Towards Circular Economy for Steel - Assessing the Efficiency of Yellow Gypsum Synthesis from BOF Slags

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Abstract

The large quantities of basic oxygen furnace (BOF) slag produced at the Tata Steel Port Talbot steelworks has no existing recycling scope and has formed a large legacy “slag mountain” over the years. Closure of all Britain’s coal power plants by 2025 potentially could create a shortage of the supply of gypsum in the UK and elsewhere. A solution to the problem may lie in production of gypsum from a by-product of the steelmaking. This will afford a potential opportunity for commercialisation in Port Talbot. This research applies the findings of ‘A method of producing calcium sulphate from LD slag waste produced during the recovery of metallic iron from LD slag’ of which patent 572/KOL/2014 has been filed, to assess the efficiency of yellow gypsum synthesis from BOF slag, while determining the feasibility for commercialisation of this process at the Port Talbot steelworks.

To provide this knowledge, an assessment of the chemical composition and particle size distribution of the BOF slag produced at the Port Talbot steelworks was undertaken, whilst developing methods to assess the efficiency of the process. X-ray fluorescence analysis was undertaken on the BOF slag samples acquired and synthetic yellow gypsum produced to determine the calcium conversion at the defined particle size distributions outlined in the thesis. Cost and market analysis were also undertaken to determine feasibility of commercialisation at the Port Talbot steelworks. This study, therefore confirmed that commercialisation of this process in the Port Talbot steelworks is feasible but would require large scale operation and further processing of the synthetic yellow gypsum produced. In addition, processing the synthetic yellow gypsum produced to products within the agriculture and construction industry would provide a higher valued final product.

Declarations and Statements

Declaration

1. This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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2. This thesis is the result of my own investigations, except where otherwise stated. Other sources are acknowledged by footnotes giving explicit references. A bibliography is appended

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3. I hereby give consent for my thesis, if accepted, to be available for photocopying and for inter-library loan, and for the title and summary to be made available to outside organisations.

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4. The University's ethical procedures have been followed and, where appropriate, that ethical approval has been granted.

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Abbreviations

ABS	Air-cooled blast furnace slag
BF	Blast furnace
BOF	Basic oxygen furnace
BOS	Basic oxygen steelmaking
CE	Circular Economy
DLS	Darlow Lloyd and Sons
DSG	Desulphogypsum
EAF	Electric arc furnace
EDS	energy-dispersive X-ray spectroscopy
EUROFER	European Steel association
EoL	End-of-life
FEECO	Fertilizer Engineering and Equipment Company
FGD	Flue Gas Desulphurisation
GBS	Granulated blast furnace slag
IS	Industrial Symbiosis
LD	Linz Donawitz
MP-AES	Microwave Plasma-Atomic Emission Spectrometer
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RCRA	Resource, Conservation and Recovery Act
SEM	Scanning Electron Microscope
TBL	Tarmac Buxton Lime
UK	United Kingdom
UVCB	Unknown or variable composition, complex reaction products or biological materials
WRP	waste recycling plant
XRF	X-ray fluorescence

1 Introduction

Annually in the United Kingdom (UK), 5.7 million tonnes of steel are produced in Basic Oxygen Furnace (BOF) steelmaking processes. However, the industry is threatened by competition from overseas, and given the global environmental crisis and the contribution of steel making emissions, as well as the critical jobs in this sector, it is more important than ever to transition the industry towards a Circular Economy (CE). This is important to reduce raw material costs, embodied emissions of steel, and mitigate costs and impacts associated with wastes. In this research project, the viability of valorisation of steel making slags thorough conversion to synthetic yellow gypsum is explored and examined. BOF slag currently has limited recycling prospects and has no high value market, due to free lime and magnesia content, which leads to problematic swelling issues. The process examined represents a potential added value application for BOF slag produced at the Port Talbot steelworks, through avoiding waste generation and producing secondary raw materials for the CE.

1.1 Circular economy

A Circular Economy (CE) describes an economic system that is based on business models which replace the 'end-of-life 'concept with reducing, alternatively reusing, recycling and recovering materials in production/distribution and consumption processes, thus operating at the micro level (products, companies, consumers), meso level (eco-industrial parks) and macro level (city, region, nation and be-yond), with the aim to accomplish sustainable development, which implies creating environmental quality, economic prosperity and social equity, to the benefit of current and future generations (1). CE is a concept that has recently gained traction in policy, business and academia to advocate a transition from a linear 'take-make-dispose' model, with raw materials on the one end and wastes at the other, towards a circular model, in which waste is a resource that is valorised through recycling and reuse (2). The appeal of CE is that it promises to reconcile environmental and economic goals by reducing resource use and stimulating economic growth at the same time. While concepts related to sustainable development come and go, CE has been very successful in gaining policy, business, and civic traction.

The world's population is growing and increases demand for raw materials. However, the crucial supply of raw materials is limited. Extraction and use of raw materials have a major impact on the environment and increases energy consumption and carbon dioxide (CO_2) emissions. It is contended that a smarter use of raw materials could potentially reduce CO_2 emissions. The main aim of CE is to redefine growth, and focus on positive, society-wide benefits. It allows a gradual decoupling of economic activity from the consumption of finite resources and is designed ideally to reduce waste (from the system). This involves sharing, leasing, reusing, repairing, refurbishing, and recycling existing materials and products, if possible, when a product reaches end-of-life (EoL). This can maximise materials usage by retention within the economy whenever possible. It is based on three key principles (3): -

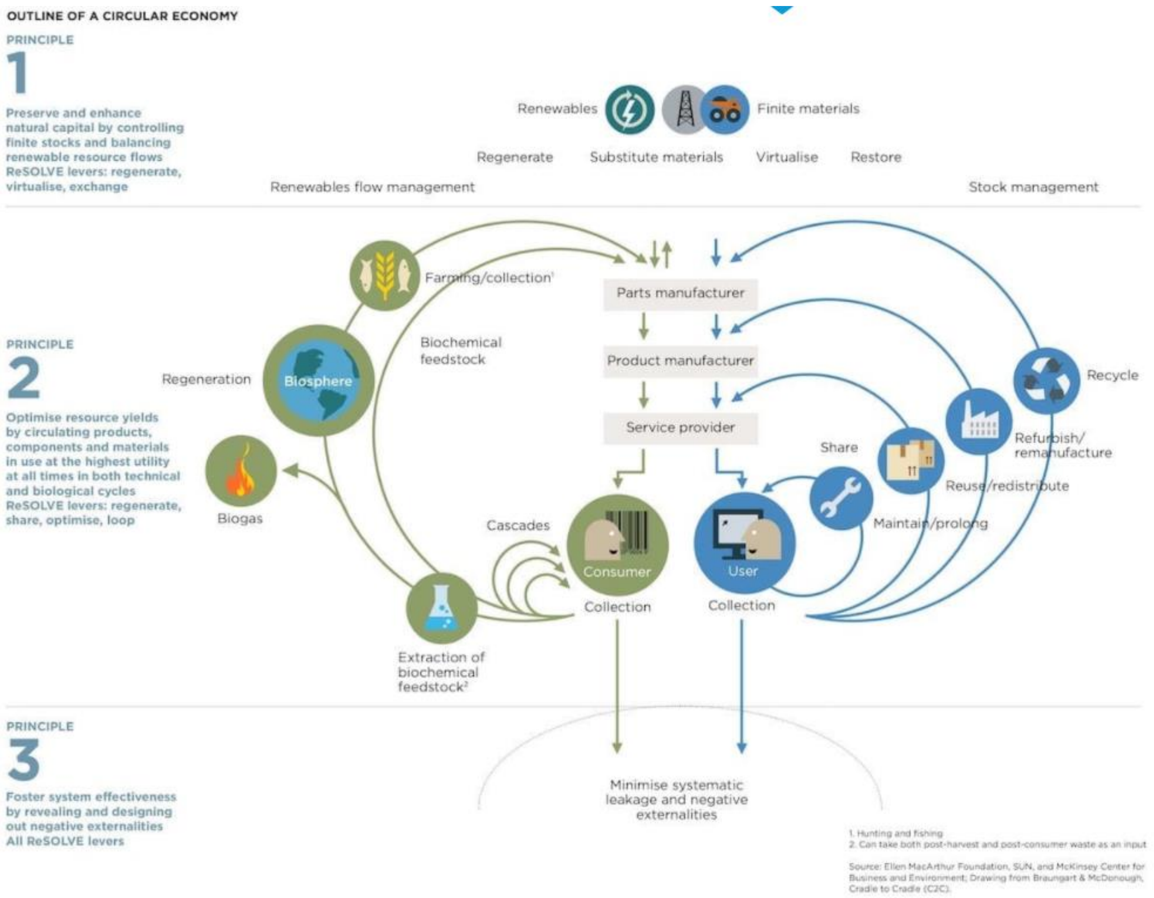
- Design out waste and pollution.
- Keep products and materials in use.
- Regenerate natural systems.

The CE model seeks to rebuild capital whether it be financial, manufactured, human, social, or natural. This ensures enhanced flows of goods and services. The system diagram in Figure 1.1 illustrates the continuous flow of technical and biological materials through the 'value circle' (3).

A CE model affords key benefits, the principals being: -

- Creation of new green industries and jobs.
- Reduced dependence of importation of raw materials.
- Avoidance of environmental damage caused by resource extraction.
- Less pollution entering the Earth's life support systems.
- Greater value creation from fewer resources.
- Material cost savings for industry.

It is contended that CE can potentially create new markets and products, create local material loops, and shorten supply chains. This may ultimately promote and boost local communities and employment. Additionally, it could further reduce the extraction and use of raw materials, which in turn will reduce the waste and pollution resulting from these processes and conserve finite natural resources.



Preserve and enhance natural capital by controlling finite stocks and balancing renewable resource flows
ReSOLVE levers: regenerate, virtualise, exchange

Optimise resource yields by circulating products, components and materials in use at the highest utility at all times in both technical and biological cycles
ReSOLVE levers: regenerate, share, optimise, loop

Foster system effectiveness by revealing and designing out negative externalities
All ReSOLVE levers

1. Hunting and fishing
2. Can take both post-harvest and post-consumer waste as an input

Source: Ellen MacArthur Foundation, SUN, and McKinsey Center for Business and Environment; Drawing from Braungart & McDonough, Cradle to Cradle (C2C).

Figure 1.1: Outline of a CE (3)

1.2 Industrial Symbiosis and Collaboration

1.2.1 Industrial Symbiosis

Industrial Symbiosis (IS) is a collective approach to competitive advantage in which separate industries create a cooperative network to exchange materials, energy, water and/or by-products. By addressing issues related to resource depletion, waste management and pollution, IS plays an important role in the transition towards sustainable development (2). Application of this concept allows materials to be used in a more sustainable way and contributes to the creation of a CE. Figure 1.2 illustrates visually the IS concept with the CE research streams. It is immediately visible that while the CE stream frames IS as a specific type of business model archetype within a much larger context.

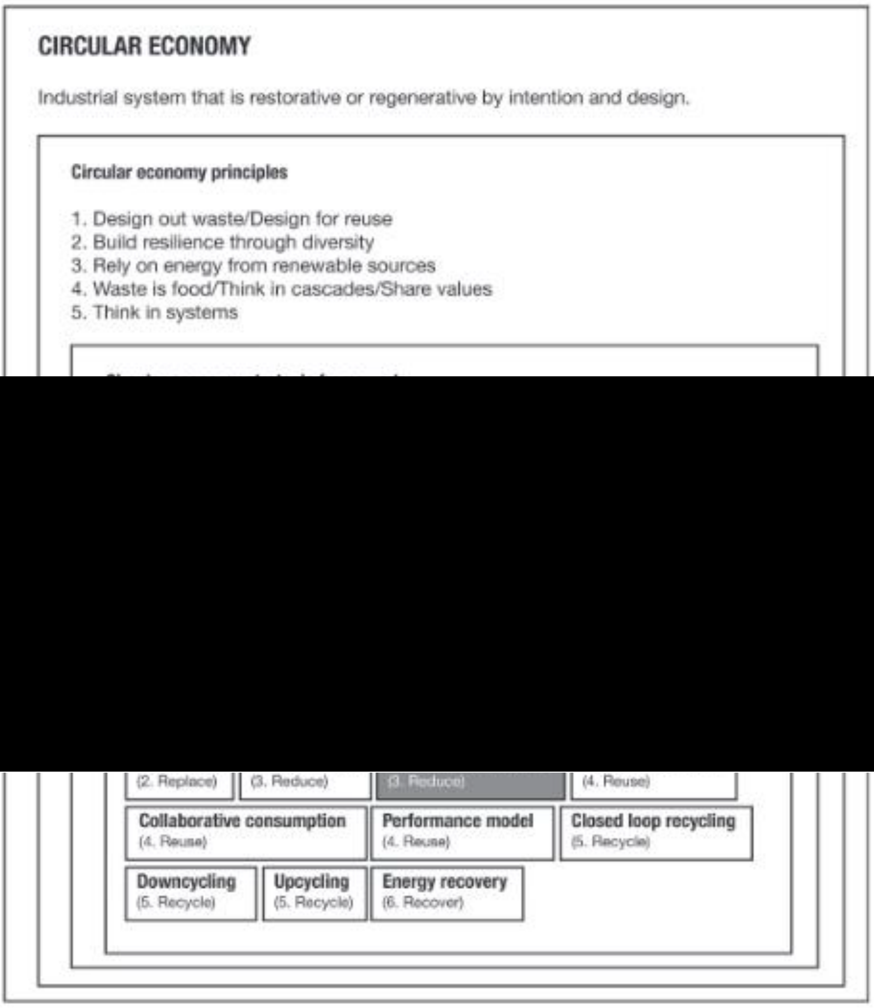


Figure 1.2 Locating IS in the CE research streams (2)

Resetting heavy industry and production strategy to a more CE represents a huge challenge. However, confronting this transition through collaborative partnerships could potentially render circularity as more accessible. IS is an innovative approach that brings together companies from different sectors to explore and use the collective valorisation of waste, improvement of resource efficiency and reduction of environmental impacts. IS affords the use and access of raw materials at lower costs. It also reduces reliance upon imports and primary raw materials, valorises waste materials which may otherwise require costly disposal. This is enabled by collaboration between organisations which potentially maximises the value which can be generated from what would otherwise be wasted resources.

There are multiple economic and environmental benefits derived from this approach. Primarily, it provides opportunities for companies within a variety of sectors to increase their profitability and competitiveness by reducing the cost of resources. Secondly, it affords substantial environmental benefits through reduced consumer demand for materials, imports, and waste.

Slag is an integral part of the iron and steelmaking process. The steel industry has committed to increasing the recycling of waste slag generated in the steelmaking process. Conserving natural resources and energy contained within this by-product is critical, due to the non-viability for being landfill material due to containing toxic ingredients such as nickel, cadmium, and chromium. Under the quality protocol you can process the correct waste steel slag to make specified unbound, semi-bound or fully bound aggregate products for use in the civil engineering and construction industries (4). Quality protocols explain when a waste derived material can be regarded as a non-waste product and no longer subject to waste controls (5). They aim to produce high quality products from waste materials to promote greater recovery and recycling.

1.2.2 Collaboration

Collaboration is a powerful business tool for companies, regardless of their size or industry. Organizations who work together to address problems and achieve goals are more effective when tackling challenging situations. By combining the effort and expertise of different organizations, all partners in the network are better equipped to innovate, grow, and increase their competitiveness. Business collaborative networking can provide companies with access to resources which routinely are beyond the scope of a single company. Individual companies can face numerous limitations when bidding to compete in global markets, including scale and expertise.

1.3 Steel

It is generally accepted that Steel is indispensable to our modern way of life and critical to economic growth. The benefits of steel make it a sustainable choice in a growing number of applications. As a permanent material, steel is fundamental to achieving a CE. Again, it is generally accepted that the efficient use of natural resources is critical to sustainability. In 2020, a total of around 1.86 billion metric tons of crude steel were produced worldwide (6). Once steel is produced, its life cycle is endless, making it a permanent resource for society. This is crucially dependent on the recoverability at EoL.

Steel is a major influence on our lives in important applications: cars/transportation; work buildings; housing; electricity-power-line towers; natural-gas pipelines; machine tools; military weapons. Steel has made our lives convenient and protected our families, thus the benefits are undoubtedly clear. Steel has a key benefit in that its high strength to weight ratio means it affords higher strength per unit mass. Steel can be easily fabricated and produced. Steel is also relatively cheap to produce compared to other products in the related market. Steel can be re-manufactured in any of these applications, thus rendering it extremely valuable due to its endless life cycle, observed in Figure 1.3.

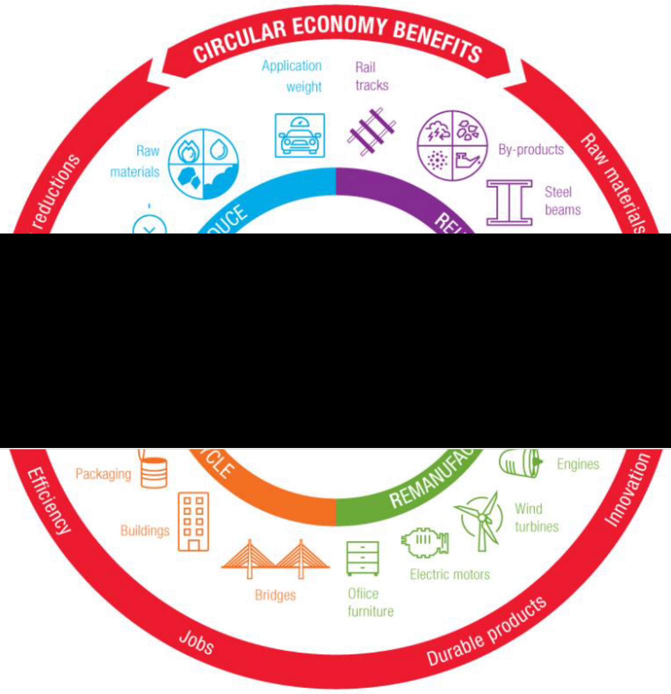


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Figure 1.3: CE of Steel (7)

Steel is regarded to be recycled repeatedly without any degradation of its properties. However, contamination with tramp elements is a major concern. Other materials are often unintentionally mixed with steel scrap in current recycling schemes, when an EoL product consisting of steel and other materials is not always dismantled and separated entirely (8). Some recycled products require minimal processing, whilst the higher value engineering steels require more metallurgical and process controls to meet tighter specifications. The final economic value of the product is not determined by recycled content, and there are many examples of high value products that contain large amounts of recycled steel. Some steel products are principally sourced via the primary route mainly because the steel specifications require low residual elements, and this can be achieved most cost-effectively using more primary material. In most cases, scrap with a low number of residual elements commands a higher market price owing to the ease of processing through the recycling routes (9).

Iron is refined to manufacture steel. To achieve this, the carbon content of hot metal is reduced to <1% by an oxidation process in a steelmaking furnace (10). Original methods of steel production consisted of “Bessemer” and “open hearth” processes, but these have been replaced by the modern methods “Basic Oxygen Steelmaking” (BOS) and “Electric Arc Furnace” (EAF) processes. Liquid pig iron with high carbon content (3.8-4.7%) is loaded into a BOF vessel and an oxygen lance is inserted, then oxygen is pumped into the melt oxidising dissolved carbon to carbon dioxide (CO_2) gas, which in turn reduces the carbon content to required levels for mechanical properties to suit the application (10). Alloying materials are added to the furnace to achieve the required chemical composition and desired mechanical properties in the final product.

The basic raw materials required for the process of large-scale steelmaking are identified within Table 1.1 with their purposes for use (10). The inputs and outputs of the BOF process utilised across the world is depicted in Figure 1.4.

Table 1.1: Raw materials required for large-scale steelmaking (10)

Raw Material	**Purpose**
Iron Ore	Treated in some way after it comes from the mine.
coal	Converted to coke.
Limestone	Remove impurities from the blast furnace when making iron.
Steel scrap	75% of iron comes from the hot metal produced by blast furnace process, the remaining 25% of the raw materials is steel scrap.
Fluxing materials	Materials used in a furnace to assist in the refinement process. They generally lower the melting point of impurities in the molten steel and combine with the impurities to form ‘slag’.
Refractory materials	Ability to provide containment of substances at high temperatures, refractories comprise of a broad class of materials having that characteristic to varying degrees, under varying periods of time and conditions of use.
Alloying elements	Elements added to steel to give it special properties to suit its application.

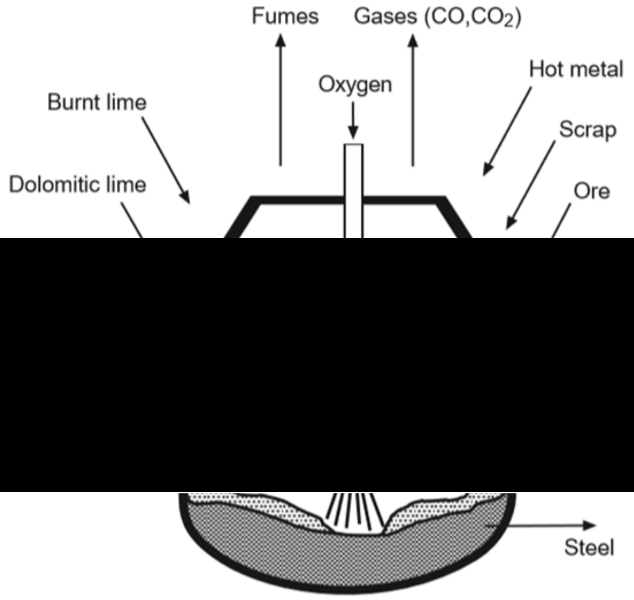

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Figure 1.4: The input and output materials in BOF process (11)

The BOF process is the primary steelmaking process employed at the Port Talbot steelworks, alternative steel production routes are recognised in Figure 1.5. The method of steel production primarily implemented at the Port Talbot steelworks is the raw material preparation, then the ironmaking process is undertaken in a BF and finally hot liquid iron is processed in the BOF. Following the BOF and EAF processing, the molten steels, after being tapped (poured) from the furnace, undergo a further stage of processing before casting to achieve final microstructure. These steps are usually called secondary steelmaking.

