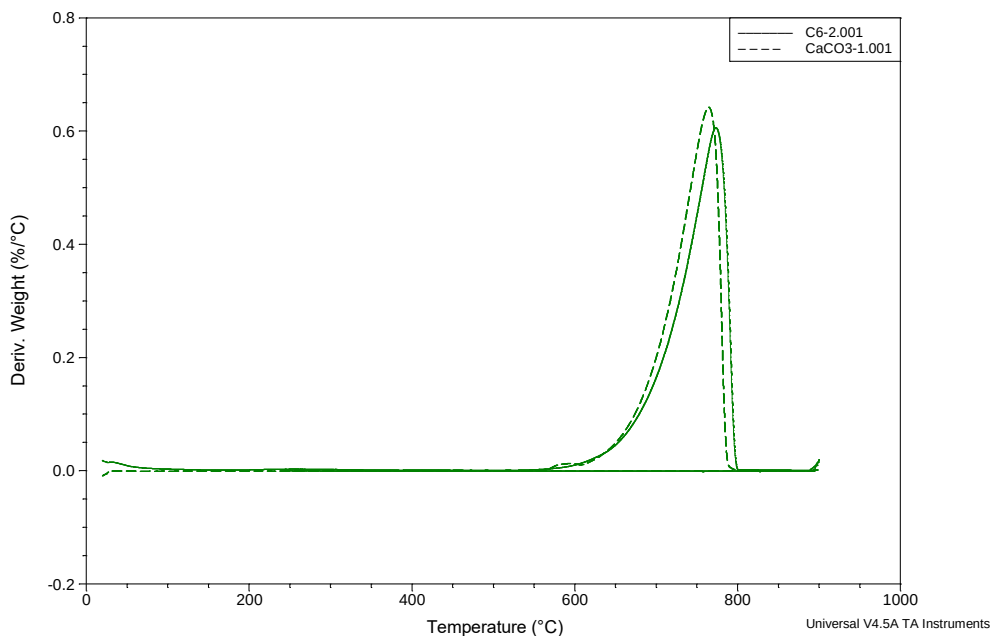


Figure 3.12: PCC produced from HMD slag (C6-1001) compared to commercial grade CaCO₃ (99.1%) (SOLVAY, SOCAL E2 Ph. Eur)

3.5.3 Precipitate morphology

SEM micrographs (Figure 3.13) indicate that all precipitates formed using bottled gas and filtered immediately have a predominantly vaterite crystalline structure and this is confirmed by XRD (Figure 3.14), though there is some calcite present in APC and BOS derived samples. Precipitates formed using flue gas, with the exception of that produced from the APC, are all in the form of calcite; this contrast is clear in the SEM images (Figure 3.12) and is confirmed by XRD (Figure 3.15). Precipitates produced from APC using flue gas are in the form of vaterite. Morphology of commercial grade PCC is unclear from SEM (Figure 3.13(i)) due to the very small particle size, but is confirmed as calcite by XRD analysis (Figure 3.4).

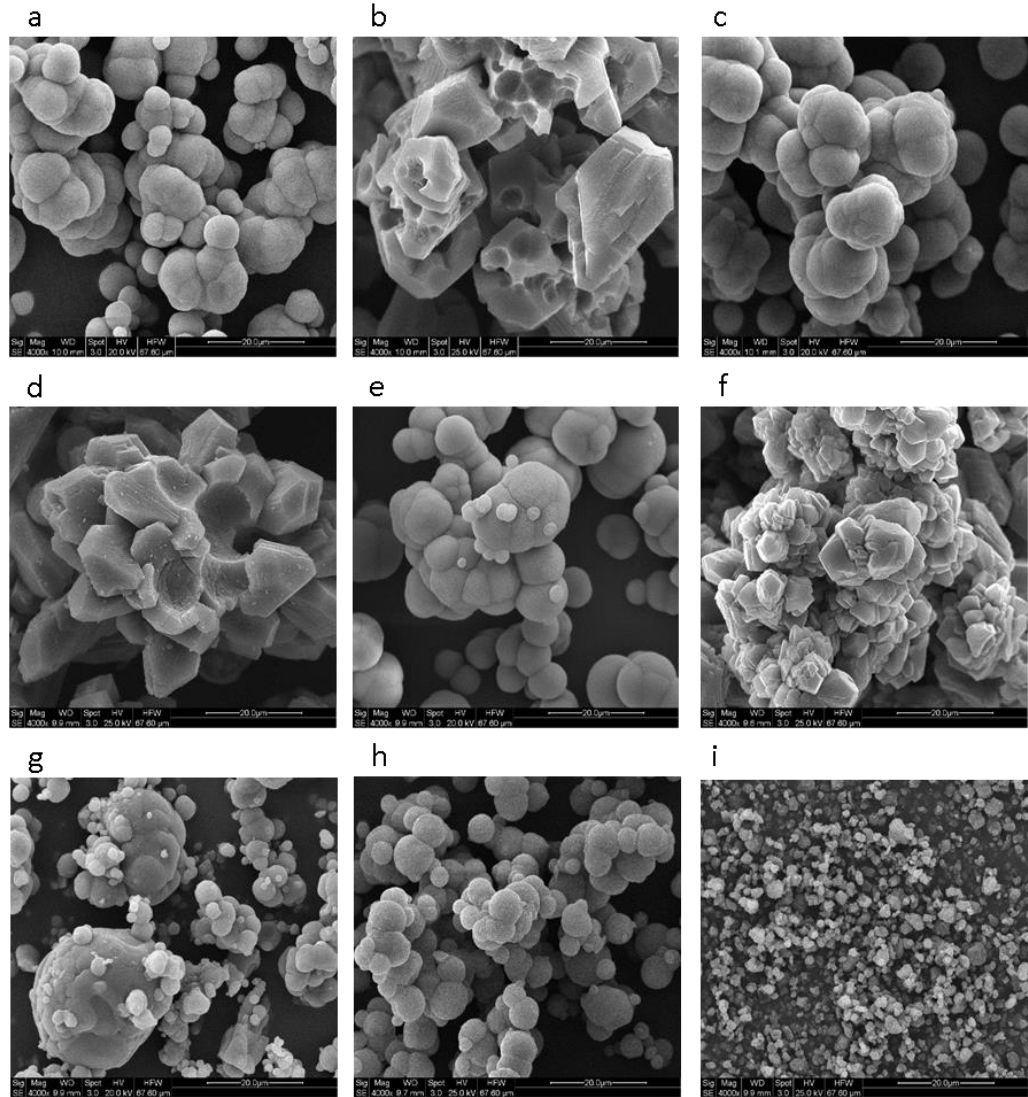


Figure 3.13: SEM micrographs at 4000x magnification of precipitates produced from; (a) BOS, (c) HMD, (e) SS and (g) APC using bottled gas, and (b) BOS, (d) HMD, (f) SS and (h) APC using steelworks flue gas. Image (i) is from the reference commercial grade PCC sample. Scale bars at the bottom right of each image are all 20 μm .

Previous works (Han *et al.*, 2006; Popescu *et al.*, 2014) indicate that the presence of ammonia in the carbonation solution can favour vaterite formation due to ammonia increasing the rate of CO_2 dissolution due to the formation of $(\text{NH}_4)_2\text{CO}_3$ causing rapid supersaturation, increasing the rate of nuclei formation and inhibiting dissolution and re-precipitation as calcite. It is likely that supersaturation is also caused by high CO_2 flow rate, inducing vaterite formation by the same mechanism (Mattila and Zevenhoven,

2014). This may help to explain the observation of initial vaterite formation in this study, due to the combination of ammonia in the carbonation liquor and high concentration of CO_2 in the gas streams.

In the flue gas treated samples, a longer period before filtering resulted in a solvent mediated transformation of vaterite to calcite (Falini *et al.*, 2009). Evidence for this is found in SEM micrographs (Figures 3.13(b) and 3.13(d)), where the remnants of dissolved vaterite spheres are clearly visible within the texture of re-precipitated calcite.

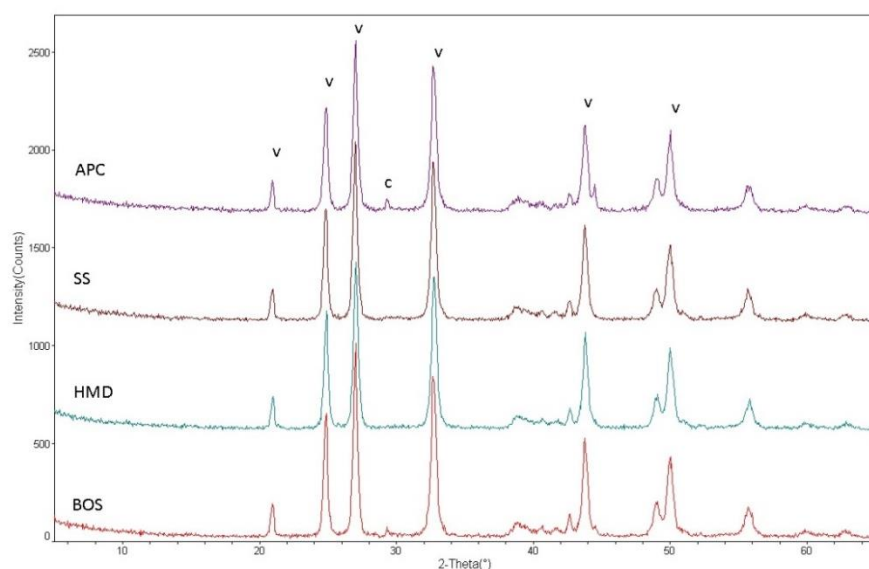


Figure 3.14: X-ray diffraction (XRD) spectra of precipitates formed during carbonation experiments using bottled gas. Labelled peaks indicate different calcium carbonate morphologies; calcite (c) and vaterite (v).

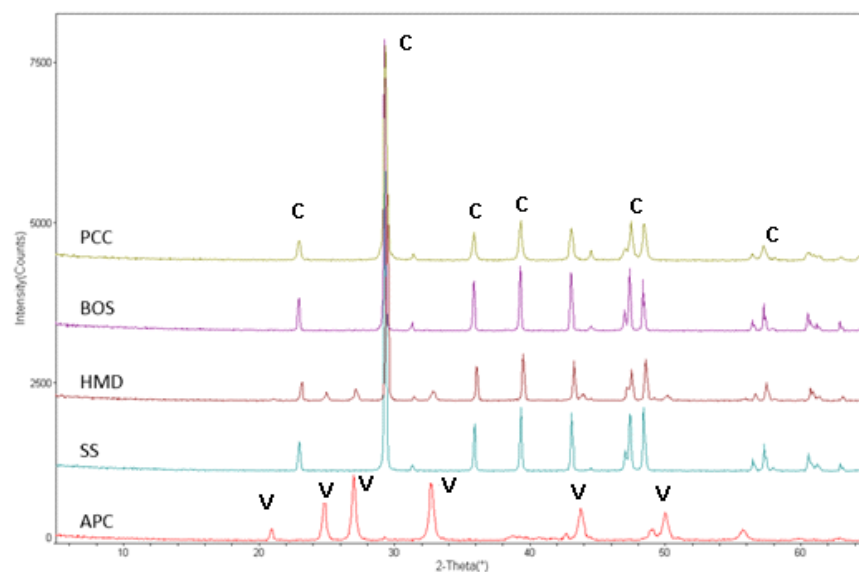


Figure 3.15: X-ray diffraction (XRD) spectra of precipitates formed during flue gas carbonation trials and compared to commercially sourced precipitated calcium carbonate (PCC). Labelled peaks indicate different calcium carbonate morphologies; calcite (c) and vaterite (v).

Particle size of precipitates produced in this study (Figure 3.13(a-h)) is larger than the BS EN ISO 3262-6:1998 (BSI, 1998) specification for PCC paint extenders, and is much larger than the commercial sample (Figure 3.13(i)), but may conform to pigment Grades I-IV (ATSM, 1986). There is evidence that the presence of sulfate can cause the aggregation of CaCO_3 crystals; Falini *et al.* (2009) found that elevated sulfate concentration caused aggregation of both vaterite (with addition of Mg/SO_4) and calcite (with addition of K/SO_4). In this study aggregation is observed in flue gas treated samples and samples from high sulfur containing residues (APC and HMD) (Figure 3.13(d,h)). Relatively large particle size due to aggregation means that milling of the PCC may be required before application, increasing the energy demand of the process.

The lack of solvent mediated transformation of vaterite to calcite in the APC precipitate in this timeframe (approximately 18 hours) (Figures 3.14 and 3.15) is interpreted as evidence of vaterite stabilisation due to a solid solution of sulfate within the crystal structure as proposed by Fernandez-Diaz *et al.* (2010). This mechanism also accounts

for the evidence of partial vaterite stabilisation in precipitate formed from the high sulfur concentration HMD slag (Figure 3.15). An implication of this is that APC is not a favourable feedstock for commercial PCC production due to undesirable precipitate morphology, the relatively low purity of the product and the lower carbonation efficiency when compared to the purity of precipitates produced from slag.

3.5.4 Summary

It has been demonstrated that the production of high purity PCC with a suitable morphology to be taken to market is technically feasible from three types of currently unutilised steelmaking residues. There is the potential for steelworks power stations burning blast furnace gas to use flue gas directly for the carbonation reaction. In this investigation, although most of the SO_2 from the exhaust gas is transferred to the product, it does not degrade the quality significantly, providing that the feed material is low in sulfur (*ie.* BOS and SS slags).

Significant sulfate accumulation from the gas was observed in both the post carbonation liquor and in the CaCO_3 precipitates at a flue gas SO_2 concentration of only around 50ppm. Use of flue gas from combustion of other works arisings such as coke oven gas (COG) is likely to have higher SO_2 concentration and compound the problem (Section 2.1), unless COG desulfurisation is deployed (Remus *et al.*, 2013).

In all PCC samples produced from slags using steelworks flue gas, calcite morphology was observed following a solvent mediated transformation from vaterite. It is likely that in a scaled up process, the reaction conditions could be optimised to precipitate calcite directly. High sulfate concentration in the carbonation liquor can degrade product purity, increase particle size due to aggregation and, at very high levels, prevent the solvent mediated transformation of vaterite to the more desirable calcite. BOS and SS slag types appear to be the most suitable to process into PCC via this route due to

the high purity of PCC produced, combined with the predominance of the desirable calcite morphology.

3.6 Chapter summary

The ammonium salt based pH swing indirect carbonation process was determined to be currently the most viable option for production of high purity carbonate from steelmaking wastes. The process compromises to some extent on calcium extraction efficiency, but produces a high purity product and uses an additive which can be recycled at minimal energy cost.

In this chapter, the two major reaction steps in the process were investigated experimentally, applied to four currently unutilised Tata Steel residues directly utilising CO₂ from a steelmaking exhaust gas.

In extraction experiments, calcium was leached from all 4 residues to a much higher extent to that reported in the literature under similar reaction conditions. A very high selectivity towards calcium was observed in extractions from slag samples, but significant co-leaching of K and likely Cl resulted in a low extraction selectivity from the APC residue. When the mineralogy of slag samples pre and post extraction was analysed, results indicated that calcium was predominantly extracted from silicate phases in BOS slag and from silicates and mixed oxide phases in SS and HMD slags. When the reaction front in individual slag grains was imaged and analysed via SEM-EDX, calcium enrichment at the edge of particles was observed suggesting calcium saturation in the solution and potentially limiting the calcium extraction extent. Formation of a silica rich precipitate in stored un-carbonated leachate indicates that silica is co-leached alongside calcium, and could lead to solids build up and fouling of process equipment when the process is scaled.

Carbonation trials were performed at a steelworks site to determine the effect of directly using steelmaking power station flue gas as a source of CO₂ for carbonation on the process and the product.

Results indicate that CaCO₃ precipitates can be successfully produced from all residue samples using flue gas directly, with varying purity. Sulfur present in flue gas (as SO₂) was stripped by the carbonation liquor and degraded the purity of precipitates slightly when compared to precipitate produced from bottled gas. Despite the reduction in purity when treated with flue gas, precipitates produced from BOS and SS samples were of a high enough purity to conform to the ISO standard for PCC paint extenders (BS EN ISO 3262-6:1998), and precipitates from HMD and APC residues were also very close to the 98% purity requirement (by 0.3% and 1.6%) respectively. Lower purity in these samples can be attributed more to high levels of sulfur in the feed material, rather than the SO₂ stripped from the flue gas.

SEM micrographs and XRD analysis of the precipitates show that initially CaCO₃ precipitation displays the vaterite morphology, but this undergoes a solvent mediated transformation to the more desirable calcite. Strong evidence of this transformation is observed in the texture of the calcite crystals.

The results presented in this chapter demonstrate that production of precipitated calcium carbonate of a marketable quality in terms of purity and morphology is technically feasible when utilising steelworks power station flue gas from at least two of the four waste samples investigated. It is likely that in a PCC production scenario where the three slag types were mixed as a single feed, then the BS EN ISO 3262-6:1998 purity requirement could be met. This scenario will be the basis for the techno-economic process evaluation for PCC production from waste slag in Chapter 4, where the process will be examined in terms of economic and environmental sustainability.

4. A techno-economic evaluation on the production of precipitated calcium carbonate from steelmaking residues

4.1 Introduction

It was demonstrated in Chapter 3 that it is technically feasible to produce precipitated calcium carbonate using waste steelmaking slags and exhaust gas CO₂ from Tata Steel sites at a high enough purity to meet both BS EN ISO 3262-6:1998 (BSI, 1998) and ASTM D1199-86 (ATSM, 1986), the international standards for PCC for use as paint extenders. The aim of this chapter is to feed the technical information from Chapter 3, into a techno-economic model to give a rough evaluation of whether the process has economic and CO₂ mitigation potential and whether the process should be further developed by Tata Steel. The following sections will detail the methods used to produce the model, discuss the optimisation of milling processes for the feed materials, make estimates for capital and operational expenditure requirements, payback period, the CO₂ mitigation capacity of the process and finally determine the sensitivity of the process economics to various unknown and assumed operating parameters.

4.2 Methodology

A techno-economic analysis of the new PCC production process from steelmaking residues using ammonium chloride was undertaken. The aim of the work was to perform a basic process design under two feed material scenarios, then to use this to make preliminary, order of magnitude capital expenditure (CAPEX) and operating expenditure (OPEX) estimates in order to indicate whether the process could be economically sustainable and should be further developed.

Two scenarios are considered for feed materials;

- A. Processing all basic oxygen steelmaking (BOS), desulphurisation (HMD) and secondary metallurgy (SS) slag which is currently sent to landfill.
- B. Processing dust collected from a filter bag plant from clean-up of sintering off gases (APC).

This design treats slag residues as a single feedstock, with a plant capacity of 250 ktonnes per annum (ktpa), based on availability from a real integrated site (Table 4.1). The residue in scenario (B) is a bag filter dust collected from sintering plant gas clean up system and is available at a rate of 20 ktpa. Experimental work has shown that this feedstock can be used to produce precipitated calcium carbonate, but at a lower purity (95% - 97%). However, as this waste currently incurs a high cost of treatment, the offset of this cost could make the process economical in itself.

Table 4.1: Summary of typical feed material production rates, calcium content, preprocessing requirements and disposal considerations. NB: BOS here is the small portion sent to landfill. Lf - Landfill; Stb – Stabilisation.

Waste	Year of data	Scenario	CaO (%) ¹⁶	Production (ktonnes/y)	Milling required?	Disposal	Cost of disposal (per tonne)
BOS ¹⁴	2006	(A)	30.4	50	Y	LF	-
SS ¹⁴	2007	(A)	34.1	176	Y	LF	-
HMD ¹⁴	2006	(A)	25.9	24	Y	LF	-
APC ¹⁷	2014	(B)	41.7	20	N	Stb->Lf	£ 94 (€ 115)

4.2.1 Plant design

A plant was designed to produce precipitated calcium carbonate from steelmaking residues using the ammonium salt pH swing process (Figure 4.1) which is discussed in

¹⁶ Taken from experimental data (see Table 3.1, Section 3.4)

¹⁷ Tata internal discussion with Simon Honingh

detail in Chapter 3. The process involves the selective extraction of calcium from residues (Equation 4.1) and filtering of the resultant liquor from the residue, followed by carbonation of the liquor by direct contact with steelworks flue gas (Equation 4.2). The resulting suspension of CaCO_3 is then filtered to yield a PCC product which is dried and stored. The ammonium chloride is regenerated in the carbonation stage (Equation 4.2) and is recycled back to the extraction stage. In addition to this, for slag materials, a size reduction process is also required to reduce the feed material to a suitable size for an acceptable calcium extraction efficiency to be achieved.

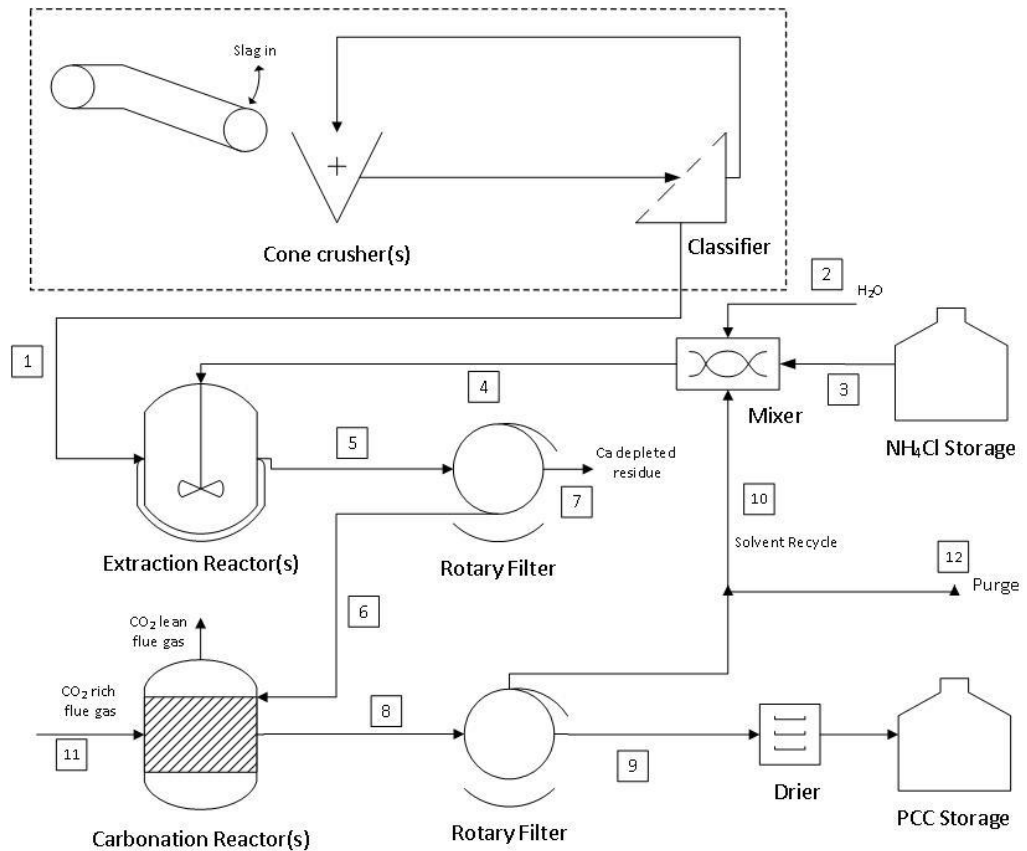
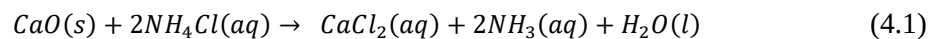
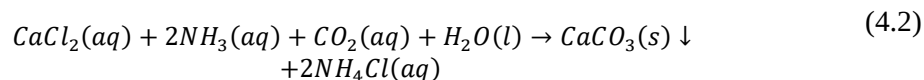


Figure 4.1: Process flow sheet. Unit operations within the dashed line are for milling and only apply to the slag scenario (A)





4.2.2 Mass

and Energy balances

Mass balances were carried out (Table 4.2) assuming an optimum solid to liquid ratio of 5 (Sun *et al.*, 2011), and an ammonium chloride concentration at 2 times the stoichiometric requirement both to ensure an excess and because high additive concentration has been observed to increase the extraction efficiency (Said *et al.*, 2013). Extraction efficiency was calculated according to particle size (see Section 4.5) and carbonation efficiency was assumed to be 0.7, based on both experimental work and literature (Kodoma *et al.*, 2008).

Both the carbonation and extraction reactions (Equations 4.1 and 4.2) are exothermic. The temperature rise in each reactor was calculated in order to determine cooling requirements, assuming a temperature of 25 °C is maintained. Enthalpies of reaction were determined to be -24.05 kJ/mol and -89 kJ/mol respectively for reactions (1) and (2). Temperature change for the slag scenario was calculated to be +4.33 °C in extraction and +11.6 °C in carbonation, assuming a heat capacity equal to that of water. It was concluded that these temperature changes could be controlled by using jacketed reactors, rather than installing dedicated heat exchangers. The process was designed to take place at 25°C and ambient pressure, as the effect of elevated heat on both reactions has previously been shown to either be minimal or undesirable (Eloneva, 2011; Mattila, 2012; Kodoma, 2008).

Solvent and water losses were calculated in order to determine the amount of makeup required. It was assumed that loss rates of 1% occur in each rotary filter, and that there is a 1% purge stream from the recycle in order to prevent accumulation of undesirable species.

Table 4.2: Simplified process mass balance for scenario (A). Refer to Figure 1 to identify streams.

	Mass flow per stream (kg/h)											
	1	2	3	4	5	6	7	8	9	10	11	12
H ₂ O	-	7673	-	142694	140612	139206	1406	137763	802	135021	-	1364
NH ₄ Cl	-	-	301	13649	1294	1281	13	11066	111	10955	-	111
NH ₃	-	-	-	4039	8013	8013	80	4818	48	4039	-	41
CaCl ₂	-	-	-	3889	13361	13227	134	3968	40	3889	-	39
CaCO ₃	-	-	-	-	-	-	-	8016	8016	-	-	-
CO ₂	-	-	-	-	-	-	-	-	-	-	27714	-
CaO	9296	-	-	-	4723	-	4723	-	-	-	-	-
Feed	28539	-	-	-	-	-	-	-	-	-	-	-
Residue	-	-	-	-	23966	-	23966	-	-	-	-	-

4.2.3 Unit operations

Cone mills were chosen for size reduction in the slag scenario (A) due to high capacity, ability to mill to fine particle size and suitability to mill hard aggregate type materials (Sinnott and Towler, 2009). The milling energy requirement was determined using Bond's law (Equation 4.3);

$$W = 10W_i \left(\frac{1}{\sqrt{P_{80}}} - \frac{1}{\sqrt{F_{80}}} \right) \quad (4.3)$$

Where W is the energy required for grinding (kWh/tonne), W_i is the bond work index of the material (kWh/tonne), P_{80} and F_{80} are 80% passing size of the product and feed respectively (μm). It was assumed that the combined slag had a W_i value equal to that given for BOS slag in Kodama (2008) of 30.4 kWh/tonne, and an average feed size of 50,000 μm (F_{80}). When evaluating mill costs, the maximum capacity for which prices are valid is 224 kW. The total power required for milling is dependent on product size chosen, but for where this is over 224 kW, multiple milling units were used.

Extraction reactors were designed based on continuous stirred tank reactors (CSTRs) with a residence time of 60 minutes to allow adequate time for the extraction reaction to take place and with a cooling jacket to allow for control of reaction temperature. From Sinnott and Towler (2009), the maximum capacity CSTR for which the cost data is applicable is 30 m^3 . As the total volume for extraction in the slag scenario was 178 m^3 , it was decided that multiple reactors would run in series to give the required volume. Reactors were sized at 3.5 m diameter and 3.1 meters high, and agitated using an axial flow impeller. Impeller power demand was determined using Table 4.3, where the extraction reaction involves the suspension of a fine slurry. There is a high solids loading in the extraction reactor, and from experimental experience the milled material is hard to maintain suspended, so a value of 2.2 kW/m^3 was used.

Table 4.3: Agitation power demand by application (Robbins and Cusack, 1997).

Agitation	Applications	Power (kW.m⁻³)
Mild	Blending, mixing	0.04-0.10
	Homogeneous reactions	0.01-0.03
Medium	Heat transfer	0.03-1.0
	Liquid-liquid mixing	1.0-1.5
Severe	Slurry suspension	1.5-2.0
	Gas absorption	1.5-2.0
	Emulsions	1.5-2.0
Violent	Fine slurry suspension	>2.0

For the carbonation reactors, jacketed CSTRs were also chosen with the same geometry and impeller in order to give good gas/liquid contact. A liquid residence time of 30 minutes was chosen based on optimisation results by Mattila *et al.* (2012), and giving a total required volume of 69 m³ in the slag scenario, meaning that 3 reactors running in parallel are required, and in the dust scenario a single 5.6m³ reactor is required with dimensions of 2 m diameter and 1.8m in height. In carbonator agitation power calculations, a value of 2 kW/m³ was used to ensure adequate gas absorption and to prevent settling of CaCO₃ particles. Flue gas is delivered to the bottom of the reactor where a value of 20% mass transfer efficiency for CO₂ dissolution is assumed (McCabe *et al.*, 2005). 10% excess dissolved CO₂ is supplied to maintain saturation.

Rotary drum vacuum filters were chosen for filtration of both the calcium depleted residue and the calcium carbonate product. A rotary drum vacuum filter operates as a horizontal axis drum with the cylindrical section covered in a medium over a grid support to allow drainage to internal manifolds. The filter operates under a negative internal pressure and is partially submerged into the slurry which is to be filtered. It is assumed that the wash water is collected through different manifolds to that of the

primary filtrate, which is recycled. A value of 1% (as NH_4Cl) per filter unit was used to estimate solvent loss, though it is accepted that this may be low and the sensitivity of the process to this parameter is tested in Section 4.6. Filtration area is the capacity value required for cost estimation and was calculated using the method given by Dahlstrom *et al.* (1997), assuming a cake thickness of 0.75 cm, final moisture value of 10% and scale up factor of 0.9. Power demand for the shaft drive was estimated from a manufacturer brochure (Andritz, 2011). In order to simplify mass balances, filters were assumed to remove solids completely from the respective process streams.

The drying unit design in the slag scenario was taken from performance data for a similar capacity foundry sand drier (Belt Roto-Louvre) with a high moisture content (Moyers and Baldwin, 1997; Table 12-25). In the dust scenario, the drier (Conveyor - continuous through circulation) was linearly scaled from generic “inorganic chemical” performance data (Moyers and Baldwin, 1997; Table 12-16) at a similar capacity. Energy (electricity and gas) demand was also estimated by linearly scaling values from these examples.

Storage vessels for ammonium chloride and the PCC product were sized as cylindrical stainless and mild steel vessels respectively, with the volumetric capacity to store two weeks supply of ammonium chloride, and four weeks of product.

4.2.4 Capital costs

Order of magnitude capital cost estimates for the plant were performed using the factorial method (Sinnot and Towler, 2009; Holland and Wilkinson, 1997). In this method, the total cost of the plant is extrapolated from the total purchased equipment cost by adding approximates for other costs such as installation, engineering, piping and instrumentation. A breakdown of these cost factors is given in Table 4.4, the sum results in a factor of 4.28 from the price of purchased major process equipment to total physical plant capital cost.

Table 4.4: Cost factors to convert delivered equipment costs into fixed capital investment for a grass roots solids-fluid processing plant (Holland and Wilkinson, 1997; Table 9-51)

Cost consideration	Factor
Equipment Installation	0.41
Piping	0.34
Electrical	0.13
Instruments	0.13
Building and service	0.3
Excavation and preparation	0.15
Auxiliaries	0.52
Field expense	0.39
Engineering	0.39
Contractor's fees, overhead	0.13
Contingency	0.39
Total fixed-capital investment	4.28

Purchased equipment costs were estimated using the exponent approach outlined by Sinnott and Towler (2009) and Holland and Wilkinson (1997), using unit operation capacity ratio exponents based on existing equipment cost data (Equations 4.4 and 4.5). These data were taken from Holland and Wilkinson (1997) (Table 9-50) and Sinnott and Towler (2009) (Table 6.2), using the capacity values for each piece of equipment outlined in the process design section. Costs were then adjusted to 2014 prices using chemical engineering process plant Cost Indices (Mignard, 2014) and, where appropriate, adjusted from USD to GDP.

$$C_2 = C_1 \left(\frac{q_2}{q_1} \right)^n \quad (\text{Holland and Wilkinson, 1997}) \quad (4.4)$$

$$C_e = C S^n \quad (\text{Sinnott and Towler, 2009}) \quad (4.5)$$

4.2.5 Direct production costs (OPEX)

The direct production costs were estimated split into workforce costs, overheads, maintenance, consumables (including electricity) and other charges (Sinnot and Towler, 2009; Table 6.6).

Workforce costs were calculated using the methodology provided in Chemical Engineering Design (Sinnot and Towler, 2009), based on a plant with three shift positions for the scenario (A) and one for (B) both with 4.8 operators per shift position. A basic salary value of £24000 was used, supervision costs were calculated at 25% of operating labour and salary overheads were estimated as 50% of workforce and supervision costs combined. General plant overhead was calculated at 65% of total workforce costs including supervision.

Electricity consumption of the plant was calculated as the sum of all independent unit operations, plus major conveyor and pumping power requirements;

- Conveyors were sized and power requirements determined for the lift required to feed material to the top of the grinding mill and top of the first extractor reactor, in addition to an assumed horizontal distance of 10m. Power requirements were calculated using Raymus (1997) Table 21-7 and converted from Horsepower to kW using a conversion value of 0.7457 kW/Hp
- Pumps were sized for carrying extraction slurry between each reactor (from bottom of one to top of the next), for pumping liquor to the top of carbonation reactors and for pumping required while recycling the solvent at an assumed distance of 60m.
- Flue gas compressors were sized assuming a pressure loss equal to the sum of frictional losses in a 30m transportation pipe and the hydrostatic pressure of the water column above the gas sparging point.

DECC data for the average electricity price of £0.07585 per kWh for industrial users (DECC, 2013) was used to estimate electricity cost.

Process water costs were calculated as the top up water demand due to losses (1% at each filter) plus the wash water required for residue and product washing (assumed to be 0.5 m³ per tonne for residue and 2 m³ per tonne for product based on the work by Tier *et al.*, 2015). Process water (demineralised) costs were estimated at £0.9 m⁻³ (Sinnot and Towler, 2009).

A crude estimate for effluent treatment cost (for wash water and purge) was made using the median estimate in Holland and Wilkinson (1997) (Table 9-61) of 0.6% of installed plant cost per year.

4.2.6 Product revenue and other considerations

Wholesale value of PCC was assumed to be £82¹ (€100) per tonne (Eloneva, 2012). When other costings were available only in US dollars, a conversion factor of £0.59 per dollar was used². When calculating the indirect CO₂ emissions associated with electricity consumption, the UK average for 2012 of 0.4968 kg CO₂ per kWh was used (DEFRA, 2012).

4.2.7 Software

The techno-economic model was developed in Microsoft Excel 2010. Optimisations were performed using the Excel “Solver” plug-in and sensitivity analyses were performed using Excel’s “Data table” function.

4.3 Milling optimisation

In order for calcium to be efficiently extracted from the slag material, it must first be reduced in size in a mill. As the APC residue is produced as a very fine powder, the milling process only applies to the feed scenario (A) and is not included in the model for (B).

¹ Using a conversion rate of £0.82 per euro (May 2014).

² May 2014 conversion rate

The power required for size reduction is proportional to the hardness of the material, often expressed as the Bond Work index (W_i), the feed size and the size to which it is reduced, typically expressed as F_{80}/P_{80} , the sieve size at which 80% of the feed/product will pass. As the hardness of the material can be treated as a constant, it follows that the milling energy required is a function of the P_{80} value (see Section 4.3.3 Equation 4.3). The energy requirement of milling begins to increase rapidly when the slag is milled to below around $100\mu\text{m}$ (Figure 4.2), however smaller particle size results in an increased calcium extraction efficiency (Eloneva, 2010). Assuming that electricity used to drive the mill will be taken from the grid, the milling process will generate indirect CO_2 emissions, offsetting those captured in the carbonation process. A compromise must be met between a particle size small enough to enable calcium to be extracted efficiently, but large enough to minimise the indirect emissions and financial costs resulting from excessive electricity consumption.

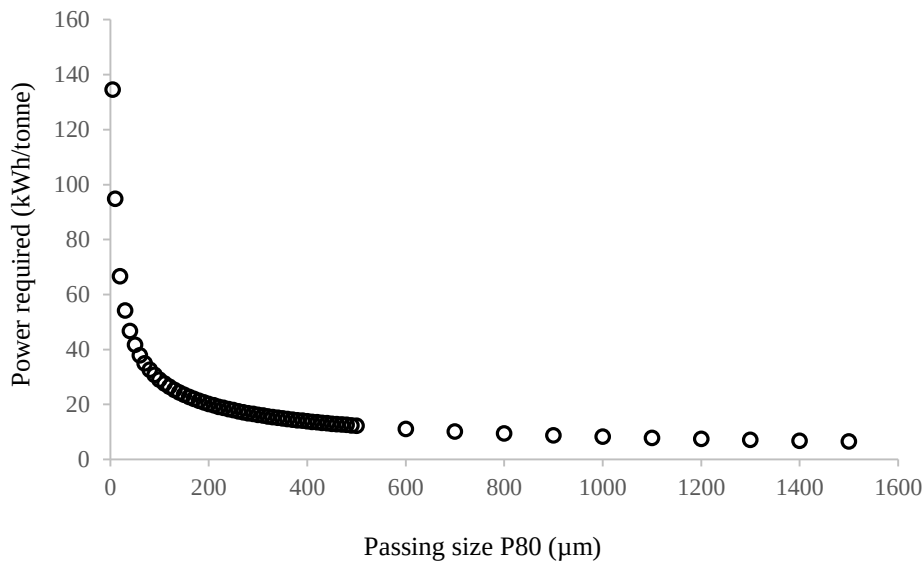


Figure 4.2: The energy required for milling vs slag particle size (P_{80}).

Experimental work was conducted by a Masters student (Paul McCreery) under the author's supervision at the University of Nottingham to determine the relationship between BOS slag particle size and the calcium extraction efficiency (Table 4.5). The

trend observed is in close agreement with that observed by Eloneva (2010) for ammonium nitrate (NH_4NO_3) (approximate values also given in Table 4.5), with the exception that slightly higher efficiencies are typically reported when using NH_4NO_3 compared to NH_4Cl .

Table 4.5: The effect of particle size on the efficiency of calcium extraction from Tata Steel BOS slag using ammonium chloride, compared to the trend observed by Eloneva (2010) (approximate values) using ammonium nitrate.

Particle size (μm)	Extraction Efficiency (NH_4Cl) (%)	Error (95% confidence)	Approximate extraction Efficiency (NH_4NO_3) (%) (Elenova, 2010)
1000-2000	9.85	5.37	~15
500-1000	19.1	4.62	~30
250-500	43.1	3.50	~51
125-250	48.6	3.51	~55
0-125	49.5	3.53	~61

The data in Table 4.5 was plotted using the mid-point of each particle size range to give a trend to input to the plant model (Figure 4.3). An equation was estimated using a logistic function (Equation 4.6);

$$\eta_{\text{extraction}} = \left(\frac{\eta_{\text{max}}}{1 + \exp(n[PS - PS_{\text{half}}])} \right) + \eta_{\text{min}} \quad (4.6)$$

Where PS is the particle size and the other terms are constants; PS_{half} is the particle size at which half the maximum calcium is extracted, n is the power term, η_{min} is the minimum calcium extraction efficiency and η_{max} is a pseudo maximum constant defined as the true maximum calcium extraction efficiency minus η_{min} . The solution was determined iteratively by minimising the sum of error squared for each experimentally determined particle size $(\eta_{\text{extraction (data)}} - \eta_{\text{extraction (model)}})^2$, using the Excel “Solver” function

to calculate a solution (Figure 4.3). Values calculated were then used to optimise the milling process (within the valid range; 50 μm – 1500 μm) to give an estimate for the optimum particle size to give the shortest payback period. This was calculated to be approximately 150 μm , and is the particle size value used to give the results which follow.

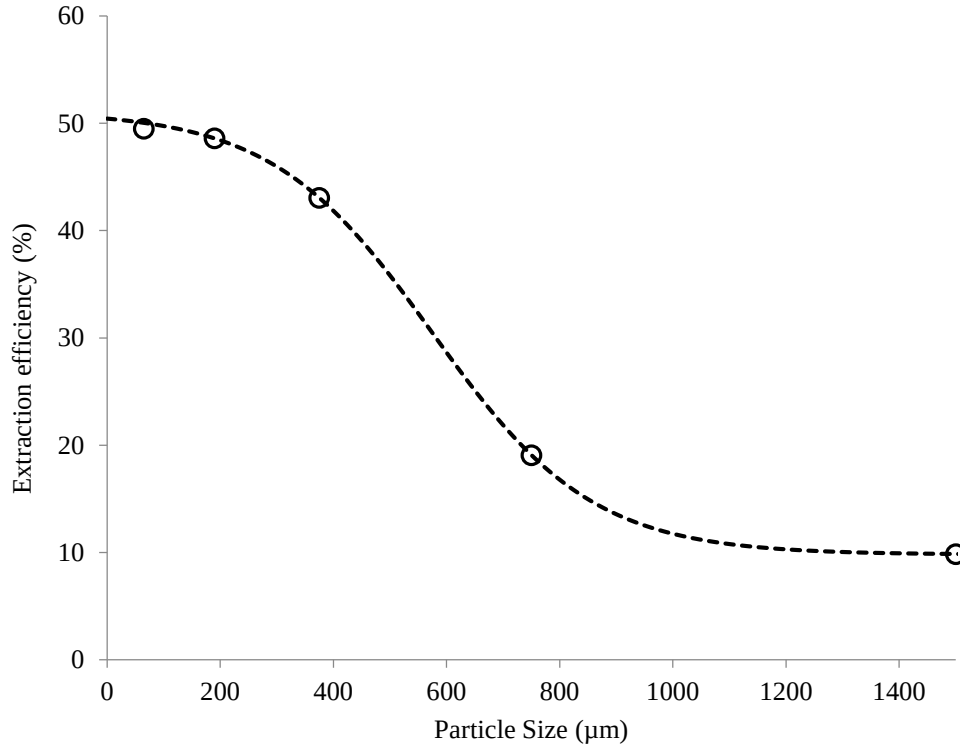


Figure 4.3: Data from Table 4.5 plotted with accompanying trend line calculated using Equation 4.6, where $\eta_{max} = 40.814$, $\eta_{min} = 9.806$, $n = 0.007$ and $PS_{half} = 580.921$.

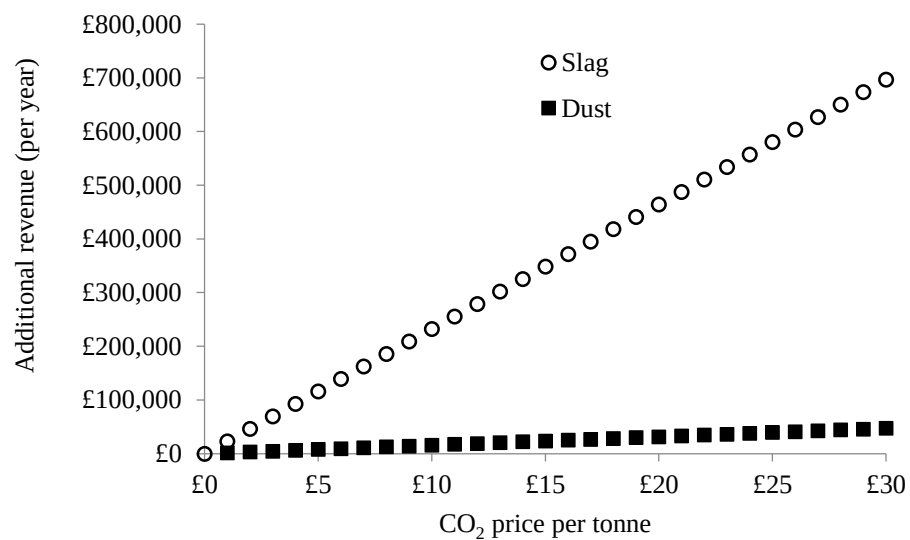
4.4 CO₂ balance

In the slag treatment scenario (A) the estimated CO₂ captured was 84.7 tonnes per day (Table 4.6). When the CO₂ emissions from operating the plant are taken into account, a CO₂ avoidance value is calculated as 63.6 tonnes per day, with a CO₂ avoidance factor of 0.75. The CO₂ capture rate in the dust scenario (B) is much lower at 5.6 tonnes per day, with operational CO₂ emissions amounting to 1.3 tonnes per day resulting in a CO₂ avoidance value of 0.77. At the scale evaluated in scenario (B), CO₂ savings are negligible and this cannot be considered as a significant CO₂ saving technology. The

potential CO₂ capture capacity in scenario (A) is significant and could result in cost benefits in terms of CO₂ credits as part of the EU ETS, if the technology were to be credited under the scheme. The potential for additional revenue is dependent on the CO₂ price but could be up to around £700,000 per year if the CO₂ price is £30 per tonne (Figure 4.4). The impact of this additional revenue on the investment payback period is discussed in Section 3.6.4. It should be noted that significant CO₂ here is regarded in terms of revenue potential from EU ETS, rather than in terms of mitigating the total emissions from an integrated site, for which this capture rate represents less than 1%.

Table 4.6: CO₂ metrics for both scenarios

Parameter	Units	Slag	Dust
CO ₂ captured	tonnes/day	84.7	5.6
CO ₂ emissions	tonnes/day	21.0	1.3
CO ₂ AF	-	0.75	0.77
CO ₂ avoided	tonnes/day	63.6	4.3

Figure 4.4: Potential additional revenue for CO₂ avoidance if CO₂ utilisation is credited under the EU emissions trading scheme.

The majority of CO₂ emissions from the plant are those arising indirectly through electricity consumption in both scenario (A) (75%) and (B) (78%), with the remainder

being produced directly from natural gas firing in the PCC drying process. Total power demand is estimated to be 1235 kW and 85 kW respectively for scenarios (A) and (B); the breakdown of this by source (Figure 4.5) indicates that the demand from reactor agitation is a significant proportion of the total demand in both scenarios. This is predominantly due to the high power demand required to suspend high density, fine particle size solids in the extraction process. Slag milling to achieve the fine particle size is the highest electricity demand when it is required (A), where it accounts for around 54% of the total energy demand. In the dust scenario where milling is not required (B), the extraction fan power demand in the dryer unit is the second highest demand. Pumping, flue gas (Fg) compression, solids conveying and filter drive power all represent low proportions of the total demand in both scenarios.

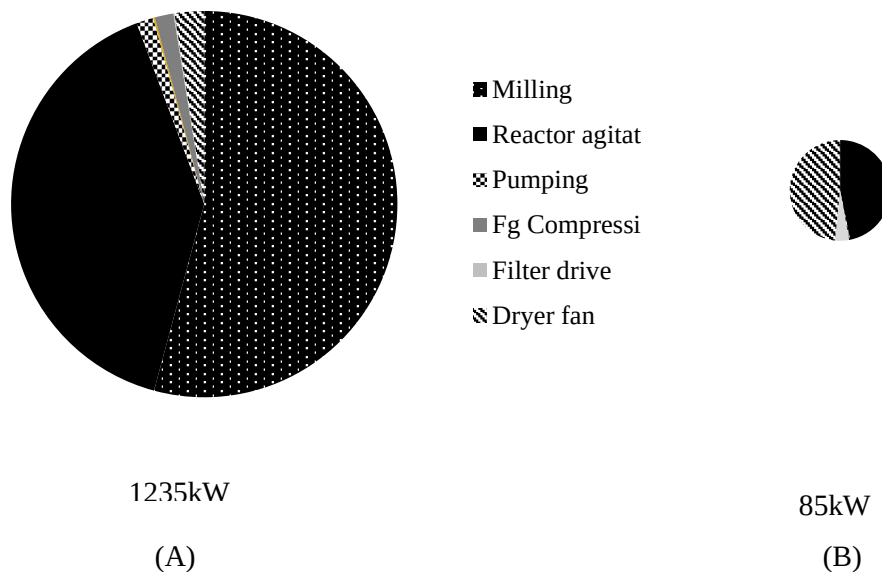


Figure 4.5: Electricity consumption split by demand for the two scenarios; (A) slag and (B) dust.

4.5 Plant economics

In Scenario (A), the revenue from PCC sale was calculated to be £5.76m per year (Table 4.7), resulting in a profit of £1.75m per year when direct production costs (Table 4.7) were deducted. The capital investment payback period was calculated by dividing the total capital investment (Table 4.8) by the annual profits, to give a period of 5.51 years

in the slag scenario (A). The cost of production was estimated using production rate and direct production costs (Table 4.9) to be £57.04 per tonne of PCC, giving an estimated profit margin of around 30%.

The total capital cost of the plant in scenario (A) is estimated to be around £9.6 million, with the largest unit cost being the milling equipment, followed by carbonation reactors and then extraction reactors (Table 4.8). Direct production costs (Table 4.9) were estimated at £4.2 million per year, with the largest single operational cost being capital charges (£965,000), closely followed by electricity (£821,000) and labour (£648,000).

Table 4.8: Capital cost estimates for each scenario

Unit	Cost	
	Slag	Dust
Conveyor to mill	£13,164	-
Cone crusher	£917,964	-
Conveyor to extractor	£13,323	-
Extraction reactors	£613,457	£35,131
Extractor pumps	£5,197	-
Rotary drum filter	£141,922	£42,863
Carbonation reactors	£313,865	£20,050
Agitators	£56,507	£7,351
Rotary drum filter	£83,899	£22,860
Product drier	£96,345	£16,834
Solids storage	£54,212	£8,437
Equipment (purchased)	£2,255,642	£109,958
Total Capex	£9,654,148	£470,622

Table 4.7: Summary of major operating parameters including CO₂ avoided, PCC production, revenue and payback period

Parameter	Units	Slag (A)	Dust (B)
CO ₂ avoided	Tonnes/year	23226	1580
PCC production	Tonnes/year	70224	4678
PCC value	Per tonne	£82.00	£82.00
Production cost	Per tonne	£57.04	£112.84
Revenue	Per year	£5,758,336	£383,609
Profit	Per year	£1,753,130	£-144,280
Payback	Years	5.51	-

Table 4.9: Direct production costs for each scenario

Direct Production Costs	Slag	Dust
Workforce total	£648,000	£216,000
Plant overhead	£421,200	£140,400
Maintenance	£482,707	£23,531
Electricity	£821,474	£56,343
Process water (DI)	£281,367	£99,904
Water treatment	£57,925	£2,824
Ammonium Chloride	£316,294	£12,816
Capital Charges	£965,415	£47,062
Insurance	£96,541	£4,706
Local Taxes	£193,083	£9,412
Total	£4,284,007	£626,682

In scenario (B), the estimated production cost is £112 per tonne of PCC, meaning that production costs are above the product value. This means that the plant is expected to make a loss of around £144,000 a year (Table 4.7) and therefore the capital cost will not be recovered. In addition, it has been shown in experimental work that it is unlikely that a high enough quality product can be produced from this feed to be able to charge a high price. However, as the feedstock is a waste which currently costs £94 per tonne to transport and stabilise (Table 4.1), the avoidance of this cost can be taken into account

under the assumption that the resultant residue is considered stable and can be directly disposed of. As the cost of treatment by PCC production is estimated to be £27.57 per tonne, the cost savings of £66.4 per tonne result in a payback period of 0.35 years, before the potential revenue from PCC sales is included. The application of the process to stabilisation of this waste is wholly dependent on the properties of the resultant calcium depleted residue, which must comply with environmental regulations and requires extensive testing beyond the scope of this project, considering the very low CO₂ capture potential. In addition, the heavy loading of solids other than calcium following the calcium extraction stage observed in experiments (see Chapter 3) means that a high purge rate will be required and it is possible that the cost of stabilisation of the waste will just be passed to treatment of the contaminated wastewater.

4.6 Sensitivity analysis

The sensitivity of the payback period was considered against a number of important operational and market variables for scenario (A). These were; the number of plant operators, recycle stream purge rate, PCC wholesale value, extraction efficiency, maintenance costs and CO₂ price (Figure 4.6). In each case a critical point is identified where the relationship between the variable and payback period transitions from linear to nonlinear. At this point, small changes to the respective variable results in very rapid increases in payback period.

Increasing the purge rate results in an increase in the required makeup NH₄Cl and process water which in turn results in higher operating costs. Between 0% and 5%, increasing the purge rate results in a linear increase in payback period, but after 5% a rapid increase in payback period is observed, up to almost 50 years at 8%. As it was concluded in Chapter 3, the actual required purge rate is highly feedstock dependent and although further testing is required to determine the actual requirement, it is unlikely to exceed 5%.

Similar to the purge rate, an increase in the solvent lost at the slag residue and product filters results in an increase in the amount of makeup NH_4Cl required and increases the operating cost. When the sensitivity of the payback period to this parameter was tested (Figure 4.6) it was found that there is a steady increase in the payback period from around 5 years to around 11 years when the solvent loss was increased from 0% to 5% at each filter. Similarly to purge rate, when losses exceed 5% per filter, the required payback period increases rapidly; reaching 60 years by 8%. This level of loss is very high and if it was determined that it would occur, solvent recovery options would have to be explored.

Payback period is relatively insensitive to both the number of plant operators required and the cost savings associated with different CO_2 prices (assuming a scenario where the technology is credited for CO_2 avoidance). Payback ranges from 3.4 years when no operators are required, to around 9 years when there are 5 plant operators (Figure 4.6), and from around 5.5 years when the CO_2 price is £0 per tonne to 4 years when the CO_2 price is £30 per tonne. Although relatively insensitive from an academic perspective, it should be noted that an increase in payback from 3.4 years to 9 years is likely to have a significantly negative impact on any decision to invest from a commercial viewpoint.

When tested against the price which can be achieved for the PCC product, payback period appears to be relatively insensitive when a sale price of above £80 per tonne can be achieved (Figure 4.6). However, if the product can only be sold for a price below this, then the payback period starts to rapidly increase as this price approaches cost of production; to around 10 years at £70 per tonne and up to almost 50 years at £60 per tonne. Similarly, the payback period is also very sensitive to the efficiency of calcium extraction from the feed; when this value drops below 50%, the period required for investment payback rises rapidly.

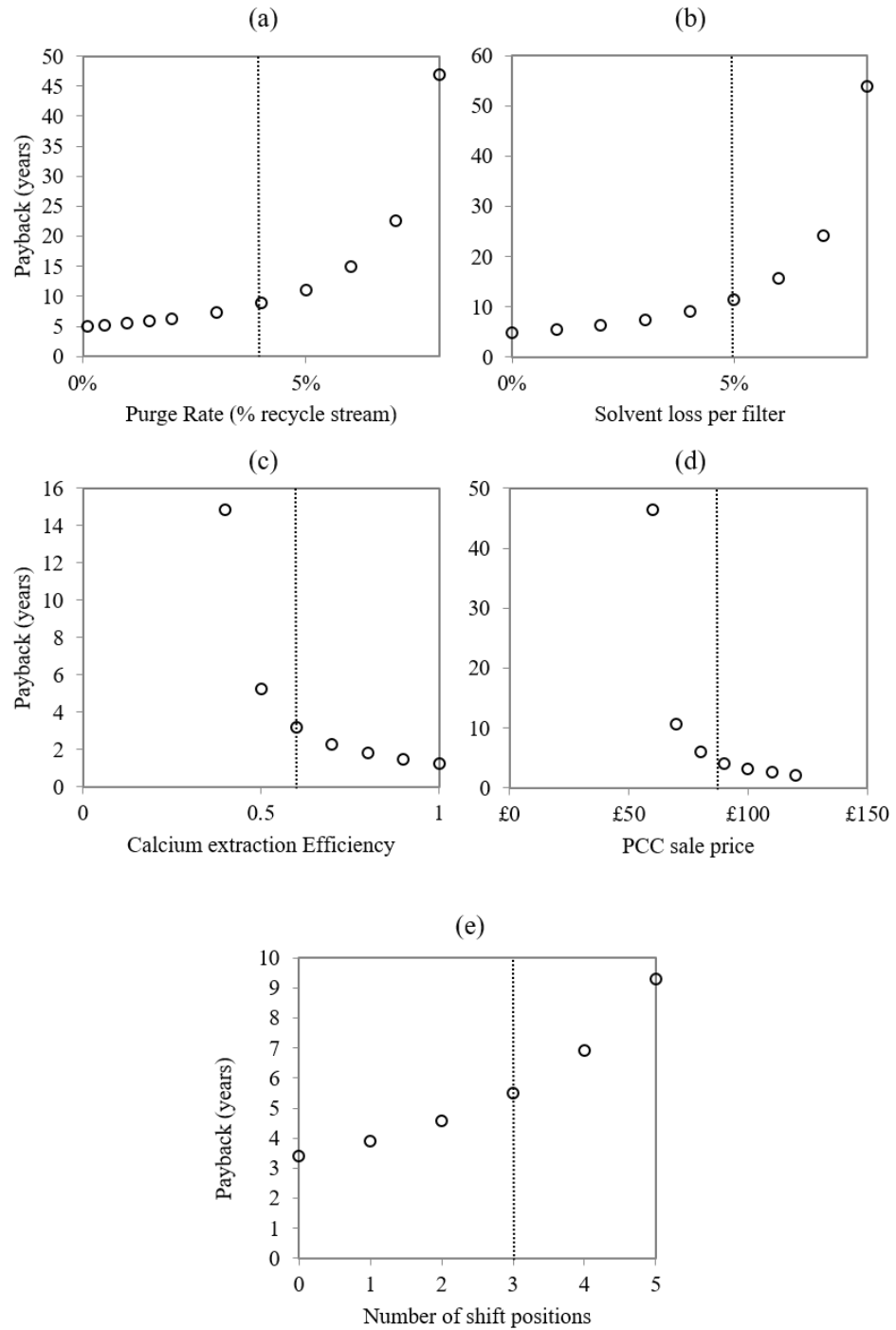


Figure 4.6: Sensitivity of payback period to (a) solvent purge rate; (b) solvent loss rate per filter; (c) calcium extraction efficiency; (d) PCC product sale price; and (e) number of shift positions required to operate the plant. Dotted lines represent the critical point at which the relationship transitions from linear to nonlinear.

4.7 Chapter summary

The techno-economic evaluation of the PCC production process presented in this chapter indicates that it has the potential to be an economically viable option for upgrading slag waste that is currently sent to landfill and utilising CO₂ directly from steelmaking exhausts. Two scenarios were considered for feedstock; (A) mixed utilisation of currently landfilled slags with a feed capacity of 250 ktpa proved promising with a positive cash flow and relatively low payback period, while (B) air pollution control dust with a feed capacity of 20 ktpa was determined to be uneconomical due to a negative cash flow.

The base case payback period for the slag scenario is estimated at 5.51 years, based on a PCC production rate of approximately 70 ktpa, a CAPEX of £9.6 million and OPEX of £4 million. PCC production cost was estimated to be approximately £57 per tonne. Under these conditions, it was estimated that the process would result in 23 ktpa avoided CO₂ emissions (not including lifecycle avoided emissions when compared to current PCC production), with the ratio of captured emissions to those indirectly produced in the process (CO₂ avoidance factor) at 0.75. Though CO₂ mitigation through the process is very low, there could be significant additional revenue created if the process were to be credited under future phases of the EU ETS. This study estimated that this would be in excess of £700,000 per year at a CO₂ price of £30 per tonne.

Milling optimisation experiments and calculations indicate that the optimum particle size for slags entering the process is approximately 150 µm.

Sensitivity analyses show that the economic viability of the process is most sensitive to both the extent of calcium extraction from the feed material and the achievable sale price of PCC, while other variables such as CO₂ price, purge rate and solvent losses during filtration have a smaller effect within their respective expected ranges of operation. These results suggest that in order to maximise the economic potential of the process,

future work should focus on increasing the extent of calcium extraction from residues and on the production of a very high quality product in order to command a higher sale price.

Though unprofitable from a PCC production perspective, the dust scenario (B) may be applicable as a waste stabilisation technology and then the process economics would benefit from the avoided very high current treatment cost of this hazardous waste. The deployment of the technology for this purpose is dependent on the environmental performance of the post extraction dust residue which must be determined experimentally. Additionally, it is possible that the hazardous components of the waste would be transferred to the leachate and the cost would just be transferred from solid waste stabilisation to wastewater treatment.