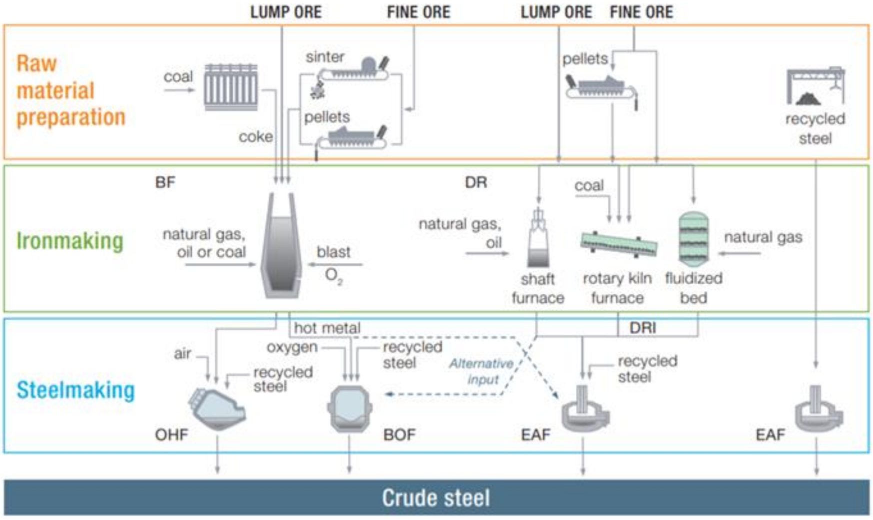

Figure 1.5: Steel production routes (12)

1.3.1 Blast Furnace

The Blast Furnace (BF) is the critical process in producing liquid pig iron for the transformation to steel. The technique was introduced in 1735 and is likely to continue to dominate the hot metal (pig iron) production in the future (13). The main objective of BF ironmaking is to produce hot metal with consistent quality for BOF steelmaking process.

The main operations of a BF are burden preparation, charging and conveying of raw materials, BF processing, generation of hot blast, direct injection of reducing agents, casting and finally slag cooling and processing. The fluxes are added to control the slag chemistry. The BF is essentially a tall shaft furnace, consisting of a steel shell protected by a refractory lining. The critical requirement in the BF operation is that the pig iron and slag are fluid, to be tapped from the furnace. The overall composition of the BF burden must therefore be chosen to produce pig iron of reproducible quality with the correct composition for subsequent steelmaking. In chorus, the flux additions and slag-forming unreduced impurity oxides in the ore and coke ash must react to form a fluid slag.

1.3.1.1 Blast Furnace Process

A BF is a closed heating system that produces liquid metals from the reaction, adding pressurised air from the tuyeres (bottom) while raw materials are added from the top. In the BF, iron oxide ores of iron are reduced by carbon, introduced in the form of coke, to produce molten pig iron. The furnace is charged semi-continuously from the top essentially with iron ore, coke, and limestone ($CaCO_3$)(11). The oxide ores are usually ‘hematite’ (Fe_2O_3) or, less frequently ‘magnetite’ (Fe_3O_4)(11). These ores also contain impurities, such as acid oxides like silica (SiO_2) and alumina (Al_2O_3)(11). To remove these impurities from the BF, they must be combined with a flux such as lime (CaO) or doloma (CaO.MgO) to form a fluid slag. This fluid slag can then be tapped from the furnace.

The raw materials consist of iron-bearing materials, additives and reducing agents which continuously fed from the top of furnace shaft, feeding the charging system. This prevents the escape of BF gas (13). The pressurised air (hot air blast) is enriched with oxygen and auxiliary reducing agents. These provide a counter current of reducing gases. The hot air blast reacts with the reducing agents to produce mainly carbon monoxide (CO), which in turn reduces the iron oxides into metal iron (13). The liquid iron with high carbon content is transported in torpedo vessels to the steel plant for conversion to steel. The BF gas is collected at the top of the furnace before being treated and distributed around the works. The gas is further used as a cost-effective fuel for heating or for electricity production.

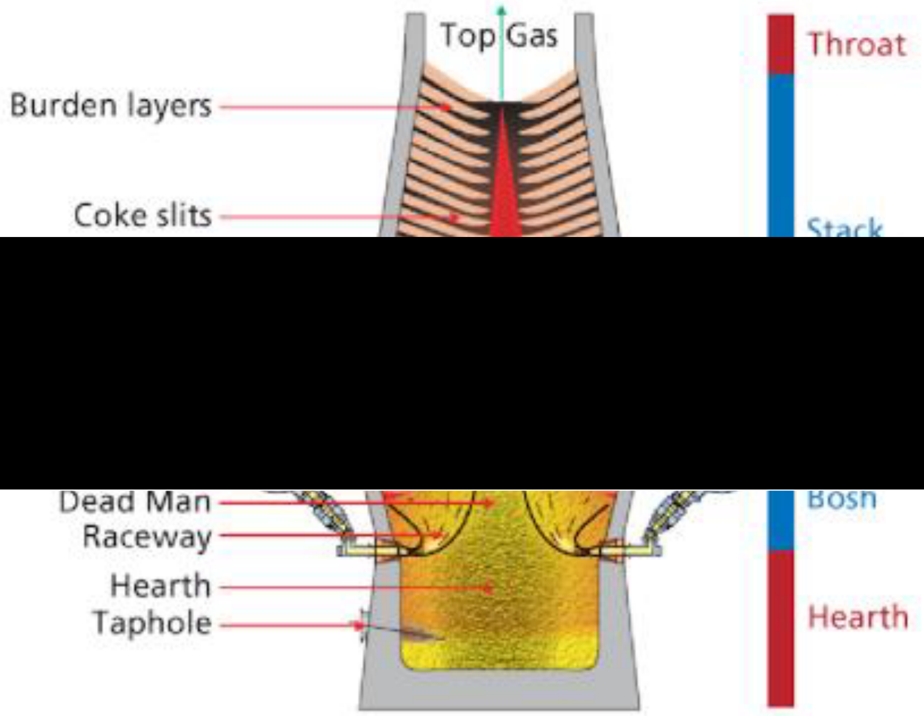

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Figure 1.6: The zones within a BF (14)

As the BF burden moves down through the furnace the temperature increases (Figure 1.6), thus it enables oxide reductions and slag formation when materials melt. The burden undergoes a series of composition changes (13):

- The iron oxide in the burden becomes increasingly reduced (forming sponge iron and finally molten hot metal).
- the oxygen from the iron ore reacts with the coke or the carbon monoxide, thus forming carbon monoxide or carbon dioxide, which is collected at the top.
- The gangue components combine with the fluxes to form slag. This slag is a complex mix of silicates of a lower density than the molten iron.
- The coke primarily serves as a reducing agent, but also as a fuel. It leaves the furnace as carbon monoxide, carbon dioxide or carbon in the hot metal.
- Any hydrogen present also acts as a reducing agent by reacting with oxygen to form water.

The key gangue components in the ferrous materials include silica, alumina, calcium oxide (lime), magnesium oxide (MgO), sulphur (S), and phosphorus (P) along with trace elements like manganese (Mn), copper (Cu), sodium (Na), potassium (K), and zinc (Zn) in the form of complex oxides (13). Most of these components are fluxed into the molten slag. Some of the impurity oxides present in the ore and coke can be wholly or partly reduced. The iron oxides consisting of ‘hematite’ and ‘magnetite’ is wholly reduced to iron. The manganese oxide is partly reduced to manganese and can be found in the iron. The phosphorus pentoxide is wholly reduced to phosphorus (P) which also collects in the iron. The silica is partly reduced to silicon (Si) which also collects in the iron while unreduced silica partitions into the slag along with alumina.

Slag is formed in the BF by the fusion of limestone (and/or dolomite) and other additional fluxes with the residues from the carbon source and the non-metallic components of iron-bearing materials (e.g. iron ore, iron sinter) (13). The BF slag is formed at temperatures exceeding 1500 °C (14). The BF slag is distinguished as 2 types: air-cooled blast furnace slag (ABS), and glassy granulated blast furnace slag (GBS) (15). The production rate of hot liquid metal is 91.3 million tonnes for all member states of the European Union, resulting in 24.6 million tonnes of BF slag as a by-product. The majority of BF slag produced (78.9%) is glassy GBS, with the rest comprising ABS slag (Figure 1.7)(15).

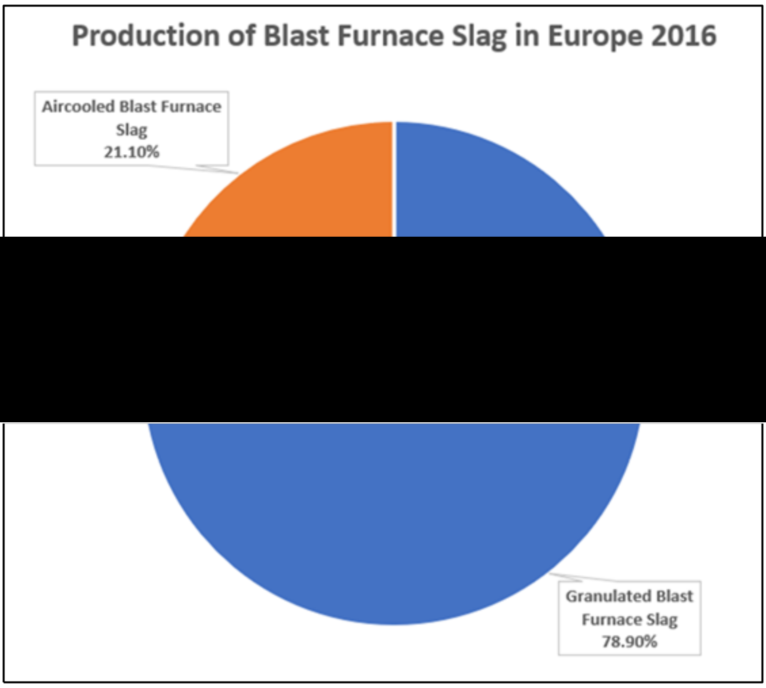

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Figure 1.7: Total production of 24.6 million tonnes of BF slag in Europe 2016 (15)

1.3.1.2 Chemicals Reactions

The basic reactions that control the ironmaking processes are relatively few and simple. This involves the reactions between carbon, oxygen, iron, and its oxides, and those that lead to the formation of slag.

Reactions of carbon:

The oxygen in the blast reacts exothermically with the coke producing very high temperatures and carbon dioxide in the following reaction:

$$\boldsymbol{C + O_2 \rightarrow CO_2} \qquad \textbf{Equation 1.1}$$

Remaining carbon rapidly reduces the carbon dioxide endothermically to produce carbon monoxide, which now enable the reduction to iron oxides:

$$\boldsymbol{C + CO_2 \rightarrow 2CO} \qquad \textbf{Equation 1.2}$$

Reactions involving iron:

The chemical reaction of iron is dependent on the temperature in the BF and occurs at different levels in the furnace. Iron ore will be reduced to iron metal in stages as charged materials descend through the furnace.

The first reaction occurs at 400-700 °C:

$$\boldsymbol{Fe_2O_3 + CO \rightarrow 2FeO + CO_2} \qquad \textbf{Equation 1.3}$$

The second reaction occurs at 700-1000°C:

$$\boldsymbol{FeO + CO \rightarrow Fe + CO_2} \qquad \textbf{Equation 1.4}$$

The third reaction occurs at 1000-1400 °C:

$$\boldsymbol{FeO + C \rightarrow Fe + CO} \qquad \textbf{Equation 1.5}$$

The fourth reaction occurs between 1400-1450 °C, the Fe melts and dissolves carbon resulting in the high carbon content of pig iron which must be reduced to suitably low levels in the subsequent steel making process.

The main reducing agent is carbon monoxide. At temperatures above 1000 °C the carbon dioxide reacts with the coke to produce more carbon monoxide as realised above.

1.3.2 Basic Oxygen Furnace

The process was initially developed between 1947 and 1949 at a steelwork in Linz and Donawitz in Austria (16). BOS is the most common and dominant primary steelmaking process used in the world today, accounting for 71% of total global steel production (17). The process was initially labelled the Linz Donawitz (LD) process, where oxygen is directed at supersonic velocities through a water-cooled lance located centrally in an open-topped barrel-shaped basic-lined converter. The main objective in the oxygen steelmaking is to burn the undesirable impurities contained in the hot metal feedstock. The main elements converted into oxides are carbon, silicon, manganese, and phosphorus. Steel is manufactured in discrete batches called heats. The furnace is a barrel shaped, open topped, refractory lined vessel that can rotate on a horizontal trunnion axis as realised in Figure 1.8.

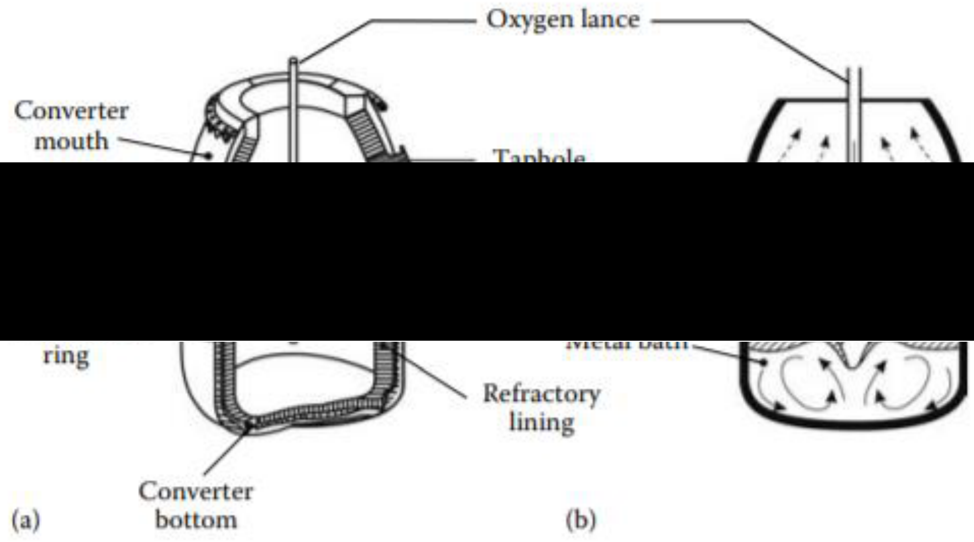

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Figure 1.8: Top blown convertor. (a) Characteristics of the vessel and (b) slag-metal-gas interaction and molten flow during blow (18)

1.3.2.1 Basic Oxygen Furnace Process

The LD process begins with charging steel scrap into the furnace and flux consisting of lime (CaO) and dolomitic lime (CaO.MgO) usually. Large ladles, capable of containing 170 tonnes of liquid metal, pour the molten iron into the furnace. During the charging process, temperatures reach 1,700 °C. The oxygen lance is then lowered into the vessel, with oxygen injection starting.

The bulk removal of silicon, phosphorus and sulphur from the liquid metal product of the BF process prior to refining in a BOF has reduced tap-to-tap time, cost, slag volume and produced steel of a higher quality (19). The selective use of slag forming reagents affords steelmakers the facility to minimise the inclusion formation, whilst modifying and controlling the shape and composition of the remaining inclusions. These practices have achieved an enhancement of the mechanical properties of steel. The operation steps during BOS are shown in Figure 1.9.

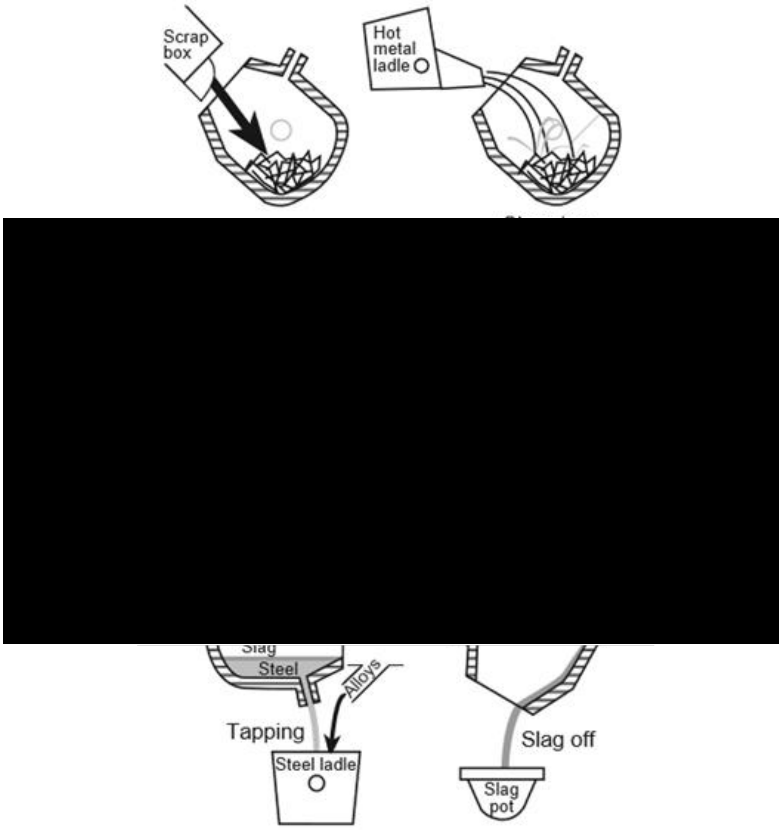

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Figure 1.9: Schematic of the operation steps during BOS (18)

1.3.2.2 Chemical Reactions

The water-cooled lance blows oxygen onto the molten bath at high velocities and then the chemical reaction commences. The oxygen is the gas that enables the removal of carbon from the molten steel by a chemical reaction that gives off heat. The lance injects a high velocity stream of oxygen onto the molten bath, supersonic jets are produced with convergent/divergent nozzles. After the ignition, fluxes (lime, dolomite lime) are dropped into the vessel through overhead chutes. The hot metal charge is refined by rapid oxidation reactions upon contact with the injected oxygen, under conditions far removed from thermodynamic equilibrium with further elements present.

The primary reason for blowing oxygen into steel is to remove carbon to endpoint specifications. This is an exothermic reaction which adds heat to the system. Other elements such as Si, Mn, and P are also oxidised and are absorbed in the slag layer. These reactions are also exothermic, further contributing to the required heat to melt scrap and raise the steel bath to the necessary temperature (19). The oxidation of the silicon is particularly important because it occurs early in the oxygen blow and the resultant silica combines with the added lime to form the molten slag. The oxidation reactions during the steelmaking process can be observed from Equation 1.6 through to Equation 1.10.

$$\boldsymbol{C+\frac{1}{2}O_2=CO} \qquad \textbf{Equation 1.6}$$

$$\boldsymbol{2CO+O_2=2CO_2} \qquad \textbf{Equation 1.7}$$

$$\boldsymbol{Si+O_2=SiO_2} \qquad \textbf{Equation 1.8}$$

$$\boldsymbol{Mn+\frac{1}{2}O_2=MnO_2} \qquad \textbf{Equation 1.9}$$

$$\boldsymbol{2P+\frac{5}{2}O_2=P_2O_5} \qquad \textbf{Equation 1.10}$$

During the refining, the oxidation products of silicon, phosphorus, manganese, and iron, combine with other oxides charged (lime, dolomite) to form a liquid slag. This floats on the surface of the metal bath. After steel tapping, slag is poured into a slag pot by tilting the convertor, and once solidified, is dumped in the slag yard from which it can be reclaimed (Figure 1.10).