5. Combined steelmaking wastewater remediation and CO₂ utilisation using microalgae

In Chapter 2, microalgal cultivation was identified as a promising technology for capturing and utilising steelworks CO₂ directly, using solar energy through photosynthesis to produce biomass which can be further processed into products such as fuel or fine chemicals. In this chapter, large-scale microalgal culture, microalgal CO₂ capture and microalgal wastewater treatment are critically reviewed, and the technological feasibility of combining CO₂ utilisation with the treatment of steelmaking wastewater is investigated experimentally through a series of microalgal cultivation trials.

5.1 Microalgae growth requirements, cultivation and uses

The term “algae” is used to describe a very large and diverse group of eukaryotic organisms, predominantly photosynthetic and aquatic, which lack some of the complex tissue types found in most terrestrial plants, for example roots, leaves and nutrient and water transport tissues (phloem, xylem). Algal diversity is illustrated by the size range from microscopic single celled species as small as 0.95 µm (for example, *Ostreococcus* spp.) (Courties *et al.*, 1994) to giant multicellular sea kelps (such as *Macrocystis pyrifera*) (Kain, 1991) that can readily reach lengths of over 45 m.

Algal species can be categorised according to their complexity, as either single celled microalgae or as multicellular macroalgae. Macroalgal species include seaweeds and kelps which are grown to a limited extent commercially for production of food, fertiliser and chemicals (for example, alginates). Microalgae are also actively cultured on a commercial scale for production of food supplements (for example *Spirulina* spp. and

Chlorella spp.), pigments and chemicals (for example, β -carotene from *Dunaliella salina* and astaxanthin from *Haematococcus pluvialis*), and feeds for aquaculture (for example, *Nannochloropsis* spp.) (Borowitzka, 2005), and passively cultured for advanced tertiary wastewater treatment (Cragg, 2006). Microalgae and macroalgae both grow by utilising CO₂ through photosynthesis, but only microalgae are suited to deployment as a means of utilising CO₂ with a view to mitigating release into the atmosphere. This is because cultures of microalgae are homogenous when mixed thoroughly and large scale cultures can be used in, and treated as, biological reactors. In contrast, culturing seaweed is more comparable to farming arable crops.

5.1.1 Microalgae growth and limiting factors

Microalgal growth in batch cultures can be split into five well defined phases: lag, exponential, growth rate decline, stationary and death (Fogg and Thake, 1987).

Lag phase: The duration of the lag stage is highly dependent on the condition of the inoculum; it tends to be short if the inoculation culture is in the exponential phase of growth and transferred to fresh media. If the inoculation culture is in a different stage of growth, or is transferred from a different type of culture medium, then a longer lag period is likely whilst the cells physiologically adapt to the new conditions.

Exponential phase: The exponential phase is the most rapid stage of growth and is when most biomass accumulates. During the exponential growth phase, the cell density increases exponentially as a function of time (Equation 5.1):

$$C_{t1} = C_{t0} \cdot e^{mt1} \quad (5.1)$$

Where C_{t1} and C_{t0} are the cell concentrations at time $t1$ and $t0$ respectively and m is the specific growth rate. The maximum growth rate in this phase depends on the species,

but is also limited by environmental factors such as light availability, temperature, CO₂ and nutrients.

Growth rate decline phase: The growth rate declines when a specific requirement for cell division becomes limiting. This phase typically occurs in dense cultures with a high biomass as a result of exhausted inorganic nutrients, light limitation if light is unable to penetrate the dense culture and limited CO₂ availability.

Stationary phase: The stationary phase in microalgal growth is defined as the point at which the net growth drops to zero. In this phase, the culture is still living but is not reproducing. This state induces a number of biochemical changes depending on the growth limiting factor. For example, in a culture limited by low nitrogen concentrations, reduced protein and increased lipid and carbohydrate concentrations are observed (Hu *et al.*, 2008). Cells can be maintained in the stationary vegetative stage for long periods (months) under certain conditions such as low light and temperature. High levels of illumination during this stage can cause cellular stress through photoinhibition and, when combined with other stresses (for example nutrient depletion), can cause the culture to enter the death phase.

Death phase: The death phase begins when the vegetative cell metabolism occurring in the stationary phase can no longer be maintained. Microalgal cell death typically occurs rapidly and is characterised by cells lysing, pigmentation loss and rapid bacterial growth.

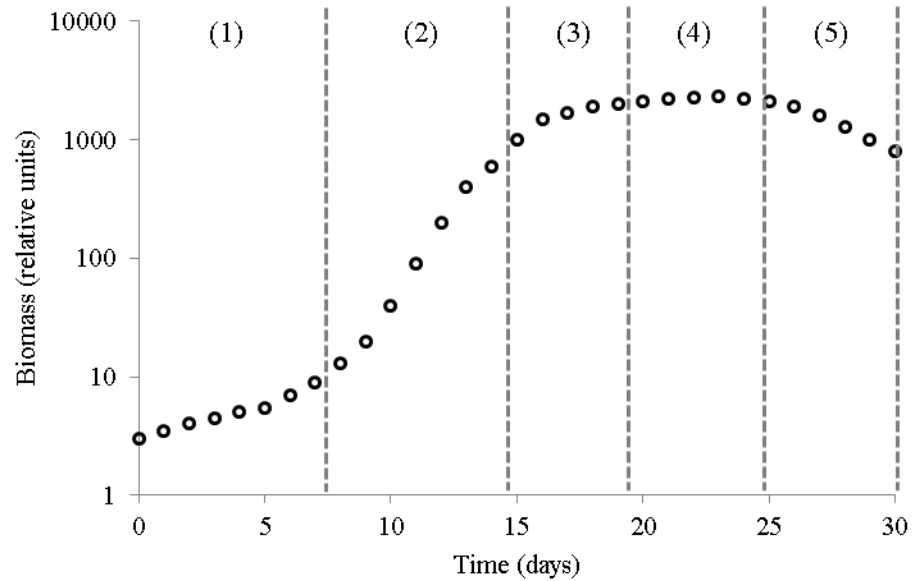


Figure 5.1: Representative diagram of algal growth in batch cultures. (1) - (5) denote the phases in growth: lag (1), exponential (2), growth rate decline (3), stationary (4) and death (5).

The rate and length of each of the growth stages described above are dependent on the environmental conditions in the culture. When an environmental condition is below optimum and is therefore limiting the growth rate this is referred to as the “growth limiting factor”. A brief outline of the most important of the requirements for photosynthetic algal growth is given below. A comprehensive description of the biological synthesis processes involved falls out of the scope of this thesis, but is widely available in the literature (for example, see Richmond and Hu, 2013).

5.1.1.1 Carbon

There are two fundamental energy sources for microalgal growth; autotrophic and heterotrophic. Autotrophic organisms are predominantly photoautotrophic, meaning that they use light energy to reduce CO₂ to build organic molecules through photosynthesis. Heterotrophic organisms take in carbon in the form of organic molecules from their environment and use them as a source of energy and as building

blocks for other complex organic molecules. When a species is able to grow *via* both of these mechanisms it is termed mixotrophic.

As CO₂ utilisation is the emphasis of this work, the focus will be on photoautotrophic growth, although it is possible that some mixotrophy could enhance wastewater treatment processes by reducing the organic carbon loading in the water, while at the same time increasing biomass accumulation.

The effect of CO₂ concentration in the culture media will be addressed in Section 5.1.3.

5.1.1.2 Nutrients

Nitrogen is an essential nutrient for microalgal growth and typically constitutes around 7% of dry algal biomass. Microalgae are able to utilise nitrogen in a range of forms including urea (CH₄N₂O), nitrates (NO₃⁻), and ammonium (NH₄⁺). Increasing the amount of available nitrogen in a culture will, up to a certain point, increase general growth rate and also the production of carbohydrates and proteins. Nitrogen deficiency typically induces formation and accumulation of lipids and results in a reduction in cellular productivity (Tebbani *et al.*, 2014). This excessive formation and accumulation of lipid molecules during conditions of nitrogen stress is of particular interest to researchers attempting to develop processes for next generation biodiesel production. Lipids can be transformed into biodiesel (alkyl esters) *via* transesterification, therefore maximising the lipid content in the harvested biomass is essential for producing a high yield of fuel (Adams *et al.*, 2013; Rodolfi *et al.*, 2009).

Phosphorus is also an essential nutrient for algal growth as it is involved in several critical metabolic pathways and is typically present in dried algal biomass at concentrations around 1%. Phosphorus is generally present in culture media as phosphate (PO₄³⁻) and must be provided in excess due to the tendency of phosphates to precipitate in the presence of some metal ions (Tebbani *et al.*, 2014).

Nutrient requirements of commercial scale microalgae cultivation systems are expected to present one of the highest variable operating costs, at between 10 and 30% (Massingil et al, 2008; Richardson, 2012).

A number of other micronutrients are also required in order to maintain healthy algal cultures. These include sulfur, iron, potassium, magnesium, copper, sodium and selenium.

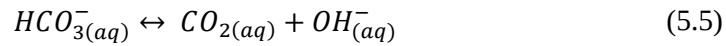
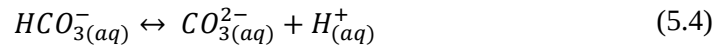
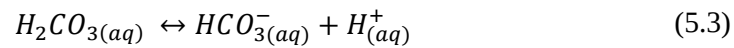
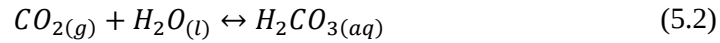
5.1.1.3 Light and photosynthesis

Light is essential to photoautotrophic algae as it is the energy source used to drive photosynthesis. The light intensity and type are important parameters in microalgal cultivation. Depending on the degree of illumination, microalgae can be either in a phase of respiration (in the absence of light), limitation (insufficient light), saturation (maximum photosynthetic yield), or inhibited (reduction of photosynthetic activity due to excessive light) (Tebbani *et al.*, 2014). In addition, the required amount of light can be different during each algal growth phase. The process of photosynthesis only utilises light within a small portion of the spectrum, called photosynthetically active radiation (PAR). PAR is usually considered to be around 43% - 45% of radiation in the wavelength range 400 to 700 nm (Carvalho *et al.*, 2006). The photosynthetic efficiency (PE) is defined as the fraction of the PAR which is eventually stored as chemical energy in biomass; however there is no agreed method for calculating an accurate value and the PE is only a theoretical maximum. In practice and especially in long term cultures, the PE is most often below 6.5% and under ideal conditions, only around 40% of the theoretical maximum yield can be reached (Laws *et al.*, 1988).

5.1.1.5 pH

Addition of CO₂ to an algal culture will at first result in a drop in pH as protons are released as it dissolves to form carbonate and then bicarbonate (Equations 5.2 to 5.5). As the microalgae grow they consume CO₂, shifting the equilibrium in Equation 5.5 to

the right and resulting in a build-up of OH⁻, increasing the pH. By carefully controlling the flow rate of CO₂ to the culture, it is possible to effectively control the pH of the culture medium (Richmond, 2004). The optimal pH for algal cultivation is species dependent but typically between neutral and slightly alkaline (pH = 7-9) (Richmond, 2004).



5.1.1.6 Growth inhibition

During photosynthesis, CO₂ is consumed and O₂ is produced. If O₂ concentrations become too high, photo-oxidation can damage chlorophyll, thereby inhibiting photosynthesis and reducing productivity (Molina *et al.*, 2011). This problem does not typically occur in open pond systems with a large surface area due to high rate of atmospheric gas diffusion, but could be a significant factor in the design of closed photobioreactors, where diffusion to the atmosphere is much less (Molina *et al.*, 2011).

In addition to photo-inhibition by O₂, other elements and compounds present in media can inhibit growth. Nakai *et al.* (2001) and Jena *et al.* (2010) showed that phenol derived compounds inhibited growth of *Microcystis aeruginosa*, and *Chlorella minutissima* respectively. Nickel also has inhibitory effects on microalgae, particularly on *Chlorella vulgaris* which can be inhibited by nickel levels as low as 0.85 ppb (Spencer and Nichols, 1983).

5.1.2 Large scale cultivation systems

5.1.2.1 *Open pond systems*

Microalgae production at industrial scales is currently almost exclusively in open pond systems. Open ponds are relatively low cost, straight forward to construct and are cheap to operate. The materials used to build and line ponds determine the durability, life and cost. Walls and floor of ponds are typically constructed from clay, concrete or plastic. Commercial plants usually use a long life plastic liner which is UV resistant and 1-2mm thick. Ponds without liners have been proposed to reduce costs but are much more susceptible to contamination, silt suspension and percolation (Richmond, 2004). There are a number of different open pond designs currently in operation (Borowitzka, 2005):

- Inclined systems where mixing is achieved by pumping and gravity
- Circular ponds with mixing by a rotating arm
- Raceway ponds; where paddle wheels continually mix in a loop
- Small scale, deep aerated ponds, where mixing is achieved *via* aeration
- Vast, shallow, open and unmixed ponds

There are a number of disadvantages to cultivation in open pond systems. Evaporation losses can be very high, contamination with other algae or bacteria strains from the environment is likely and temperature is difficult to control. Although productivities of $>50 \text{ g m}^{-2} \text{ d}^{-1}$ have been reported in the literature, long term productivity from commercial raceway ponds rarely exceeds $15 \text{ g m}^{-2} \text{ d}^{-1}$ (even in areas with high solar irradiation). However, the relatively low capital and maintenance cost of open systems, when compared to those in closed systems means that they are currently the only microalgal production technology operated commercially. The estimated cost of algal biomass production from raceway ponds is between £7.50 and £14 kg⁻¹ (Richmond, 2004).

5.1.2.2 Closed cultivation systems

Photobioreactor (PBR) is the term used to describe closed systems of algal culture. These systems typically consist of a transparent glass or polymer container or tubing through which the microalgal culture flows. The closed nature of the system means that PBRs have a number of potential advantages over open systems. These include a more controllable environment for optimising growth and the ability to minimise evaporation and the risk of contamination (Ugwu *et al.*, 2008). PBR design is a very active research area and a large number of designs have been proposed, including tubular, flat plate, helical and bubble column arrangements, in addition to hybrids incorporating two or more of these designs (Chen *et al.*, 2011). The working volume of test PBR designs and the reported productivity of algal cultures grown in them show a high degree of variation (Table 5.1), but these productivities are typically much higher than from the same strain in an open pond system.

PBR operating costs are anticipated to be higher than those of open pond systems. This is due to energy requirements for pumping culture through the reactor geometry, maintenance costs due to fouling on internal PBR surfaces and increased labour requirement as a result of increased maintenance requirements and complexity of the system. Operating costs have been estimated to be approximately 50% higher in the case of PBRs compared to open pond systems (Richardson *et al.*, 2012).

PBR systems have so far been limited to pilot and demonstration scale and are currently not suitable for commercial deployment due to a combination of the high operating costs outlined above, and also very high capital costs. There is a great deal of uncertainty surrounding the actual cost of large scale PBR systems due to the lack of commercially operating plants; estimates of capital costs range from 25% higher (Richardson *et al.*, 2014) to tenfold (Kunjapur and Eldridge, 2010) those of a raceway pond system of the same production capacity.

Table 5.1: A selection of types of photobioreactor, including the volume, species and reported productivity in each (Ugwu, 2008).

Reactor type	Volume (L)	Microalgae strain	Productivity (g L ⁻¹ d ⁻¹)	Reference
Airlift tubular	200	<i>Porphyridium cruentum</i>	1.50	Camacho Rubino <i>et al.</i> (1999)
Airlift tubular	200	<i>Phaeodactylum tricornutum</i>	1.20	Acien Fernandez <i>et al.</i> (2001)
Airlift tubular	200	<i>Phaeodactylum tricornutum</i>	1.90	Molina <i>et al.</i> (2001)
Inclined tubular	6	<i>Chlorella sorokiniana</i>	1.47	Ugwu <i>et al.</i> (2002)
Undular row tubular	11	<i>Arthrospira platensis</i>	2.70	Carlozzi (2003)
Outdoor helical tubular	75	<i>Phaeodactylum tricornutum</i>	1.40	Hall <i>et al.</i> (2003)
Parallel tubular	25,000	<i>Haematococcus pluvialis</i>	0.05	Olaizola (2000)
Bubble column	55	<i>Haematococcus pluvialis</i>	0.06	García-Malea López <i>et al.</i> (2006)
Flat plate	440	<i>Nannochloropsis</i> sp.	0.27	Chen-Wu <i>et al.</i> (2001)

5.1.3 Products from microalgae

The vast majority of recent literature approaches microalgae production as a potential source of next generation biofuels, and from a CO₂ utilisation point of view this is an obvious route to pursue due to the large market capacity.

The primary focus of recent research relating to microalgae is the production of biodiesel, exploiting the high cell lipid concentrations present in some microalgae species and converting it to biodiesel *via* transesterification. Other options for fuel production include production of biogas *via* anaerobic digestion or production of bioethanol *via* fermentation of cellulosic material. Anaerobic digestion of algal biomass could be attractive due to the process's ability to treat a wet feed material, meaning that the energy intensive biomass drying stage can be avoided (Ras *et al.*, 2011).

There is the potential for production of high value products from algae, for example pigments (β -carotene from *Dunaliella* spp.), pharmaceuticals, human nutrients (*Spirulina* spp., *Chlorella* spp.) and animal food supplements (astaxanthin from *Haematococcus* spp., aquaculture feed from *Nannochloropsis* spp.) (Borowitzka, 2005).

Combining production of multiple products in an integrated system called a “bio-refinery” has also been suggested as a way to maximise revenue and ensure optimum utilisation of the biomass (Vanthoor-Koopmans *et al.*, 2012). As the focus of this current Chapter is concerned with remediation of industrial wastewater combined with direct capture of steelworks exhaust CO₂, determining the quality and biosafety of the algae was not considered here. Whilst it is unlikely that the algal biomass resulting from the test processes would be considered suitable as a feedstock for higher value products due to potential contamination and the implications of this entering the food chain, other uses such as harnessing lipids for subsequent biodiesel production may be a possibility.

5.1.4 Use of microalgae in wastewater treatment

Another significant industrial use of microalgae is in tertiary wastewater treatment. In contrast to the processes described above, in these systems the aim is to utilise the nutrient consuming nature of algae growth to remediate wastewater. Therefore in these systems, rather than attempting to maximise algal productivity and biomass, the plant is designed to maximise absorption of nutrients from the waste.

Wastewater treatment processes based on microalgae were pioneered by William Oswald in the 1950s in the USA as part of the advanced integrated wastewater pond system technology which was designed as an alternative low cost treatment option to conventional aeration pond technologies (Oswald *et al.* 1957; Craggs, 2006). In these systems, raceway type ponds called high rate algal ponds (HRAPs) are used as a step in the water treatment process before the culture is sent to an algal settling pond for biomass removal.

There is a general consensus among researchers that advanced wastewater treatment is currently the only economical source of microalgae for production of fuels (Rawat *et al.*, 2013). In these systems, wastewater treatment is the primary objective and the reason for capital expenditure, with biomass and/or biofuel production being only a minor by-product.

5.1.4.1 Hybrid systems

Addition of CO₂ to HRAP wastewater treatment systems has a number of advantages over conventional air diffusion at the pond surface. CO₂ addition enhances biomass productivity by reducing carbon limitation, enhances the removal of O₂ to prevent photoinhibition, allows a high degree of control over the pH and increases nutrient uptake as a result of increased growth (Craggs *et al.*, 2012). A recent study in New Zealand using a large-scale facility (5 ha) observed an increase in biomass productivity of up to 100% when CO₂ was added to the culture (Craggs *et al.*, 2012).

5.1.5 Direct flue gas utilisation at steelworks

There are a number of examples of successful algal cultivation trials where CO₂ was supplied directly from a process exhaust stream, including from steel plant exhausts (Chiu *et al.*, 2011; Li *et al.*, 2011; Zimmerman *et al.*, 2011).

An investigation into the potential of utilising CO₂ from the exhaust of the power plant at Tata Steel's Long Products UK site in Scunthorpe as a CO₂ source for cultivating

microalgae was undertaken in 2010 in conjunction with the University of Sheffield (Zimmerman *et al.*, 2011). A 2.2 m³ photobioreactor was constructed using a patented technology to generate microbubbles as the gas inlet system. The bioreactor was used to cultivate *Dunaliella salina* in a growth medium dosed with exhaust gasses from the central power station (CPS) at Scunthorpe works (the same location as used for the carbonation tests in Section 3.5).

Two growth trials were conducted using the reactor, in both trials steady state growth was observed and there was a 100% survival rate. Exhaust gas was pumped into the reactor at between 10 and 80 L min⁻¹ at a temperature of 15-22 °C and with a CO₂ concentration in the feed exhaust gas of around 23%. An average of 14% of the available CO₂ was absorbed by the microalgae, corresponding to a high uptake rate of around 0.1 g L⁻¹ h⁻¹ or 2.4 g L⁻¹ d⁻¹ (Zimmerman *et al.*, 2011).

Evidence from the two growth trials using the reactor suggested that the process was not mass transfer limited, and that the oxygen depleted stack gas stripped dissolved O₂ to the equilibrium level (5% in the stack gas). The use of exhaust gas rather than air as a source of CO₂ benefited the system in two different ways; CO₂ is in high concentrations in the exhaust meaning that the availability of CO₂ was much higher and the low O₂ content of the exhaust (around one quarter of that in air) meant that the O₂ was more efficiently removed from the culture medium (preventing photoinhibition). High dosing of CO₂ and efficient stripping of O₂ meant that the liquid phase was consistently saturated with CO₂. With efficient O₂ stripping, inhibition is removed allowing for higher density and faster rates of growth (Zimmerman *et al.*, 2011).

In addition to work at Scunthorpe, Tata Steel is also currently involved in a microalgae project at Strip Products UK in Port Talbot in collaboration with Swansea University as part of the larger EU funded EnAlgae project. This project uses flue gases from coke ovens under firing to provide CO₂ to microalgae cultures cultivated in a wastewater

provided by the municipal wastewater company Dŵr Cymru Cyf, another project partner (Swansea University, 2015). This work is still ongoing and the results are as yet unpublished.

There have also been publications from two research projects on direct capture of CO₂ using microalgae from coke ovens located in China and Taiwan. Li *et al.* (2011) cultivated *Scenedesmus obliquus* in a 100 L bioreactor dosed with flue gas and achieved a maximum CO₂ uptake of 67% at a CO₂ concentration in the gas of around 12%. Chiu *et al.* (2011) cultured *Chlorella* sp. in a 50 L reactor dosed with flue gas containing around 25% CO₂ and achieved a removal efficiency of around 13% after the reactor was under CO₂ saturation conditions. In addition to CO₂, NO and SO₂ concentrations in the inflow and outflow to the reactor were measured. It was found that the reactor removed both SO₂ and NO from the gas stream by 55% and 73% respectively, without any adverse effects on algae growth. It should be noted however, that initial concentrations of these gases were very low, 87 ppm and 78 ppm for SO₂ and NO respectively.

The success of these tests indicate that cultivation of microalgae is highly tolerant to impurities in the exhaust streams such as NO_x and SO_x, and that microalgal cultivation processes are suitable for direct CO₂ utilisation.

5.2 Wastewater production at an integrated steelmaking site

Integrated steelmaking sites consume very large quantities of water in a variety of processes including heat transfer, direct and indirect cooling and flue gas clean up processes. Many of the water types used either do not need treatment before discharge (for example, water from cooling towers) or are very highly contaminated with iron or other metals, but not with significant nutrients which would be able to support algal growth (for example cold rolling wastewater and blast furnace gas de-dusting scrubber effluent). The most promising wastewater source from an integrated works is that

discharged from the biological effluent treatment plant. This water has a relatively high nitrogen content, making it potentially attractive for algal nutrition.

5.2.1 Biological Effluent Treatment (BET) Plant

Substantial quantities of wastewater are produced from operations at the coke oven by-products plant. Water is used in the by-products plant predominantly in gas cooling and stripping systems, with a large fraction of this water being derived from that which was present in the coking coal and some produced chemically as a result of the coking process (i.e. that which is condensed from the raw COG (see Chapter 2 Section 2.2)). Water for stripping and cooling is typically stored in the ammonia liquor storage tank, and surplus is stripped of ammonia by distillation. Wastewater following ammonia stripping contains various organic compounds, residual ammonia and cyanides at concentrations which would be highly polluting if discharged directly. This wastewater is typically produced at a specific rate of 0.31 to 0.69 m³ per tonne of coke in Europe and is sent for treatment at a biological wastewater treatment plant, sometimes following mixing with other steelmaking wastewaters (Remus *et al.*, 2013).

Biological treatment of this wastewater is usually in the form of an aerobic activated sludge system, with more advanced systems combining this with a nitrification or nitrification-denitrification system. In the aerobic activated sludge process, a dense sludge of microorganisms oxidise organic molecules to form CO₂ and H₂O. The required oxygen for the process is supplied by sparging pure oxygen to the bottom of the tank. Heavy metals are adsorbed onto the surface of the sludge, and removed when excess sludge is dewatered. Dewatered excess sludge is blended with coal and returned to the coke ovens. An additional nitrification step is deployed where there is a restriction on the permitted amount of nitrogen which can be discharged as ammonium. In this process one or more additional, high residence aerobic cell(s) are added, where nitrifying bacteria convert ammonium to nitrate. When there are even more stringent

limits on the total nitrogen which can be discharged, the nitrification stage can be preceded by an anoxic denitrification cell, with a high recirculation rate from the nitrification cell(s) (Remus *et al.*, 2013).

5.2.2 Treatment of BET effluent with microalgae

Treated coke oven effluent was identified by Christenson and Sims (2011) as a potentially suitable stream for algal cultivation. Only one study to date has investigated this experimentally; Yun *et al.* (1997) studied the possibility of combined CO₂ capture and remediation of steelmaking wastewater using *Chlorella vulgaris*. The exact source of the wastewater was not detailed in the paper, but when the information provided (composition, treatment description) is compared to the wastewater streams requiring treatment at a steelmaking site, it can be speculated that they used post-treatment effluent from a cokemaking by-products plant. The authors cultivated *C. vulgaris* in wastewater at three different CO₂ concentrations; ambient (0.03%), 5% and 15% and measured growth rates. The highest algal growth rate was observed when cultures were dosed with 5% CO₂, with lower and comparable growth observed in air and 15% CO₂ dosed samples respectively.

The large variation in treatment methods, permitted discharge compositions and processes deployed at coke oven by-products plants within Europe means that the final discharged effluent from these plants can vary enormously between different steelmaking sites. For this reason, effluents produced by Tata must be tested in order to determine their suitability to microalgae cultivation, and to determine the effectiveness of microalgae as a tertiary treatment method.

5.3 Materials and Methods

The main aim of this investigation was to test the technical feasibility of combined BET effluent remediation and CO₂ utilisation using microalgae. In this context, remediation specifically refers to removal of ammonium-N from the effluent prior to discharge to a

water body. To achieve this aim, a series of laboratory-scale trials were undertaken in which two algal species were cultured in BET discharge effluent. This section gives a detailed description of the experiments performed and the analytical methods used.

5.3.1 Microalgal species, source and maintenance

Chlorella vulgaris (CCAP 211/63) and *Scenedesmus obliquus* (CCAP 276/7) were purchased from the Culture Collection of Algae and Protozoa (CCAP) and cultured in Jaworski's Medium (JM) under controlled conditions (20 °C, continuous lighting and aeration). Stock cultures were regularly sub-cultured into fresh JM (Appendix B). Aseptic technique was used throughout and media sterilised (autoclaved, 15 mins, 103 kPa, 121 °C) prior to use. *C. vulgaris* was chosen as the primary species for cultivation trials due its high growth rate, ability to grow mixotrophically and because it has previously been demonstrated that this species performs consistently well when cultivated in wastewater, and under steelworks flue gas dosing (Ji, 2013; Su, 2012; Chiu *et al.*, 2011). *S. obliquus* was chosen as a comparative second species for growth and nitrogen removal comparisons relative to *C. vulgaris*; this species can also withstand coke oven exhaust gas conditions (Li *et al.*, 2011). Jaworski's Medium (JM) stocks were also purchased from CCAP.

5.3.2 Cultivation trials

Trials were conducted using BET effluent collected from the final discharge point of a biological effluent treatment plant (BET) treating coke-making wastewater in Northern England. Effluent was stored in airtight containers at 4°C until required and immediately prior to use, samples were filtered under vacuum through a Whatman 540 (8µm) filter in order to remove suspended solids. Multiple BET samples were collected during the project and variability in sample composition is reported in Section 5.4. The sample which was used in each experiment is indicated.

Four consecutive microalgal trials were undertaken as outlined below:

- 1) BET EFFLUENT toxicity and capacity for supporting algal growth were tested using *C. vulgaris*.
- 2) Based on the findings of trial 1, nitrogen-use efficiency of *C. vulgaris* was determined for BET EFFLUENT when other nutrients were at optimum concentrations.
- 3) N-use efficiency of *S. obliquus* was evaluated using BET EFFLUENT with supplementary PO₄-P only.
- 4) Nitrogen use efficiency of *C. vulgaris* and *S. obliquus* was evaluated when PO₄-P amended BET EFFLUENT was sparged with CO₂.

Further details of each trial are as follows:

Trial one was split into two separate stages, the first, (a) to determine the toxicity of BET effluent to *C. vulgaris* and the second, (b) to determine whether BET effluent could act as the sole nutrient source for *C. vulgaris*. Toxicity was determined by diluting JM (Appendix B) with BET effluent by 10%, 20% and 30%, in order that all required nutrients were present for algal growth. Undiluted (100%) JM was used as the control. To test nutritional capacity for maintaining algal growth, BET effluent was diluted to 10%, 20% and 30% in deionised water rather than in JM.

Trial two consisted of diluting BET effluent to 30%, 40% and 50% in a nitrogen deficient JM medium (JM-n) which was prepared by omitting the nitrate-containing JM stocks 1 and 8 (see Appendix B) (CCAP, 2014) during preparation of the media. *C. vulgaris* was cultured in the solutions and undiluted (100%) JM was used as the control.