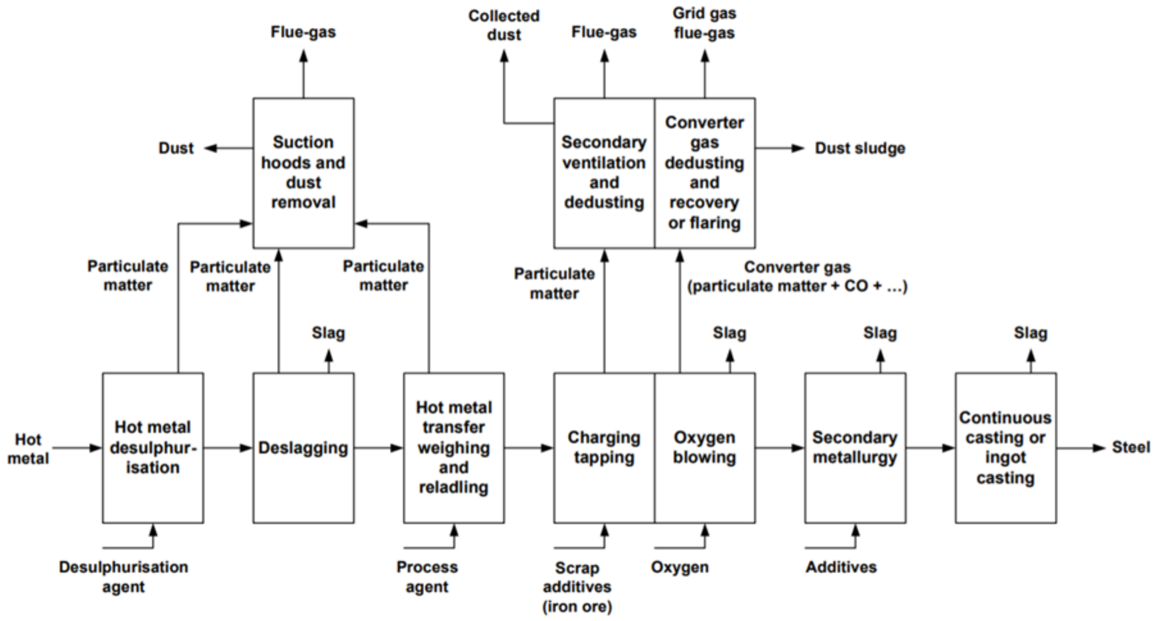

Figure 1.10: The sequence of oxygen steelmaking indicating the individual emission sources (13)

One cycle of steelmaking (‘heat’) takes 40-45 minutes and produces an average of 158 tonnes of molten steel (13). The slag is generated by the addition of fluxes, such as limestone during the blowing oxygen into the melt. Due to oxidising conditions some elements are oxidised, and this contributes to the formation of slag. Some components are either oxidised to gas such as carbon, while other components are chemically bound to the slag such as silicon and phosphorus. The liquid slag has tapping temperatures of 1600 °C and is air-cooled under controlled conditions in pits (20). Once the liquid slag has cooled it forms into crystalline slag. In 2020, a total of around 1.86 billion metric tons of crude steel were produced worldwide (6). BOF slag represents 56.7% of the steelmaking slag produced with the EU, which equates to 10.41 million tonnes of slag produced in 2016 demonstrating large economic potential for valorisation (Figure 1.11).

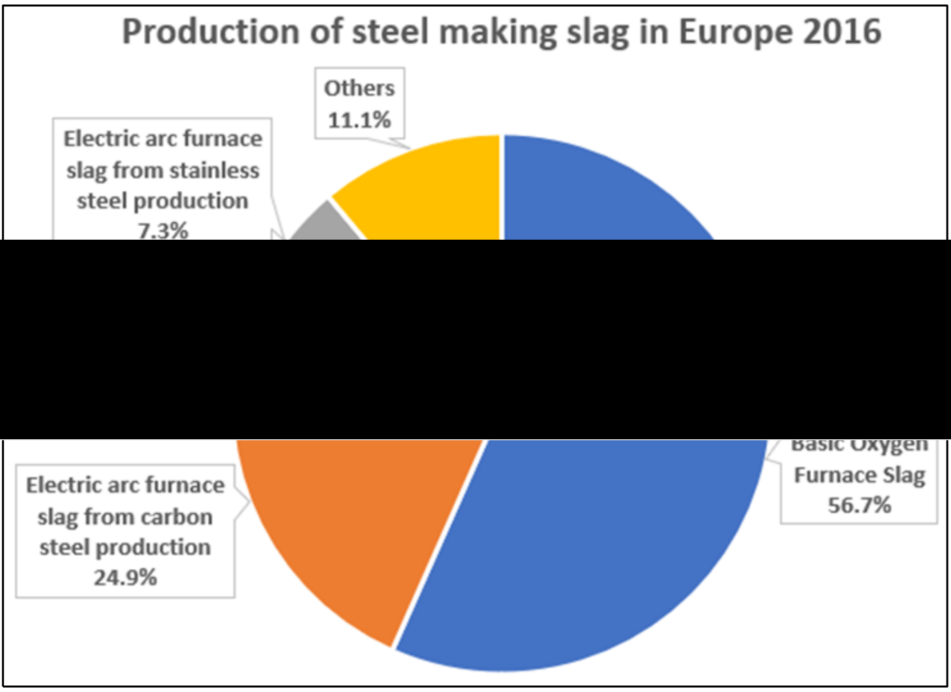

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Figure 1.11: Total production of 18.4 million tonnes of steel making slag in Europe 2016 (15)

1.3.3 Slag

Slag is the glass-like by-product left over after a desired metal has been separated (i.e., smelted) from its raw ore. Slag usually consists of a mixture of metal oxides and silicon dioxide. However, slags can contain metal sulphides and elemental metals. While slags are generally used to remove waste in metal smelting, they can also serve other purposes, such as assisting in the temperature control of the smelting. Additionally, it minimises any re-oxidation of the final liquid metal product before the molten metal is removed from the furnace and used to cast solid metal.

Ferrous slag is generated during the iron and steel making processes. Depending on the steel production method, various slag types can be generated. The following slag families are most common in Europe and can be seen in Figure 1.12.

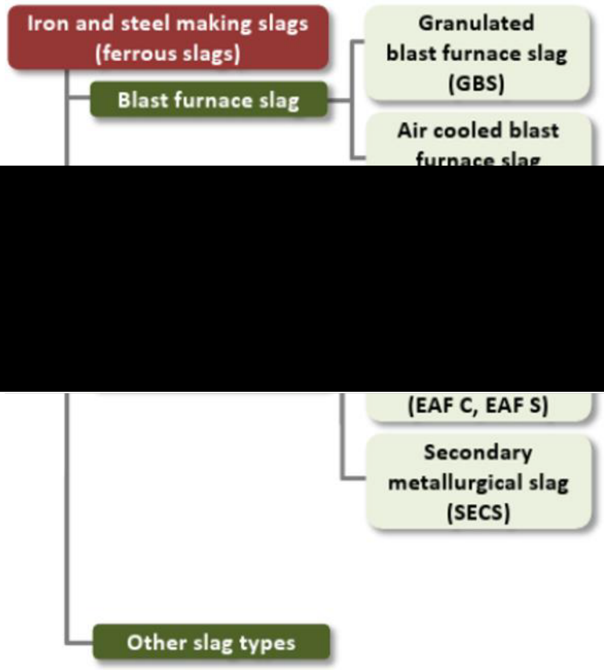

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Figure 1.12: Iron and steel making slag types (15)

In 2007, the implementation of the REACH regulation (21), in agreement with European Steel association (EUROFER) introduced a process for the registration of iron and steel slags as substances. EUROFER represents the entirety of steel production in the European Union (20). The consensus is that slags in general are not wastes but by-products or products/secondary raw materials. Agreement was reached to register all slag types as unknown or variable composition, complex reaction products or biological materials (UVCB) - substances which are best described by their production processes. A UVCB substance has many different constituents, some of which may be unknown. The composition can be variable or difficult to predict. The production processes of the various slag types are the most important criteria for their identification.

1.3.3.1 Chemical Composition of Slag Variations

The BF and BOF slags from different global markets can be characterised by their chemical composition and are generally comparable and independent of their producers. Weathered samples will have a higher Loss on ignition (LOI) due to carbonation. The typical chemical composition of steelmaking slag is shown in Table 1.2 (22). Slag is mainly non-metallic by-product which is made up of silicates, alumina silicates, calcium aluminium silicates and iron oxides (23). During the BOS process, a portion of molten iron partitions into the slag and cannot be recovered, so elemental iron is often observed in the slag (24). The phosphorus, present in slag, jeopardizes internal steel making recycling, as it has a marked influence on steel quality (degradation of weldability and toughness properties) (25). The proportions of each element will vary from each batch, depending on raw materials and processing conditions (22). The physical properties of various steelmaking slag can be observed within Table 1.3.

Table 1.2: Constituents of steel slag (22)

Slag Type	**Chemical Composition (%)**							
	FeO	**MnO**	**P_2O_5**	**SiO_2**	**CaO**	**Al_2O_3**	**MgO**	**TiO_2**
BOF slag	10-35	2-15	0.2-3.0	8-20	30-55	1-6	5-15	0.4-2.0
EAF slag	15-30	3-10	0.1-2.0	9-20	35-60	2-9	5-15	-

Table 1.3: Physical properties of steelmaking slag (26)

Property	
Specific gravity	3.1 to 3.5
Bulk density	1600-1760 kg/m^3
Aggregate crushing value	12 to 25
Aggregate impact value	18 to 24
Aggregate abrasion value	3 to 4
Water adsorption	0.2 to 2
Polished stone value	53 to 72

The presence of calcium silicate in BOF slag as dicalcium silicate (Ca_2SiO_4), tricalcium silicate (Ca_3SiO_5), and wollastonite ($CaSiO_3$) induces BOF slag to have cementitious properties (22). In order to remove metallic iron, the slag is crushed in order to undertake separation, using rotating magnetic drum process (27). The processing involves: -

- cooling within the slag pits where the slag cools naturally with the help of water sprays, which form an outer crust (Figure 1.13).
- Crushing and size screening

The magnetic separation process and the crushing process are often repeated several times to increase the quantity and quality of metallic iron which can be recovered from the process (28).

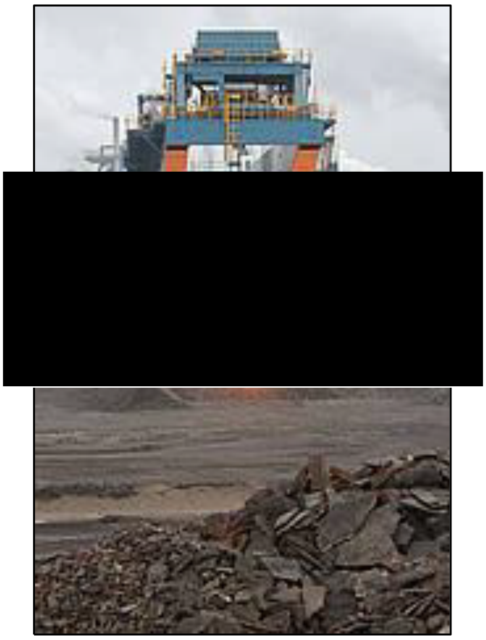

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Figure 1.13: Molten slag within cooling slag pits (15)

The chemical compositions of steel slag from BOF, EAF and ladle are given in Table 1.4. The constituents identified in the table are iron (II) oxide (FeO), manganese (II) oxide (MnO), phosphorus pentoxide (P_2O_5), silicon dioxide, calcium oxide, aluminium oxide, magnesium oxide and titanium dioxide. Table 1.4 presents how various slag constituents vary making it an UVCB substance. It can be observed from the literature, that the calcium oxide percent varies for BOF slags. This is dependent on type of process used to produce the crude steel, the cooling conditions of the slag, chemical composition, and the valorisation process. Fresh and weathered BOF slag chemical compositions differ due to processing and weathering (29). The calcium oxide, silicon dioxide and iron oxide content decreases for weathered slag in comparison to the fresh slag in the literature, while the manganese oxide content increases. Ladle slag from cited references have a much larger calcium oxide content than comparing to BOF slag, representing over 50% (Table 1.4).

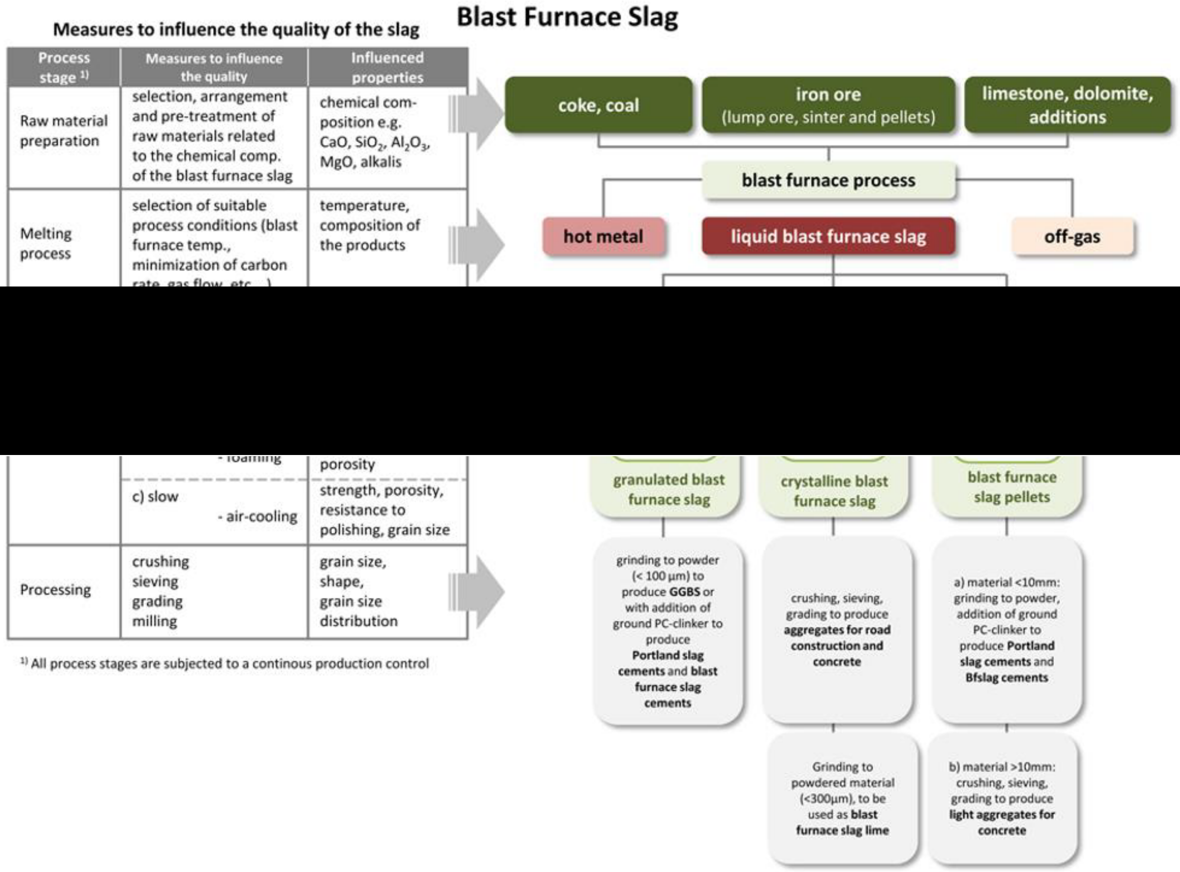
Table 1.4: Chemical composition of various slag types

		Chemical composition (%)											
Reference	**Type**	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**FeO**	**Fe_2O_3**	**Fe Total**	**SO3**	**MnO**	**TiO_2**	**P_2O_5**	**Free CaO**
Das et al. (30)	BOF	47.9	12.2	1.2	0.8	26.3	-	-	0.3	0.3	-	3.3	-
Juckes (31)	BOF	36.4-45.8	10.7-15.2	1-3.4	4.1-7.8	-	-	19.0-24.0	0.1-0.2	2.7-4.3	-	1.0-1.5	2.5-12.0
Mahieux et al. (32)	BOF	47.5	11.8	2	6.3	-	22.6	-	-	1.9	0.5	2.7	-
Poh et al. (33)	BOF	52.2	10.8	1.3	5.04	17.2	10.1	-	-	2.5	0.6	1.3	10.2
Shen et al. (34)	BOF	39.3	7.8	0.98	8.56	-	38.06	-	0	4.2	0.9	-	-
Shi (22)	BOF	30-55	8.0-20.0	1.0-6.0	5.0-15.0	10.0-35.0	-	-	0.1-0.2	2.0-8.0	0.4-2.0	0.2-2.0	-
Tossavainen et al. (35)	BOF	45	11.1	1.9	9.6	10.7	10.9	-	-	3.1	-	-	-
Waligora (36)	BOF	47.7	13.3	3	6.4	-	24.4	-	-	2.6	0.7	1.5	9.2
Belhadj (29)	Fresh BOF	45	10.8	1.9	4.5	-	32	-	0.4	2.6	0.5	1.4	-
	Weathered BOF	40.1	8.6	1.9	5.5	-	30.8	-	0.4	2	0.5	1.4	-

	High Lime content BOF	41.7	13.1	1.7	6	-	29.3	-	0.4	4.1	0.9	2.4	-
	Low Lime content BOF	42.9	11.3	2.1	7.5	-	28.3	-	1.2	3.7	0.7	2	-
Shi (22)	EAF	35.0-60.0	9.0-20.0	2.0-9.0	5.0-15.0	15.0-30.0	-	-	0.1-0.2	3.0-8.0	-	0.0-0.3	-
Tossavainen et al. (35)	EAF	38.8	14.1	6.7	3.9	5.6	20.3	-	-	5	-	-	-
Luxán et al. (37)	EAF	24.4	15.4	12.2	2.9	34.4	-	-	-	5.6	0.56	1.2	-
Manso et al. (38)	EAF	23.9	15.3	7.4	5.1	-	-	42.5	0.1	4.5	-	-	0.5
Shi (22)	Ladle	30.0-60.0	2.0-35.0	5.0-35.0	1.0-10.0	0-15.0	-	-	0.1-1.0	0-5.0	-	0.1-.0.4	-
Tossavainen et al. (35)	Ladle	42.5	14.2	22.9	12.6	0.5	1.1	0.4	-	0.2	-	-	-
Nicolae et al. (39)	Ladle	49.6	14.7	25.6	7.9	0.44	0.22	0.17	0.8	0.4	-	0.2	-
Qian et al. (40)	Ladle	49.5	19.59	12.3	7.4	-	0.9	-	-	1.4	-	0.4	2.5
Setién et al. (41)	Ladle	50.5-57.5	12.6-19.8	4.3-18.6	7.5-11.9	-	1.6-3.3	-	-	0.4-0.5	0.3-0.9	0-0.01	3.5-19.0

1.3.3.2 Recycling and Valorisation

BF slag is characterised as ABS and GBS. After crushing and screening, ABS provides an eminently suitable material for use as a construction aggregate in bound or unbound form, like any rock (15). GBS however exhibits cementitious properties and is thus used as hydraulic binder for cement, concrete, mortar, and grout (Figure 1.14)(15). For these purposes, it is ground, separately or together with Portland cement clinker and calcium sulphate (15). This is referred to as ground granulated blast furnace slag (GGBS). Unground GBS can be used as an aggregate. BF slags are routinely recycled, whilst the utilisation of BOF slag is more challenging. The disposal and exploitation of residues from steelmaking plants are an open problem due to the huge quantity and remarkable variety of waste materials.



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Measures to influence the quality of the slag

Process stage [1]	Measures to influence the quality	Influenced properties
Raw material preparation	selection, arrangement and pre-treatment of raw materials related to the chemical comp. of the blast furnace slag	chemical composition e.g. CaO, SiO_2, Al_2O_3, MgO, alkalis
Melting process	selection of suitable process conditions (blast furnace temp., minimization of carbon	temperature, composition of the products
[redacted]	[redacted]	[redacted]
		porosity
	c) slow - air-cooling	strength, porosity, resistance to polishing, grain size
Processing	crushing sieving grading milling	grain size, shape, grain size distribution

[1] All process stages are subjected to a continous production control

Figure 1.14: Utilisation of BF slag (15)

1.3.3.3 Free Lime Volume Instability

The recycling process for BOF slag is impacted by its free lime and magnesia content which in turn leads to problematic swelling, and these further compromises civil engineering applications. It was discovered that steel slag is volumetrically unstable compared to BF slag, due to the content of expansive oxides such as magnesium oxide and calcium oxide (42). Steel slag is stored in large stockpiles in storage yards located outdoors, and this makes the slag vulnerable to short and long-term hydration of lime and magnesium oxides. This process is known as 'free lime volume instability.' The reuse of steelmaking slag is limited as potential applications are located outside where moisture could cause potential volume expansion (43). To illustrate, if the slag is used in a road surface which acquires moisture, the free lime expansion may cause the road surface to fracture (25). The volume expansion of steelmaking slag has been recorded as up to 10% (44). The reaction of the free lime and water can be expressed by Equation 1.11. Under ambient conditions the reaction proceeds to the right, while reaction proceeds to left only at 547 °C or above.

$$\boldsymbol{CaO + H_2O \leftrightarrow Ca(OH)_2} \quad \textbf{Equation 1.11}$$

1.3.3.4 Free Lime Volume Stabilisation

In recent times two methods have been developed to stabilise the free lime content in the slag, to prevent volume expansion. The two processes developed are: -

1. Air oxidation.
2. Carbothermic reduction.

The first method involves the slag being heated to a temperature of 1673 K under an air atmosphere, then cooled down to room temperature at a rate of 5 K/minute. Once the slag is heated up in air, the wüstite (mineral form of iron oxide) is oxidised to form hematite, as realised in Equation 1.12. The hematite reacts with the free lime (~1370 °C) and precipitates the mineral brownmillerite ($Ca_2(Fe_xAl_{1-x})_2O_5$) during solidification, seen in Equation 1.13. This method eliminates the free lime content from the slag, enabling more possibilities for recycling methods (45).

$$\boldsymbol{4FeO + O_2 \rightarrow 2Fe_2O_3} \quad \textbf{Equation 1.12}$$

$$\boldsymbol{2CaO + xFe_2O_3 + (1-x)Al_2O_3 \rightarrow Ca_2(Fe_xAl_{1-x})_2O_5} \quad \textbf{Equation 1.13}$$

In the second method, the BOF slag undertakes a carbothermic reduction reaction. The iron, phosphorus and calcium oxide are reduced. Carbon (5-8 wt%) alumina and silica are added to a homogenous powder of BOF slag. These are mixed, dried and placed into a furnace at 1600 °C for one hour, followed by water quenching (46). As the amount of carbon is increased the phosphorous-rich moved from the slag to the metal. This means that the carbon addition must be kept to a minimum to avoid contamination of metallic iron. The silicon dioxide is added to stabilize the free lime and causes carbon disulphide (C_2S) to form, which has cementitious properties, and its strength gradually increases when it ages. Therefore, the slag can be used as some kind of cement product (46).