Trial three was designed to determine whether BET effluent could provide all the necessary nutrients for microalgal growth (nitrogen and micronutrients) apart from phosphate, and to establish the effect of two different phosphate concentrations on algal growth and nitrogen removal from the wastewater. Two concentrations of phosphate were added to BET effluent (as K₂HPO₄), the first treatment was based on the optimum

concentration (when no other nutrients are limiting) of 18 mg PO₄³⁻ L⁻¹ present in JM and in the second treatment this was doubled to 36 mg PO₄³⁻ L⁻¹. *S. obliquus* was independently tested in this trial and was also grown in undiluted (100%) JM as the control treatment.

Trial four was conducted to determine the effect of elevated CO₂ concentration on the growth rate and nitrogen remediation rate of *C. vulgaris* and *S. obliquus* in BET effluent. Treatments were prepared by adding 18 mg L⁻¹ of phosphate (as K₂HPO₄) (based on results from trial 3) to filtered BET effluent. After inoculation with each species, treatments were sparged with two simulated flue gas mixtures (CO₂:N₂) at differing CO₂ concentrations (5% and 20%) (BOC, certified).

Treatment and environmental conditions for each trial are summarised in Table 5.2. All cultures were continuously illuminated by T5/HO 830 and 840 lamps (54W) in controlled temperature rooms. Distance between the culture and the lamp was 50 cm in trials 1, 2 and 3 and 40cm in trial 4. This difference is due to the fact that lamps were relocated to a fume cupboard in order to give adequate ventilation for CO₂ experiments.

Table 5.2: Treatment and environmental conditions for each trial.

Trial	Added nutrients			Lighting period (h)	Gas flow (appx. L min ⁻¹)	Temp (°C)
	N	P	Micro			
1(a)	-	-	-	24	0.1	20
1(b)	x	x	x	24	0.1	20
2	-	x	x	24	0.1	20
3	-	x	-	24	0.1	20
4	-	x	-	24	0.1	20

In all trials, microalgae were cultured in 200 mL of the appropriate treatment in 250 mL conical flasks after autoclaving JM solutions at 121 °C and 103 kPa (gauge) for 15 minutes. With the exception of the CO₂ dosed treatments, all other treatments were

sparged with air at an approximate gas flow rate of 0.1 L min⁻¹. All treatments were inoculated under sterile conditions with 1 mL of stock culture, which had been sub-cultured and maintained in JM. All experiments were set up in a randomised block design with three replicates per treatment.

5.3.2.1 Determination of growth rates and biomass

Following gentle agitation (swirling) to ensure uniform cell suspension, 1 mL samples were aseptically removed from each experimental flask on days 2, 4, 7 and 9 of cultivation in trial 1; on days 0, 3, 5, 7, 10 and 13 in trial 2; on days 0, 3, 5, 7, 10, 12, 14 in trial 3; and on days 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 in trial 4, before being frozen (-20°C) until required for analysis.

Immediately prior to analysis, samples were defrosted overnight at 4°C, and centrifuged at 11000rpm for 10 minutes. A 0.9 mL aliquot of supernatant was decanted from the above samples and the remaining biomass pellet was re-suspended in 0.9 mL deionised water via gentle mixing prior. Centrifugation and resuspension was carried out in order to minimise the effect that differing culture media composition may have had on optical density.

Optical density (OD) was used to estimate algal relative growth rate in each trial; OD at a wavelength of 660 nm (OD₆₆₀) was recorded for each sample using a UV-VIS photospectrometer (Cecil CE 1010) after being zeroed with deionised water. The author accepts that there are limitations to measuring growth *via* optical density, particularly at high OD values and those for mature cultures when the accuracy of OD for estimating cell density can have a high margin of error (Rodrigues *et al.*, 2011). Nevertheless, optical density (OD) can be used as a proxy for microalgal growth by measuring the turbidity of the culture relative to other cultures within the visible light spectrum (~400 nm - ~700 nm) (Odlare *et al.*, 2011; Chen *et al.*, 2012; Ras *et al.*, 2011). In order to

support and validate the OD measurements, the final algal biomass for each treatment was measured on the final day of each trial. Final biomass was determined by measuring the dry weight from a known volume for each treatment. A sample of suspended culture (50 mL) was centrifuged at 4000 rpm for ten minutes and 45 mL of supernatant removed and stored for analysis before the pelleted biomass was re-suspended in 45 mL of deionised water. This process was repeated again to remove any soluble species from the residue. Samples were then dried in an oven at 80 °C overnight and dry weight determined gravimetrically.

5.3.3 Analyses

Prior to experimentation, BET effluent composition was analysed as follows: Ammonium and nitrate (using an automated photometric analyser, Gallery™, Thermo Scientific), phosphate (photometrically by the vanadomolybdophosphoric acid method), total phenol (photometrically by the 4aminophenazone method), Chemical Oxygen Demand (COD) in accordance with BS ISO 15705:2002, free cyanide (CN⁻) (photometrically *via* Konig's reaction after fixing immediately after sampling with 10 NaOH pellets per 500mL). Photometric analyses were conducted using a Merck Spectroquant Nova 60 unless otherwise stated. The above analysis was performed on behalf of the author by Tata Steel Testing Solutions Ltd.

Supernatant from OD samples taken in trials 2, 3 and 4 were diluted and analysed for total nitrogen concentration using a Shimadzu combined TOC-V/TNM-1 instrument. Supernatant from OD samples in trials 3 and 4 were also analysed for total organic carbon (TOC) using the same instrument.

Phosphorus and trace element concentrations in the effluent were measured both before and in the supernatant following trial 2 *via* ICP-MS (Thermo Scientific iCAP Q ICPMS).

5.3.4 Calculations

Nitrogen removal rates from the culture media (trials 2, 3 and 4) were calculated using Equation 5.6, where N_t and N_0 are nitrogen concentrations (total nitrogen) (mg L⁻¹ d⁻¹) at the start (t_0) and end (t_c) of the experiment (days).

$$\text{Nitrogen removal rate (mg L}^{-1}\text{d}^{-1}\text{)} = \frac{N_t - N_0}{t_c - t_0} \quad (5.6)$$

5.3.5 Statistical analysis

Data were analysed by repeated measures analysis of variance (OD, TN, TOC, N-removal measurements) and one-way ANOVAs (final biomass) using Genstat Release 15.1 (Lawes Agricultural Trust). Normality was tested by plotting residuals against expected normal quantiles and post-hoc comparisons between means was based on least significant differences at the 0.05 probability level (for repeated measures ANOVAs) and Tukey's Test (for one-way ANOVAs).

5.4 Results and Discussion

5.4.1 BET plant effluent composition and variability

Four samples of BET effluent were collected over the duration of the project and were each analysed separately in order to give an indication of sample variability (Table 5.3). The most obvious variation in composition is the reduction in total nitrogen present in the effluent over time. This is a direct result of ongoing efforts at the BET plant to reduce nitrogen in the discharged effluent in order to comply with the European BAT AEL target of 50 mg L⁻¹ (Remus, 2013; see Chapter 2)²⁰. This reduction has implications in the current work, as the total available nitrogen for algal nutrition is set to be reduced to around half per unit volume when compared to the original samples

²⁰ From internal discussions with Tata Steel staff

used for trial 1 and 2. The total nitrogen concentration in the effluent (total-N) reduced from 108 mg L⁻¹ in January 2013, to 69 mg L⁻¹ in October 2014 (Table 5.3). Nevertheless, the nitrogen concentration measured in October 2014 should still be more than adequate to sustain microalgae growth as nitrogen concentration in the standard JM growth media is only around 15.5 mg L⁻¹.

Phosphate concentration in the effluent is low (0.5-1 mg L⁻¹) (Table 5.3). This indicates that the effluent is unlikely to be able to sustain algae growth without additional phosphate.

The level of organic carbon in the effluent is relatively low (24 – 32 mg L⁻¹). If suitable, it is possible that a microalgal culture may utilise this carbon source to grow mixotrophically. However the low TOC concentration means that if this does occur, it will likely be insignificant in terms of total growth.

Two types of chemical species which are known to cause growth inhibition in microalgae, cyanide and phenols, are present in the effluent at concentrations of up to 0.11 mg L⁻¹ and 5.4 mg L⁻¹ respectively. Total phenols appear to be well below the toxicity limit (IC₅₀) for *Scenedesmus quadricauda* (403 mg L⁻¹) (Tisler and Zagorc-Koncan, 1997), indicating that growth inhibition by phenols is unlikely. In contrast, cyanide levels appear to be above those at which growth inhibition could be expected to occur; Gensemer *et al.* (2006) observed growth inhibition in *S. quadricauda* cultures at CN concentrations as low as 30 µg L⁻¹. This sensitivity to cyanide does however appear to be highly species dependent, as *Chlorella* sp. was reported to be tolerant up to levels as high as 30 mg L⁻¹ (Gensemer *et al.*, 2006).

Table 5.3: Variability of BET plant effluent composition from four samples over a two and a half year period.

Component	Unit	Sample date and reference			
		Jan-13 (A)	Feb-13 (B)	Oct-13 (C)	Oct-14 (D)
CNS	mg L ⁻¹	0.7	0.8	-	0.7
Mono-phenol	mg L ⁻¹	0.7	1	1	1.1
Total phenol	mg L ⁻¹	4.8	5.4	2.8	4
DOC	mg L ⁻¹	29	32	-	24
Phosphate	mg L ⁻¹	0.5	0.7	1	0.8
Total N	mg L ⁻¹	108	104	79	69
Free cyanide	mg L ⁻¹	0.05	0.11	0.07	-
COD	mg L ⁻¹	-	104	98	90

5.4.2 Trial 1: Toxicology Screen

Substantial algal growth was observed in all dilutions of BET effluent (Sample “A”) in JM and in JM alone (trial 1(a) (Figure 5.2), but very little growth was recorded in the BET/water combinations (Figure 5.4; trial 1b) so these data were not included in the statistical analyses. BET effluent does not contain sufficient nutrients to support algal growth and adding nutrients by substituting JM with BET resulted in measurable algal growth. In cultures grown in BET/JM combinations, OD significantly increased between days 4 and 7 (time as a single factor, $P < 0.001$), but not between days 7 and 9. When BET was diluted with JM, the highest average OD value was obtained for algae growing in 30% BET/JM (OD 0.607 at 660nm), which was significantly different from the other BET/JM combinations apart from the JM alone (OD 0.568 at 660nm) (BET/JM mix as a single factor, $P = 0.015$; $LSD = 0.167$). Average final biomass in trial 1(a) ranged from 0.35 g L⁻¹ in the 20% BET effluent treatments to 0.76 g L⁻¹ in the 30% BET effluent treatments on day 9 of cultivation. The 30% BET treatment yielded a significantly higher algal biomass than other treatments (BET/JM mix as a single factor, $P = 0.007$; Figure 5.3). The data suggest that BET effluent does not have a toxic effect on *C. vulgaris*. The fact that there is no significant difference in OD between cultures in the BET effluent and in the JM medium alone indicates no inhibition of *C. vulgaris*.

by species in the effluent such as cyanide. However, the N-concentrations in each BET/JM mixture were not kept constant and the 30% BET/JM contained the highest concentration of total N (Table 5.3 and see Figure 5.5) and JM medium the least. It is likely that the increased N in the 30% BET treatment benefited algal growth. However, if the only explanation for the higher biomass is increased N in the medium, the 20% treatment should have also yielded a greater biomass than the JM medium alone, but it was similar to that from the JM and the 10% BET treatments. The NO₃⁻/NH₄⁺ ionic ratio was different in each solution with the JM containing 100% NO₃⁻ and the BET treatments containing both NO₃⁻ (from the JM) and NH₄⁺ (from the BET) with the ratio depending on the BET/JM combination. *C. vulgaris* is able to assimilate nitrogen from both NO₃⁻ and NH₄⁺ although ammonium is generally preferred because nitrate must be converted to ammonium within the algal cell in order to be assimilated (L'Helguen *et al.*, 2008). Petrovič and Simonič (2015) demonstrated complete removal of ammonium in < 3 days and 81% nitrate removal in 4 days by *C. sorokiniana* from a starting point of 30 mg L⁻¹ NH₄⁺ and 50 mg L⁻¹ NO₃⁻. In contrast, Podevin *et al.* (2015) showed that *C. vulgaris* (strain K-1006) preferred sodium nitrate to ammonium-N sources, although the authors state that most *Chlorella* species would normally show a preference for ammonium. It is likely that the increased biomass obtained from algae grown with 30% BET/JM is due to preferential assimilation of the NH₄⁺-N within the medium and the lower biomass of algae grown in JM alone is due to the energetic costs of assimilating nitrate. It is not known whether the algae in the current investigation preferentially took up ammonium or nitrate, but the experimental cultures were obtained from stocks maintained in JM (containing nitrate). Either the algae adapted to the new medium remarkably well, or the increased growth observed with 30% BET was the result of some other phenomenon. One alternative explanation is that the 30% BET may have induced a stress response, possibly because of low concentrations of free cyanide, estimated to be 0.015 mg L⁻¹ in the 30% BET/JM medium. Whilst this is less than the

concentration that is known to harm algae ($> 0.16 \text{ mg L}^{-1}$), sub-lethal concentrations may have induced compensatory growth, a phenomenon that occurs in plants and has been reported in algae (Qin and Peng, 2012).

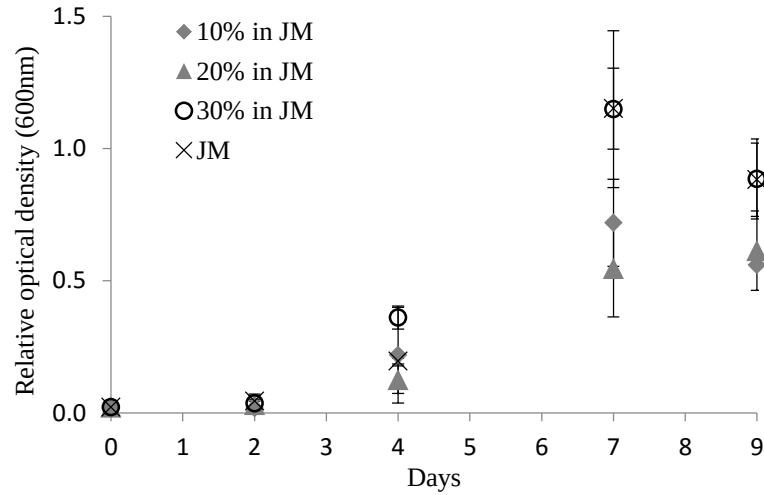


Figure 5.2: Optical density of algal cultures in trial 1(a) over time. Algae were cultured in 100% JM and in three dilutions of BET effluent in JM to give the following ratios of BET/JM: 10% BET/90% JM, 20% BET/80% JM and 30% BET/70% JM. ANOVA (repeated measures): treatment as a single factor $P = 0.015$; $LSD = 0.409$

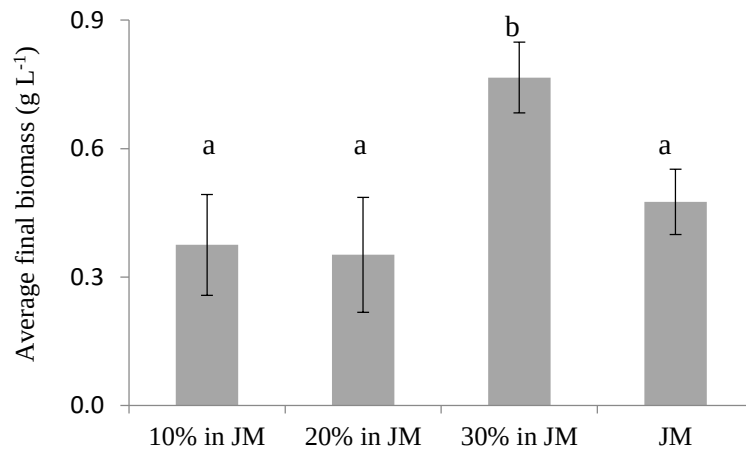


Figure 5.3: Average final biomass for treatments in trial 1(a). ANOVA: Treatment as a single factor $P = 0.007$; columns similarly superscripted are not significantly different (Tukey's Test, $P < 0.05$).

Little growth was observed in *C. vulgaris* cultures grown in dilutions of BET effluent (Sample “A”) in water (trial 1(b)) (Figure 5.4) and final biomass was negligible in all treatments and is therefore not presented.

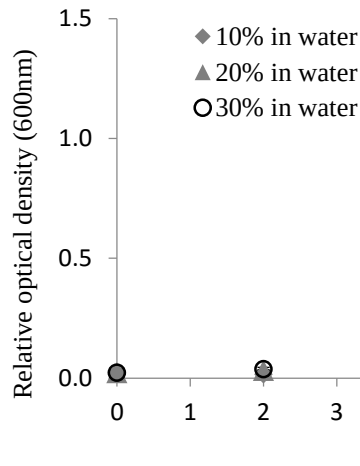


Figure 5.4: Optical density of algal cultures in trial 1(b) over time. Algae were cultured in three dilutions of BET effluent in deionised water to give the following ratios of BET/water: 10% BET/90% water, 20% BET/80% water and 30% BET/70% water.

5.4.3 Trial 2: N use efficiency

5.4.3.1 Microalgal growth

The BET effluent acted as the sole source of nitrogen for *C. vulgaris* at dilutions of 30%, 40% and 50% BET (Sample “B”) in combination with JM minus added N (JM-n; Figure 5.5). Neither optical density ($P = 0.992$) nor final biomass ($P = 0.837$) were significantly different between BET effluent supplemented with N-free JM and standard JM (plus N) (Figure 5.5 and 5.6). No growth was observed in the JM-n control, indicating that the nitrogen in the BET effluent was utilised by the algae.

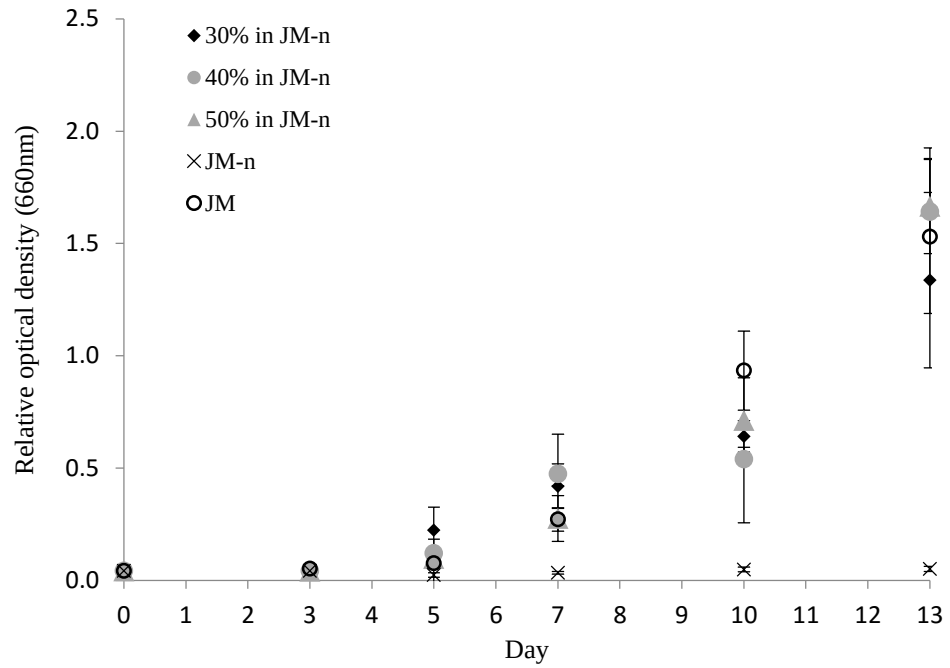


Figure 5.5: Optical density of algal cultures in trial 2 over time. Algae were cultured in 100% JM, in JM-n and in three dilutions of BET effluent in JM-n to test the effectiveness of BET as the sole source of nitrogen. ANOVA (repeated measures): Treatment as a single factor $P = 0.992$; time as a single factor, $P < 0.001$ (JM-n treatment was excluded from statistical analysis)

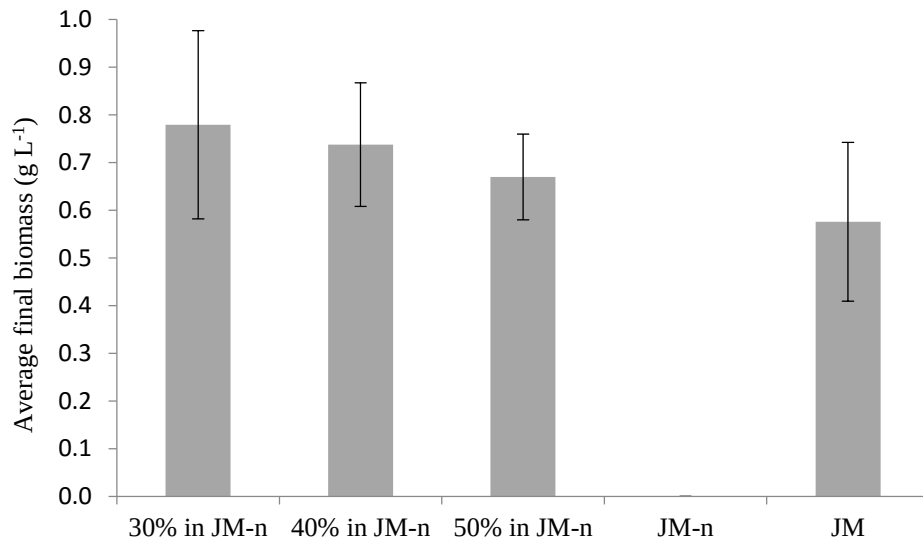


Figure 5.6: Average final algal biomass ($\pm$ standard error) for treatments in trial 2 after 13 days. No significant treatment effects were observed when JM-n was removed from the analysis.

5.4.3.2 Nitrogen removal

A profile of total nitrogen (TN) concentrations within the culture media across the 13 day cultivation period (Figure 5.7) shows a substantial drop in TN concentration in the first three days within the three treatments containing BET effluent. The drop in TN concentration on day 3 was 32.5%, 47.5% and 54.4% for treatments 30% BET, 40% BET and 50% BET effluent respectively. As this occurred in the lag phase of algal growth before increases in optical density were observed, it is likely to be due to volatilisation of ammonia in the BET effluent, as described by Zimmo *et al.* (2003). This was not observed in the JM treatment because the main N-source was NO₃⁻. Nevertheless, Petrovič and Simonič (2015) reported rapid ammonium removal in < 3 days; these authors also reported increased NO₃⁻ uptake when a carbon source was added to their algal growth medium. BET contained small amounts of DOC (29 mg L⁻¹), which may have stimulated initial NO₃⁻ uptake, although this concentration is smaller than the honey and sucrose concentrations (250-500 mg L⁻¹) used by Petrovič and Simonič (2015). However, since the OD did not increase until day 5, it is unlikely that N-removal prior to that was due to algal growth. The increase in total N observed over the first 3 days in the JM-n treatment is likely to be due to ammonium leakage from algal cells as a result of N-limiting conditions (Kleiner, 1985; Howitt and Udvardi, 2000). All calculations determining algal uptake of nitrogen and nitrogen removal efficiency were therefore calculated by taking initial TN concentrations from day 3 and not day zero (t_0 = day 3). Throughout the trial (from day 3 onwards), solution N concentrations were highest in the 50% BET treatment, with the 40% and 30% BET solutions being similar to each other and the JM treatments having the lowest total N concentrations (Repeated Measures ANOVA: Treatment as a single factor, $P < 0.001$). By the end of the 13-day trial, all treatments had similar concentrations of N; any differences on day 13 were not significant, whilst previously they had been (Repeated Measures ANOVA: Treatment x time interaction, $P < 0.001$).

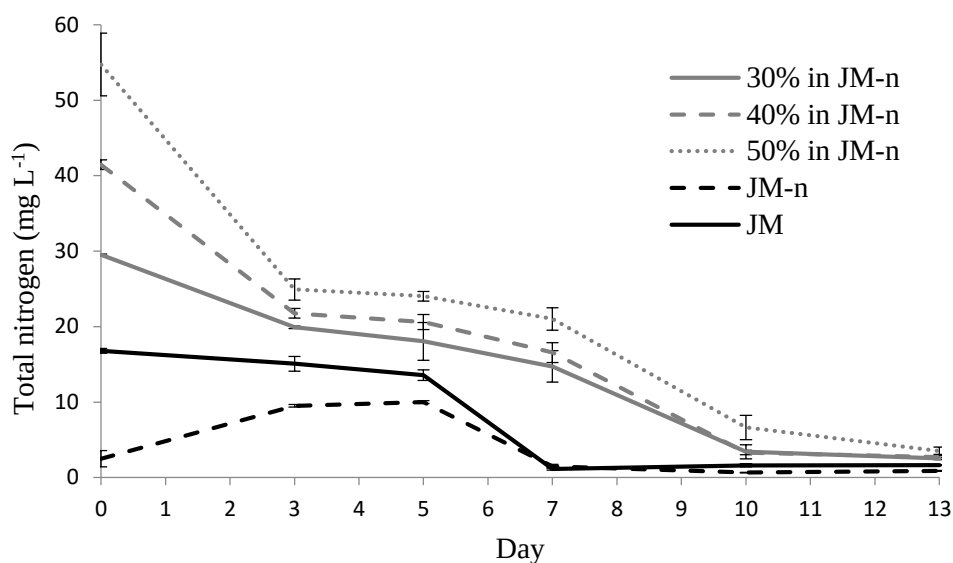


Figure 5.7: Change in total nitrogen concentration in the media throughout the cultivation period in trial 2 (*C. vulgaris*). Data are means $\pm$ standard error. ANOVA (both with and without inclusion of day 0 data): ANOVA: Treatment as a single factor and Treatment $\times$ Time interaction, $P < 0.001$ (from Day 0); $P < 0.001$ (from Day 3); LSD = 3.14

Since the starting concentration of N was different in each treatment, the nitrogen removal rates from the solutions are of more interest. Despite the apparent trend towards a more rapid N-uptake rate with increasing BET concentration, there was no significant difference between solutions containing BET, although the average daily uptake rate was slower from the JM treatment (ANOVA: $P < 0.001$; Figure 5.8). Despite this, the percentage efficiency of N-removal from day 3 to day 13 was not statistically different (Table 5.4).

A longer lag phase prior to nitrogen removal (attributed to the algae) was observed in solutions containing BET effluent relative to the JM treatments (Figure 5.7). The highest rate of nitrogen removal was observed from the JM treatment between days 5 and 7, compared to days 7 and 10 in treatments containing BET effluent. It is hypothesised that the increased lag phase is due to algal cells adjusting from a nitrate source in the stock culture medium (100% JM) to an ammonium nitrogen source in the BET effluent. When $\text{NH}_4^+\text{-N}$ is used as the sole nitrogen source, pH generally falls

because of the utilisation of bicarbonate (Mayer *et al.*, 1997), however pH was not observed to fall significantly in this work.

Table 5.4: Nitrogen removal efficiency for trial 2. (t_0 = day 3) ANOVA: $P=0.299$

Treatment	N - Removal Efficiency
30% in JM-n	0.873 ± 0.013
40% in JM-n	0.875 ± 0.021
50% in JM-n	0.859 ± 0.047
JM	0.901 ± 0.017

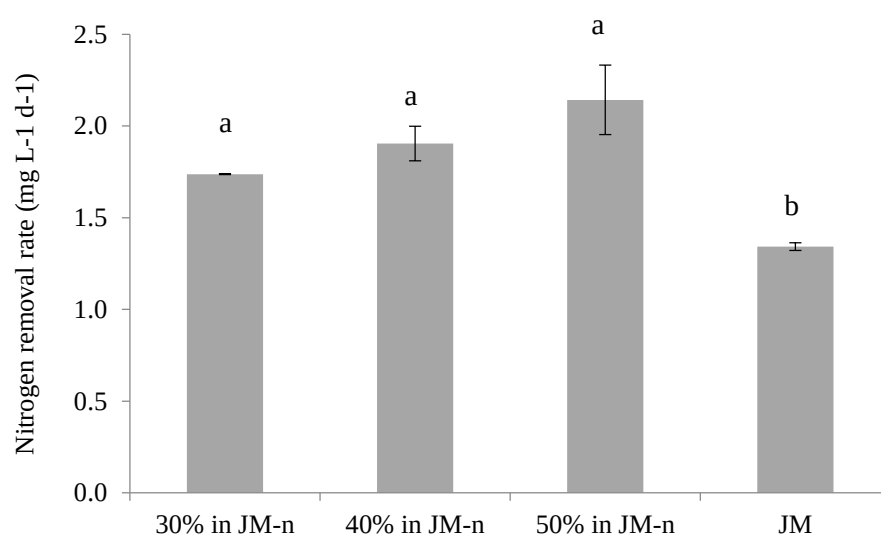


Figure 5.8: Nitrogen removal rate for different treatments in trial 2. Data are means $\pm$ standard error. ANOVA: $P = <0.001$. Columns similarly superscripted and not significantly different (Tukey's Test, $P < 0.05$)

High efficiencies of nitrogen removal were achieved (Table 5.4). Efficiencies of removal were within a narrow range for BET effluent media (0.86 - 0.87), and appear slightly higher in the JM control (0.90), although this difference is not significant ($P = 0.299$). The nitrogen removal rate was, however, statistically higher in high BET

effluent treatments (30%, 40% and 50% BET effluent, Figure 5.8) ($P = <0.001$), due to the fact that initial TN concentration was higher in high BET effluent treatments.

5.4.4 Trial 3: *S. obliquus* N-use efficiency with added PO₄

5.4.4.1 Microalgae growth

No treatment (as a single factor) differences in growth (OD) were observed, indicating that *S. obliquus* is well suited to cultivation in the BET effluent, and that it can grow in undiluted BET when sufficient phosphate is added at a comparable rate to when cultivated in JM. Although initial growth rate appears higher in the JM culture (Figure 5.9), the phosphate/BET effluent (Sample “C”) treatments recover and proceeded to accelerate beyond the OD of JM treatments by day 12. The initial lag phase in BET samples is likely to be due to adjustment to the new media conditions. Although there was no treatment effect as a single factor, the OD of the JM cultures was significantly lower at day 14 than that of the other treatments; there was no difference between the two PO₄-P treatments (Repeated Measures ANOVA; $P = 0.032$; Figure 5.9).