1.3.3.5 Leaching Behaviour of Steelmaking Slag

With utilisation of steelmaking slags in various applications, there is a potential hazard that metals contained within the steelmaking slag may begin to leach out, causing issues such as water or soil pollution (47). Leaching tests in both acidic and neutral conditions have been performed on slag samples from 59 steel plants across the United States (48). The samples included BF, BOF, and EAF slags. Each slag was leached at pH 2.8 and the slag leachate concentrations were recorded. None of the materials which were leached exceeded the safe criterion outlined in the Resource, Conservation and Recovery Act (RCRA) for the United States (49). RCRA oversees the disposal, storage, treatment, generation, and transportation of hazardous and non-hazardous solid waste in the United States. Metals are more susceptible to leaching under acidic conditions. The results suggest that metals are unlikely to leach out of steelmaking slags under neutral solution. This means that generally slag may be categorized as a non-hazardous waste from the steel industry, with potential for recycling elsewhere. Similar results and conclusions were reported by Geiseler (50).

1.3.4 Utilisation of Slag

The improvement of existing technologies and development of new technologies has been extended to achieve a future “zero waste” target. The utilisation of slags can benefit the steel industry and transform previously regarded waste by-products with minimal value or disposal cost, into a high value saleable product.

Steel slag contains waste steel, which can be reclaimed through methods such as crushing, sorting, magnetic separation, and screening process. The application of slag is closely related with their technical properties.

Due to growing environmental concerns and stricter regulations for managing industrial by-products, there is a global emergence for increased research into the properties of by-products and alternative methods of recovery. Critically this is to valorise these wastes as secondary raw materials and establish IS opportunities. Non-reproducibility of mineral raw material reserves is especially significant sustainable development standpoint. There is a clear need to preserve the finite mineral raw material reserves, and additionally to continuously research and explore new reserves, whilst simultaneously utilising existing processes.

The physical properties of iron and steel making slags are dependent on the chemical composition in addition to the cooling condition. The slag formed can be influenced by its processing once removed from the furnace. Steel slag and crystalline BF slag is produced through slow cooling. Quenching the liquid slag (e.g. granulation) on the other hand will generate a vitreous slag with latent hydraulic properties. The uses of BF and steelmaking slag can be observed within Figure 1.15 and Figure 1.16, respectively. While the current treatments of BOF Slag can be observed in Figure 1.17

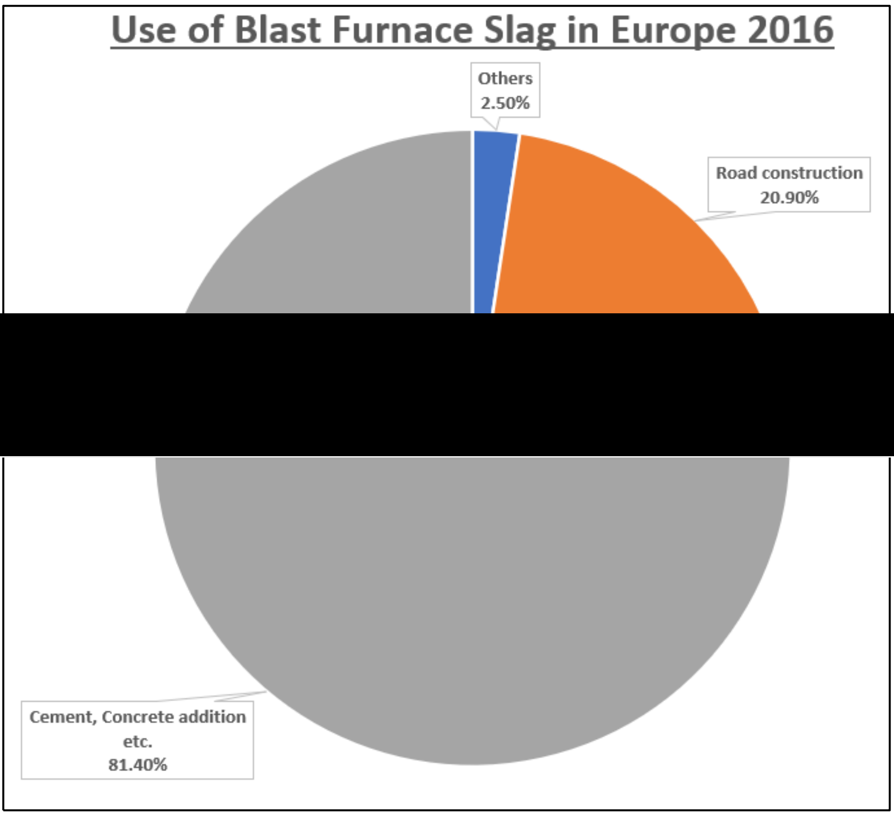

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Figure 1.15: Total use of BF slag of 14.2 million tonnes in 2016 (15)

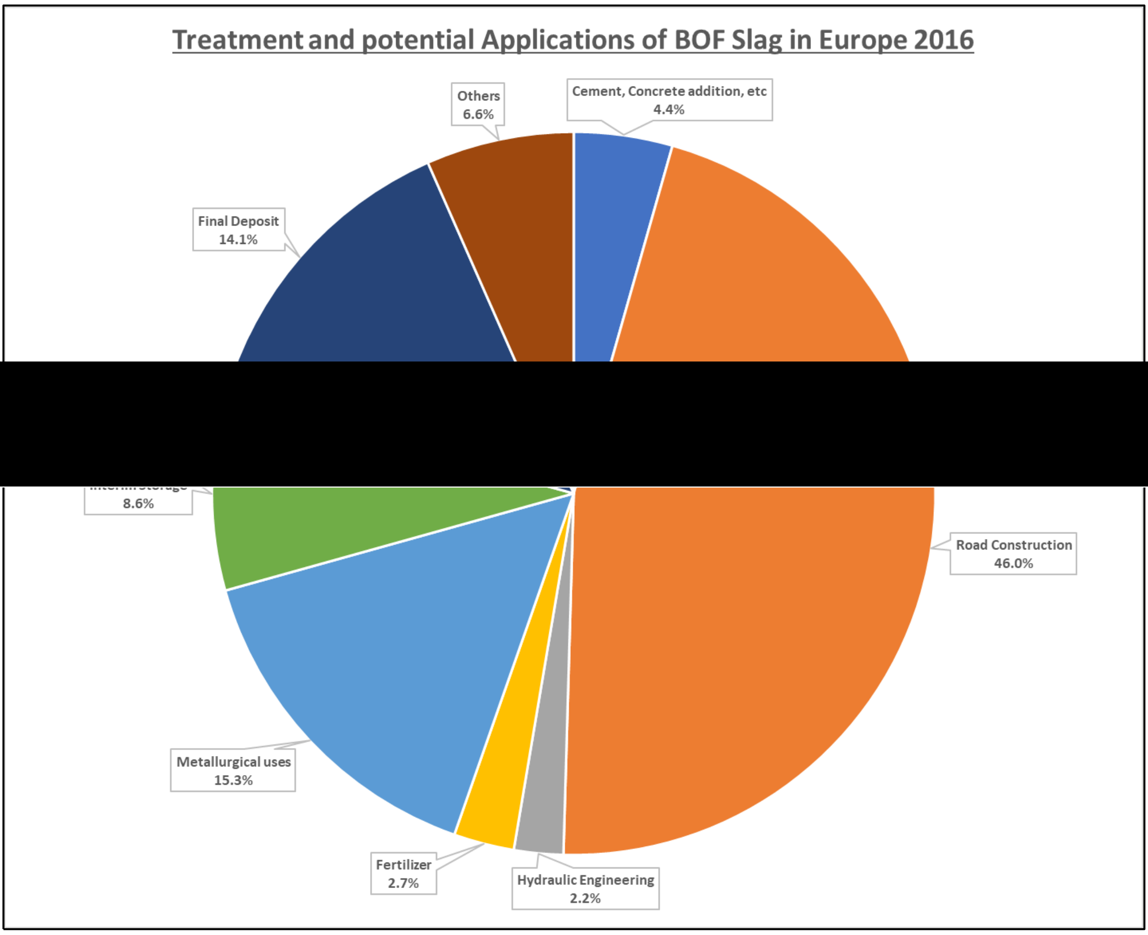

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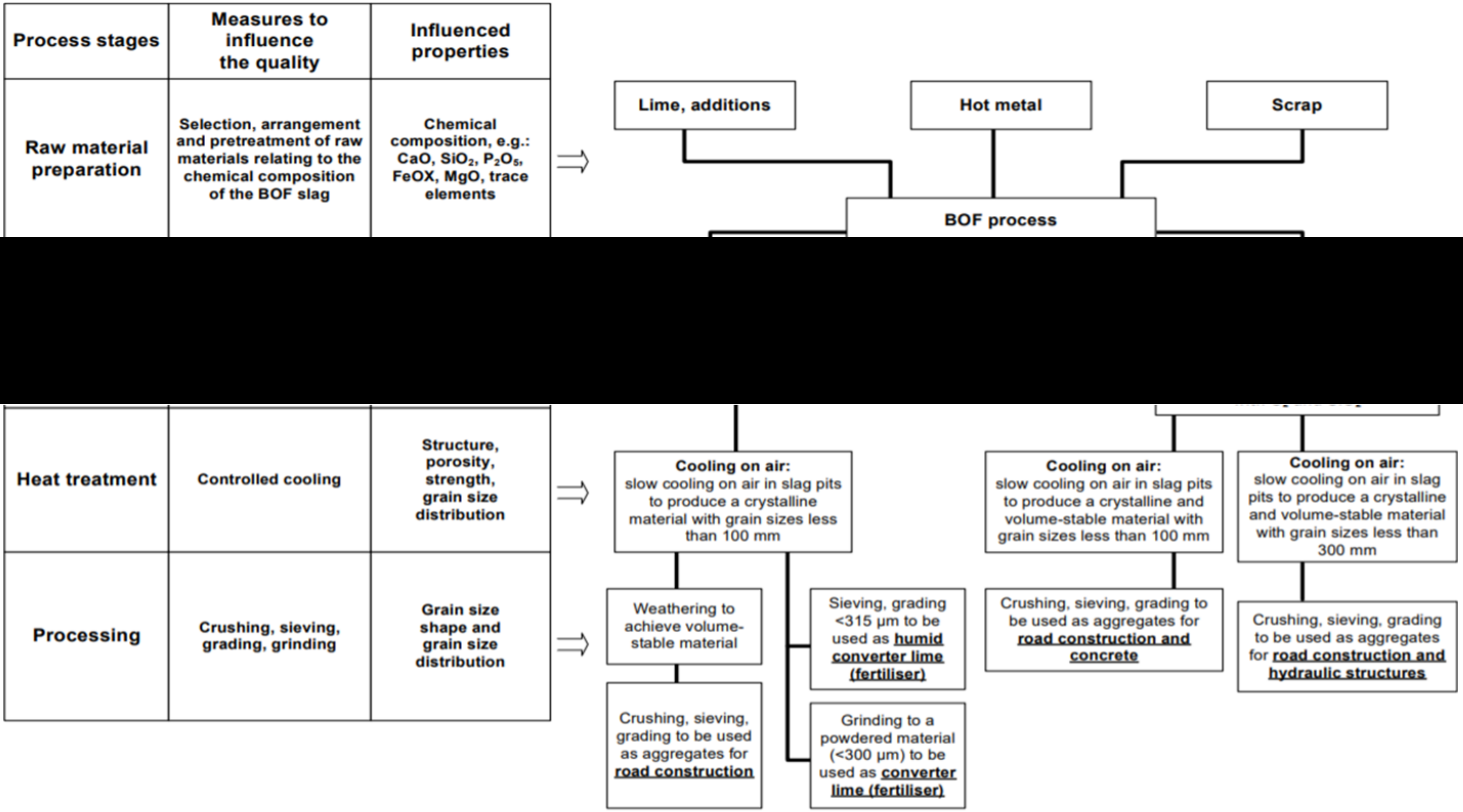
Figure 1.16: Total treatment and potential applications of 14.2 Million tonnes BOF slag in 2016 (15)



Process stages	Measures to influence the quality	Influenced properties
Raw material preparation	Selection, arrangement and pretreatment of raw materials relating to the chemical composition of the BOF slag	Chemical composition, e.g.: CaO, SiO_2, P_2O_5, FeOX, MgO, trace elements
[redacted]	[redacted]	[redacted]
Heat treatment	Controlled cooling	Structure, porosity, strength, grain size distribution
Processing	Crushing, sieving, grading, grinding	Grain size shape and grain size distribution

Figure 1.17: Treatments of BOF slag (51)

1.3.4.1 Reuse within the Steelworks

One approach to finding specific uses through which to recycling steel slag is to re-use the slag within the process itself. If oils and greases can be removed, the potential arises to use slag as an iron ore replacement in iron making process. This potentially reduces the cost and implications of mining and transportation; these factors contribute to the overall carbon footprint of steel production. However, it must be remembered that re-use in steel production is very limited.

In European countries, 30% of BOF slags are recycled into the BF (30). The high content of CaO in the slag can be used to substitute limestone as a fluxing material, and this will reduce the cost of steelmaking. The use of BOF slag as a replacement for limestone is a process used globally. Steel slags contain higher quantities of phosphorus and sulphur, which affects the direct recycling to iron and steel making processes. Steel slag is subjected to metal recovery prior to its application outside of the iron and steel making processes. The method of slag processing is varied, dependent on cooling method, chemical and mineralogical composition, and its application. Steel slag processing consists of crushing or grinding, screening and magnetic separation. Figure 1.18 demonstrates the internal recycling of steel slag within the steelworks (52).

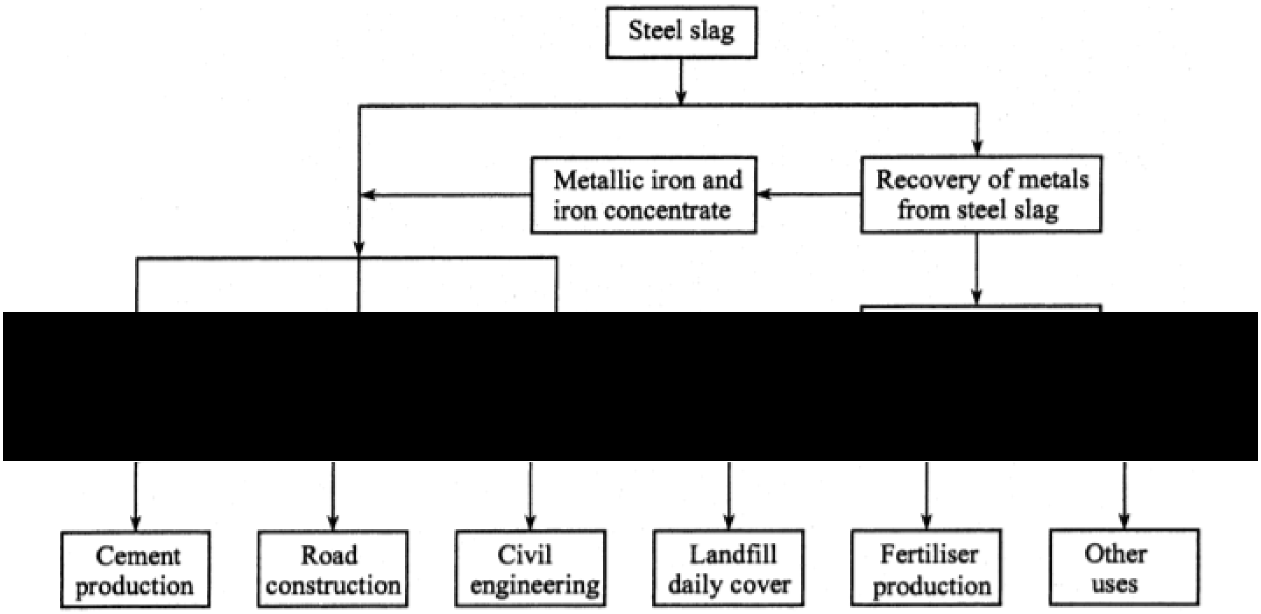


Figure 1.18: Utilisation of steel slag (52)

1.3.4.2 Civil Engineering

The primary recycling of steel slag is in road construction which represents 46% of the total consumption of steelmaking slag (Figure 1.16)(15). For many years steelmaking slags have been utilised and recycled in civil engineering applications as cement, roadbed material, aggregate in cement and in the stabilisation of riverbanks (53). Once the crystalline slag is air-cooled within the slag pits or ground bays, the slag is treated for the desired technical properties for a specific use, the treatments involve weathering, crushing, and/or sieving. BOF slag has suitable physical, chemical, and mineralogical properties for use as aggregate in civil engineering projects. BOF slag has increased skid resistance and because of its high level of strength compared to natural rocks, it is an ideal aggregate for road construction. The processing of the solid and crystalline slag (e.g. crushing and screening) is undertaken to ensure that the produce aggregates and mixtures conform to requirements of the European standards and regulations.

1.3.4.3 Concrete

In the production of concrete, two components are required, in addition to aggregates and pastes. Aggregates occupy about 70-75 vol% of concrete (54). Traditionally concrete mixture ratio consists of 1-part cement, 3-parts sand, and 3-parts aggregate. Natural sand is dredged up from riverbeds, which can be damaging to the environment (55). During the 1980s scientists began to consider recycling waste materials to replace aggregate in concrete. Lupu et al (2006) explored the potential of cementitious and pozzolanic by-products such as fly ash, granulated BF slag and condensed silica fume which could be used as aggregate in the production of concrete (56). The addition of BF slag as a substitute for natural sand in aggregates, matched the strength properties. Mehta discovered that in some cases the use of BF slag cement was stronger than the use of natural sand cement (57).

Subathra and Gnanavel (2014) identified that the replacement of coarse and fine aggregates with steelmaking slag resulted in a reduction in tensile strength (58). This is realised in Figure 1.19, where the strength of concrete is identified for the optimum loading conditions.

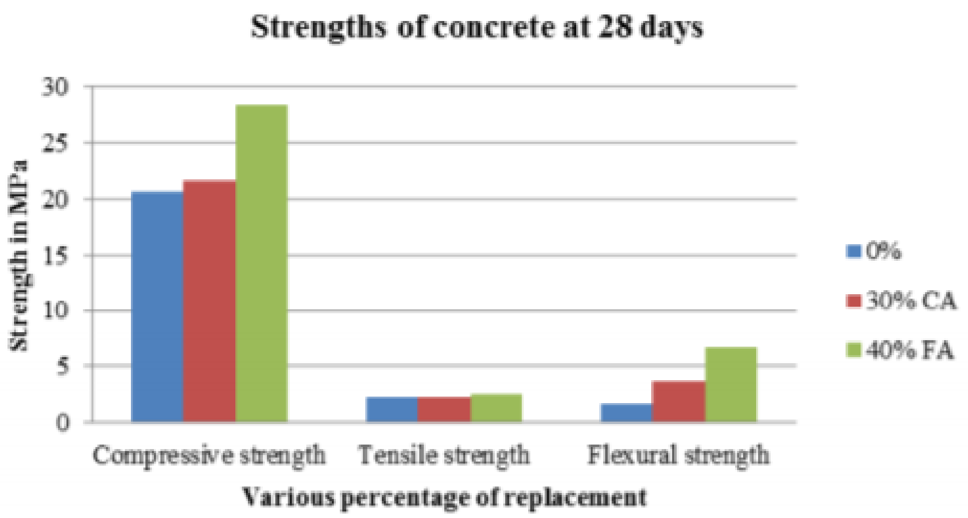


Figure 1.19: Figure showing the compressive, tensile and flexural strength of concrete after 28 days made with optimum amounts of course aggregate (CA) and fine aggregate (FA) compared to sand (58)

1.3.4.4 Fertiliser

During the 1950s BOF slag was used in Germany as fertiliser for crops. The slag caused the crops to grow in larger quantities, without any adverse effects in the soil in the short term. The use of BOF slag as fertilizer did not have any negative impacts on the soil fertiliser through long term application of BOF slag, although there were significant increases of chromium and vanadium contents recorded. Steel slag has also shown good use as a liming material when spread over acidic soils to help to raise the pH to a more neutral level (59). As a consequence of the increase in pH, aluminium solubility decreases and absorption of phosphorus is favoured, while an increase in calcium and magnesium contribute to an increase in yield (60). An increase in yield will have corresponding benefits for animals through grazing.

1.3.4.5 Slag wool

In Wales, slag wool has been manufactured since around 1840 from steelmaking waste products. The production of slag wool involves melting the slag and drawing it through a tap hole. The slag then passes through a jet of air, which disperses the slag into a cone of liquid droplets, which then develop into long fibres. The long fibres are then placed into a chamber to dry where small additions of limestone and silica may be added to enhance the properties. Slag wool is often used as insulation in houses due to its outstanding thermal, fire resistance and sound absorption properties (61). Slag wool is resistant to attack from pests, oxidation and is entirely incombustible. All these properties mean it is extremely suitable to be used for home insulation. During the 1970s slag wool became the prominent usage of steelmaking slag (26).

1.3.4.6 Marine Applications

Steelmaking slags have beneficial applications to the marine environment due to its high porosity and large surface area. Due to this reason, research into marine applications of steelmaking slag has increased significantly over past years (62).

1.3.4.7 Carbstone Process

The conversion of steelmaking slag into a strong structural material through high gravity carbonation was identified by Chang et al (2012) (63): this process is now known as the carbstone method, which consists of three-steps: pre-treatment, shaping and curing (64).