The average final biomass (Figure 5.10) confirms that growth of cultures in BET treatments exceeded that in JM; average final concentrations of 0.83 g L⁻¹ and 0.90 g L⁻¹ were observed in BET effluent treatments with 18 and 36 mg L⁻¹ PO₄³⁻ added respectively, compared to an average value of 0.63 g L⁻¹ in the JM culture (ANOVA: $P = 0.009$). Final biomass results also indicate that increasing the phosphate to 36 mg L⁻¹ does not significantly affect the algal growth rate or biomass accumulation.

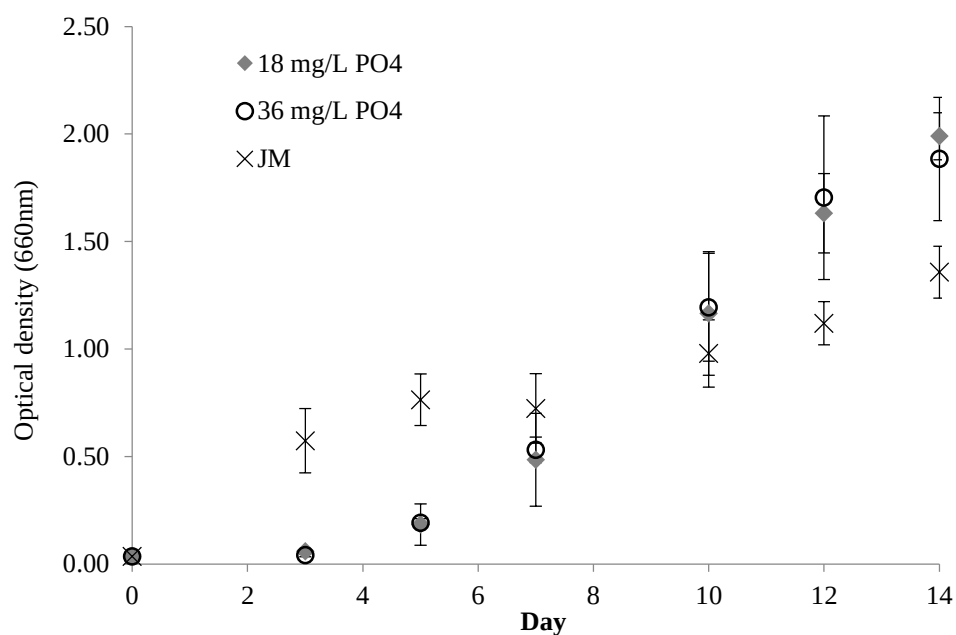


Figure 5.9: Average optical density of algal cultures ($\pm$ standard error of the mean) in trial 3 over time to determine the effect of phosphate concentration (18 mg L⁻¹, 36 mg L⁻¹ and JM; x-axis) on growth rate of *S. obliquus*. ANOVA (repeated measures): Treatment x Time interaction, $P = 0.032$; LSD = 0.479

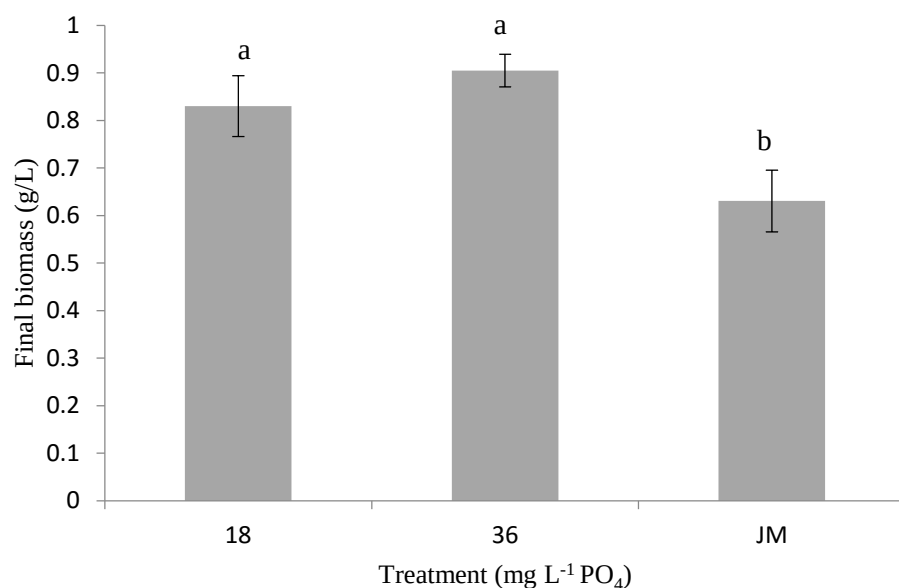


Figure 5.10: Average final (Day 14) biomass ($\pm$ standard error) of *S. obliquus* cultures in trial 3. ANOVA: $P = 0.009$. Columns similarly superscripted and not significantly different (Tukey's Test, $P < 0.05$)

5.4.4.2 Nitrogen removal

Reduction of TN concentration was again observed during the lag phase of algal growth for BET effluent treatments in trial 3 (Figure 5.11), indicating some volatilisation of

ammonia, but this was to a lesser extent when compared to that observed in trial 2. The TN profile for the JM treatment is consistent with that observed in trial 2, with peak nitrogen removal occurring between days 3 and 5. In the BET treatments, a lag in nitrogen removal was observed until day 5, at which point the nitrogen concentration rapidly decreased. This is consistent with the lag phase observed in the OD measurements in these treatments, and with the lag phase also observed in nitrogen removal from BET treatments in trial 2. Total nitrogen concentration during the cultivation period was significantly different ($P < 0.001$) in BET-based treatments compared to cultures in JM. Final TN concentration appears to remain higher in samples from trial 3 when compared to the final day in trial 4 ($3.6\text{--}6.3\text{ mg L}^{-1}$ in trial 3; $1.7\text{--}3.5\text{ mg L}^{-1}$ in trial 2). This difference is due to the fact that starting TN concentration in this trial is higher than that in trial 2 ($\sim 58\text{ mg L}^{-1}$ on day 3 of trial 3 compared to $\sim 25\text{ mg L}^{-1}$ on day 3 of trial 2); and in fact the removal efficiency is higher in trial 3 ($>90\%$ for BET samples) (Table 5.5) when compared to trial 2 ($85.9\% - 87.5\%$). Nitrogen removal rate in trial 3 is more than double that in trial 2 ($4.5\text{ mg L}^{-1}\text{ day}^{-1}$ compared to $2.1\text{ mg L}^{-1}\text{ day}^{-1}$ in trial 2) (Figure 5.12); indicating that the culture is not overburdened with nitrogen at the current BET outlet concentration. Nitrogen removal efficiency ($P = 0.004$) and rate ($P < 0.001$) was significantly higher in BET treated samples than in JM cultures.

Table 5.5: Nitrogen removal efficiency by *S. obliquus* for treatments in trial 3. ANOVA: $P = 0.004$

Treatment	N - removal efficiency
$18\text{ mg L}^{-1}\text{ PO}_4$	0.915 ± 0.007
$36\text{ mg L}^{-1}\text{ PO}_4$	0.908 ± 0.016
JM	0.771 ± 0.037

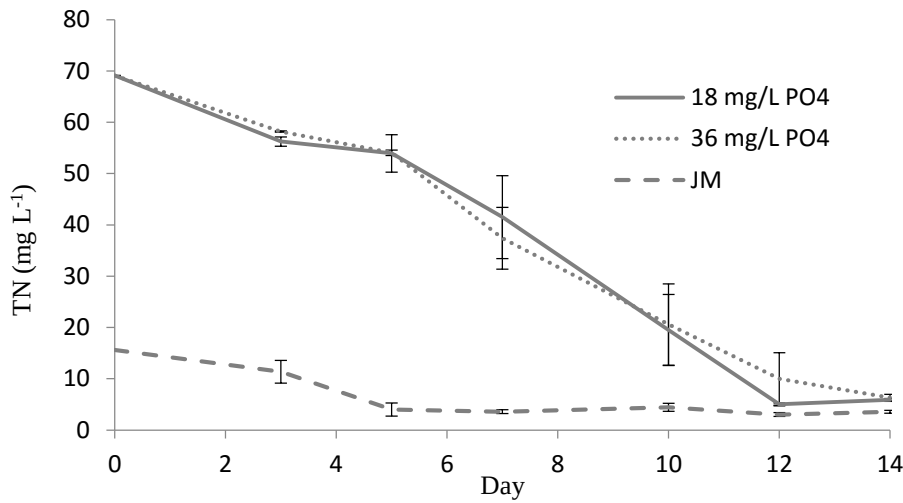


Figure 5.11: Average total nitrogen concentration ($\pm$ standard error) in the media throughout the cultivation period in trial 3 (*S. obliquus*). ANOVA: Treatment as a single factor $P < 0.001$; Treatment x Time interaction, $P < 0.001$; LSD = 12.4

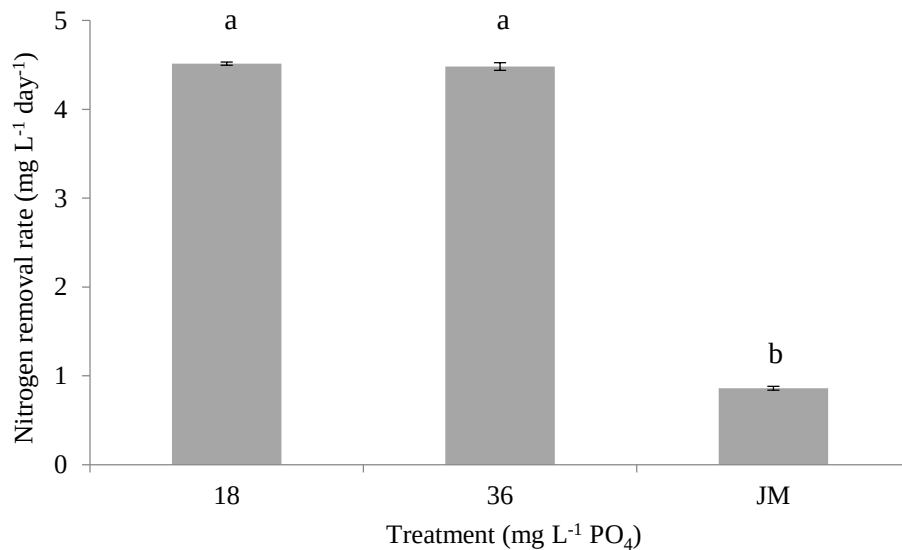


Figure 5.12: Nitrogen removal rate for treatments in trial 3. ANOVA: $P = < 0.001$. Columns similarly superscripted and not significantly different (Tukey's Test, $P < 0.05$)

In trial 3, concentration of total organic carbon (TOC) in the treatments was analysed across the cultivation period (Figure 5.13). In the BET treatments, TOC concentrations are initially high (due to the presence of dissolved organic carbon in the BET effluent) and these fall during the exponential phase of algal growth (day 3 to day 10). In contrast, the JM treatment possesses a low TOC concentration at the start of the trial (1.6 mg L⁻¹

¹) (TOC in JM is from low concentrations of vitamins; cyanocobalamin, biotin, thiamine and EDTA), but this increases by day 5 to the same level as the BET to around 40 mg L⁻¹ by day 5 before following a similar pattern to the other treatments. TOC in the JM treatments was significantly lower at the start of the trial and at the end of the investigation (Treatment x Time interaction, $P < 0.001$; $LSD = 9.559$) than the concentrations recorded in the BET media.

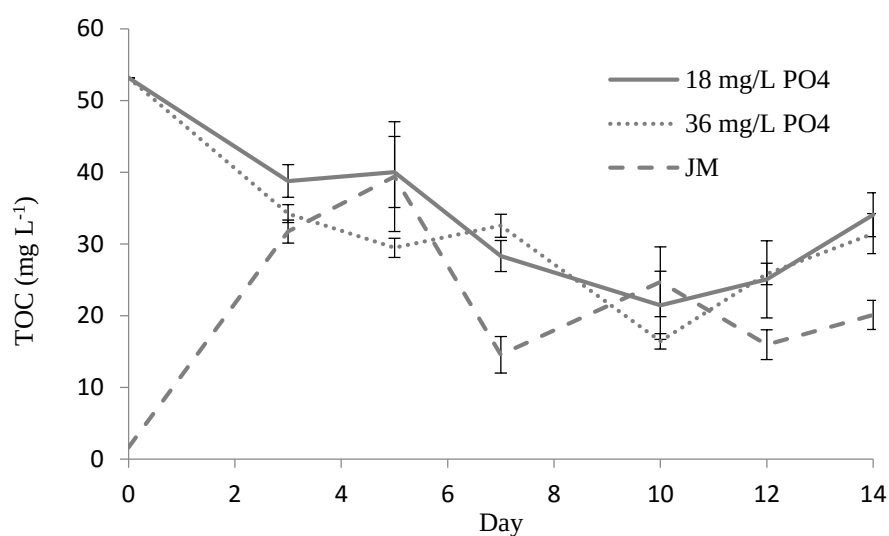


Figure 5.13: Average total organic carbon concentration ($\pm$ standard error) throughout the cultivation period. ANOVA: Treatment as a single factor $P = 0.004$, $LSD = 4.977$; Treatment x Time interaction, $P = <0.001$, $LSD = 9.559$

The results from this trial indicate that BET effluent can sustain growth of *S. obliquus* when phosphate is added and cultures in these treatments outperformed those cultured in JM. *S. obliquus* removed nitrogen from the BET wastewater with an efficiency in excess of 90% over a 14 day period. Increasing the phosphate added to the BET effluent to double that present in the JM media did not significantly affect the rate of nitrogen removal from the wastewater, nor growth rate.

5.4.5 Trial 4: N-use efficiency with PO₄ and CO₂ amendments

5.4.5.1 Microalgal growth

In trial 4, all treatments were prepared using BET effluent sample “D” with added phosphate (18 mg L⁻¹ based on results from trial 3) and dosed with different concentrations of CO₂. OD measurements for both *C. vulgaris* and *S. obliquus* indicate that for both species, growth in the treatments dosed with 20% CO₂ suffered a longer lag period than the lower CO₂ treatments, with exponential growth phases not starting until day 4/5 compared to day 2/3 in lower concentration CO₂ treatments (Figures 5.14 and 5.16; Time x Treatment interaction, $P = 0.018$). The different CO₂ concentrations as a single factor did not affect the OD of *S. obliquus* ($P = 0.088$).

S. obliquus cultures in air appear from OD measurements to grow more slowly than CO₂ dosed treatments. This observation is confirmed in final biomass measurements, where biomass in both 5% and 20% CO₂ treatments is significantly higher ($P = 0.010$) than in the air treatment (1.82 g L⁻¹ - 1.88 g L⁻¹ compared to 1.09 g L⁻¹) (Figure 5.15). When final biomass for *S. obliquus* in trial 4 is compared to trial 3 it is clear that 9 days is an adequate cultivation period; no statistical difference in biomass was produced from a trial duration of 14 days in trial 3 compared to 9 days in trial 4.

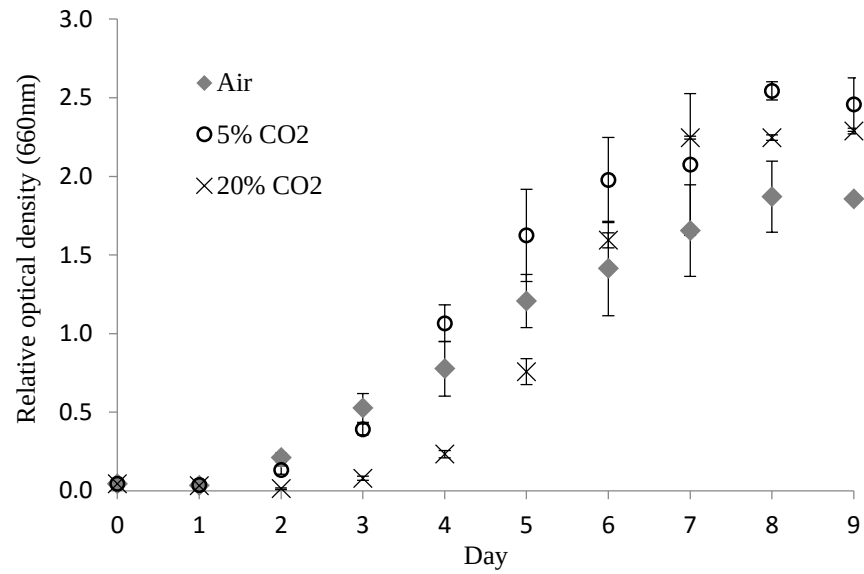


Figure 5.14: Average optical density measurements ($\pm$ standard error) for *S. obliquus* in trial 4. Effect of CO₂ concentration on growth of *S. obliquus*. ANOVA: Treatment as a single factor, $P = 0.088$; Time x Treatment, $P = 0.018$; LSD = 0.491

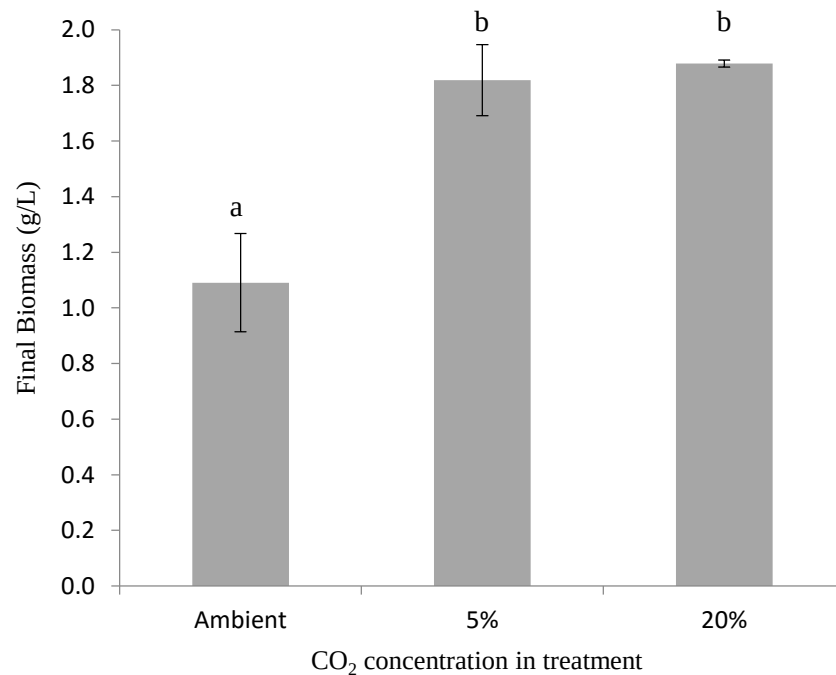


Figure 5.15: Average final (Day 9) biomass concentration of *S. obliquus* cultures in trial 4. ANOVA: $P = 0.010$. Columns similarly superscripted and not significantly different (Tukey's Test, $P < 0.05$)

In *C. vulgaris* cultures, a significant treatment effect was observed during the exponential phase of growth on days 3-7 (treatment x time interaction, $P < 0.001$). However, biomass measurements on the final day (Figure 5.17) indicate that there was no statistical difference ($P = 0.621$) in biomass between cultures on the final day (day 9); average final biomass concentration was 1.55, 1.55 and 1.37 g L⁻¹ for air, 5% CO₂ and 20% CO₂ treatments respectively. This suggests that any treatment effect observed during the linear phase of growth was subsequently lost. The final biomass data are in contrast to the study by Yun *et al.* (1997), where final biomass in *C. vulgaris* cultures dosed with 5% CO₂ was higher (1.58 – 1.72 g L⁻¹) than in treatments dosed with both air (1.30 – 1.32 g L⁻¹) and 15% CO₂ (1.25 – 1.49 g L⁻¹) over a 100 hour cultivation period. However, the current investigation continued for ~216 hours; at 4 days (equivalent to Yun *et al.*'s 100 hours), clear differences in OD were observed (Figure 5.16) that show maximum growth with 5% CO₂ and least growth with 20% CO₂ which corroborates their findings.

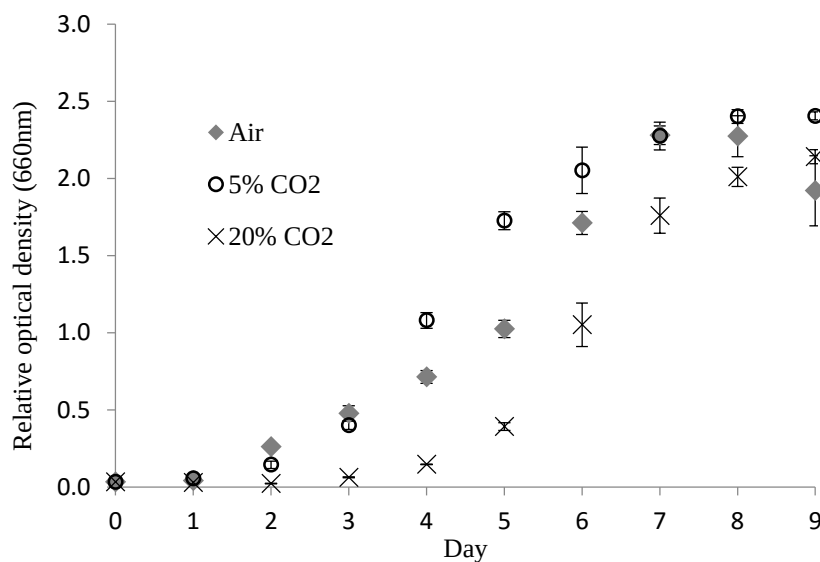


Figure 5.16: Average optical density measurements ($\pm$ standard error) for *C. vulgaris* in trial 4. Effect of CO₂ concentration on growth of *C. vulgaris*. ANOVA: Treatment x Time $P < 0.001$; LSD = 0.238.

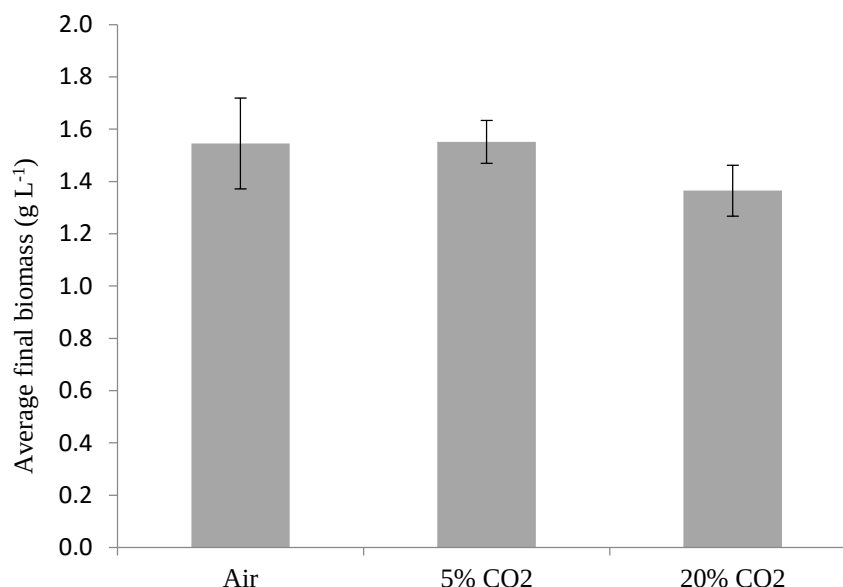


Figure 5.17: Final (Day 9) biomass of *C.vulgaris* cultures in trial 4. Data are means $\pm$ standard error. There was no significant treatment effect.

When final biomass measurements for *C. vulgaris* in trial 4 (Figure 5.17) are compared to the same measurements in trial 1 (Figure 5.3) and trial 2 (Figure 5.6) it is clear that the biomass obtained in trial 4 (1.37 – 1.55 g L⁻¹) is significantly higher than similar treatments in other trials (0.35 – 0.76 g L⁻¹ in trial 1; 0.670 – 0.779 g L⁻¹ in trial 2). It is possible that the higher nitrogen concentration in trial 4 treatments (~69 mg L⁻¹) (Figure 5.19) compared to other *C. vulgaris* trials (29-54 mg L⁻¹ in trial 2, not taking account of NH₃ volatilisation) (Figure 5.7) is a contributing factor; and this is supported by evidence that despite the higher initial concentration, nitrogen in the media is removed to virtually the same extent in both trials (Tables 5.4 and 5.6). In addition, the higher light intensity due to the difference in distance between lamps and the culture between trials (50cm in trial 1, 2 and 3; 40cm in trial 4) is likely to be another factor contributing to higher final biomass in *C. vulgaris* treatments in trial 4. The intensity, duration and quality of light affect photosynthetic efficiency and growth; whilst reduced duration

generally results in lower biomass production, light, CO₂ and nutrient interactions are complex (e.g. Al-Qasmi *et al.*, 2012).

5.4.5.2 Nitrogen removal

The longer lag phase observed in cultures grown with 20% CO₂ resulted in slower N removal from the BET medium (Figures 5.18 and 5.19). Nitrogen concentrations did not fall until day 4 of cultivation, in agreement with OD measurements (Figures 5.14 and 5.16), where significant growth was not observed until the same day. After day 4 the drop in N concentration in 20% CO₂ dosed treatments was more rapid in *S. obliquus* cultures than *C. vulgaris* ones; TN concentration dropped below 10 mg L⁻¹ by day 6 in *S. obliquus* cultures compared to day 7 in *C. vulgaris* cultures. These results appear to show slightly lower final nitrogen concentrations following treatment than those reported by Yun *et al.* (1997), where nitrogen was removed from steelmaking wastewater using *C. vulgaris* to a final concentration of around 15 mg L⁻¹.

Thus in *S. obliquus* cultures, N removal was least in BET treated with 20% CO₂ although the Treatment x Time interaction was only weakly significant (P=0.066; Figure 5.18). In contrast, N removal from *C. vulgaris* cultures was significantly affected by CO₂ amendment with 20% being least effective and 5% CO₂ the most effective over the period of linear algal growth (Figure 5.16)

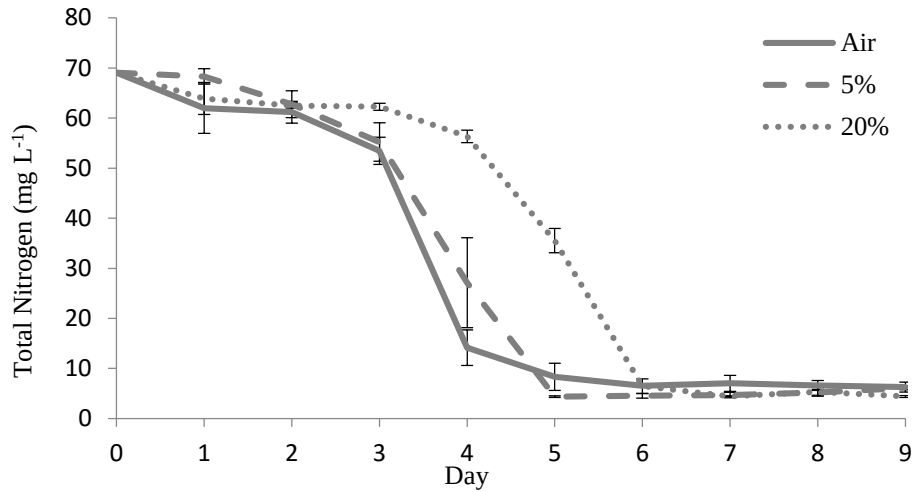


Figure 5.18: Total nitrogen concentration in the media throughout the cultivation period in trial 4 (*S. obliquus*). Data are means $\pm$ standard error. ANOVA: Treatment as a single factor was not significant ($P = 0.141$); Treatment $\times$ Time, $P = 0.066$

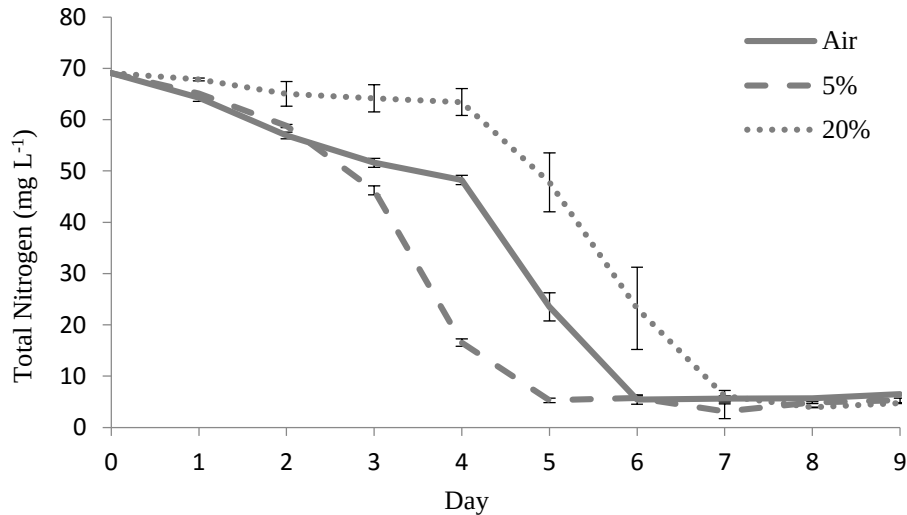


Figure 5.19: Total nitrogen concentration in the media throughout the cultivation period in trial 4 (*C. vulgaris*). Data are means $\pm$ standard error. ANOVA: Treatment as a single factor, $P = <0.001$; Treatment $\times$ Time; $P = 0.004$; LSD = 7.99

Efficiency of nitrogen removal from the wastewater in treatments for both species was high, all achieving an average above 90% (Table 5.6). The efficiency with which *S. obliquus* removed N from the BET medium was unaffected by the CO₂ treatments. In contrast, N removal efficiency by *C. vulgaris* was lowest when cultured with air and highest when grown with CO₂ amendments although there was no difference between the two CO₂ concentrations (Treatment effect, $P=0.015$; Table 5.6).

Table 5.6: Nitrogen removal efficiency for treatments in trial 4. ANOVA: $P = 0.015$ (*C. vulgaris*); $P = 0.093$ (*S. obliquus*)

Treatment	Nitrogen removal efficiency		Error ($\pm$)	
	<i>C. vulgaris</i>	<i>S. obliquus</i>	<i>C. vulgaris</i>	<i>S. obliquus</i>
Air	0.906	0.909	0.028	0.008
5%	0.923	0.911	0.010	0.012
20%	0.931	0.934	0.003	0.003

Nitrogen removal rate (Figure 5.20) followed a similar trend to nitrogen removal efficiency, with no significant effect of CO₂ treatment on N removal by *S. obliquus*, and a higher rate of removal in *C. vulgaris* cultures amended with CO₂ rather than with air (Treatment effect, $P=0.015$; Figure 5.20).