The BOF slag is firstly homogenised into a powder, then mixed with the appropriate quantity of water. The optimum water quantity in this method was 10%, but this is dependent on the moisture content of the slag. This mixture is then compacted into a desirable shape through use of a hydraulic press (75-609 kgf/cm^2)(64). The shape is dependent on the desired application of the slag block. The block is then placed into an autoclave at 20-140 °C, for a duration of 16 hours, with a CO_2 enriched atmosphere at a pressure of 0.5-1 MPa (64). The final product displays excellent compressive strength and environmental properties, thus enabling it for effective use in construction. One advantage of this process is the elimination of the need for additional binder (65).

1.4 Gypsum (Calcium Sulphate)

Calcium sulphate is an inorganic compound (chemical formula $CaSO_4$): one hydrate of calcium sulphate is gypsum. Gypsum - chemical name calcium sulphate dihydrate ($CaSO_4.2H_2O$) - is a mineral which has many applications in the construction industry (66). Gypsum - also known as hydrated calcium sulphate - is a mineral commonly found in marine evaporites, and in permian and triassic sedimentary formations. Under certain geological conditions (high temperature and pressure), gypsum is converted to anhydrite ($CaSO_4$ with no water) (67). It is found in layers formed under saltwater millions of years ago. When water evaporated, the mineral was left behind. The largest gypsum quarries in Europe are located in France, Germany, Italy, Poland, Spain, Ukraine and the UK (68).

Gypsum is found in both crystal and rock form and has two main forms: natural gypsum (mined) and synthetic gypsum. Gypsum occurs naturally as a mineral ore which is conventionally quarried. Synthetic gypsum is created as a by-product of industrial processing. Currently, the most important industrial processing occurs through flue gas desulphurisation, a process which removes synthetic gypsum from the flue gases at coal-fired power stations. However, closure of all Britain's coal power plants by 2025 potentially will lead to a shortage of gypsum in the UK and elsewhere. There are a variety of forms of synthetic gypsum dependent on the acid-neutralising industrial processes. These include (67): -

- Desulphogypsum (DSG), a by-product of flue gas desulphurisation (FGD) at coal power plants.
- Citrogypsum, a by-product of citric acid manufacturing.
- Fluorogypsum, a by-product of hydrofluoric acid manufacturing.
- Phosphogypsum, a by-product of phosphoric acid manufacturing.
- Titanogypsum, a by-product of titanium dioxide manufacturing.

The demand for gypsum is principally driven by the construction sector, where it is required in the manufacture of building products such as cement, plaster, and plasterboard. As the demand for new housing increases, the requirement for new schools, hospitals and offices will also increase. This will increase the need for construction products. The manufacture of synthetic gypsum provides significant economic and environmental benefits. Economically, manufacturing synthetic gypsum produces additional revenue from a by-product which resulted in waste management costs. The production of this valuable by-product reduces the material sent to landfill, which in turn reduces the pollution from landfills. The use of synthetic gypsum will reduce the need to mine natural gypsum, which will conserve the material and preserve natural capital.

1.4.1 **Applications of Gypsum**

The most important application of Gypsum is the production of plaster, plasterboards, gypsum fibreboard and gypsum blocks. The mineral is key for a large industry producing a wide range of building products. Gypsum has also been used for over 200 years as soil amendment and fertiliser.

Synthetic gypsum is used in a range of applications, which includes cement, drywall, glass manufacture, plaster, and soil amendments. When gypsum is ground to powder and heated to remove three-quarters of its water, this results in a hemi-hydrate plaster ($CaSO_4.1/2H_2O$), forming plaster of Paris (69). This powder can be mixed with water to re-produce gypsum, and this can be achieved indefinitely for CE (Figure 1.20). Synthetic gypsum is more widely used for plasterboard, while natural gypsum is more suitable for production of plaster due to its clay contents which improves the workability of the plaster.

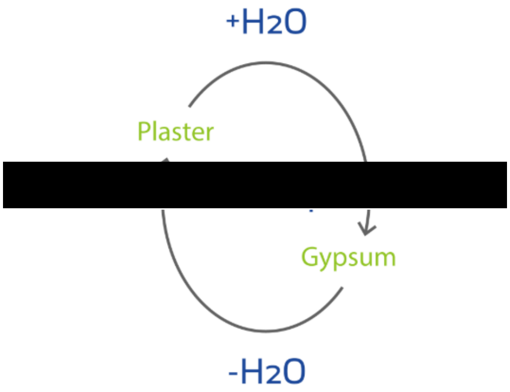


Figure 1.20: Formation of plaster (70)

High purity natural gypsum is used to produce special plasters, such as plaster moulds in the pottery industry and for surgical/dental work. High purity gypsum is also used in confectionary, food, brewing industry, pharmaceuticals, sugar beet refining, as cat litter and as an oil absorbent (70). Gypsum is known to have low thermal conductivity, crucial for its use making drywalls or wallboards. Gypsum-based products and solutions have several qualities in construction such as (70):

- Gypsum is non-combustible and acts as a fire barrier.
- Gypsum acts as a sound regulator by providing physical barrier to sound.
- Gypsum acts as a thermal insulator for inside of buildings when combined with insulating materials, due to its low thermal conductivity.
- Gypsum equilibrates humidity and heat peaks.
- Gypsum is impact resistant, thanks to its high degree of hardness equivalent to a thick wall heavy masonry construction.

Gypsum is used within the agriculture sector; it is generally added to soils either as a source of nutrients or to modify and improve soil properties. It can be a valuable source of both calcium and sulphur for plants and may provide benefits for soil properties in specific conditions. It may also be used for removing sodium from soils which have excess salinity. Pure gypsum is 23.3% calcium and 18.6% sulphur (71). Additionally, the sulphur in gypsum is in sulphate form, a form that plants can utilise. The sulphur in gypsum is readily available, so gypsum can be used where a quick response to sulphur is required. Gypsum has little if any effect on soil pH and cannot be used as a substitute for lime to correct soil acidity (72). The benefits of gypsum on soil chemical properties include increased subsoil calcium, decreased subsoil acidity and reduced exchangeable aluminium (73). The physical benefits include increased infiltration, increased aggregation, decreased sodium absorption, reduced root impedance and reduced restriction of hardpans (73).

Some soils benefit from application of gypsum as a source of calcium. In soils with excess sodium (Na), the calcium released from gypsum will tend to bind with greater affinity than sodium on soil exchange sites, thus releasing the sodium to be leached from the rootzone. Where gypsum has been used in the remediation of high sodium soils, it generally enhances soil’s physical properties-such as reducing bulk density, increasing permeability, and water infiltration, and decreasing soil crusting. In most conditions, adding gypsum by itself will not loosen compacted or heavy clay soils (66). A well-known use of gypsum is to supply calcium for peanuts, which have a unique growth pattern. Gypsum is most commonly spread on the soil surface and mixed in the rootzone. Equipment exists that allows finely ground gypsum to be distributed through an irrigation system.

1.4.2 Flue Gas Desulphurisation

One of the main substitutes to natural gypsum is FGD which is generated by coal-fired power stations during the process designed to clean sulphur from the exhaust gases. Flue gasses are produced when coal is burned to generate electricity, and these gases contain sulphur dioxide. Due to the mandate given by the Clean Air Act Amendments of 1990, sulphur dioxide must be removed from flue gases in order to control environmental pollution (74). DSG is the largest production of synthetic gypsum, it is a by-product of FGD. The most common FGD process is limestone wet scrubbing process, which uses limestone or lime as an absorbent and produces synthetic gypsum as a by-product. The process may be clearly realised in Figure 1.21 (75).

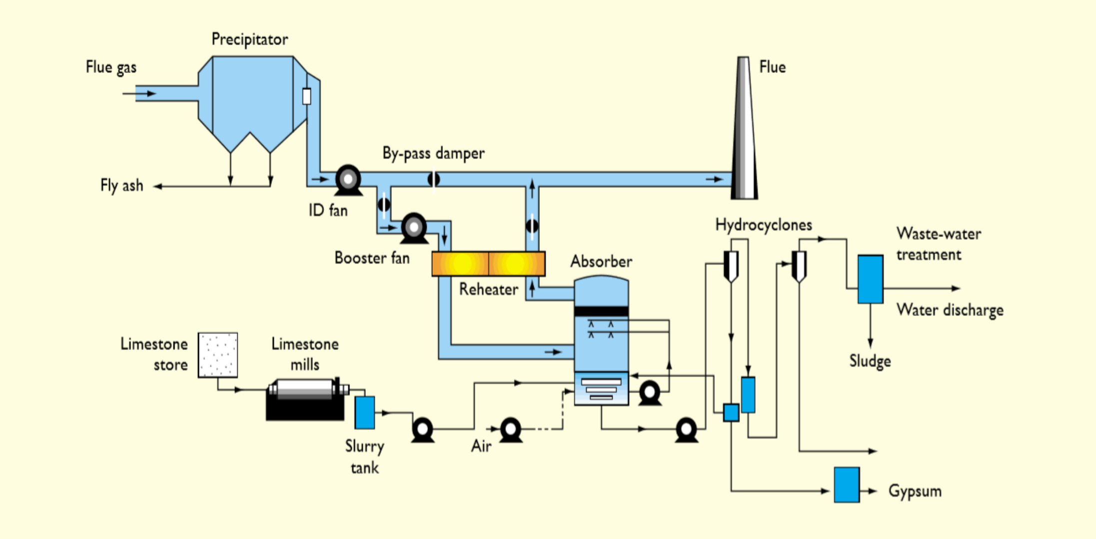


Figure 1.21: Schematic of a limestone gypsum FGD process (75)

DSG is formed through the chemical reaction: -

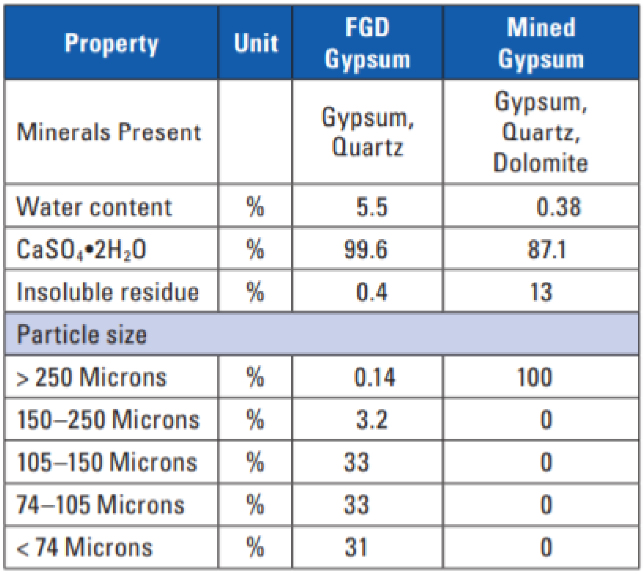
$$CaCO_3 + SO_2 + 2H_2O \rightarrow CaSO_4.2H_2O + CO_2 \quad \textbf{Equation 1.14}$$

It is formed due to the reaction between the limestone slurry and sulphur dioxide in the flue gas. DSG has a higher purity of 96% than natural gypsum (80%) and weighs less, which enables efficient plasterboard manufacture in less time (76). While the disadvantage of use of DSG is its higher moisture levels (8-12% free moisture), more energy is required for drying (76).

The first FGD plant installed in Nottinghamshire was Ratcliffe: production started in 1994, and has since averaged 260,000 tonnes per annum (77). In Wales, FGD was utilised at the Aberthaw power station prior to closure in 2020 (78). The 3 x 500 MW coal-fired power station was based near Cardiff. The Aberthaw power station was the last coal-fired power station in Wales, there now remain only a handful of coal-fired power stations left in the UK (78). The European Union introduced regulations in 2008, requiring all coal powered stations to limit their sulphur dioxide emissions. DSG is produced from non-sustainable energy sources, the EU have set a target to achieve 20% of the EU’s energy to be sourced from renewable sources (79). The closure of all coal power stations by 2025 will create a shortage of synthetic gypsum, producing new markets. The closure of Aberthaw power station could negatively impact the supply of synthetic gypsum in Wales. Provision of synthetic gypsum from the slag produced at Port Talbot steelworks, however, could afford increased environmental and economic benefits.

1.4.3 Desulphogypsum

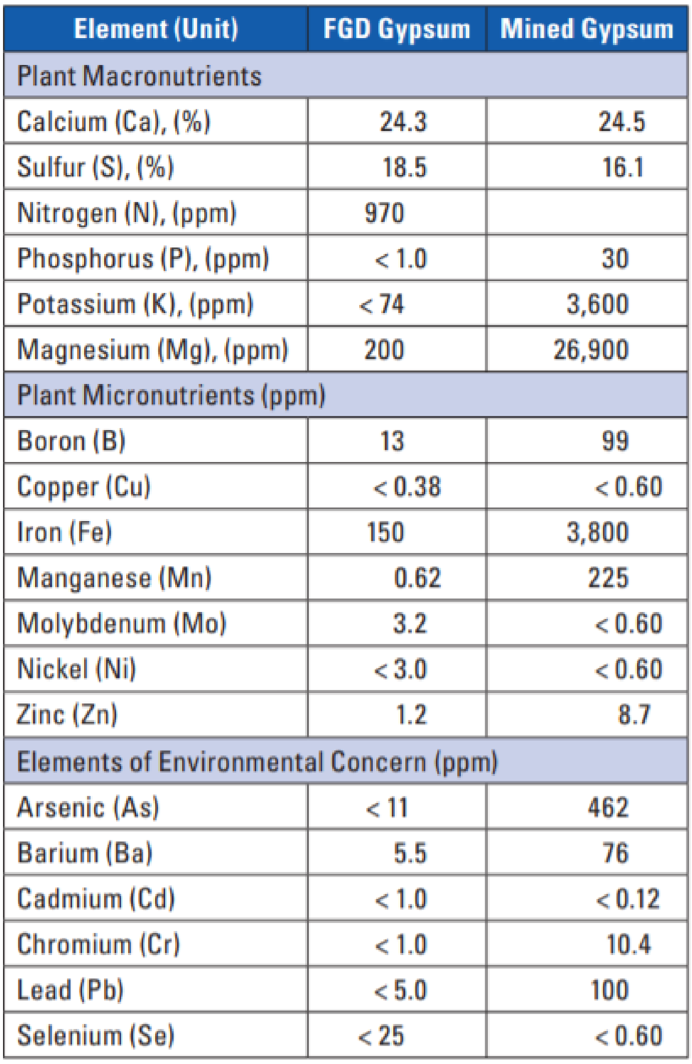
Production of Flue Gas Desulphurisation (FGD) gypsum has gradually increased over the past several years. Different sources of gypsum have specific mineralogical, physical, and chemical properties. Properties of FGD gypsum are often compared with results for the same measurements that are obtained for mined gypsum, which is currently used in agriculture. Mineralogical and physical properties of FGD gypsum from the W. H. Zimmer Station of Duke Energy (Moscow, Ohio) and mined gypsum from the Kwest Group (Port Clinton, Ohio) are shown in Figure 1.22 (80). The mineral composition of FGD gypsum and mined gypsum is predominantly $CaSO_4.2H_2O$. Occasionally, FGD gypsum contains minor amounts of quartz (SiO_2). Mined gypsum contains both quartz and dolomite ($CaMg(CO_3)_2$). FGD gypsum usually possesses a much smaller and more uniform particle size (more than 95% < 150 microns) than agricultural mined gypsum which is granulated to produce a final size of 2–4 mm (80). However, FGD gypsum can also be processed to form larger-sized granules.



Property	Unit	FGD Gypsum	Mined Gypsum
Minerals Present		Gypsum, Quartz	Gypsum, Quartz, Dolomite
Water content	%	5.5	0.38
$CaSO_4 \cdot 2H_2O$	%	99.6	87.1
Insoluble residue	%	0.4	13
Particle size			
> 250 Microns	%	0.14	100
150–250 Microns	%	3.2	0
105–150 Microns	%	33	0
74–105 Microns	%	33	0
< 74 Microns	%	31	0

Figure 1.22 : Some Mineralogical and Physical Properties of FGD Gypsum from the W. H. Zimmer Station of Duke Energy (Moscow, Ohio) and Mined Gypsum from the Kwest Group (Port Clinton, Ohio). (80)

The chemical composition of FGD gypsum is influenced by the type of coal, scrubbing process, and sorbent used in the desulfurization process. The FGD gypsum can have a purity as high as 99.6% in Figure 1.22 (80). Concentrations of other chemical elements in FGD gypsum from the W. H. Zimmer Station of Duke Gypsum as an Agricultural Amendment: General Use Guidelines 7 Energy (Moscow, Ohio) and in mined gypsum from the Kwest Group (Port Clinton, Ohio) are also shown in Figure 1.23 (80).



Element (Unit)	FGD Gypsum	Mined Gypsum
Plant Macronutrients		
Calcium (Ca), (%)	24.3	24.5
Sulfur (S), (%)	18.5	16.1
Nitrogen (N), (ppm)	970	
Phosphorus (P), (ppm)	< 1.0	30
Potassium (K), (ppm)	< 74	3,600
Magnesium (Mg), (ppm)	200	26,900
Plant Micronutrients (ppm)		
Boron (B)	13	99
Copper (Cu)	< 0.38	< 0.60
Iron (Fe)	150	3,800
Manganese (Mn)	0.62	225
Molybdenum (Mo)	3.2	< 0.60
Nickel (Ni)	< 3.0	< 0.60
Zinc (Zn)	1.2	8.7
Elements of Environmental Concern (ppm)		
Arsenic (As)	< 11	462
Barium (Ba)	5.5	76
Cadmium (Cd)	< 1.0	< 0.12
Chromium (Cr)	< 1.0	10.4
Lead (Pb)	< 5.0	100
Selenium (Se)	< 25	< 0.60

Figure 1.23: Chemical Properties of FGD Gypsum from the W. H. Zimmer Station of Duke Energy (Moscow, Ohio) and Mined Gypsum from the Kwest Group (Port Clinton, Ohio) (80)

1.4.4 Coal Power Plants

Coal rapidly became the dominant fuel for electricity generation in the UK: in 1950 it provided 97% of all electricity produced (81). In 2015 the UK Government was the first in the world to announce its ambition to phase out the use of unabated coal power generation entirely from the Great Britain grid - target for the end of 2025 (81). On the 21st of April 2017, Britain went a full day without using coal power for the first time since the industrial revolution (82). In November 2015, the government announced its intention to consult on proposals to end unabated coal generation in UK by 2025. In 2018 the UK Government ordered all remaining coal-fired power stations to close by 2025 as part of its carbon emission reduction strategy (78). Figure 1.24 shows the success in reducing coal generation and the increased role of renewables.

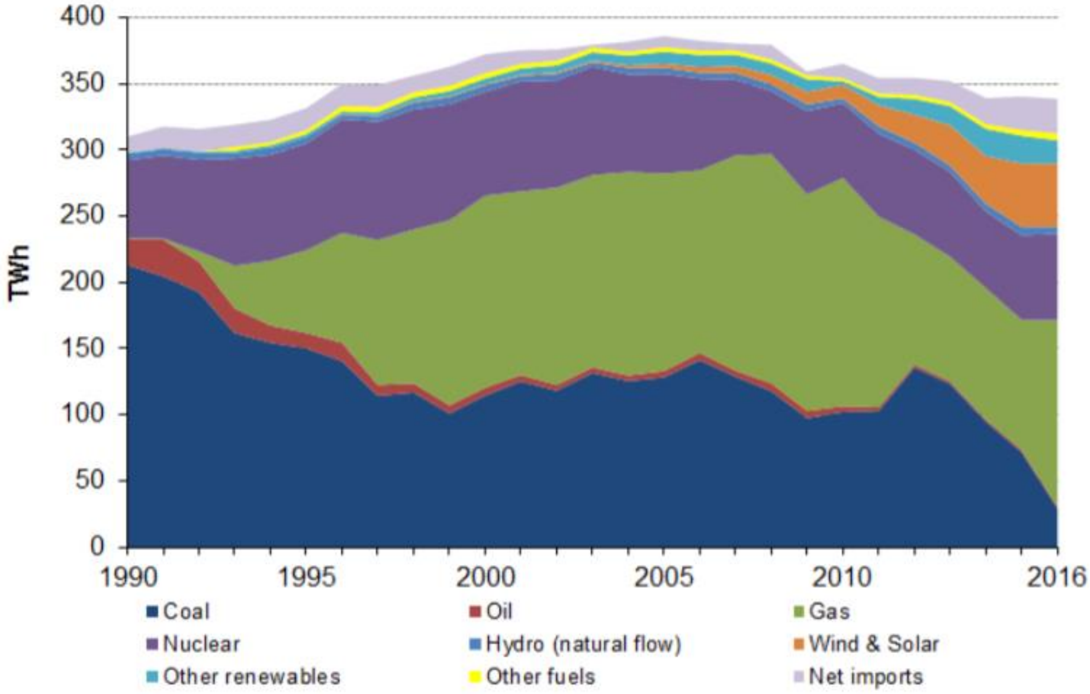


Figure 1.24: Electricity supplied by fuel type in the UK, 1990-2016 (83)

Coal is the most carbon intensive fossil fuel and the decline in coal generation over the last few years has led to a significant reduction in the carbon intensity of the power sector (Figure 1.25). The reduction in coal will reduce harmful air pollutants such as Sulphur Dioxide (SO_2), Nitrogen Oxides (NO_x) and particulate matter (PM).

This will improve air quality, while also reducing negative impacts on human health and the environment.

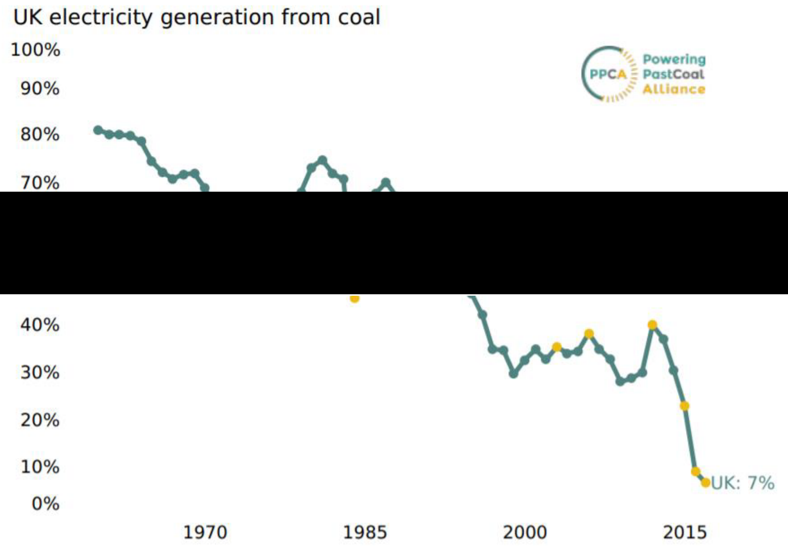


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Figure 1.25: UK electricity generation from coal (81)

The phasing out of coal powered generation will significantly impact the production of synthetic gypsum through FGD in the UK. The last coal-fired power station in Wales has closed, this could provide a potential market opportunity to supply synthetic gypsum to FGD synthetic gypsum operators.

1.4.5 Alternative Sources of Gypsum

Gypsum has "closed recycling loop" which means it is continually recyclable. It maintains high quality, which affords significant commercial product development benefits. The use of synthetic gypsum creates revenue from a by-product which incurs waste management costs. This will have significant positive environmental impacts, such as reducing the landfill waste material and conserving natural gypsum.

Gypsum products are amongst the very few construction materials where 'closed loop' recycling is achievable. Waste gypsum can be used to make the same product and not just recovered for use in other 'down-cycling' applications like other construction products. Increased recycling of Gypsum products waste is occurring from construction sites (84). Once collected, the plasterboards are broken down into a fine powder, which is then re-introduced into the manufacturing process (85). The destination of end-of life construction products is diverse. Construction products may be re-used, recovered, or disposed of through landfill.

1.5 Patent 572/KOL/2014

An Indian patent application bearing application number 572/KOL/2014 has been filed based on ‘A method of producing calcium sulphate from LD slag waste produced during the recovery of metallic iron from LD slag’ (86). This method relates to the utilisation of LD slag produced in steel industry processes. This invention uses the availability of sulphuric acid and lime fines generated during the production of lime from limestone. With the increased costs for disposal and utilisation of by-products becoming increasingly more important, a demand arises for a process that will reduce the amount of LD slag waste to be disposed of and result in a reusable product.

1.5.1 Summary

This process advantageously includes a method for treating LD slag waste fines (below 6 mm), after the recovery of metallic iron with sulphuric acid, to form a slurry containing insoluble calcium sulphate, excess unreacted sulphuric acid, and other soluble metal sulphates (87). LD waste slag contains the highest levels of calcium as calcium silicate and as free lime and calcite along with metals like iron, titanium, magnesium, aluminium etc. The slurry formed is further neutralised using the lime fines and dried to produce the yellow calcium sulphate (87). The yellow calcium sulphate product can include calcium sulphate dihydrate ($CaSO_4.2H_2O$), anhydrite forms, co-products (like Iron sulphate, Aluminium sulphate). This method disclosed will produce a final product of Yellow Gypsum (Calcium sulphate).

The chemical composition of LD slag fines used in this process from the waste recycling plant (WRP) at the Jamshedpur steelworks can be seen in Table 1.5 (86). The LD slag fines of 250 µm or smaller chemical composition in this process can be observed in Table 1.6 (86). Grinding will increase the costs associated with this invention while gathering slag fines of 250 µm or smaller for use in Port Talbot steelworks will depend on availability.

Table 1.5: Averaged of X-ray fluorescence (XRF) analysis LD slag fines taken randomly from WRP at Tata Steel plant, Jamshedpur, India (86)

Components	**Weight Percent (wt%)**			
	Average	**Minimum**	**Maximum**	**Variance**
Calcium Oxide (CaO)	51.36	37.35	60.06	7.79
Silicon Dioxide (SiO2)	15.71	10.97	26.51	2.1
Magnesium Oxide (MgO)	2.09	0.12	6.16	0.58
Aluminium Oxide (Al2O3)	0.931	0.52	3.76	0.05
Titanium Dioxide (TiO2)	1.14	0.6	2.43	0.03
Iron (Fe)	18.2	10.1	28.67	7.64
Sulphur (S)	0.016	0.005	0.177	0.01
Manganese Oxide (MnO)	0.446	0.18	4.41	0.03
Chromium Oxide (Cr_2O_3)	0.156	0.04	0.22	0
Phosphrous Pentoxide (P_2O_5)	3.24	2.06	5.65	0.16

Table 1.6: Chemical analysis of LD slag fines of 250 µm or smaller used in the process (86)

Parameters	**LD Slag fines Weight Percent (wt%)**
Iron (Fe(T))	14.17
Iron (II) Oxide (FeO)	11.61
Iron (III) Oxide (Fe_2O_3)	7.39
CaO	49.15
SiO2	11.75
P_2O_5	2.32
MgO	4.21
MnO	0.397
Al_2O_3	1
TiO_2	0.934
Loss on ignition	11
Sodium Oxide (Na_2O)	0.029
Potassium Oxide (K_2O)	0.008

1.5.2 Producing Calcium Sulphate from LD Slag Waste

The process digests the LD slag fines with sulphuric acid. The sulphuric acid solution reacts with calcium silicate, calcite and calcium hydroxide forming the slurry containing insoluble calcium sulphate and other soluble metal sulphates (87).

LD slag fines consists of a mixture of compounds compromised of some or all of the following chemical groupings: carbonates, silicates of calcium, magnesium, oxides of iron, aluminium, phosphorus, hydroxides of calcium and some amount of free lime (87). There may also be low concentrations of heavy metals such as cadmium, chromium, lead, mercury, nickel, platinum, and palladium. LD slag fines produce a highly alkaline solution (pH 11-13.5) when mixed with water: this alkalinity is primarily due to the presence of calcium hydroxide in the slag fines, or the slacking of calcium oxide occurs in the solution (87).

LD slag fines 250 μm or smaller, were used as the starting material, as observed within Figure 1.26, and the fines larger than 250 μm were grinded down. The starting material was then subjected to atmospheric leaching with sulphuric acid. LD slag fines, sulphuric acid and water were taken in the ratio specified as 1:1.4:7.6 and heated to 100-105 °C with continuous stirring in the reactor (stage 03) in Figure 1.26 to obtain a slurry (87). The slurry that was formed contained in-soluble calcium sulphate and other soluble salts in the solution. This slurry was then neutralised (stage 05) to pH 7 as observed within Figure 1.26 using 20% lime solution (87). The solid and liquid components were then separated, and the solid is then further dried at 50-60 °C for 24 hours (87). The dried material was designated as yellow calcium sulphate (gypsum). The filtrate was reused in this process, the filtrate was neutral and was added at the reactor (stage 03a) (87). The reuse of the filtrate meant the process was designated a zero-discharge process.

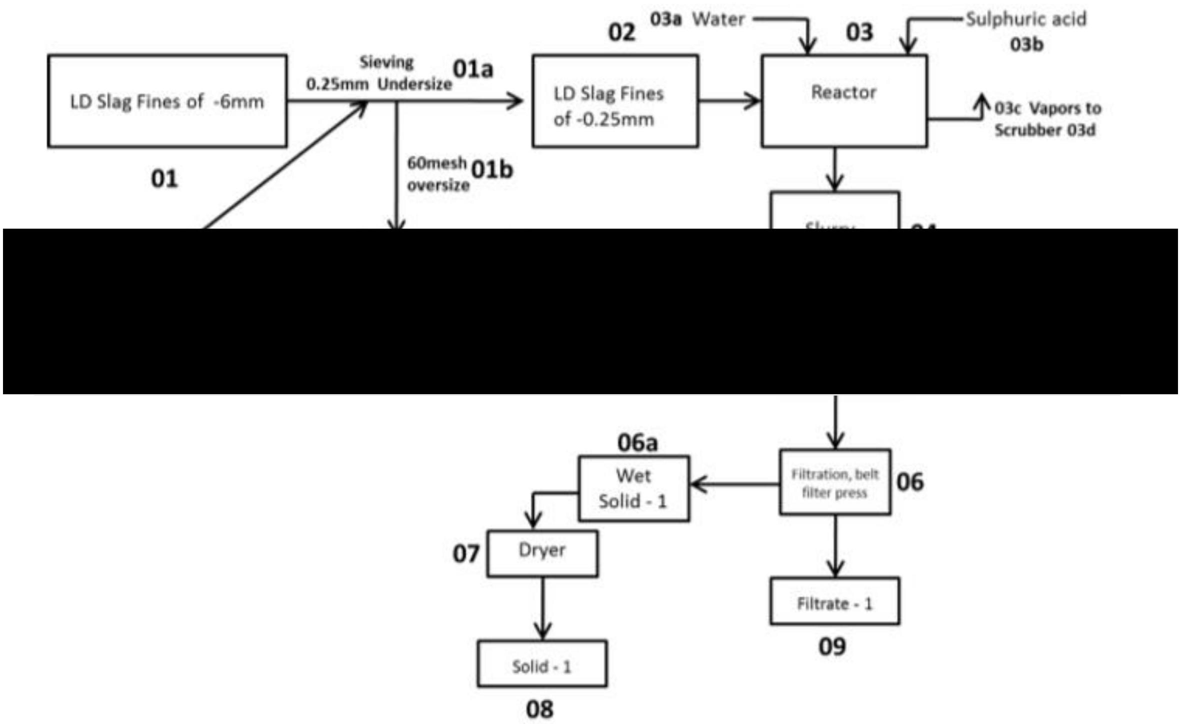

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Figure 1.26: Process flow sheet of yellow gypsum preparation (87)

The purity of the yellow calcium sulphate produced from the process of reacting LD slag fines using sulphuric acid solution varies directly with the corresponding abundance of silica in the LD slag fine (87). Silica remains insoluble along with calcium of LD slag fine and decreases the purity of the calcium sulphate formed. The purity will also be dependent on the sulphuric acid used for the digestion. The yellow colour of the calcium sulphate produced from the process, is due to the presence of iron sulphate along with calcium sulphate (88). The colour turns to red as the iron increases and decreases to pale yellow with any decrease in iron content in the LD slag fines (88). LD slag samples with higher concentrations of calcium, tended to produce the highest purity of yellow calcium sulphate product.

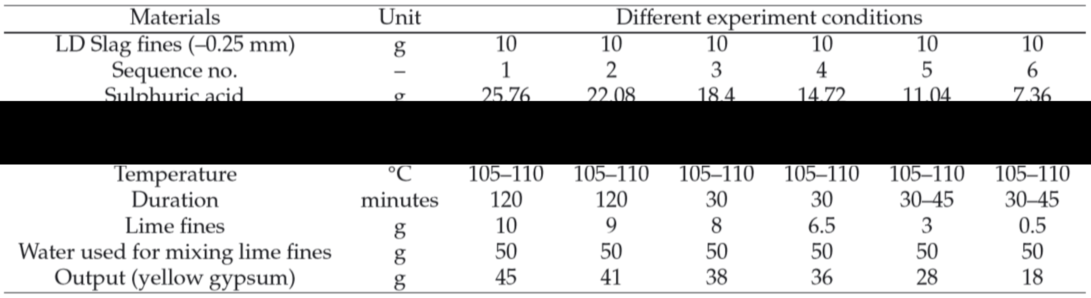
Due to the increased costs associated for dumping waste valuable products, alternative uses are being explored. Each hazardous waste has its inherent complications: toxicity, environmental pollutants and simply the quantity of waste generated. Sulphuric acid waste is toxic and is regulated as a hazardous waste, with the primary disposal method being incineration (86). The incineration of waste, or spent sulphuric acid is expensive and it has many regulatory disposal requirements. An objective identified in patent 572/KOL/2014 is to use lime fines generated in the lime making process and provide a use for sulphuric acid (which is a hazardous by-product from the copper concentrate smelting industries)(86). The potential use of other by-products within the process has IS opportunities.

A limitation of the process is the quality of calcium sulphate produced through treatment of LD slag fines with sulphuric acid. This is due to the constituents of the LD slag fines which vary both qualitatively and quantitively. It is also dependent on the quantity of sulphuric acid used for the treatment. Increase in quantity of sulphuric acid will require more quantity of lime fines for the neutralisation (stage 05).

1.5.3 Process Optimisation

From the literature relating to the patent, different process conditions were undertaken and evaluated. The controlled variable in the process optimisation was the mass of 250 µm or smaller LD slag fines and temperature of experiment (87). The independent variables were (87): 1. the quantity of sulphuric acid, water, lime fines and 2. the duration of the experiment. The dependent variable was the mass of the calcium sulphate produced. Through undertaking different process conditions an optimum process was identified. It was observed that sequence one produced the best yield when varying the independent variables.

From the research undertaken in the literature, an input of 10 g of LD slag fines, 25.76 g of sulphuric acid and 86 g of water was digested and then neutralised with 10 g of limes fines mixed with 50 g of water – this produced 45 g of yellow gypsum (87). Through the literature, a process efficiency of 98.33% was acquired (87). In order to compare the repeatability of this process, it needs to be repeated using the same experimental conditions and same quantity of materials inputted using LD slag fines from Port Talbot, UK.



Materials	Unit	Different experiment conditions					
LD Slag fines (–0.25 mm)	g	10	10	10	10	10	10
Sequence no.	–	1	2	3	4	5	6
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Temperature	°C	105–110	105–110	105–110	105–110	105–110	105–110
Duration	minutes	120	120	30	30	30–45	30–45
Lime fines	g	10	9	8	6.5	3	0.5
Water used for mixing lime fines	g	50	50	50	50	50	50
Output (yellow gypsum)	g	45	41	38	36	28	18

Figure 1.27: Different process conditions used for process optimisation (88)

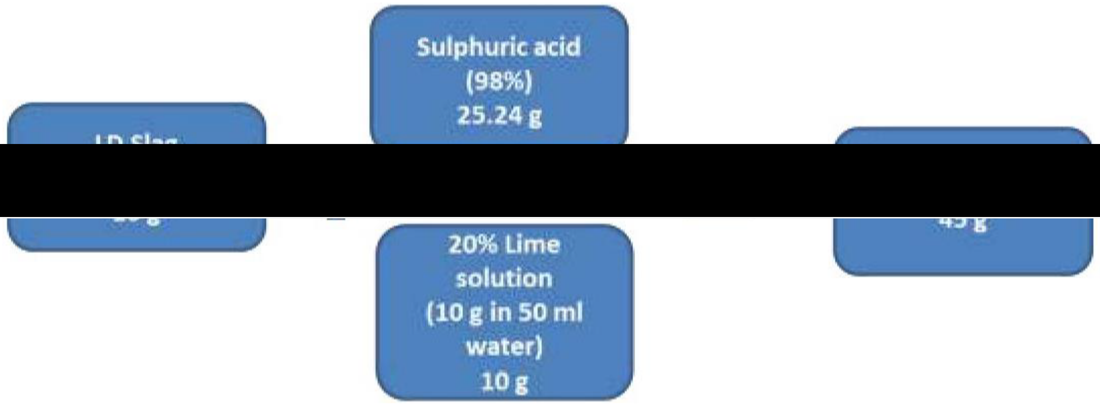


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Figure 1.28: Optimum mass balance profile of yellow gypsum synthesis process (87)

1.5.4 Chemical Reactions

Due to the composition and quantity of calcium within the LD slag fines, there are fluctuations due to various types of oxides along with calcium. A more accurate manifestation of the reactions of sulphuric acid with calcium compounds from Equation 1.15 through to Equation 1.24 (86): -

$$CaO + H_2SO_4 + H_2O \rightarrow Ca(OH)_2 + H_2SO_4 \qquad \textbf{Equation 1.15}$$

$$CaSiO_4 + H_2SO_4 + H_2O \rightarrow CaSO_4 + 2(H_2O) + SiO_2 + O \qquad \textbf{Equation 1.16}$$

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4.2H_2O + CO_2 \qquad \textbf{Equation 1.17}$$

The reaction of the excess sulphuric acid left after the digestion of the LD slag fines neutralised with the lime fines (86): -

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2(H_2O) \qquad \textbf{Equation 1.18}$$

While a manifestation of reactions involved can be represented (86): -

$$CaSiO_4 + H_2SO_4 + H_2O \rightarrow CaSO_4 + 2(H_2O) + SiO_2 + O \qquad \textbf{Equation 1.19}$$

$$P_2O_5 + 3(H_2SO_4) + 3O \rightarrow 2(H_3PO_4) + 3(SO_4) \qquad \textbf{Equation 1.20}$$

$$MgO + H_2SO_4 \rightarrow MgSO_4 + H_2O \qquad \textbf{Equation 1.21}$$

$$Fe_2O_3 + 2(H_2SO_4) \rightarrow 2(FeSO_4) + 2(H_2O) + O \qquad \textbf{Equation 1.22}$$

$$TiO_2 + H_2SO_4 \rightarrow TiSO_4 + H_2O + O \qquad \textbf{Equation 1.23}$$

$$Al_2O_3 + 3(H_2SO_4) \rightarrow Al_2(SO_4)_3 + 3(H_2O) \qquad \textbf{Equation 1.24}$$

This process was thought to have potential use as a method of valorisation of the BOF slag produced at the Port Talbot steelworks. In order to exploit this method at the Port Talbot steelworks, an assessment was undertaken to verify this process, identifying the chemical composition and particle size distribution of the BOF slag produced. Whilst conducting cost-benefit analysis and identifying potential IS opportunities and collaboration to commercialise this process.

1.6 Summary

1.6.1 Introduction

Iron and steel slag are registered as substances, by-products, or primary/secondary raw materials. These by-products must be re-used rather than the traditional methods of landfill. The steel industry over the last few decades has focussed its efforts on the improvement of by-product recovery and quality, centred not simply on existing processing and technologies, but development of innovative sustainable resolutions. Developing new innovative solutions has led the steel industry to save natural resources and reduce its environmental impact. BF slags are routinely utilised for recycling purposes, whilst the utilisation of BOF slag is far more challenging. The recycling of BOF slag is limited by its free lime and magnesia content leading to problematic swelling. The increasingly rigorous European regulation and the escalating disposal costs currently affect manufacturing industries, leading them to strengthen their efforts to improve the recycling rate of their by-products and waste. The potential utilisation of BOF slag at Port Talbot steelworks will have economic and environmental benefits from the large legacy stockpile of BOF slag readily available.

Closure of all Britain’s coal power plants by 2025 may potentially result in shortages of the gypsum supply in the UK and globally. Production of gypsum from a by-product of the steelmaking process, may provide commercial opportunities at the Port Talbot steelworks.

The process identified to produce yellow calcium sulphate from LD slag fines utilises the availability of sulphuric acid and lime fines which are generated during the production of lime from limestone in Jamshedpur, India. This invention utilises the availability of some of the major inputs of the process to produce yellow calcium sulphate, which may not be readily available in Wales. The invention also utilises LD slag fines of 250 μm or smaller, particle size distributions analysis of slag acquired from the Port Talbot steelworks which will increase the availability of slag fines. An assessment of the efficiency of yellow gypsum synthesis will be undertaken on BOF slag acquired from the Port Talbot steelworks.

The aims of this research are to assess the efficiency of the process of synthesis of yellow gypsum from various steelmaking slags from Port Talbot steelworks, and to carry-out detailed market analysis. In addition, to make recommendations regarding feasibility of commercialisation of this process at the steelworks. Analysis will be undertaken on the available BOF slag at the Port Talbot steelworks and synthetic yellow gypsum produced. The study will outline the chemical composition, particle size distribution, efficiency of synthesis of yellow gypsum, cost analysis and potential IS opportunities and collaboration to commercialise this process at the Port Talbot steelworks.

1.6.2 Deliverables

The overall research aim is to assess the efficiency of yellow gypsum synthesis from BOF slags from the Port Talbot steelworks. To ensure that the research is guided, and efficient, specific deliverables have been generated through collaboration with Tata Steel: -

- To assess the efficiency of the process of synthesis of yellow gypsum from various steelmaking slags, from Port Talbot steelworks.
- Conduct process optimisation steps where necessary, towards superior cost-benefit, environmental outcomes, and maximum resource efficiency.
- Conduct cost-benefit analysis on optimised process.
- Carry-out detailed market analysis and make recommendations regarding feasibility of commercialisation of the process of synthesis of yellow gypsum from steelmaking slags from Port Talbot steelworks in the UK.