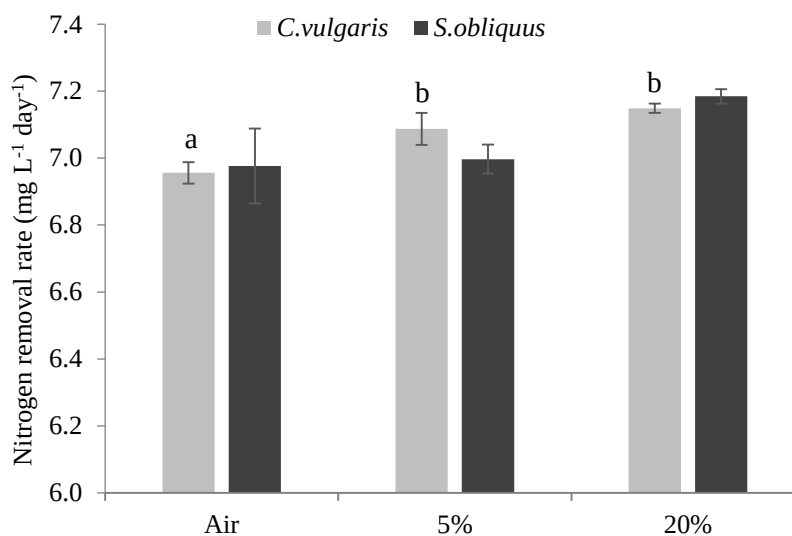


Figure 5.20: Nitrogen removal rates from BET media amended with air, 5% CO₂ or 20% CO₂ in trial 4. Data are means $\pm$ standard error. ANOVA: $P = 0.095$ (*S. obliquus*); $P = 0.015$ (*C. vulgaris*). Columns similarly superscripted (*C. vulgaris*) are not significantly different (Tukey's Test, $P < 0.05$)

The TOC concentration profile across the cultivation period for both species (Figures 5.21 and 5.22) appears to follow a similar trend for all treatments, and is in close agreement with the TOC observations made in trial 3 (Figure 5.13). The relatively high initial TOC concentration (53.2 mg L⁻¹) which rapidly falls to a minimum of 8.7 mg L⁻¹ by day 3 of cultivation is possibly an artefact of storing the BET prior to

conducting the experiment. The first value is that measured on collection of the BET sample and the measurement on day 1 is from the experimental flasks after set-up. The apparent fall in TOC concentration is most likely because of bacterial utilisation prior to filtering and/or removal of suspended organic matter during filtering before experimental use. Therefore, statistical analyses were performed on data from day 1 onwards. In both sets of cultures, TOC increased with time ($P < 0.001$ for both species). TOC was unaffected by treatment (CO₂/air) in *S. obliquus* cultures but lower TOC concentrations were apparent in 20% CO₂-amended *C. vulgaris* cultures from day 6 onwards (Treatment x time, $P = 0.020$). This trend is consistent with the algal growth over this period (Figure 5.16).

The observed trend in TOC concentration across the cultivation period is in contrast to other studies where microalgae are cultured in wastewater; Mahapatra *et al.* (2014) observed a staged but consistent drop in TOC concentration coinciding with growth

phases, although the starting concentration was much higher ($>200 \text{ mg L}^{-1}$) than in this study and the wastewater source very different (municipal).

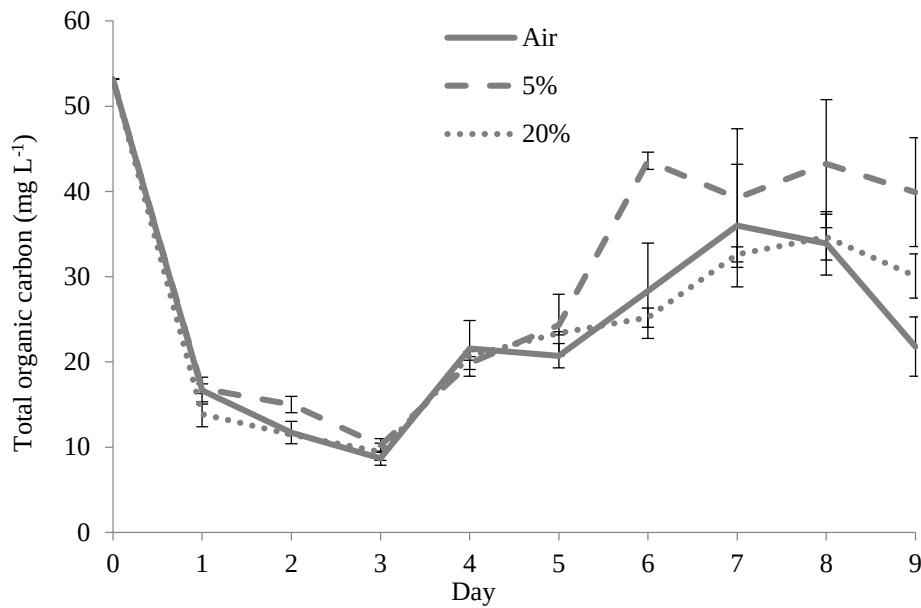


Figure 5.21: Total organic carbon concentration in the media throughout the cultivation period in trial 4 (*S. obliquus*). Data are means $\pm$ standard error. ANOVA: Treatment only, $P = 0.163$; Treatment $\times$ Time; $P = 0.181$.

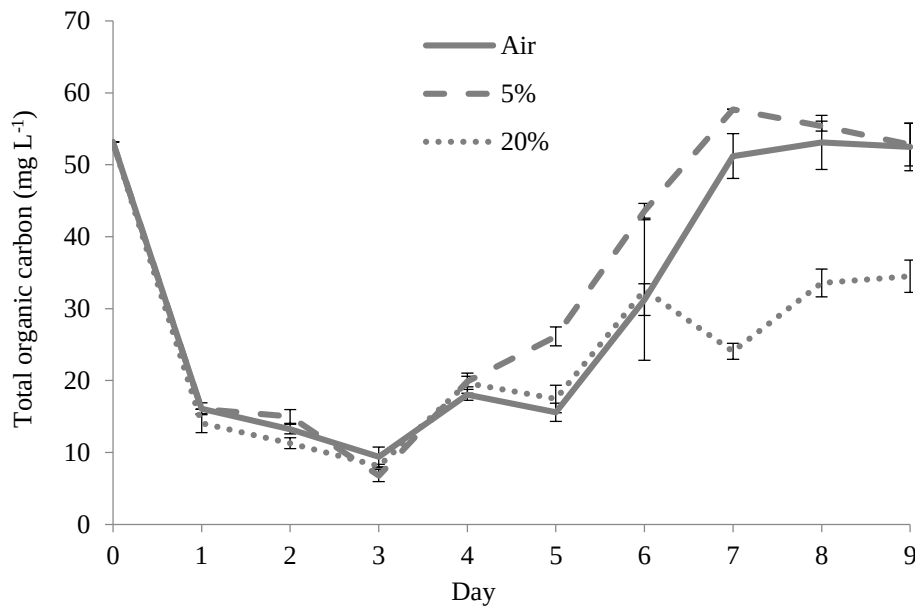


Figure 5.22: Total organic carbon concentration in the media throughout the cultivation period in trial 4 (*C. vulgaris*). Data are means $\pm$ standard error. ANOVA: Treatment only, $P = 0.022$; Treatment $\times$ Time; $P = 0.020$; LSD = 9.127

5.5 Chapter summary and conclusions

A review of literature on microalgal cultivation indicates that open pond systems are the only commercially viable option for large-scale production. Current commercial examples of microalgal production centre on high value products with relatively low markets. Most of these products are used in human or animal nutrition and it is unlikely that this market would accept a product produced from steelmaking wastewater and CO₂ due to fears of contamination. Currently, commodity products such as biofuels cannot be produced economically from microalgae except when produced as the by-product of a wastewater treatment system where high rate algal ponds are deployed. In these systems, it has been demonstrated that CO₂ addition to the cultures can result in a number of benefits, including a substantial increase in microalgae productivity. This hybrid system is an attractive option for combining CO₂ utilisation with wastewater treatment. The technical feasibility of supplying CO₂ to microalgae cultures *via* direct contact with steelworks derived exhaust gas has been demonstrated in a number of publications, including gases from Tata Steels own integrated sites; from both coke ovens at Strip Products UK and the power station at Long Products UK.

A wastewater stream from Tata Steel operations was identified as potentially suitable for microalgae cultivation and a series of 4 cultivation trials was devised to test the feasibility of treating this wastewater with algae to produce biomass.

Results indicate that although the wastewater is deficient in phosphate, when this is added to the culture it can sustain growth of both species of microalgae that were tested, *C. vulgaris* and *S. obliquus*. Moreover, in some tests the cultures grown in wastewater had a higher final biomass concentration than those cultured in the standard culture media.

Measurements of nitrogen concentration in the media throughout the cultivation period show that both *C. vulgaris* and *S. obliquus* can be very effective in remediating nitrogen

from this effluent; removal efficiency was greater than 85% in all trials, and a maximum of 93.4% was observed in trial 4 for *S. obliquus* cultured in 20% CO₂.

When simulated flue gas (20% and 5% CO₂) was added to cultures grown in wastewater, a significant increase in the final biomass was observed for one algal species, *S. obliquus*, but not for *C. vulgaris*. No significant difference was observed between the final biomass of *S. obliquus* in 5% CO₂ and those in 20% CO₂. This suggests that *S. obliquus* may be the best suited of the two species tested to being grown in a CO₂ enriched environment, but that use of a low CO₂ concentration flue gas (for example from sintering processes) may be as effective at enhancing growth and accelerating nitrogen remediation than higher concentration sources.

6. A techno-economic evaluation of combined microalgae production and wastewater treatment at an integrated steelmaking site.

6.1 Scope and process description

In Chapter 5, it was demonstrated that microalgae can be used to reduce the ammonium levels in this effluent while at the same time capture CO_2 and produce a biomass product. In this chapter, a techno-economic analysis is presented in order to assess the technical and economic potential and possible synergies of siting a microalgae water treatment and biomass production facility at an integrated steelworks.

The approach of this chapter is to conduct a preliminary techno-economic assessment on microalgae based wastewater treatment and CO_2 capture based on technology that is currently available for commercial deployment, and not considering technologies currently under development. The two most mature technologies for microalgae production and wastewater treatment are raceway ponds and high rate algal ponds (HRAP's) respectively. As the objective of the production is to combine wastewater treatment with CO_2 utilisation (the rate of which is directly proportional to biomass production rate), it was decided that the plant design would be a hybrid of these technologies.

In the present model, the BET plant effluent used for Chapter 5 experiments is used as a water and nitrogen nutrient source, is supplemented with phosphate and fed to a series of open raceway ponds where algae are cultivated. The ponds are supplied with CO_2

taken directly from a coke oven underfiring exhaust (24% v/v CO₂) in order to enhance the microalgae productivity and utilise CO₂ emissions.

The process incorporates microalgae cultivation and biomass processing into existing operations at a typical integrated steelmaking site (Figure 6.1). The design was chosen to minimise energy consumption where possible, for example processing biomass as slurry rather than dry, and to produce products of direct benefit to steelmaking operations. Anaerobic digestion was chosen as the biomass processing route due to the ease of integrating the biogas into existing fuel gas distribution at a steelworks, and due to the potential for nutrient recycling.

In order to quantify any advantage gained from using the nitrogen present in wastewater rather than to add it as a fertiliser, a second scenario was modelled where urea is used as a nitrogen source.

Microalgae are cultured in BET effluent in raceway ponds before mature culture is pumped from the raceway ponds for an initial concentration stage in settling ponds followed concentration to 4% dry weight in a dissolved air floatation (DAF) unit. A fraction of the overflow from the settling ponds is recycled as necessary back to the raceway ponds and the remainder is discharged as treated effluent. In the DAF unit, the overflow is still relatively highly concentrated and is therefore recycled back to the settling ponds to maximise the yield.

The 4% biomass slurry outflow from the DAF is fed to an anaerobic digester where it is converted into a primary biogas product and secondary solid and liquid digestates. The liquid digestate is recycled as a nutrient source back to the raceway ponds while the solid digestate is sold as a terrestrial fertiliser. The biogas product is fed back to steelmaking operations and either mixed directly back with cleaned COG, or is used to enrich lower calorific value fuel gases on the works such as blast furnace gas or BOS gas. A flow diagram of the process is shown in Figure 6.1.

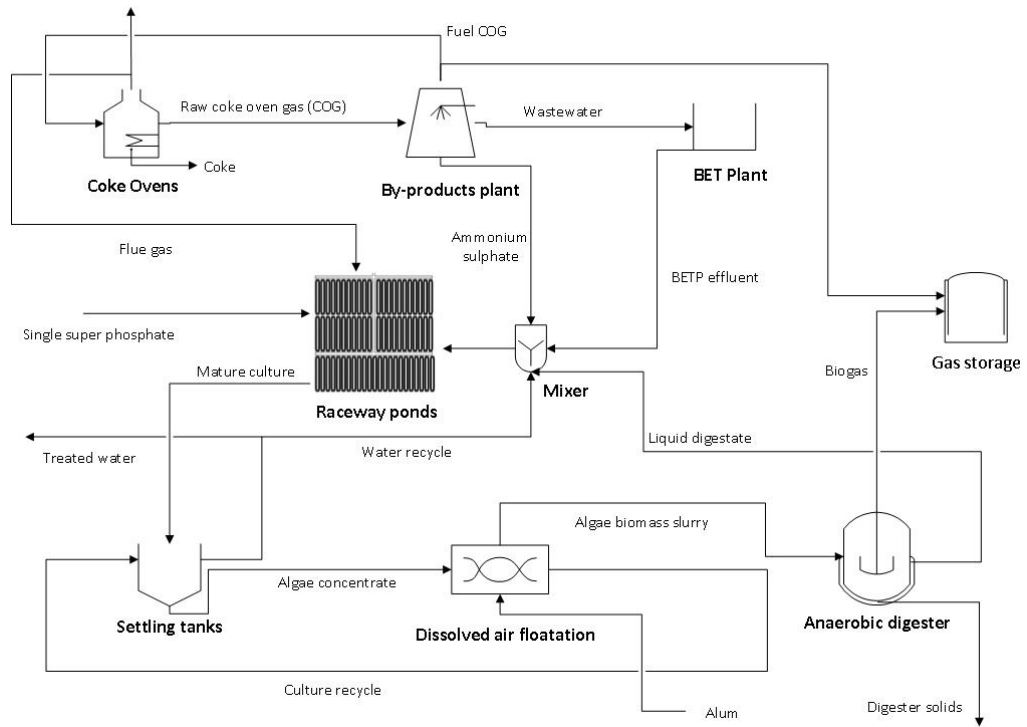


Figure 6.1: Flow diagram of microalgae production integrated into steelmaking operations

6.2 Methodology

6.2.1 Microalgae cultivation

The open pond cultivation process was designed to sit between the biomass production optimisation described by Borowitzka (2005) and the system described for advanced wastewater treatment by Craggs (2006). A raceway pond arrangement was modelled, with individual pond dimensions of 20 m by 200 m and a depth of 0.5 m. This gives an area of 0.4 hectares and a total volume of 2000 m³ per pond. Ponds are arranged in rows and are fed at one point per pond by a water (and nutrient) delivery pipe, a flue gas delivery pipe and a harvest pipe (see electricity requirements, Section 6.2.5). Although laboratory cultures of *S.obliquus* cultured in BET effluent achieved growth rates as high as 200 g L⁻¹ m⁻³ (Chapter 5; Trial 4), real outdoor cultures would almost certainly be very low in comparison. This is due to the inability to optimise growth conditions, shorter irradiance period (day/night cycle) and relatively poor mixing. In

this work, low base case algal productivity of $15 \text{ g m}^{-3} \text{ d}^{-1}$ was assumed based on the lower estimate by Craggs (2006) to account for the relatively low temperature and solar irradiation in the UK, giving an algal dry weight concentration of 120 g m^{-3} for harvesting following an 8 day residence time. The culture in the ponds is agitated through the use of paddlewheels, which maintain a low culture velocity of 0.1 m s^{-1} . A base case scenario was developed using a typical volumetric outflow of BET plant effluent from an integrated steelworks ($2100 \text{ m}^3 \text{ day}^{-1}$), diluted to a factor of 0.5 to give $4200 \text{ m}^3 \text{ day}^{-1}$ inflow of water to the cultivation plant. This equates to a baseline total pond area of 6.72 hectares.

6.2.2 Harvesting

Microalgae biomass harvesting was modelled using two processes; an initial concentration stage using a natural settling process in large settling ponds, and a second concentration process to increase the solids loading to 4% in a dissolved air floatation unit.

6.2.2.1 *Algae settling ponds*

Algae settling ponds promote natural sedimentation of the algae biomass and act as an initial harvesting stage to concentrate the biomass adequately for dissolved air floatation. The settling ponds modelled have a hydraulic residence time of one day in order to achieve a 75% recovery of algal biomass (Craggs, 2006). The pond size is dependent on the inflow to the raceway ponds but a length to width ration of 5:1 is used as recommended by Craggs (2006). Two ponds operate in series, one is in settling operation while the other is emptied of biomass. A proportion of the settling pond outflow water is recycled back to the raceway ponds as necessary, while the remainder is discharged as a treated effluent. Harvested algae biomass leaving the settling ponds is assumed to have a dry matter concentration of 1%.

6.2.2.2 Dissolved air floatation

Dissolved air floatation (DAF) is commonly applied at wastewater treatment facilities and is described in detail as an option for harvesting microalgae biomass by Elder (2011). The process involves a portion of the effluent from the DAF being saturated with compressed air where it dissolves. The air saturated liquid is then pumped into the algae concentrate which has been mixed with a flocculent. The dissolved air forms microbubbles (30-100 μm diameter) due to the pressure reduction and these bubbles carry the suspended biomass to the surface where it is skimmed off as concentrated slurry.

In this model, alum ($\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) is added as a flocculant at 30ppm to the DAF unit inflow (30 g m^{-3}) in order to achieve solids recovery of 65% with a dry solids concentration of 4% (Elder, 2011). The solids depleted effluent has a relatively high biomass load (35% of inflow) and so is recycled back to the settling ponds.

6.2.3 Anaerobic digestion

The concentrated algal slurry produced from DAF operations is fed to an anaerobic digester where the algal biomass is digested to form a primary biogas product and liquid and solid digestate by-products. The gas yield from anaerobic digestion can be calculated using the volatile solids content of the microalgae (82% assumed) and a conversion factor derived from experimental results. For this model results from Samson and LeDuy (1982) were used; for *Spirulina maxima*, $0.26 \text{ L CH}_4 \text{ g VS}^{-1}$ was used and corrected to total gas using a methane content of 68% (v/v). The heating load of the anaerobic digester is assumed to be met using low grade waste heat from steelmaking operations, at no additional cost.

6.2.4 Nutrient requirements

Nutrient requirements were estimated using the empirical values derived from biochemical composition of the algae by Collet *et al.* (2011). Values of 61 g N and 9.1 g P per kg dry algae were used (Collet *et al.*, 2011).

6.2.4.1 BET effluent

Final effluent from biological effluent treatment plants treating coke making wastewater was identified as a source of nitrogen (ammonium) rich wastewater, suitable for microalgae cultivation. BET plants are standard processes used to clean coke production and the effluent is typically discharged to the environment. Cultivation of microalgae in such effluents can act as a tertiary wastewater treatment stage and reduce the ammonium loading considerably, reducing the potential to cause damage to the environment. The nitrogen concentration in the wastewater was determined experimentally and this concentration was included in the model to allow for excess nutrient requirement calculations.

6.2.4.2 Ammonium sulphate

A source of nitrogen nutrients in addition to that provided by BET effluent is ammonium sulphate produced at coke oven by-products plants on integrated steelmaking sites. Ammonium sulphate is produced during the process of stripping coke oven gas (COG) of nitrogen and sulphur so that it can be used as a fuel gas on site. Although historically this has been sold as a fertiliser by-product, more recently it has become less favourable in agriculture to nitrate and urea based fertilisers and thus it has become difficult to market²¹.

6.2.4.3 Urea

²¹ From internal Tata discussions

The use of bought in urea fertiliser as a source of nitrogen was also explored in order to determine the lifecycle benefits and synergy of using waste and by-product sourced nitrogen.

6.2.4.4 Single super phosphate

Although nitrogen nutrients can be sourced on site from BET effluent and ammonium sulphate, there is not an easily accessible and soluble source of phosphate at an integrated steelworks. Therefore phosphate must be brought to the site in the form of single super phosphate fertiliser. For this work, single super phosphate is assumed to have a phosphate concentration of 20%.

6.2.5 Electricity requirements

6.2.5.1 Water and flue gas pumping

Calculations on electricity requirements for pumping of water and flue gas to supply the raceway ponds were based on the methodology of Rickman *et al.* (2013). It was assumed that flue gas and water would be pumped continuously into one point at each pond and that water would also be pumped out of each pond, through the same geometry to algal settling ponds for harvesting. Length of pipe required L_{pipe} , was calculated using Equation 6.1, where L_{pond} is pond length, and n_{div} is the number of pipes diverging from the main (Equation 6.2). Diverging pipes are located before the first row of ponds and at every two pond lengths thereafter, rounded to the closest integer.

$$L_{pipe} = (\sqrt{A_{total}} - L_{pond}) + (\sqrt{A_{total}} * n_{div}) \quad (6.1)$$

$$n_{div} = \left\lceil 1 + \frac{\sqrt{A_{total}}}{2 \cdot L_{pond}} \right\rceil \quad (6.2)$$

In order to allow scaling without manually changing pipe diameter, appropriate fluid velocities were assigned to both water (1 m s^{-1}) and flue gas (15 m s^{-1}) (Sinnott and Towler, 2009), and pipe diameter (D) was back calculated from this using Equation 6.3,

$$D = 2 \sqrt{\frac{Q}{2n_{sub}/v\pi}} \quad (6.3)$$

Where Q is the volumetric flow rate and v is the fluid velocity. In the case of flue gas pumping, an assumption was made that 10% of CO₂ delivered would be dissolved and therefore would be available for algal growth, based on evidence from Becker (1994) that 80-90% of CO₂ delivered to raceway ponds using a sump is vented to atmosphere due to the short duration for mass transfer at the gas/liquid interface. Flow rate of flue gas required was calculated from required CO₂ to produce total biomass output and an example steelworks power station stack CO₂ concentration of 24% v/v. Reynolds number (Re) was then calculated using Equation 6.4 where kinematic viscosity, ν is 0.001002 for water and 0.00002 for flue gas.

$$Re = \frac{vD}{\nu} \quad (6.4)$$

Pressure drop (ΔP) across the pipe length (L_{pipe}) could then be calculated to provide a basis for power rating calculations (Equation 6.5). Where density (ρ) is 1000 kg m^{-3} and 1.8 kg m^{-3} for water and flue gas respectively (Rickman *et al.*, 2013) and f_D is the Darcy friction factor, estimated in Equation 6.6 (Blasius law for friction coefficient in turbulent pipe flow).

$$\Delta P = f_D \cdot \frac{L_{pipe}}{D} \cdot \frac{\rho v^2}{2} \quad (6.5)$$

$$f_D = 0.3164Re^{-0.25} \quad (6.6)$$

Pumping power requirements were calculated using the pressure loss (ΔP), volumetric flowrate (Q) and pump efficiency (η), where $\eta = 0.8$ and 0.7 for flue gas blower and

water pump respectively (Rickman, (2013); Internal Tata discussions on pumping efficiency).

$$P = \frac{\Delta P \cdot Q}{\eta} \quad (6.7)$$

6.2.5.2 Paddlewheel power

For paddlewheel power consumption, Equation 6.8 was used (Hadiyanto, 2013), where η_{paddle} is 0.17 (Borowitzka, 2005), Q is the flow rate ($U_{\text{culture}} \cdot A_{\text{flow}}$) (m^3s^{-1}) and Δd is the head difference across the paddle wheel (Equation 6.9);

$$P = \frac{9.804 \cdot Q \cdot \rho \cdot \Delta d}{\eta_{\text{paddle}}} \quad (6.8)$$

$$\Delta d = L_{\text{pond}} U_{\text{culture}}^2 n^2 / r_h^{1.33} \quad (6.9)$$

Where n is the roughness of the wall (0.013 for smooth concrete (Borowitzka, 2005)), r is hydraulic radius (area of flow/wetted perimeter) and U_{culture} is the culture velocity (base case 0.1ms^{-1}).

6.2.5.2 Harvesting

A figure of 0.3 kWh m^{-3} (inflow) was used for the power demand of the DAF process (Viitasaari, 1995).

6.2.5.3 Anaerobic digestion

Anaerobic digestion mixing electricity demand was estimated using power requirements for mild agitation in a baffled tank from “Chemical Engineering Design” (Sinnot and Towler, 2009). A value of 0.04 kW m^{-3} was used in calculations.

6.2.6 CO₂ balance

Total microalgae biomass produced per day was calculated by multiplying productivity ($\text{g m}^{-3} \text{ day}^{-1}$), retention time (days) and water input ($\text{m}^3\text{day}^{-1}$). Total mass of microalgae

produced was converted to CO₂ captured using the lower estimate for conversion factor given by Vasumathi (2012) of 1.65 tonnes CO₂ per tonne of microalgae.

Total CO₂ produced during cultivation was calculated as the sum of total electricity consumption related emissions and all nutrient derived emissions. CO₂ avoidance factor was then determined to display the CO₂ balance of the whole system and is defined as:

$$CO_2 \text{ avoidance factor} = CO_{2_{\text{captured}}} / CO_{2_{\text{emitted}}}$$

6.2.6.1 Indirect emissions

When calculating the CO₂ emissions associated with electricity consumption, the UK average for 2012 of 0.4968 kgCO₂/kWh was used (DEFRA, 2012). Emissions arising indirectly from the production of nitrogen and phosphate nutrients were calculated from the total requirements for nutrients in the form of commonly used fertilisers (urea and single superphosphate) using current market prices and average European values for CO₂ emissions resulting from their production (Wood and Cowie, 2004). In the scenario where ammonium sulphate is used to replace urea, it is assumed that there are no associated emissions due to its nature as a by-product of coke production.

6.2.7 Operational expenditure

6.2.7.1 Workforce

Workforce costs were calculated using the methodology provided in Chemical Engineering Design (Sinnot and Towler, 2009), based on a plant with two shift positions and 4.8 operators per shift position. A basic salary value of £24000 was used, supervision costs were calculated at 25% of operating labour and salary overheads were calculated at 50% of workforce and supervision costs combined. General plant overhead was calculated at 65% of total workforce costs including supervision.

6.2.7.2 Electricity

Operating costs of electricity demand was calculated using DECC data for the average electricity price of £0.07585 per kWh for industrial users (DECC, 2013).

6.2.7.3 Consumables

Single super phosphate and urea costs were calculated using current market values of £110 and £185 per tonne respectively. The alum flocculent was priced at £0.19 per kg (Hendricks, 2006).

6.2.8 Capital expenditure

6.2.8.1 Ponds, piping and pumps

Capital costs for raceway pond construction were estimated using the capital estimates from the US Department of Energy comprehensive review on microalgal open ponds in 1996²² (Bennemann and Oswald, 1996) and adjusted for inflation using chemical engineering plant cost indices (Mignard, 2014).

Estimates for piping costs (both water and flue gas) were calculated using correlations between pipe diameter and cost per meter (Sinnott and Towler 2009):

For A106 Carbon steel 25-200mm, \$/m = $880d_i^{0.74}$

250-600mm, \$/m = $1900d_i^{1.73}$

For 304 Stainless steel 25-200mm, \$/m = $2200d_i^{0.94}$

250-600mm, \$/m = $4700d_i^{1.7}$

²² The author accepts that this is a dated reference; however, this economics analysis was deemed to be the best available resource for estimating cost in this case. In addition, this piece of work has been used for cost estimates in recent published literature by both Davis *et al.* (2011) and Gallagher (2011).

Where d_i is the pipe internal diameter (m). A106 Carbon steel was used in the case of water and algal culture pumping, and 304 Stainless was used for flue gas pumping to minimise corrosion from acid gases.

Pumps, blower and motors were priced using capacity ratio exponents (Equation 6.10) based on existing cost data and exponent factors given in Perrys Engineering Handbook (Holland and Wilkinson 1997; table 9-50) and corrected for inflation using cost indices.

$$C_2 = C_1 \cdot \left(\frac{q_2}{q_1}\right)^n \quad (6.10)$$

Where C_2 is the new price, C_1 is the cost of the equipment at a known capacity or size (q_1), q_2 is the capacity or size of the equipment being priced and n is the exponent, dependent on the equipment.

6.2.8.2 Harvesting

Cost estimates for settling ponds were made assuming that they would require earthworks similar to the raceway ponds per unit area but with a cost factor of two due to the increased depth. In addition to this, it is assumed that the settling ponds will be lined with a concrete liner with a thickness of 0.2 m at a cost of £50 m⁻³.

Cost estimates for dissolved air floatation were calculated using equations given by the US EPA in “Development Document for the CWT Point Source Category: Chapter 11 Cost of treatment technologies”. The calculations are based on the capacity of the unit.

6.2.8.3 Anaerobic digestion plant cost

Digester costs are based on the market cost given for high rate digesters in Zamalloa *et al.* (2011) of £413 m⁻³ (reported by Zamalloa *et al.* (2011) as €500).

6.2.8.4 Cost factors

The cost of purchased equipment and materials must be converted into an installed capital cost taking into account a number of cost factors such as installation, electrical, engineering, contractor's costs and contingency. In this work, cost factors were taken from in Perry's Engineering Handbook (Holland and Wilkinson 1997; Table 9-51) and are shown in Table 6.1

Table 6.1: Cost factors for adjusting purchased equipment costs into capital investment cost (Holland and Wilkinson 1997).

Cost factor	
Installation	0.76
Electricals	0.09
Engineering	0.41
Fees/overheads	0.17
Contingency	0.39
Location factor	0.02

6.2.9 Data analysis

The model was constructed and all data analysis was performed in Microsoft Excel 2010. Sensitivity analysis was performed using Excel's "What-If Analysis" tools.