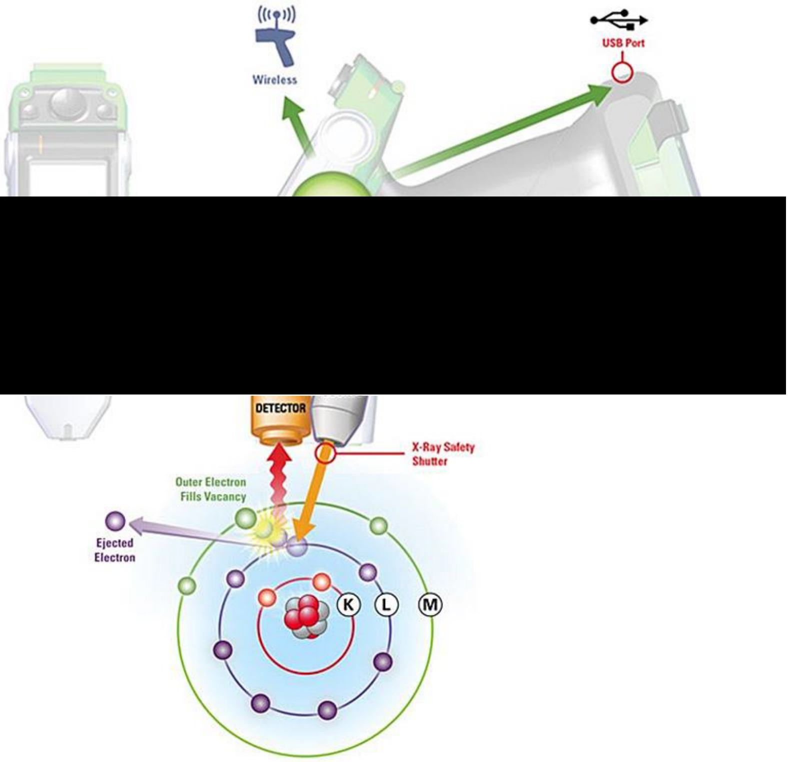
2 Experimental- Techniques and Procedures

This chapter outlines details of experimental techniques used in acquisition of results presented in subsequent chapters.

2.1 X-ray Analysis

2.1.1 X-ray Fluorescence

X-ray Fluorescence (XRF) is a non-destructive analytical technique to determine the elemental composition of materials (89). XRF analysers determine elemental composition by measuring the fluorescent (or secondary) X-rays emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-ray emissions that are unique for a specific element. XRF spectroscopy provides qualitative and quantitative analysis of material composition.



[redacted]

Figure 2.1: XRF process (90)

XRF occurs when a sample is irradiated by x-rays, and an electron can be ejected from its atomic orbit. To fill this space, an electron from a higher orbit (energy level) drops to lower orbit and emits a second x-ray (Figure 2.1). The energy (wavelength) of this fluorescent x-ray is characteristic of a particular element. This provides a means to qualitatively establish the elemental composition and quantitively measure the concentration of these elements (91). Measurements by XRF are carried out directly on the solid material (or liquid) with little to no sample preparation.

2.1.1.1 Instrument

All analyses were conducted with a Fischer Instrumentation Fischerscope XDALFD system and Fischer WinFTM software. Manufacturer recommended settings for detection of elements i.e. a 50 keV x-ray beam with Aluminium primary filter. A beam with circular cross-section with varying diameter between 0.3-1.0 mm was used. The appropriate beam diameter was selected for the size of the component being analysed, and to focus analysis on portions of components. Elements present were identified by emission signals indicated at the characteristic energies.

2.1.2 X-ray Diffraction

X-ray Diffraction (XRD) was utilised in this study to determine the elemental composition of slag samples and the synthetic yellow gypsum produced following treatment of the slag with sulfuric acid. This information is used to work out the conversion rate or yields of gypsum synthesis from the slags.

XRD is a powerful non-destructive technique for characterising crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample (92). The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material.

The structures of crystals and molecules are often being identified using x-ray diffraction studies, which are explained by Bragg’s Law. The law explains the relationship between an x-ray light shooting into and its reflection off from crystal surface. The law states that when the x-ray is incident onto a crystal surface, its angle of incidence (θ), will reflect back with a same angle of scattering (θ) as realised in

Figure 2.2. And, when the path difference (d) is equal to a whole number (n), of wavelength, a constructive interference will occur.

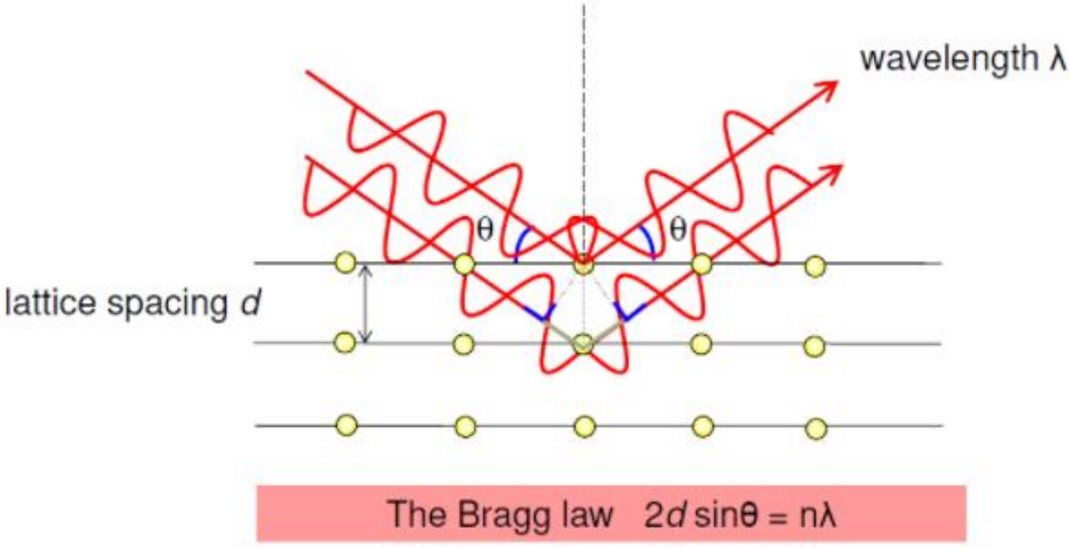


Figure 2.2: Bragg's Law

2.1.2.1 Instrument

All analyses were conducted using Bruker D8 Discover. This XRD combines a Eulerian cradle, allowing sample positioning and movement in 5 axis, and a 40kV Copper twist-tube source, for both point and line focus jobs, provide effective diffraction of "as is" components. In addition, the 1D Lynx-eye detector provides increased data acquisition rates, speeding up testing considerably, allowing both qualitative and quantitative measurements of a wide range of materials. Samples can be up to 500g in weight with heights up to 500mm.

2.2 Differences Between XRF and XRD

In summary, the difference between XRF and XRD is simple: XRF analyses for Chemistry while XRD determines the mineralogy. XRD identifies and measures the presence and amounts of minerals and their species in the sample, as well as identify phases. XRF will produce and assay by giving information on the chemical composition of your sample, without indicating what phases are present in your sample.

XRF analysis determines the elemental composition of a sample but does not provide information about how the various elements are combined. Such mineralogical information is only available through X-ray diffraction (XRD). XRD is a versatile and non-destructive analytical technique that reveals detailed structural and chemical information about the crystallography of materials.

2.3 Scanning Electron Microscopy

Scanning electron microscope (SEM) obtained high resolution images of the slag and synthetic gypsum samples during this study. SEM is an electron probe method, which provides high resolution images of samples, by irradiating their surfaces with a focussed beam of electrons in a raster scanning pattern and detecting secondary or backscattered electron signals.

Since SEM uses excited electrons for imaging, the electron microscope must act in scope in a high vacuum environment, such that the electrons are not absorbed by atmospheric molecules as they move to the sample and detector. The sample must be able to complete an electric circuit, meaning it must be conductive or made to be conductive by sputter coating. The greatest disadvantage here, is that surface is cloaked with the coating, which means that the information on the sample’s atomic number information is lost. In addition, the topography of the surface can be adjusted, or incorrect atomic information can be collected.

2.3.1 Instrument

Analysis of slag composition was conducted with a Hitachi TM3000 tabletop microscope running BrukerQuantax 70 software. SEM imaging of platinised counter-electrodes at 5 kV using a 30-micron aperture (Figure 2.3).

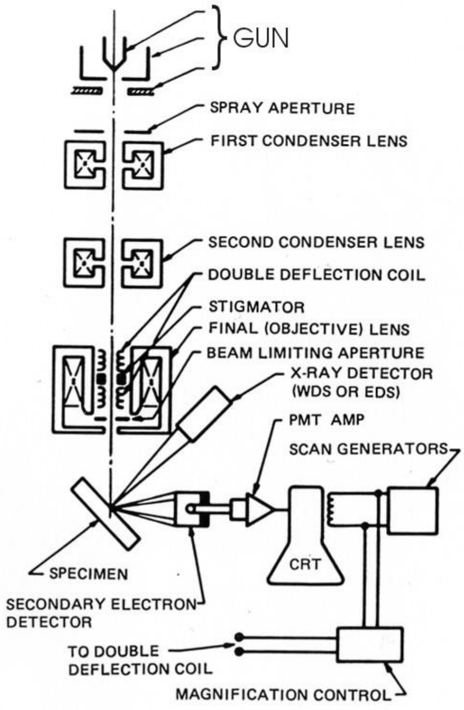


Figure 2.3: Schematic drawing of the SEM

2.4 Energy Dispersive X-ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDS) was applied in this study to determine elemental composition of slag and synthetic gypsum samples during this study. EDS is an analytical technique that enables the chemical characterisation/elemental analysis of materials. A sample excited by an energy source (such as the electron beam of an electron microscope) dissipates some of the absorbed energy by ejecting a core-shell electron. A higher energy outer-shell electron then proceeds to fill its place, releasing the difference in energy as an X-ray that has a characteristic spectrum based on its atom of origin. This allows for the compositional analysis of a given sample volume, that has been excited by the energy source. The position of the peaks in the spectrum identifies the element, whereas the intensity of the signal corresponds to the concentration of the element (93).

As previously stated, an electron beam provides sufficient energy to eject core-shell electrons and cause X-ray emission. Compositional information, down to the atomic level, can be obtained with the addition of an EDS detector to an electron microscope. As the electron probe is scanned across the sample, characteristic X-rays are emitted and measured; each recorded EDS spectrum is mapped to a specific position on the sample. The quality of the results depends on the signal strength and the cleanliness of the spectrum. Signal strength relies heavily on a good signal-to-noise ratio, particularly for trace element detection and dose minimization (which allows for faster recording and artifact-free results). Cleanliness will impact the number of spurious peaks seen; this is a consequence of the materials that make up the electron column.

A SEM equipped with EDS analytical capabilities is a powerful tool for carrying out elemental analysis of the input and output of the process. Signals produced in an SEM/EDS system include secondary and backscattered electrons that are used in image forming for morphological analysis, as well as X-rays that are used for identification and quantification of chemicals present at detectable concentrations. EDS can detect major and minor elements with concentrations higher than 10 wt% (major) and minor concentrations (concentrations between 1 and 10 wt%). The detection limit for bulk materials is 0.1 wt% therefore EDS cannot detect trace elements (concentrations below 0.01 wt%) (94).

A system by which quantitative analysis of target elements in EDS, can be conducted without using the standard specimen in each analysis. Standardless electron probe microanalysis provides quantitative composition data from evaluating a recorded X-ray spectrum by means of fundamental physical formulas and extensive atomic databases (95). Modern standardless analysis is sufficiently accurate and reliable for a wide range of applications in research, education, environmental protection, production, and many other fields. The ease of use and reliability of standardless electron probe microanalysis are unique features, which, among others, account for the wide acceptance of this analysis method.

2.4.1 Instrument

Analysis of waste thermocouple filaments was conducted with a Hitachi TM3000 tabletop microscope running BrukerQuantax 70 software for EDS analysis. A 15 kV beam was used.

2.5 Microwave Plasma-Atomic Emission Spectrometer

Microwave Plasma-Atomic Emission Spectrometer (MP-AES) was utilised in this study to determine the contents of this filtrate produced during the experimental analysis undertaken. MP-AES analysis was utilised to determine if any worth could be utilised from the filtrate.

MP-AES consists of a microwave induced plasma interfaced to an atomic emission spectrophotometer (AES). It is used for simultaneously multi-analyte determination of major and minor elements. MP-AES employs microwave energy to produce a nitrogen plasma discharge supplied from a gas cylinder or extracted from ambient air. A schematic diagram for an MP-AES can be observed in Figure 2.4.

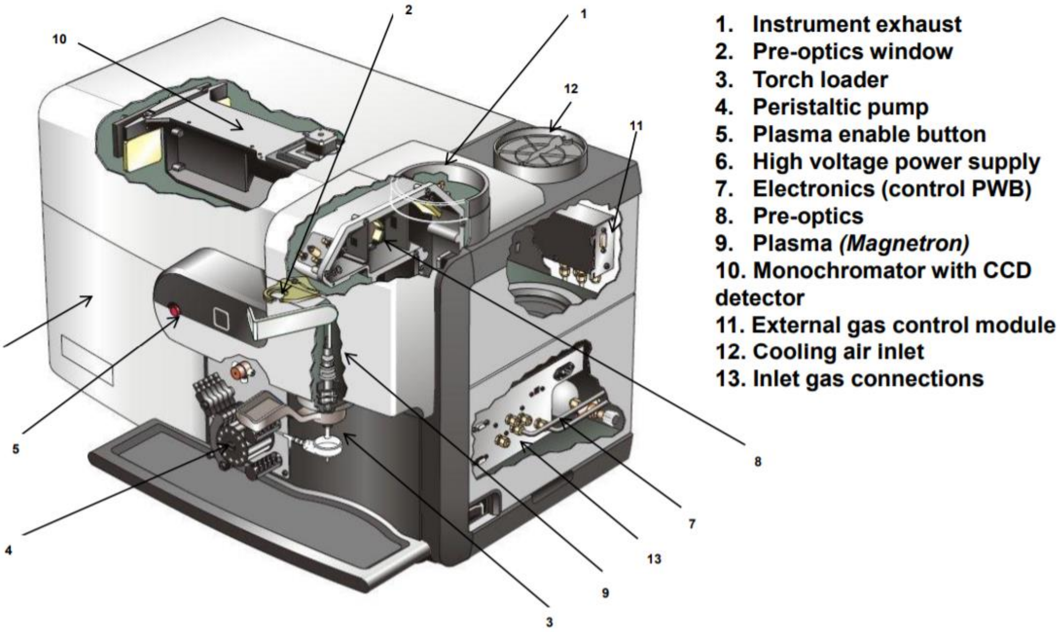


Figure 2.4: Schematic Diagram of the MP-AES

Samples are typically neutralised prior to interaction with the plasma in MP-AES measurements. The atomised sample passes through the plasma and electrons are promoted to the excited state. The light emitted electrons return to the ground state, light is separated into a spectrum and the intensity of each emission line measured at the detector. Most determined elements can be measured with a working range of low part per million (ppm) to weight percent (wt%).

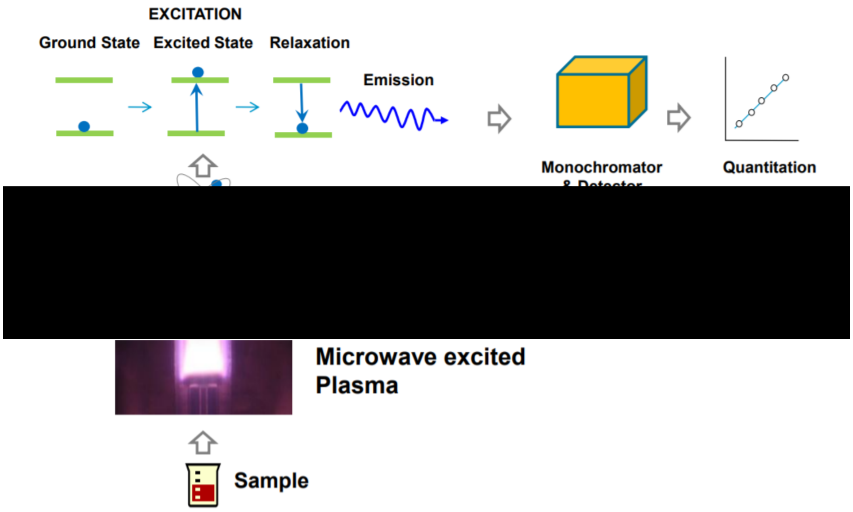


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Figure 2.5: Microwave plasma emission overview (96)

2.5.1 Instrument

MP-AES analysis was undertaken using an Agilent 4200 MP-AES system, determining the element content at the associated wavelengths: -

- Calcium (393.366 nm)
- Iron (371.993 nm)
- Zinc (213.857 nm)

2.6 Sieving

This method was utilised in this study to determine the particle size distribution of the slag acquired from Tata Steel, Port Talbot. Particle size distribution is an index indicating what sizes (particle size) of particles are present in what proportions in the sample particle group to be measured.

Sieving is a separation technique based on the difference in particle size. The sieve is responsible for retaining the larger particles. Sieve analysis is a technique used to determine the particle size distribution of a given material. This method is performed by sifting a sample through a stack of wire mesh sieves and separating it into discrete size ranges. A sieve shaker is used to vibrate the sieve stack for a specific period. Vibration allows irregularly shaped particles to reorient as they fall through the sieves.

Figure 2.6: Example of a sieve shaker equipment and wire cloth sieves

3 The Development and Evaluation of Sampling and Experimental Procedures

It was essential to obtain an accurate characterisation data for the BOF Slag from the Tata Steel, Port Talbot to compare to results obtained in Jamshedpur. Before undertaking characterisation of the input of the process, procedures for appropriate sample preparation, processing and analysis must be identified.

3.1 Sampling

Sampling is a sequence of selective and non-selective operations ending with the selection of one or several assay portions submitted to the analytical process in their entirety (97). The sample may be described as homogenous or heterogenous, a homogenous sample is composed of strictly identical constitutive units, contrasted with the heterogenous sample composed of non-strictly identical constitutive units.

Regardless of how the sample is obtained, its composition must be representative of the bulk of material from which it was removed, and this allows the analytical results to be meaningful. Non representative sampling results in incorrect analysis, process failure and unacceptable final products. To achieve samples of appropriate quantities, the coning and quartering method was applied. It is essential that the samples selected for measurement and analysis, should be representative of the bulk in particle size distribution and the relative fractions of their various constituents. This is irrespective of whether a physical or chemical assay is to be calculated, since these characteristics are in-dependent (98). Statistically, the goals of the sampling process are (99):

1. To obtain a mean analyte concentration that is an unbiased estimate of the population mean. This goal can be realised only if all members of the population have an equal probability of being included in the sample.
2. To obtain a variance in the measured analyte concentration that is an unbiased estimate of the population variance so that valid confidence limits can be found for the mean, and various hypothesis tests can be applied. This goal can be reached only if every possible sample is equally likely to be drawn.

Both goals require obtaining a random sample. The reduction in size of a granular or a powdered sample was achieved by formation of a conical heap which is spread out into a circular, flat cake. The cake is divided radially into quarters and two opposite quarters are combined. The other two quarters are discarded. This process is repeated to achieve a desired quantity for final use (e.g. as the laboratory sample or as the test sample). If the process is performed only once, coning and quartering is no more efficient than taking alternate portions and discarding the others.

Great care must be undertaken when obtaining a sample through coning and quartering. As the initial powder sample is poured, it will undertake a range of processes that will result in the segregation of particles according to relative size. This is due to their flowability being the poorest, the finer particles will collect at the centre of the cone, the coarser particles will flow towards the edges of the cone. Hence, each quarter of a poured cone will become severely segregated by the act of pouring, making the process of subdivision and recombination critical (Figure 3.1). It is not unusual to obtain large standard deviations in particle-size results when this method is used to obtain a sample.

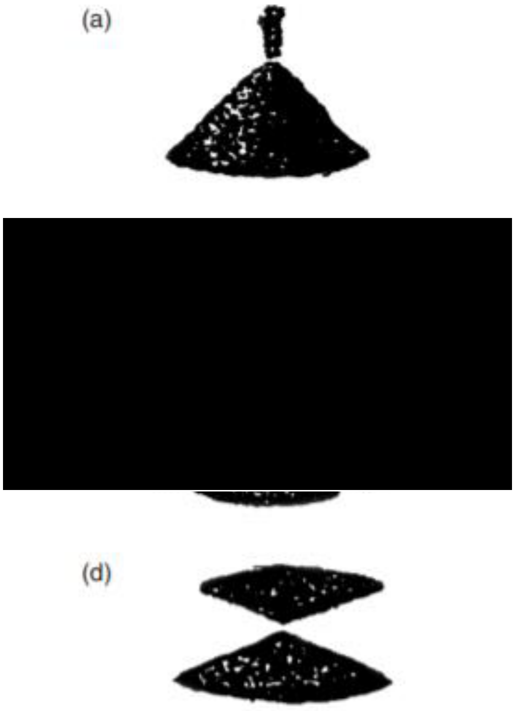

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Figure 3.1: Performance of coning and quartering showing (a) pouring of the initial cone, (b) division of the flattened cone into halves, (c) further division of the flattened cone into quarters, and (d) removal of alternate quarters to define the subdivided sample (99)

3.2 Precision and Accuracy Development

To improve the reliability and to obtain the variability of the results, three portions (replicates) of the sample were acquired for the entire analytical procedure. The mean was identified as the central value for a set of replicate measurements (the mean is also called the arithmetic mean or the average). Obtaining an average of a set of results is often used to improve precision. The mean ($\bar{x}$) is obtained by dividing the sum of the replicate measurements by the number of measurements in the set: -

$$\textbf{Mean } (\bar{x}) = \frac{1}{N}\sum_{i=1}^{N} x_i \qquad \textbf{Equation 3.1}$$

where x_i represents the individual values of x making up the set of N replicate measurements. Towards calculating the precision of the equipment to calculate the chemical composition of the input and output of the process, a sample standard deviation (s) was obtained. The standard deviation is estimated by examining a random sample taken from the population of the steelmaking slag. Thus, the sample standard deviation (s) is given by the equation: -

$$s = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \bar{x})^2} \qquad \textbf{Equation 3.2}$$

Where $\bar{x}$ is the mean of the sample, the denominator $N - 1$ is the number of degrees of freedom in the vector. Standard deviation is a number used to tell how measurements for a group are spread out from the mean value.