6.3 Results and discussion

6.3.1 Pond design

In order to give an accurate account of the potential benefits of a microalgae production plant, the cultivation pond design parameters were optimised to minimise energy consumption from paddlewheel operation and pumping. Total paddlewheel power required to maintain the base case culture velocity of 0.1 m s^{-1} can be minimised by

selecting an optimum pond width (Figure 6.2). Considering the length to width ratio and practical pond size (Borowitzka, 2005), an optimum width of 20 m was chosen. Similarly, pond depth can have a significant effect on the overall CO₂ balance (Figure 6.3); too shallow and the area to which water must be pumped means pipe length is very long and results in a negative CO₂ balance due to excessive pumping energy cost. Conversely if the pond is too deep then the culture will be light limited, effecting productivity and total biomass production. The chosen pond depth of 0.5 m was a compromise between the shallow optimum depth for commercial microalgae production (Borowitzka, 2006) and the deeper pond depth recommended for high rate algal ponds (HRAP's) in wastewater treatment.

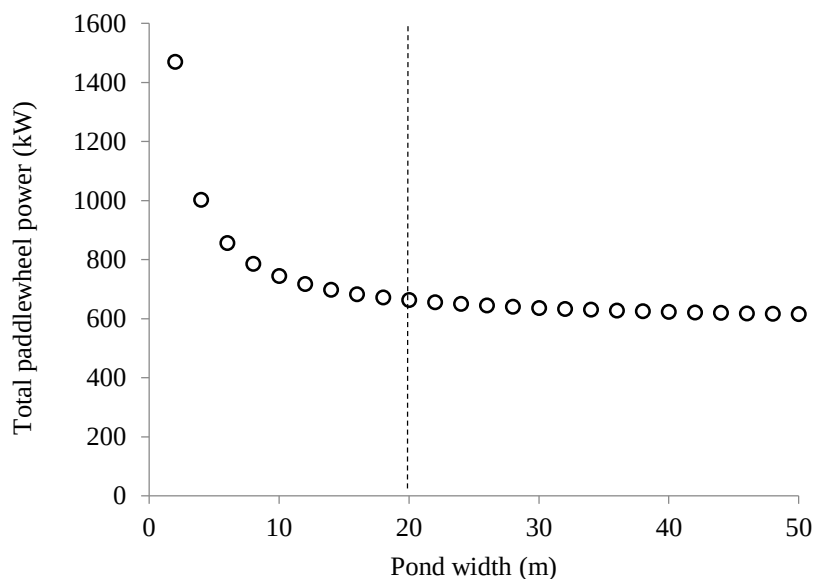


Figure 6.2: Effect of pond width on total required paddlewheel power at a culture velocity of 0.1ms^{-1} .¹ Dashed line represents optimum pond width of 20m chosen for calculations.

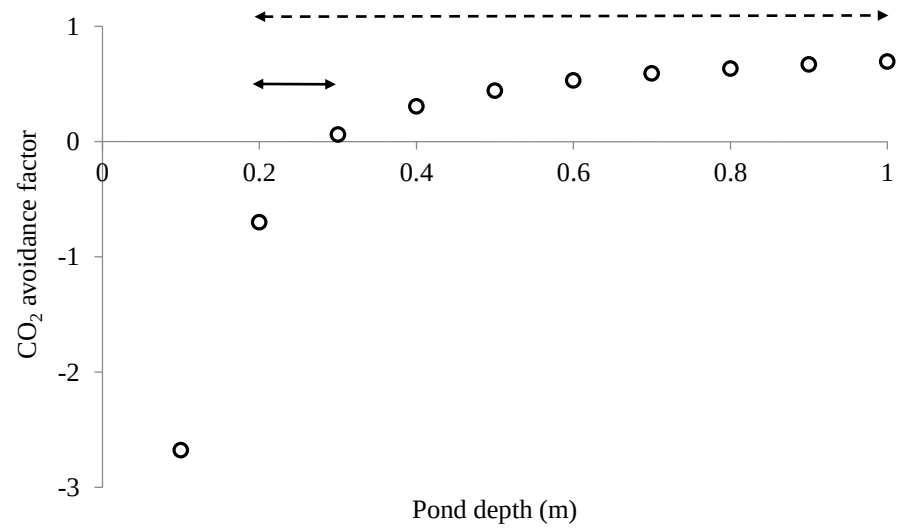


Figure 6.3: Pond depth vs CO₂ avoidance. Solid arrow represents typical range in depth for commercial raceway pond design for microalgae production (Borowitzka, 2005). Dashed arrow represents range in typical design depth for waste water treatment high rate algal ponds (HRAPs) (Craggs, 2006).

6.3.2 CO₂ balance

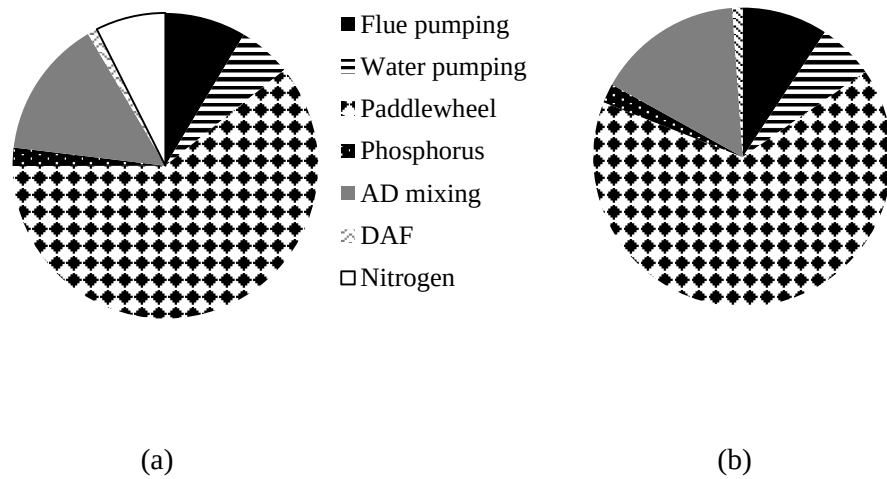


Figure 6.4: Indirect CO₂ emissions split by source for scenario (a) nitrogen imported as urea and (b) nitrogen supplied by wastewater and coke by-products ammonium sulfate

When total CO₂ emissions are split by source for the base scenario (Figure 6.4), it is clear that paddlewheel power consumption dominates, accounting for 66% of emissions in the baseline scenario (utilising wastewater) (Figure 6.4a). Paddlewheel power consumption is often considered in terms of cost but not in terms of associated CO₂ emissions in other techno-economic studies (Norsker *et al.*, 2011; Rickman *et al.*, 2013). In studies where paddlewheel energy was analysed; Collet (2011) determined a lower value than the one reported in this study (31.2%), and Zamalloa (2011) determined that mixing at a velocity of 15 m s⁻¹ would require 20 kWh d⁻¹ Ha⁻¹ compared to a value of around 98 kWh d⁻¹ Ha⁻¹ calculated in this study, though this difference is likely due to a reduced pond depth.

Indirect emissions from fertiliser production account for approximately 9% of total emissions in the scenario where all nutrients are bought in; urea and single super phosphate (SSP) account for 7% and 2% respectively. This means that using wastewater and coke oven ammonium sulfate as sources of nitrogen can provide a 7% reduction in CO₂ emissions (Figure 6.4b) and, if a local source of soluble phosphate or phosphate rich wastewater can be found to replace SSP, this saving could be increased further to 9%. This combined estimate is also very close to the estimated 10-30% production cost from nutrients quoted for outdoor algal production by Borowitzka (2005). The required SSP may also be reduced by recycling of the nutrient rich liquid digestate.

As the size of the cultivation area increases, the number of pipes diverging from the main increases in steps. When a further diverging pipe is required for gas and water delivery, the CO₂ avoidance factor falls sharply due to the increased electricity demand caused by substantially increased pipe length (Figure 6.5). At a total pond area of around 60 hectares, the CO₂ avoidance factor drops to around 0.15. This result supports the conclusion of Rickman *et al.* (2013) that smaller scale, localised microalgae cultivation

is favoured in order to reduce the demands of pumping water and gas over large distances. When all the parasitic energy demands are considered, the breakeven point for CO₂ avoidance (CO₂AF = 0) in terms of pond area is around 250 hectares (Figure 6.5) compared to around 550 ha reported by Rickman *et al.* (2013). This difference can be explained by a combination of the lower algal productivity used in this study; 15 g m⁻³ d⁻¹ here vs 15 g m⁻² d⁻¹ used in the Rickman *et al.* (2013) study, which was modelled to be located in New Mexico, USA. As the plant is designed to be located in the North of England, there would be considerably less solar irradiation and lower temperatures year-round; average solar irradiation in Albuquerque NM is 5.6 kWh m⁻² day⁻¹ (NREL, 2015), compared to an average of around 2.1 kWh m⁻² day⁻¹ in Hull, UK (Boxwell, 2014)

The maximum total CO₂ avoided per day is achieved at a pond area of around 140 hectares (Figure 6.6), although this is misleading as the total CO₂ avoided per day at this scale is only 2.4 tonnes.

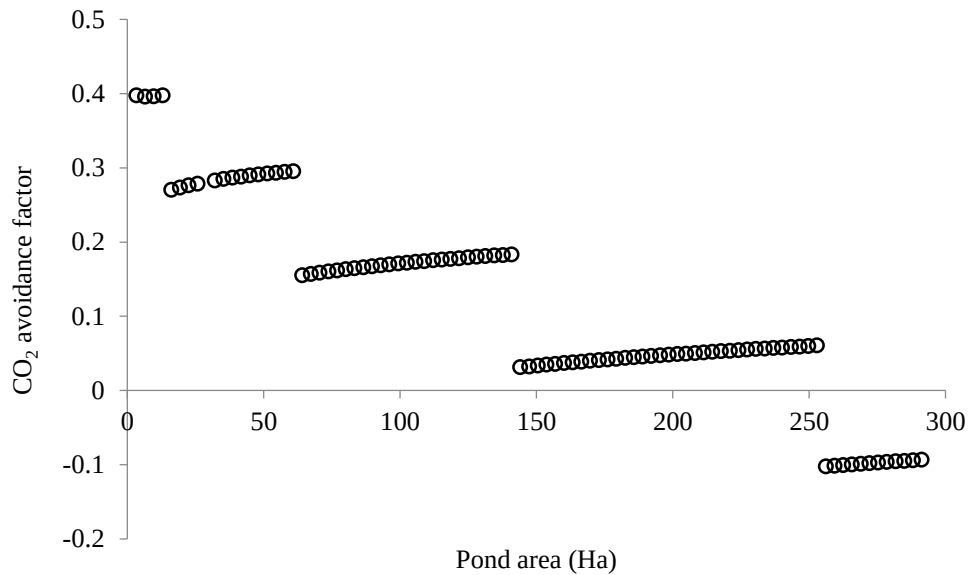


Figure 6.5: Effect of plant scaling on CO₂ avoidance factor. Note that the steps correspond to an increase in the number of diverging gas and water delivery pipes, where an extra diverging pipe means that a large amount of extra pipework is required and results in a jump in the energy requirement for pumping.

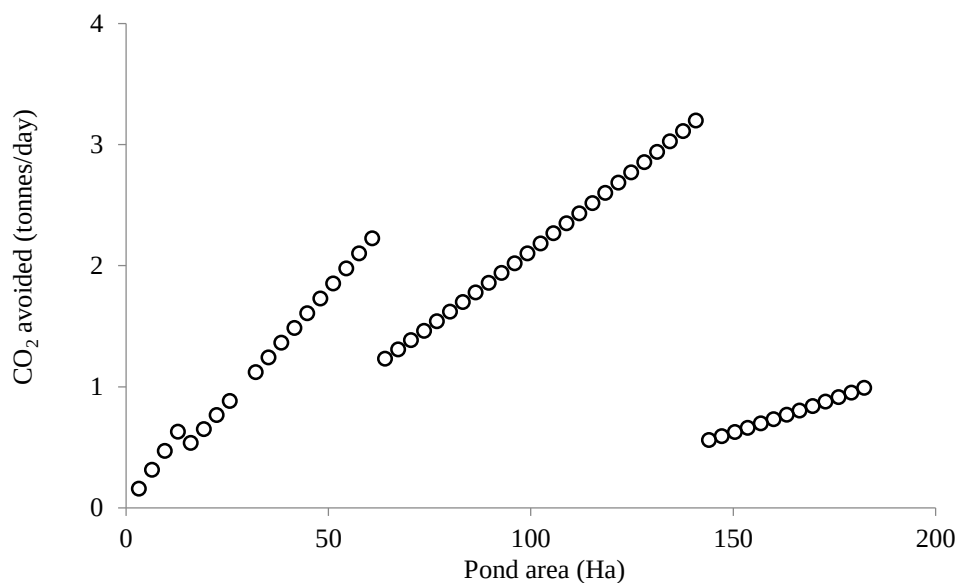


Figure 6.6: Change in net CO₂ avoided per day as total pond area is increased

6.3.3 Plant economics

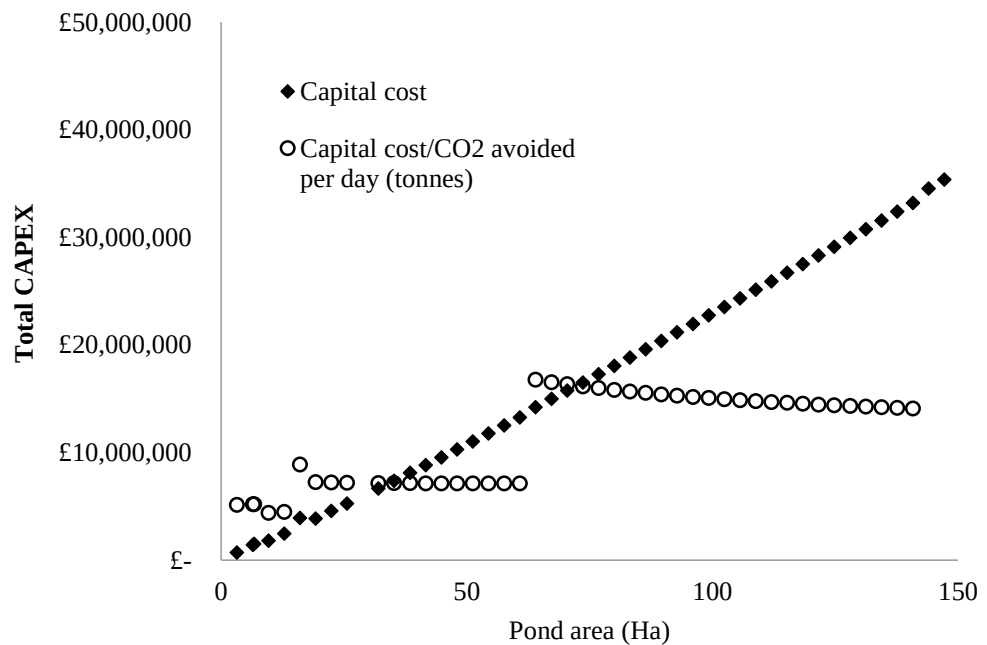
The baseline (6.72 Ha, 17 ponds, 4200 m³ d⁻¹ inflow) plant capital cost was estimated at just over £1.5m, with the cultivation process being the single largest cost accounting for over 30% of the total (Table 6.2). Capital cost increases linearly with plant size in this modelling scenario (Figure 6.7); though in reality there would likely be some economy of scale factors. The capital cost estimates in this model are likely to be underestimated as they assume pipe length for pumping of culture between harvesting and anaerobic digestion and piping for biogas is negligible. They also do not include the cost of land purchase if required²³ or pumping of water and CO₂ from the source to the plant. The capital cost per tonne of CO₂ avoided per day (Figure 6.7) shows the investment cost per unit of capture capacity as the plant is scaled. This increases as the plant size increases in steps which correlate to the number of diverging pipes, as the cost of piping is one of the highest individual capital costs (Table 6.2). Smaller plants are favoured

²³ Integrated steel works sites typically have large areas that underutilised but already owned by the steel producer, so land purchase may not be required.

for CO₂ capture as the investment required per unit captured is much lower for smaller pond area; price per unit CO₂ avoided is around a third for 12 hectares compared to 60 hectare

Table 6.2: Capital cost estimates for the baseline scenario

Plant	Estimated cost (£)
Raceway ponds	£526,282
Earthworks	£62,687
Structural	£51,351
Piping and pumps	£203,800
Paddlewheels	£30,428
Installation	£178,014
Harvesting	£79,343
Settling ponds	£98,902
DAF unit	£28,875
Anaerobic digestion	£120,201
Electricals	£65,324
Engineering	£297,589
Fees/overheads	£123,390
Contingency	£283,072
Location factor	£14,516
Total	£1,509,720

Figure 6.7: Effect of total pond area on process capital cost estimates and investment required per tonne CO₂ avoided per day

Operating expenditure (OPEX) is estimated at £1.37m per year based on continual operation (Table 6.3). Electricity costs account for the largest proportion of this (47.9%), followed by workforce costs (31.8%) and plant overheads (20.5%). When operating costs are presented as operating cost of production (Figure 6.8) it is clear that although the smallest plant size offers benefits in terms of CO₂ avoidance, the cost of biogas/biomass production is very high due to the low output but high workforce cost. The baseline cost of biogas production is estimated at £5.74 per kWh while the minimum cost of production was estimated as £3.56 per kWh and is achieved at a cultivation pond area of approximately 60 hectares. Projected production costs for biogas do not take into account payback of capital investment and are already orders of magnitude higher than current market gas prices per kWh (average 2.54p 3rd quarter 2013) (DUKES, 2013). Operational cost per tonne of CO₂ avoided is extremely high (Figure 6.9); at its lowest (~12 ha) the cost is approximately £8,500 per tonne avoided, not including capital cost considerations and in the baseline scenario the cost is £11,400 per tonne avoided.

Table 6.3: Operational expenditure (OPEX) for baseline scenario

OPEX summary	Cost (£/year)	% of total
Electricity	£657,688.67	47.92%
Consumables	£1,992.85	0.15%
Phosphate	£1,912.26	0.14%
Urea	£0.00	0.00%
Alum (DAF)	£80.59	0.01%
Workforce	£432,000.00	31.48%
Labour	£230,400.00	16.79%
Supervision	£57,600.00	4.20%
Salary overheads	£144,000.00	10.49%
Plant overhead	£280,800.00	20.46%
OPEX Total	£1,372,481.52	100%

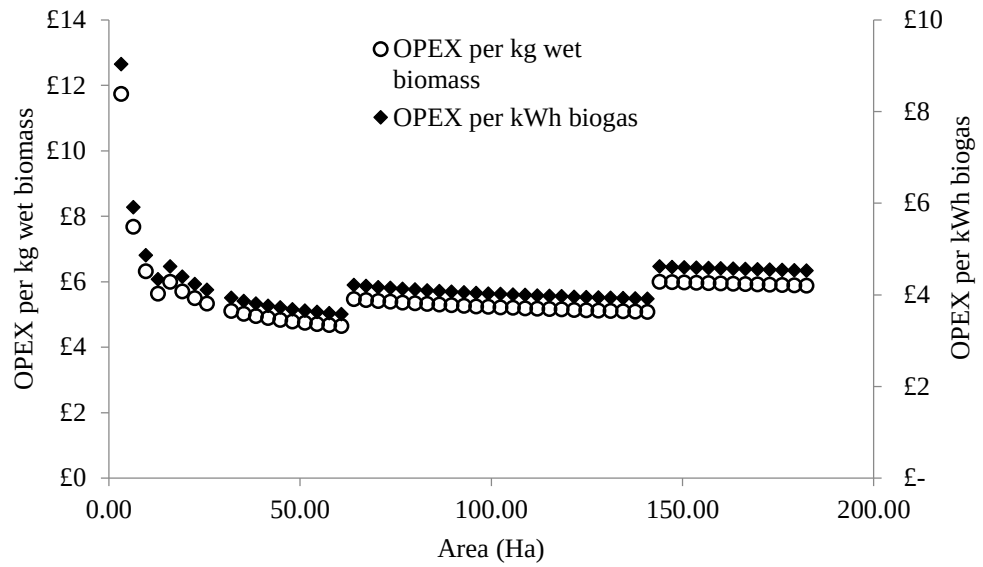


Figure 6.8: Estimated production cost for wet biomass (dry weight as 4% slurry) and for biogas per kWh

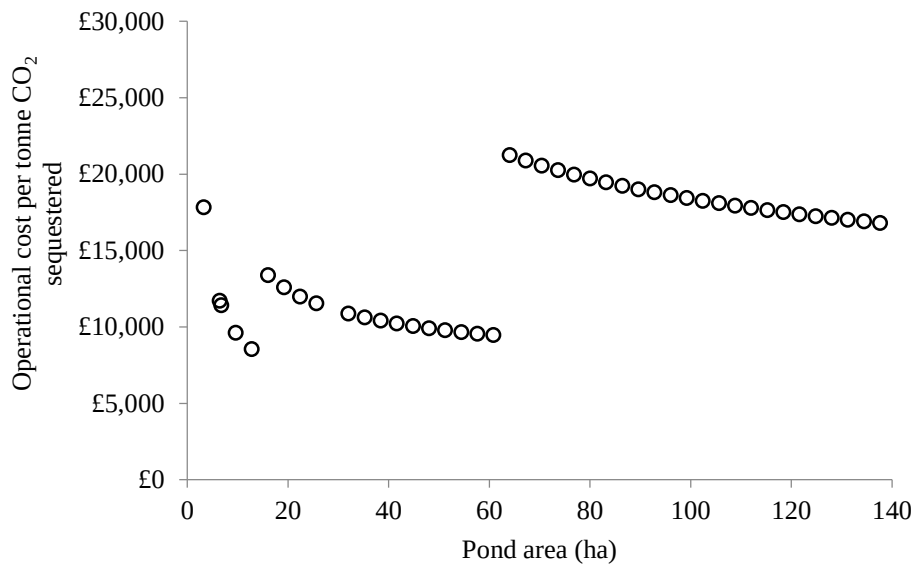


Figure 6.9: Operational cost per tonne of CO₂ sequestered per day against pond area

6.3.4 Optimised scenario

An optimum scenario is proposed based on the results at a plant size of 12 hectares, the maximum plant capacity which can be fed by only one diverging pipe. Wastewater treatment is the primary objective in this scenario, but additional capacity is added in order to maximise CO₂ avoided and minimise production cost of the product(s).

At a cultivation pond area of 12 hectares, the capital cost is estimated at £2.3m, with operating costs of £1.9m per year and a biogas production cost of £4.43 per kWh (Table 6.4). This equates to a reduction in biogas production cost of 22.9% over the baseline scenario. However, this cost is still an order of magnitude above the current price of natural gas (2.54 p/kWh), and so based on this case study investment in deploying this technology is not currently recommended.

Table 6.4: Key operational parameters values in both the baseline and optimised scenarios

Parameter	Units	Scenario	
		Baseline	Optimised
No. ponds	-	17	30
Pond area	Ha	6.72	12
Biomass production	tonnes/day	0.504	0.900
Biogas produced	kWh	655	1169
CO ₂ AF	-	0.396	0.349
CO ₂ avoided	tonnes/day	0.329	0.518
Parasitic energy	kWh/day	990	1764
CAPEX total	£	1,509,720	2,312,467
OPEX total	£/year	1,372,482	1,896,213
Biogas production cost	£/kWh	£5.74	£4.43
Biomass production cost (as 4% slurry)	£/kg	£6.88	£5.17
Operating cost of CO ₂ avoidance	£/tonne	£11,416	£8,767

6.4 Opportunities for improvement

Opportunity for improving both economics and the CO₂ capture potential of this process lies mainly within two areas; (1) reducing electricity demand, (2) increasing volumetric productivity of the microalgae culture. A third option would be to change to production of a high value product, however this would not positively impact the CO₂ mitigation potential of the process, and so falls out of the scope of this work.

One of the largest opportunities for improving the situation as presented in this work is that it may be possible to significantly reduce the electricity cost for pumping flue gas

by increasing the efficiency of CO₂ delivery to the culture. This could be achieved by having a step to dissolve CO₂ in a packed column of slightly alkaline media as proposed by Rickman (2012), or in an airlift-loop type gas/liquid contact vessel, potentially using microbubble technology (Zimmerman *et al.*, 2012) prior to distribution of the media to ponds; potentially increasing mass transfer efficiency from 10% to up to 90% (Putt *et al.*, 2011). Such solutions will, however increase the CAPEX of the plant and therefore should be assessed on a cost/benefit basis.

The productivity of the microalgae culture is the single most important factor in improving the economics of the process. The actual impact of increased productivity on the CO₂ capture potential of the process will be discussed in detail in the next chapter, but the productivity itself is highly dependent weather and therefore on the location of the production facility.

The proposed location of the site, close to an integrated steel works in the North of England does not offer optimum conditions for industrial culture of microalgae. Both solar irradiation and temperature is very low in winter, meaning that average performance over the year is likely to be less than that which is assumed for this model. There may be much more opportunity for development of microalgae based CO₂ utilisation processes in other areas of the world that Tata Group operate, for example in India.

6.5 Chapter summary

A process consisting of open pond microalgae cultivation, harvesting and anaerobic digestion was modelled in order to determine the potential for CO₂ mitigation, biogas production and capital and operating costs. Waste and co-products from steelmaking operations were incorporated into the model in order to quantify any advantages gained by siting an algae production facility at an integrated steelworks.

Synergies between steelmaking operations and microalgae production are present in nutrient supply, wastewater remediation, waste heat delivery to anaerobic digesters, localised availability of CO₂ and an existing infrastructure for water delivery. It is estimated that the use of wastewater and coke oven by-product derived ammonium sulphate as nutrients can achieve a CO₂ reduction of 7% on the whole process when compared to urea for both the baseline and optimised scenarios.

The potential for CO₂ avoidance by microalgae production at an integrated steelworks was found to be very low; the maximum achievable was calculated to be approximately 3.2 tonnes per day, and this is at an exceptionally high operational cost of over £16,000 per tonne of CO₂ avoided.

In the optimised scenario, biogas production cost even before capital investment considerations are over a hundred times the current natural gas price of 2.54p per kWh, indicating that gas production is not feasible as a primary objective.

7. Technology appraisal, conclusions and recommendations

7.1 Technology appraisal

Two CDU technologies were chosen in Chapter 2 as the basis for further research based on their combined market capacity, potential for integration into steelmaking operations and due to their ability to utilise CO₂ directly from exhaust gases, without being first dependent on the deployment of carbon capture and storage technology. A number of gaps in knowledge were identified from the literature for each technology, and the purpose of Chapters 3 and 5 was to attempt to address these knowledge gaps through experiments. A discussion on technical feasibility is presented in each of these experimental chapters and will not be repeated here.

Techno-economic studies on each technology have been presented in Chapters 4 and 6. The following sections will expand on these Chapters to analyse the two processes side by side in two areas; economic potential and CO₂ mitigation potential, both at present and under projected future CO₂ emissions from grid electricity.

7.1.1 Economical potential

In order to make a preliminary assessment of their economic potential, techno-economic studies were conducted for each technology. A model was developed for a microalgae wastewater treatment plant dosed with CO₂ to enhance productivity. The plant was designed to treat harvested biomass slurry via anaerobic digestion to produce biogas as a product that could be fed back to steelmaking operations.

Under this model, it was not possible to adjust the value for microalgae productivity to the point where biogas could be produced at an economical price. Even when the

productivity level of the algae is raised to a hypothetical $500 \text{ g m}^{-3} \text{ day}^{-1}$ (2.5 times the maximum productivity achieved under laboratory conditions), the production cost of biogas (not including capital charges) was around 58 p kWh^{-1} , around 20 times the 2013 price of natural gas (2.54 p kWh^{-1}) (DUKES, 2013). It should be noted that this result indicates only that the process tested is uneconomical, and not microalgae culture systems in general. The choice to model the production of a biogas was based on the potential to integrate into steelmaking processes and minimise energy consumption, but may have led to the process appearing less economical than if a higher value fuel product was chosen. It was decided not to pursue modelling production of a higher value product as the primary aim of this thesis is CO_2 utilisation, the capacity of which is not altered by altering the final product²⁴ and due to the fact that it is unlikely that Tata Steel would invest in microalgae technology unless the focus was CO_2 reduction.

In contrast to the microalgae process, the economic assessment for the new PCC production process from waste steel slag indicates that the process could be economically viable. A plant was designed to produce 70,224 tonnes of PCC per year and it was calculated that this could be achieved at a production cost of £57.04, meaning that as long as the product can be sold above this price there is a positive cash flow. The market price for PCC was estimated at £82 (€100) based on literature, resulting in an estimated profit of around £1.75 million per year and resulting in a payback period of 5.51 years on the estimated £9.65 million capital cost of the plant. These values are derived from academic, order of magnitude cost estimates and should be used as an indication of economic potential and as the basis for further work, rather than be seen as precise cost estimates (accuracy of capital cost estimates is estimated to be approximately $\pm 50\%$ based on the cost estimation method). Limitations of the

²⁴ The addition energy burden from production of other fuel products (*ie.* biodiesel, bioethanol) would almost certainly result in poorer CO_2 avoided values to the ones presented in Section 7.1.1, due to biomass drying requirements and more intensive processing than in the production of biogas.

carbonation economic study in this thesis, and an outline of future work required for process development is given in Section 7.2.6.

7.1.2 CO₂ mitigation potential

In the open pond water treatment based microalgae cultivation model developed for this thesis, CO₂ avoided by the process was found to be limited to around 3.2 tonnes per day under baseline conditions. This value is very low, and is predominantly as a result of the fact that scaling up the plant does not linearly increase the CO₂ captured, partly due to exponentially increasing water and flue gas delivery pipe lengths and the resulting indirect emissions from high pumping energy requirements. The values for CO₂ avoided from the PCC production process are much higher than those for the microalgae process; and are estimated to be around 64 tonnes CO₂ avoided per day.

It is important, however to consider values for CO₂ avoidance in context. An integrated site will typically produce on average around 1.815 tonnes of CO₂ per tonne of finished product (rolled coil, rail, construction beam, etc.) (Carpenter, 2012). To illustrate, if a steel plant with an annual output of 4 Mt of steel is considered, the annual CO₂ emissions can be estimated to be around 7.26 Mt. CO₂ avoided from production of PCC from waste slag at the scale discussed in Chapter 4²⁵ would account for 0.32% of this value and the CO₂ avoided in the optimised²⁶ microalgae scenario discussed in Chapter 6 would account for 0.016% of this value. The relationship between the cultivation scale and the CO₂ avoided value is non-linear and this means that the CO₂ avoided value for microalgae cannot simply be increased by increasing the scale of the plant. In contrast in the case of slag carbonation, it is possible to increase the value of total CO₂ avoided by increasing scale; the 250 ktpa feed capacity considered in Chapter 4 was based on that which is sent to landfill at one specific plant, and is very low when compared to the

²⁵ 250 ktpa slag feed rate

²⁶ 12 hectare pond area, 15 g m⁻³ day productivity.

total amount of suitable slag produced at an integrated works. It was calculated during the ULCOS programme (see Chapter 2 Section 2.5) that the theoretical maximum CO₂ capture using all of the slag produced at a typical integrated site is around 0.1 Mtpa, or around 1.3% of the total CO₂ emissions from the plant (Birat, 2010). However, at this scale slag would have to be re-diverted from current utilisation routes to the carbonation process, and the PCC production route would no longer be a favourable option due to the huge volumes of calcium depleted residue that would require disposal.

It is possible that a direct carbonation process would be able to process the total slag volume to produce an aggregate of similar or greater quality to the original slag, with utilisation of the material being delayed until after the carbonation process. However, as the value of the product in this case would be low (virtually the same as the feed material) it is unlikely that such a process would be economically viable without a high CO₂ price, rendering it in effect a competing (but much lower in capacity) technology to CCS.

If the technologies were deployed as outlined in Chapters 4 and 6 and the CO₂ avoided was credited under the EU ETS, approximate savings of £6000 and £120,000 per year could be made for microalgae cultivation and PCC production respectively under the current CO₂ price²⁷, or £34,800 and £697,000 per year under a carbon price of £30 per tonne. This value is so low that it is virtually insignificant in the case of microalgae cultivation, but is significant in the case of PCC production, accounting for 2% of total PCC production plant revenue under the current CO₂ prices and increasing to 12% at CO₂ price of £30 per tonne. This means that despite the very low emissions reduction in the context of the steelworks as a whole, the process could to some extent reduce the

²⁷ Approximate CO₂ price of €8 (EXX, 2015) and exchange rate of 1.40EUR/GBP for August 2015

exposure of the company to costs from emissions beyond those that are allocated allowances under the EU ETS system.

7.1.3 Impact of reductions in CO₂ emissions from grid electricity

The microalgae and PCC processes considered in this thesis were estimated have CO₂ avoidance factors of 0.349 and 0.750 respectively for base case scenarios. This means that for every tonne of CO₂ captured by the process, indirect emissions during process operations mean that a net value of only 0.349 and 0.750 tonnes of CO₂ are avoided. These values are, with the exception of nutrients production in the microalgae process, from the CO₂ emissions associated with electricity production and are based on the UK electricity grid average of 0.4968 kgCO₂/kWh (DEFRA, 2012). Due to ongoing efforts in the UK to reduce this value, it is projected that CO₂ emissions from grid electricity in the UK will fall to 0.1 kgCO₂/kWh by 2030 (DECC, 2013). This reduction will significantly increase the CO₂ avoidance value for both technologies; the value for PCC production rises to 0.89 and for microalgae production the value raises to 0.657. At this value, CO₂ avoided scales linearly for the microalgae production process²⁸, meaning that substantially higher CO₂ savings can be made than in the base case scenario. Although the CO₂ avoided value increases in line with the size of the plant under this scenario, in order to achieve CO₂ savings equivalent to the PCC process under 2012 conditions (~64 tonnes CO₂ avoided per day) the cultivation area required would be around 650 hectares (6.5 km²), with over 1600 ponds. This is a huge area requirement for what, in relative terms, would be a very small volume of CO₂ avoided. In addition, the economics of the process would remain relatively unchanged except for potentially from an additional contribution from EU ETS cost avoidance, which would be very small relative to the high capital and operating costs of such a large plant.

²⁸ The relationship was found to be linear modelled to a pond area of 700 hectares, $R^2=0.9955$

In the case of the PCC production process, an increase in the CO₂ avoidance factor value due to the projected reduction in indirect emissions from grid electricity results in an even stronger business case. Under the 250 kt waste slag scenario the total CO₂ avoided per day would increase from 64.0 tonnes per day under present conditions to 75.4 tonnes per day under projected 2030 conditions resulting in EU ETS savings increasing from £697,000 to around £825,000, or from 12% to 14% of total PCC plant revenue.

7.1.4 Advances in microalgae biotechnology

Though microalgae biotechnology has been deemed to be currently unviable for short term deployment, as the area is the focus of intense research at present there is the possibility that future developments in the field may make this route a more attractive option. In the authors view, there are two significant and interlinked developments which must be realised before microalgae CO₂ utilisation technology in the steel industry can be considered viable; these are (1) the development of low capital cost and scalable photobioreactors, which in turn can allow; (2) an increase in the volumetric productivity of large scale cultures by at least an order of magnitude.

To illustrate the effect of productivity, CO₂ avoided by the process as a percentage of total emissions from a typical steel plant was modelled for increasing pond area for 4 different levels of algal productivity; 15 g m⁻³ day⁻¹ (baseline), 50 g m⁻³ day⁻¹, 100 g m⁻³ day⁻¹ and 200 g m⁻³ day⁻¹ (the approximate maximum achieved in laboratory cultures in Chapter 5). It is assumed that the scaled up photobioreactor system would only be able to achieve the same volume of culture per unit area due to the effect of shading. As the productivity value increases, the relationship between pond area and CO₂ avoided becomes linear, and total CO₂ captured begins to become significant. Approximately 1% and 2% of total steel plant emissions are avoided at a pond area of 300 Ha for productivities of 100 and 200 g m⁻³ day⁻¹ respectively. If productivity values

as high as this could be maintained in outdoor cultures at a relatively low capital costs, microalgae production could become an attractive option for CO₂ mitigation.

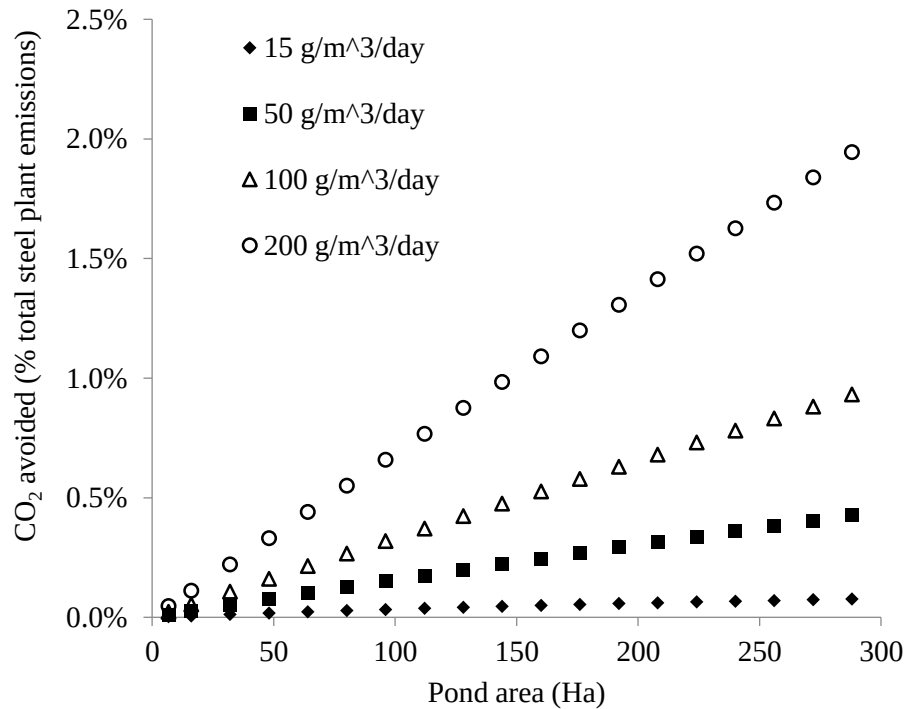


Figure 7.1: Microalgae pond area vs the percentage of typical steel plant CO₂ emissions avoided for four different algal productivity values

7.2 Conclusions

Two technologies were determined to be potentially suitable for short term deployment based on their product market capacity, energy required for conversion, potential to use by-products and wastes from steelmaking wastes and ability to utilise CO₂ directly from exhaust gases. The ability to utilise exhaust gases directly as a source of CO₂ was established as an essential criteria as it means that the technology is not co-dependent on deployment of carbon capture and storage which is likely to be uneconomical in the steel industry until at least the 2030s (see Chapter 2 Section 2.6). The chosen technologies were;

- Production of precipitated calcium carbonate (PCC) via indirect carbonation of steelmaking waste materials

- Combined biomass production and steelmaking wastewater remediation using microalgae cultures supplemented with CO₂

7.2.1 PCC production process

The PCC production process comprises two steps that were both investigated experimentally in this work. In the first step, calcium is extracted from the waste material into solution using aqueous ammonium chloride and in the second step, the calcium rich solution is contacted with CO₂, precipitating a high purity calcium carbonate product.

The focus of work into the extraction process was the mineralogical effects of the process on the slag, and the significance of resulting leachate chemistry. It was found that ammonium chloride selectively dissolved calcium at efficiencies of up to 60% from a number of mineral phases within the slag, predominantly from dicalcium silicate and free lime. Additional petrographic observations gave an insight into the mechanism of the extraction from dicalcium silicate at a granular scale. Results from work presented on the extraction process in this thesis were published in *Minerals Engineering* in 2014 (Hall *et al.*, 2014).

The use of flue gases directly as a source of CO₂ for carbonation was assumed to be feasible in the PCC production process in previous studies, but had not been demonstrated experimentally; in fact, the feasibility of using flue gases directly was identified as a major knowledge gap across all carbonation processes in a high profile review of mineral carbonation by Sanna *et al.* (2014). The ability of the process to be able to take flue gases directly was determined essential to its short term deployment, and so it was decided that an attempt would be made to address the knowledge gap by performing a series of trials using steelworks exhaust gas as a source of CO₂ for the carbonation step. Results indicated that there was some loss in purity due to dissolution of SO₂ in the exhaust gas, and subsequent transfer of sulfur into the product. However,

it was found that at the SO₂ concentration tested (~50 ppm), precipitates produced from two of the waste materials were of a high enough purity to conform to the international standards for PCC to be used as extenders for paints. It can be concluded from the results presented that flue gases can be used directly for production of PCC, providing that the SO₂ concentration in the gas is relatively low, and that the feed material has a low sulfur concentration. Results from work carried out on carbonation using steelworks flue gases are currently in preparation for publication in *Environmental Science & Pollution Research*.

A techno-economic assessment of the new PCC production process presented in this thesis suggests that short term deployment of the PCC production process is unlikely to result in CO₂ savings beyond a fraction of a percentage (0.32%) of the emissions from a typical integrated plant, but could reduce exposure to the EU ETS system by around £100,000 per year under current market conditions, or up to £825,000 by 2030. In addition, deployment of the technology would allow Tata Steel to diversify their revenue streams in addition to reducing mass sent to landfill by around 14%²⁹.

7.2.2 Combined CO₂ capture and wastewater treatment using microalgae

A review of literature revealed that the only microalgae production processes that are currently at a mature enough development stage for deployment at a commercial scale are the production of high value products for use in human or livestock nutrition, and in the tertiary treatment of wastewater, with both technologies deploying similar open pond systems. The water treatment process route was chosen for further development due to potential contamination issues and the low market capacity in the high value products, and also because wastewater treatment processes would enable better integration into steelmaking operations by utilising a waste stream. In addition,

²⁹ This value is based on the difference between flow of slag in and flow of calcium depleted residue out of the filters following calcium extraction.

evidence in the literature indicated that CO₂ addition to wastewater microalgae cultures can be beneficial to the process.

A microalgae based combined wastewater treatment and CO₂ utilisation concept was developed, and a wastewater stream from a Tata Steel biological effluent treatment plant was identified as a potentially suitable feedstock to the process. A series of four cultivation trials were undertaken to determine the suitability of the effluent for culturing two species of microalgae that had previously been shown to be tolerant of utilising CO₂ directly from flue gases and to determine the potential for effluent remediation by these microalgae. Results from cultivation trials indicated that the process was technically viable. Cultivation of microalgae in the effluent was found to be successful when additional phosphate was added to the culture. Biomass production rate in the effluent was found to be to a similar and under some conditions to a greater extent than cultures grown in a specially prepared growth medium. The cultures were observed to remove nitrogen from the wastewater with a high efficiency (up to 93.4%), and in one species (*S.obliquus*) the efficiency of nitrogen removal was found to increase significantly when the cultures were dosed with synthetic flue gas.

Results from a techno-economic study indicate that the CO₂ avoidance potential a large scale open pond microalgae production plant is very low, and limited by low expected volumetric productivity combined with the high indirect emissions from electricity required for culture pumping and paddlewheel operation. In addition, the production cost of the biogas product was determined to be orders of magnitude above its value, rendering the process uneconomical using currently available technology.

7.2.3 Overall conclusions

In the introduction to this thesis, the overarching aim of the research was stated as;

“To provide Tata Steel with a basis from which they are able to make an informed decision as to whether short term implementation of carbon dioxide utilisation can be

technologically feasible and economically sustainable as a means to reduce CO₂ emissions from primary steelmaking processes.”

From the results presented in this thesis it must be concluded that carbon dioxide utilisation is unlikely to make a meaningful contribution to climate change mitigation in the European steel industry in the short term. This is simply because the CO₂ volume which can be sequestered economically by technically mature CDU processes is very small relative to the scale of emissions from primary steelmaking operations.

Of the two processes examined in this work, only production of precipitated calcium carbonate has the potential to be economically sustainable in the short term, and could reduce to some extent Tata Steel's exposure to the EU ETS, in addition to providing an additional revenue stream.

The microalgae wastewater treatment and CO₂ capture processes was, despite being demonstrated to be technically feasible, found to be currently highly uneconomical and have very limited potential in terms of CO₂ reduction.

7.2.5 Recommendations to Tata Steel

In the short term, resources in the area of CO₂ utilisation should be focused on carbonation, and in particular the PCC production process as this technology could be commercially viable even without credit for CO₂ mitigated due to the high value of the product.

Additionally, efforts should be made within the company to ensure that any CO₂ savings made by deploying the technology are credited under phase VI of the EU ETS, as this could increase the revenue of the process by up to 14% by 2030.

It is recommended that research into CO₂ sequestration using microalgae in open ponds is not pursued in the short term, and that microalgae research in general is not allocated any resource until significant advances in the technology result in an large increase in

capacity to capture CO₂ per unit of volume, combined with a substantial reduction in the capital and operational costs.

7.2.6 Recommendations for further work

Recommendations for future work outlined in this section are based on major requirements to enable the scale up and deployment of the PCC production process from steelmaking wastes. A number of uncertainties (where assumptions were used in this work), were identified in the sensitivity analysis in Chapter 4 to have a significant impact on the economic sustainability of the process. A list of important factors including required additional work required and potential additional process equipment requirements is given below.

1. **Calcium extraction efficiency;** in this work, the maximum extraction efficiency obtained from slag was 60% (HMD) but the value was generally much lower for other slags. Finding an economical way to improve this efficiency would provide the best way to improve the overall performance of the process as the efficiency value for most slag is in the range to which payback period is highly sensitive (between 40% and 60%; see Chapter 4, Figure 4.6). Some other studies (Eloneva *et al.*, 2012) have achieved slightly higher extraction efficiencies but typically these involve very high liquid to solid ratios, and would require extremely large reactors to process reasonable volumes of slag material. One route which deserves more investigation is the use of ultrasound to enhance the dissolution of calcium; Said *et al.* (2015) increased the extraction from BOS slag from 65% to over 95% using this method, but more work is required in order to understand the energy cost of the process.
2. **Purge rate;** scaled up experiments are required in order to determine the effect and significance of dissolved inorganic components when the solvent is cycled numerous times and thus determine the required solvent purge rate for the process.

3. **Solvent loss during filtration;** this parameter has an effect on the amount of solvent that is lost from the system and must be made up either fresh or through more advanced recycling. The base case scenario assumed rates of 1% for NH_4Cl loss at each of the two filter units, and also assumed that these filters would have separate manifolds for primary filtrate to be recycled and wash water produced from washing the residual NH_4Cl from the residue/product. It is possible that rather than being treated as a waste it could be economic to concentrate ammonium chloride in the filter wash water for recycling through a process such as reverse osmosis. This could both reduce the required make up NH_4Cl and reduce the ammonium loading in the water sent to wastewater treatment; however a full cost benefit analysis would be required to determine the feasibility of this.
4. **Ammonia losses during carbonation;** free ammonia present in the calcium laden solvent following the extraction process could be entrained and leave with the exhaust gas, causing potential environmental damage. The techno-economic work presented in this thesis assumed that the ammonia losses were negligible based on the work by Eloneva *et al.* (2011), and no mitigating equipment was included in the process design. However, the tests by Eloneva *et al.* (2011) were in the laboratory and must be validated by testing at a larger scale. If it is found that ammonia vapour is entrained to a significant degree, this could impact on the economics of the process considerably. An HCl stripper would be required to remove the ammonia from the exhaust and reform it to ammonium chloride for recycling. Recycling the ammonia in this way would also result in a build-up of chloride in the system, also requiring removal.
5. **Solids handling;** this work has assumed that the facilities for solids handling and storage (excluding milling and conveying between plants) are already present at the slag processing area of the site. In reality, additional CAPEX may be required to prepare a new storage site for raw slag and calcium depleted residue.

6. **Product particle size distribution;** the assumption was made that the reaction conditions could be optimised to produce the required product particle size characteristics. If the process conditions cannot be optimised to produce a product with a size distribution that will conform to BS EN ISO 3262-6:1998 (BSI, 1998) and/or ASTM D1199-86 (ATSM, 2986), an additional product mill may be required to grind the product to a suitable size. Further work is required in order to determine whether the required PSD characteristics can be produced through process optimisation, or whether a final milling stage would be required.
7. **Product quality and sale price;** The PCC produced by the process is assumed to be suitable for use as a filler for industrial processes, and was estimated to have a market value of £82 per tonne based on previous publications from Finland (Elenova *et al.*, 2012). Recent publications by (and discussions with) the Finish group indicate that a price point closer to £130 may be achievable if a high quality precipitate can be developed for paper manufacture to replace GCC (Tier *et al.*, 2015). At a £130 per tonne sale price, the process becomes very attractive with a payback period of only 1.85 years. It is therefore important that any future work is undertaken with the aim of producing a specific high value product, ideally in collaboration with the end user of the PCC.

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Appendix A: Supplementary data on analysis of PCC

The following charts are supplementary data for Chapter 3. Figures A.1 to A.4 present results from thermo-gravimetric analysis (TGA) (TA Instruments, Q500) of the precipitates produced using flue gas, each compared to high purity commercial grade PCC (SOLVAY, SOCAL E2 Ph. Eur). Peaks indicate the temperature at which peak mass loss occurs, and for all samples there is one major peak at between 700-800°C. Mass loss within this temperature range is characteristic of the calcination process where CaCO_3 is thermally degraded to CaO and CO_2 . In addition, mass lost in each sample was calculated to be $44 \pm 0.5\%$, the molar mass ratio of CO_2 to CaO in CaCO_3 . This evidence supports conclusions in chapter 4, that the precipitates are high purity calcium carbonate.

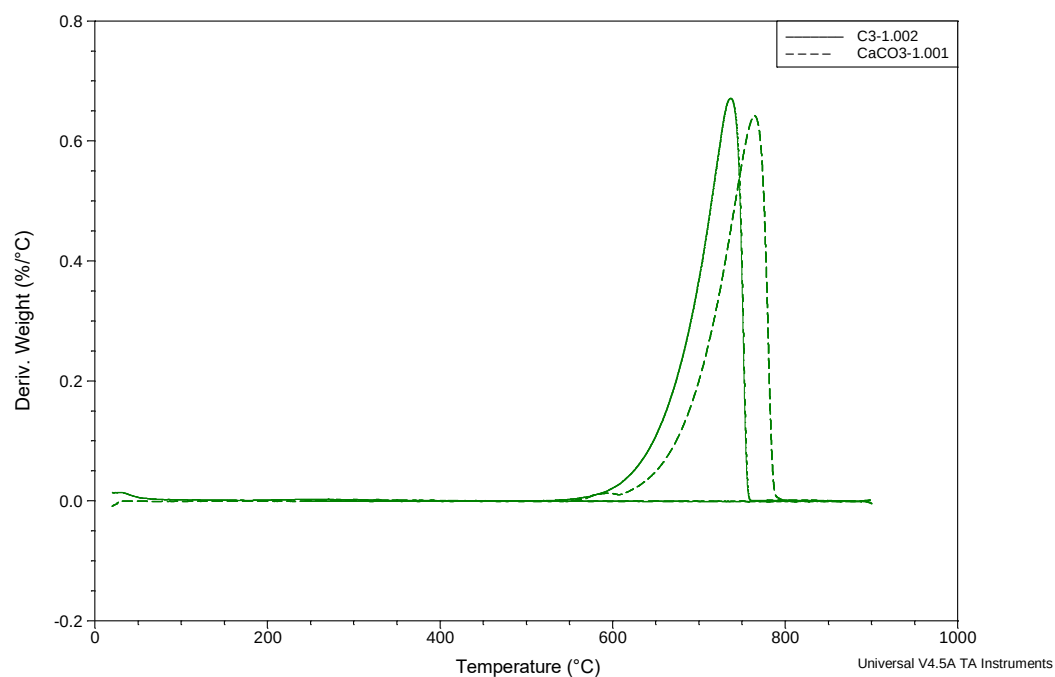


Figure A.1: PCC produced from BOS slag (C3-1002) compared to commercial grade CaCO_3 (99.1%) (SOLVAY, SOCAL E2 Ph. Eur)

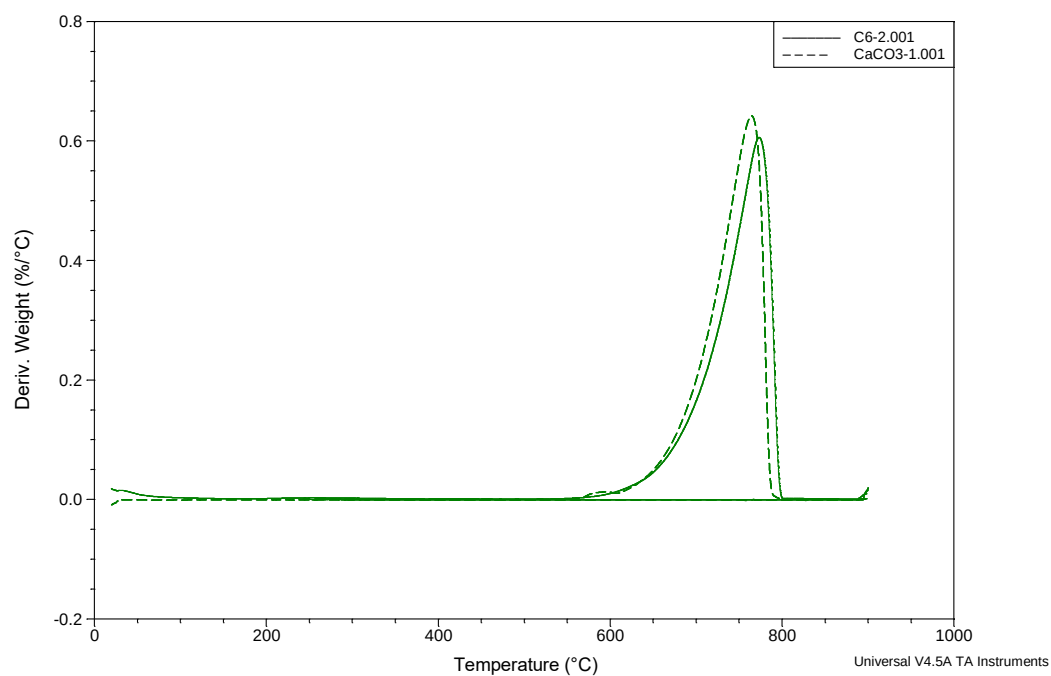


Figure A.2: PCC produced from HMD slag (C6-1001) compared to commercial grade CaCO_3 (99.1%) (SOLVAY, SOCAL E2 Ph. Eur)

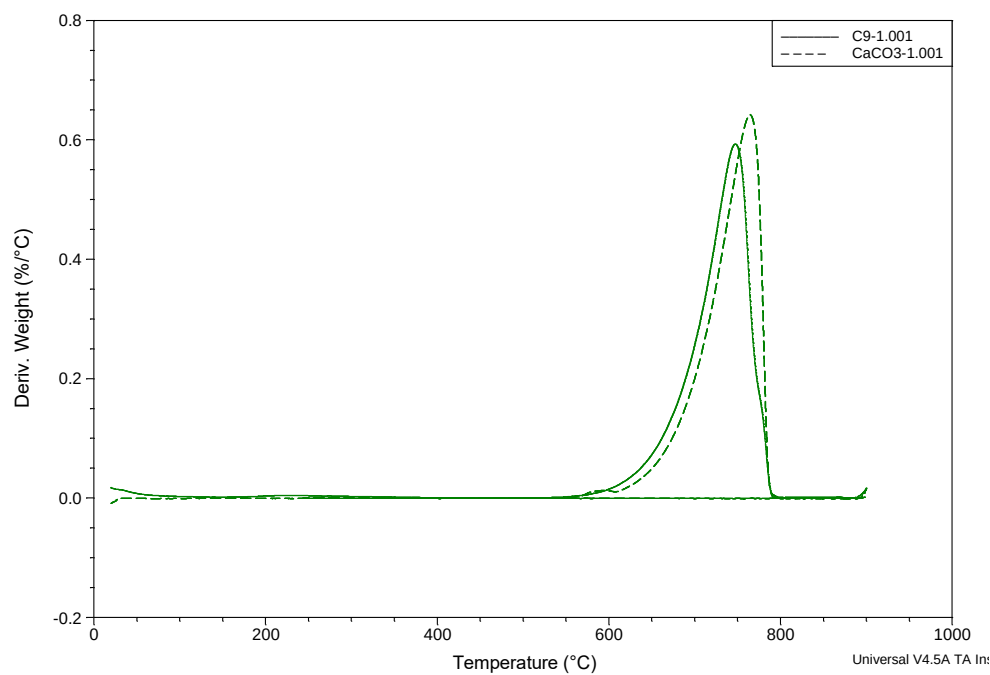


Figure A.3: PCC produced from SS slag (C9-1001) compared to commercial grade CaCO₃ (99.1%) (SOLVAY, SOCAL E2 Ph. Eur)

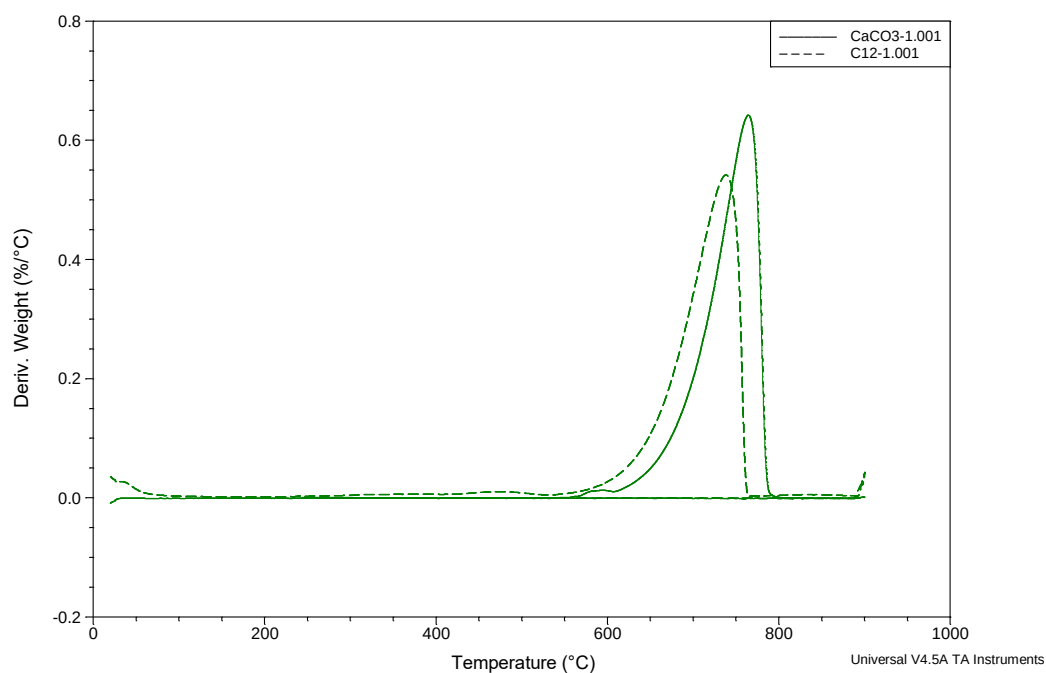


Figure A.4: PCC produced from APC residue (C12-1001) compared to commercial grade CaCO₃ (99.1%) (SOLVAY, SOCAL E2 Ph. Eur)

Appendix B: Culture medium composition

Table B.1: Calculated Jaworski's Media (JM) composition. Stocks in bold were omitted in preparation of the JM-n medium.

Stock	g/200ml	mg/l
Ca(NO₃)₂·4H₂O	4	20
KH ₂ PO ₄	2.48	12.4
MgSO ₄ ·7H ₂ O	10	50
NaHCO ₃	3.18	15.9
EDTAF _e Na	0.45	2.25
EDTANa ₂	0.45	2.25
H ₃ BO ₃	0.496	2.48
MnCl ₂ ·4H ₂ O	0.278	1.39
(NH₄)₆Mo₇O₂₄·4H₂O	0.2	1
Cyanocobalamin	0.008	0.04
Thiamine	0.008	0.04
Biotin	0.008	0.04
NaNO₃	16	80
Na ₂ HPO ₄ ·12H ₂ O	7.2	36
Sum of ammonia-nitrogen (NH ₄ ⁺ -N), nitrate-nitrogen (NO ₃ ⁻ -N) and nitrite-nitrogen (NO ₂ ⁻ -N)		15.5
Total PO ₄ ³⁻		18.21484