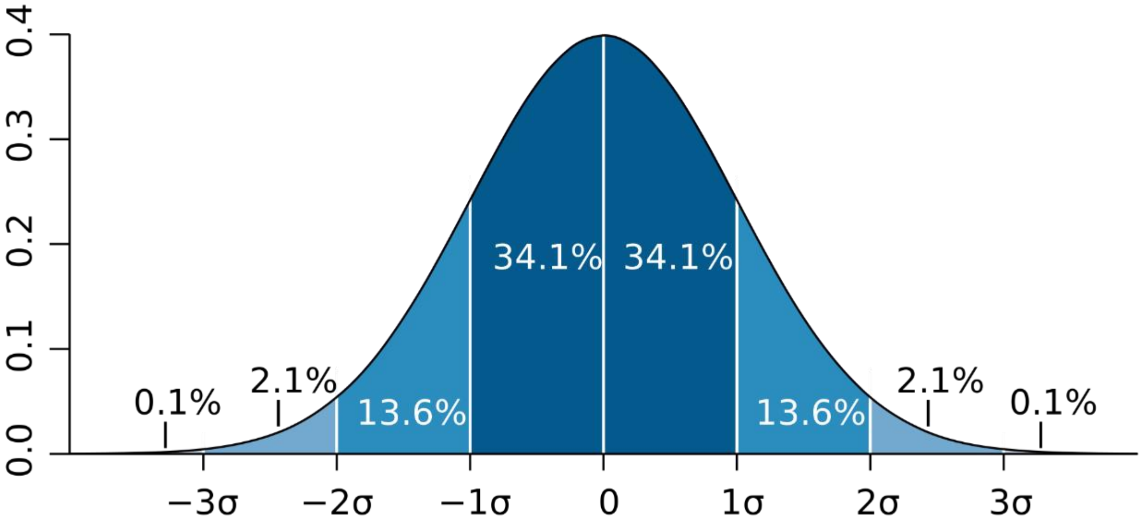

Figure 3.2: Gaussian distribution function

The area beneath a gaussian distribution function may be used to describe the physical events (Figure 3.2). The gaussian distribution is a continuous function which approximates the exact binomial distribution of events. Within one standard deviation of the mean, 68.3% is under the Gaussian curve. Thus 68.3% of the results within the samples are within parameters. For normal distributions, the two points of the curve which are one standard deviation from the mean are also the inflection points.

The standard deviation of each mean is identified as the standard error of the mean and is given the symbol, s_m. The standard error is inversely proportional to the square root of the number of data points N used to calculate the mean. Thus, the standard error of the mean is given by the equation: -

$$\mathbf{s_m = \frac{s}{\sqrt{N}}} \qquad \textbf{Equation 3.3}$$

These equations will be used to determine the precision and accuracy of an analytical process. This will ensure that the instrument used while undertaking analytical procedures proves to be accurate and correct.

3.3 Experimental Procedure

3.3.1 Synthesis of Yellow Gypsum (Calcium Sulphate)

For the synthesis of yellow gypsum, LD/BOF slag fines were taken as the starting material and subjected to atmospheric leaching with sulphuric acid. LD/BOF slag fines, sulphuric acid and water were taken in the ratio 1:1.4:7.6 and heated to 105-110 °C for two hours for continuous stirring to obtain the slurry. The slurry was neutralised to pH7, using different neutralising agents. The solid and liquid components were then separated through filtration and the solid product was dried at 50-60 °C in a hot air oven. The dried material was designated as yellow gypsum.

3.3.2 Process

To repeat the process for calcium sulphate production from BOF slag created at the Port Talbot steelworks, the corresponding process must be repeated at laboratory scale. Thus it would reflect the process optimisation undertaken in the literature (87). It was essential whilst undertaking this experiment for the same quantity of slag, sulphuric acid, water in the reactor (stage 03) in Figure 1.26 whilst maintaining the constants such as the temperature and time. The main processes undertaken in the process is the sample digestion, neutralisation, filtration and drying.

- Digestion: The decomposition of a sample into liquid form by treatment with enzymes or strong acids or alkalis.
- Neutralisation: An acid-base reaction in which an acid reacts with a base to form salt and water. The pH of the neutralised solution depends upon the acid strength of the reactants and their concentrations.
- Filtration is a physical or chemical separation process that separates solid matter and fluid from a mixture using a filter medium that has a complex structure through which only the fluid can pass.
- Drying is the process of using evaporation to remove water from a solution, suspension, or other solid-liquid mixture.

3.3.3 Experimental Procedure

The slags sourced from the Port Talbot steelworks, firstly undertook sampling utilising coning and quartering, and was further separated into desired particle size distributions. The sieve shaker was utilised for 10 minutes to separate 1kg of slag into desired particle size distributions. The sieves utilised throughout this research can clearly be observed in Figure 3.3.

Figure 3.3: Sieves

The desired particle size distributions obtained are realised below: -

a) 250 µm or smaller
b) 250-500 µm
c) 500-710 µm
d) 710-1000 µm 1
e) 1000-1400 µm
f) 1400-2360 µm
g) 2360 µm or greater

Slag sourced from the Port Talbot steelworks, sulphuric acid (ACS Reagent, 95-98%) and distilled water were taken in the ratio 1:1.4:7.6. An analytical balance was utilised when undertaking measurements of the inputs and outputs of the procedure. Analytical balance measure masses from around 320 g to sub-milligram (320-0.0001 g), this ensures that measurements taken for inputs and outputs of the process were reliable and accurate. Atmospheric leaching (reactor) was undertaken on the mixture, using a clamped 500 ml beaker with a magnetic stir clamped on a hot plate containing a magnetic stirrer. Whilst in the reactor, the mixture was heated to 105-110 °C for two hours with continuous stirring. The resultant slurry was then neutralised to pH-7 using a neutralising agent. Calcium Hydroxide (ACS Reagent ≥95%) mixed with distilled water were utilised as the neutralising agents throughout this research. The slurry once neutralised was vigorously tested using pH paper to ensure pH-7 was achieved. Once pH-7 was achieved, vacuum filtration was undertaken using a clamped büchner flask with conical filter adapter with filter paper, and a vacuum applied to the side arm of the filter flask. The solution to be filtered is poured into the funnel and drawn through the perforated plate by the vacuum. Once the solid and liquid components are separated, the solid product is then dried in a laboratory oven at 50-60 °C for 24 hours, to remove all moisture. The resultant solid (output) is then weighed and stored for further analysis.

3.4 Percentage Yield

Percentage yield is the percentage ratio of actual yield to theoretical yield. It is calculated to be the actual (experimental) yield divided by the theoretical yield multiplied by 100% as realised in Equation 3.4. This is utilised within this research to assess conversion within the procedure.

$$\textbf{Percentage Yield} = \frac{\textbf{Actual Yield}}{\textbf{Theoretical Yield}} * \mathbf{100\%} \qquad \textbf{Equation 3.4}$$

Where:

- Actual yield is the mass of product obtained from a chemical reaction.
- Theoretical yield is the mass of product obtained from the stoichiometric using the limiting reactant to determine product.
- Units for actual and theoretical yield need to be the same (grams or moles).

The actual yield is usually less than the theoretical yield. The reasons for this include:

- Incomplete reactions, in which some of the reactants do not react to form the product.
- Human error.
- Practical losses during the experiment such as filtering or neutralisation.
- Side reactions.

The higher percentage yield will have an economical cost associated with this recycling process. This will be calculated when repeating the process for direct comparison with the literature.

To assess the repeatability of this process, we need to identify if repeating this process with slag from Port Talbot results in a match. Through the literature, a mass balance was taken by taking the ratio of the sum of the weight of the input materials in the process to yield weight of the process. The simple mass balance flow profile is represented, and process efficiency calculation is shown by: -

$$\boldsymbol{Process\ efficiency} = \left(\frac{\boldsymbol{Output\ of\ the\ process}}{\boldsymbol{Inputs\ to\ the\ process}}\right) * \mathbf{100} \qquad \textbf{Equation 3.5}$$

3.5 Analysis of Calcium Conversion

Determining the quantity of calcium sulphate produced during the leaching process of the synthesis is crucial. One of the main chemical reactions that is undertaken during the synthesis of yellow gypsum from the manifestation of reactions can be seen in Equation 3.6: -

$$\boldsymbol{CaSiO_4 + H_2SO_4 + H_2O \rightarrow CaSO_4 + 2(H_2O) + SiO_2 + O} \qquad \textbf{Equation 3.6}$$

To monitor the calcium being converted from input of the process to the output of the process, elemental analysis was essential. To determine the yield of calcium converted during the leaching of recovered BOF slag, XRD elemental analysis was undertaken on the recovered BOF slag (input) and the synthetic gypsum produced (output). To ensure that the conversion of calcium was accurate, neutralisation with a twenty percent lime (calcium hydroxide) solution is unsuitable to determine the calcium converted from the slag to the gypsum. To produce synthetic gypsum, neutralisation of the slurry produced from leaching was required. Using the methods from the literature, neutralising the excess sulphuric acid left after the digestion process with the lime fines will produce additional calcium sulphate. This additional calcium sulphate will impact the yield of calcium being converted from the slag to the gypsum.

$$\boldsymbol{Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2(H_2O)} \qquad \textbf{Equation 3.7}$$

To accurately determine the yield of calcium converted during the leaching process, an alternative inorganic compound was identified. Sodium hydroxide (NaOH) was identified as an alternative inorganic compound to neutralise the excess sulphuric acid. When sodium hydroxide reacts with sulphuric acid completely, it leads to the formation of sodium sulphate and water as a product as realised in Equation 3.8: -

$$\boldsymbol{2NaOH + H_2SO_4 \rightarrow NaSO_4 + 2(H_2O)} \quad \textbf{Equation 3.8}$$

Neutralisation with sodium hydroxide will mean no additional calcium sulphate is produced from the neutralisation stage, which means the only calcium converted at any stage of the process will be the leaching of recovered BOF slag. As the recovered BOF slag is the only source of calcium, determining the mass of calcium within the recovered BOF slag and mass of calcium within the synthetic gypsum produced allows the calcium yield to be calculated. Elemental analysis will determine the amount of calcium oxide (CaO) present within the recovered BOF slag and the synthetic gypsum. Once the quantity for calcium oxide is identified, next is to calculate the quantity of calcium the molecular weight: -

Calculation 3.1

$$\boldsymbol{CaO = 56.0774\ g/mol}$$

$$\boldsymbol{Ca = 40.078\ g/mol}$$

$$\boldsymbol{O = 15.994 g/mol}$$

$$\boldsymbol{Ca\%\ in\ CaO = \frac{40.078}{56.0774} * 100 = 71.469\%}$$

Calcium represents 71.45% of calcium oxide. Once the elemental analysis is complete, the weight percent of calcium can be identified. Throughout the process of producing synthetic gypsum, the measurement of each input to the process was logged. To calculate the mass of calcium in the slag and gypsum, the following equation was used: -

$$\boldsymbol{Mass\ of\ Ca\ in\ sample = Weight\ percent\ Calcium * Mass\ of sample}$$

Equation 3.9

The yield of calcium could be calculated from the following equation: -

$$\boldsymbol{Yield(\%) of\ Ca = \frac{Mass\ of\ Ca\ in\ input}{Mass\ of\ Ca\ in\ output} * 100}$$ **Equation 3.10**

The yield of calcium was monitored when monitoring the affects the leaching of recovered BOF slag. The experimental procedure defined in chapter “3.3.3 Experimental Procedure” is repeated, but Sodium Hydroxide (ACS reagent, ≥97.0%, pellets) is utilised as the neutralising agent as a replacement for Calcium Hydroxide (ACS reagent ≥95.0%).

3.6 EDS/XRD Precision and Accuracy Comparison

Establishing the precision and accuracy of the readily available standardless EDS at Swansea University compared to XRD at the Port Talbot steelworks would permit less reliance on Tata Steel for XRD analysis and enable more research to be undertaken in the agreed timeline. The EDS method was utilised as it has a high speed of data collection and ease of use, enabling analysis to be done quickly and when required. The XRD at Tata Steel is used daily to determine the chemical composition of the liquid slag produced during each ‘heat’ and the liquid steel produced from the BOF process. The XRD results obtained were considered precise and accurate in this study, because the XRD used daily in the Port Talbot steelworks, regularly tested, and maintained.

Standardless EDS analysis is undertaken throughout this research. To identify the precision of the EDS for elemental analysis, three methods were identified. Different magnifications were selected, to select the most precise magnification, and thus the standard error was identified for each. The results obtained through EDS analysis would be compared with XRD analysis, and the identical sample would be used for both analytical techniques.

Slag fines of 250 µm or smaller were acquired, then cone and quartered until a suitable sub-sample was identified for elemental analysis. This was important for the analytical analysis to be undertaken on the input and output of the process, also enabling key cost-effective recommendations to be made. EDS specimens must be sputtered with conductive coating to avoid charging issues with electrons.

Elemental analysis was undertaken to identify the optimum precision of the EDS going forward in the experimental procedure. The instrument precision was being tested to ensure this method was accurate, when using the data acquired from this experiment set out later when assessing the synthesis of gypsum. The following magnification were selected: -

- At 100x magnification
- At 500x magnification
- At 1000x magnification

At each location the mean, standard deviation, relative standard deviation, range, and standard error were calculated for each repeat of each location on the sub-sample. The average for each of the six locations was then calculated, allowing comparison on how the results vary depending on the magnification. The standard error was calculated to identify the optimum magnification for elemental analysis. These values were calculated to see how the results vary when repeating the analysis multiple times on one location to identify the variance in repeated results. Once the optimum magnification is selected, all elemental analysis using the EDS would be undertaken at this magnification.

Table 3.1: Magnification comparison for elemental analysis of the slag

	100X Magnification		**500X Magnification**		**1000X Magnification**	
Element	**Average (wt%)**	**Standard Error**	**Average (wt%)**	**Standard Error**	**Average (wt%)**	**Standard Error**
Oxygen	46.66	0.33	47.65	0.73	47.94	0.54
Calcium	27.55	0.78	28.11	1.32	28.76	1.41
Carbon	10.59	0.29	10.59	0.73	7.62	0.46
Iron	5.26	0.30	4.85	0.66	5.31	0.68
Silicon	4.79	0.30	4.37	0.35	4.71	0.42
Magnesium	2.21	0.23	1.75	0.27	2.40	0.55
Aluminium	1.83	0.19	1.67	0.26	1.86	0.38
Sulphur	0.49	0.06	0.52	0.09	0.48	0.10
Manganese	0.49	0.08	0.38	0.11	0.72	0.17
Phosphorus	0.10	0.04	0.10	0.06	0.18	0.09

As realised in Table 3.1, the standard error was calculated for each element at each magnification to allow comparison to determine the accuracy of the findings at each magnification. To calculate the accuracy of EDS, the result would be compared with results from XRD analysis. This would be undertaken to determine the accuracy of the results obtained from EDS analysis. XRD analysis was undertaken in Tata Steel, Port Talbot and these results were viewed as accurate. The EDS findings were compared with XRD, comparing the elemental findings for oxygen, calcium, iron, and silicon.

Table 3.2: EDS and XRD elemental comparison

Particle Size Distribution	**Analysis**	**Elemental Analysis Average (wt%)**			
		Oxygen	**Calcium**	**Iron**	**Silicon**
250um or smaller	EDS	46.66	27.55	5.26	4.79
	XRD	29.89	21.13	15.63	7.41
250-510um	EDS	45.20	17.90	10.04	3.84
	XRD	16.14	20.79	18.26	8.39
510-710um	EDS	47.88	24.40	5.32	4.21
	XRD	16.59	22.06	18.12	6.81
710-1000um	EDS	47.45	18.58	8.36	4.41
	XRD	17.09	22.63	18.76	6.70
1000-1400um	EDS	48.16	16.30	8.07	4.01
	XRD	17.22	23.28	18.45	7.13
1400-2360um	EDS	48.37	19.45	3.51	4.15
	XRD	17.24	24.31	17.54	6.76
2360um or greater	EDS	43.22	27.19	4.87	4.98
	XRD	18.95	28.27	17.83	6.91

One additional difficulty associated with EDS analysis is the thickness of the sample. Sample thickness can bring energy levels closer together, thus making electrons easier to move to outer energy levels, which can in turn cause deviation in the results. Additionally, X-rays are not particularly effective at penetrating beyond several nanometres in samples, which means that only surface layers can be efficiently measured by the technique. As such, if there is a discrepancy between the outer and inner material layers, it will not necessarily appear in EDS. If the concentration of an element in the sample is too low, the amount of energy given off by X-rays after hitting the sample will be insufficient to adequately measure its proportion. These are limitations of EDS that must also be selecting a favoured analytical approach.

EDS is generally considered semi-quantitative elemental analysis method. Standardless EDS analysis was undertaken throughout this research due it ease of use and reliability. For analyses requiring higher degree of quantitative accuracy, standards can be incorporated into the quantification routine. In most cases systematic errors of about 1% can be achieved even when using pure element standards or simple compounds.

As realised in Table 3.2, the elemental average varies for EDS and XRD results. The same sub-samples were used for the EDS and XRD analysis. As the same sub-sample for each particle size distribution is used for both analytical procedures, it is expected that the results would be consistent. When comparing all four elements, the results are not consistent and not comparable. There are large variances in the results for EDS and XRD. As the results are not consistent with each other, it was decided the use of XRD would produce more accurate and reliable results. XRD measures relatively large sample volumes (up to 10 grams), resulting in a more representative characterisation of the sample. The same sub-sample was analysed for both procedures, and XRD analysis takes a larger sample than EDS analysis, thus results may vary depending on the location and magnification analysed when undertaking EDS analysis.

3.7 Summary

The sampling procedure has been outlined for this research, to gain a representative sample for the bulk of the material obtained. The experimental procedure has been outlined for laboratory scale operation employing Patent 572/KOL/2014. The precision and accuracy of experimental techniques has been undertaken (on the sample acquired). The favoured analytical procedure in obtaining elemental analysis for slag obtained from the Port Talbot steelworks and the synthetic yellow gypsum produced through use of the process has been discussed above. A method has been developed to examine the calcium conversion during the process, assisting in assessment for the yield of calcium throughout the investigation.

4 Development of Methods for Analysing Yellow Gypsum Synthesis

The ‘analysis’ undertaken is an estimation of a series of critical contents. Analysis directly provides the chemical composition and the size distribution of the samples acquired from the Port Talbot steelworks.

4.1 Chemical composition (Port Talbot)

The primary components of LD slag are calcium silicate, calcium carbonate, calcium hydroxide and free lime, which collectively account for a range of 30-60% of the BOF slag produced in Tata Steel Port Talbot. Other compounds can proportionately vary in chemical composition, due to the composition of the feed materials to the BOF convertor, operating temperatures, and time of slag generation in the steelmaking process.

The total chemistry given in Table 4.1 is the sum of all the oxide components and iron. In identifying the mean chemical composition of BOF slag at Port Talbot steelworks, specific historical data was acquired. That is, 7325 data samples were acquired, and statistical analysis were undertaken. The mean, minimum, maximum, variance, standard deviation, relative standard deviation, and range were all calculated. The standard deviation determines the measure of dispersion, the deviation being a measurement of the spread between data. This data was identified through XRF analysis at the Port Talbot steelworks. These 7325 samples were acquired directly from the BOF, cooled and then XRF is undertaken on each sample. Each sample represents one ‘cycle’ of BOS. These results acquired represent historical data for the liquid slag produced at Port Talbot steelworks. XRF analysis was not undertaken on the liquid slag produced at Tata Steel plant, Jamshedpur, India in the literature and unfortunately sourcing this data during this study was unachievable.

Table 4.1: Liquid BOF slag composition at the Port Talbot steelworks

Components	**Mean (wt%)**	**Minimum (wt%)**	**Maximum (wt%)**	**Variance**	**Standard Deviation (1σ)**	**Relative Standard Deviation (%)**	**Range**
Fe	19.13	9.37	33.73	9.66	3.11	0.16	24.36
CaO	44.33	30.14	60.64	9.34	3.06	0.07	30.50
SiO_2	14.25	7.71	32.67	2.59	1.61	0.11	24.96
MgO	7.64	3.38	19.85	2.33	1.53	0.20	16.47
Al_2O_3	2.30	1.03	10.40	0.38	0.62	0.27	9.37
MnO	2.26	1.11	11.23	0.29	0.53	0.24	11.12
P_2O_5	1.34	0.44	4.02	0.06	0.24	0.18	3.58
S	0.02	0.00	0.29	0.00	0.01	0.43	0.29
TiO_2	0.75	0.26	1.37	0.02	0.13	0.17	1.11
V_2O_5	0.68	0.19	1.58	0.05	0.21	0.32	1.39

The historical data acquired at the Port Talbot steelworks can be compared to the data acquired at the Tata Steel plant, Jamshedpur, India. XRF analysis was undertaken at both sites to determine chemical composition. As observed in Table 4.2, the average weight percentage of calcium oxide is 7% lower at the Port Talbot steelworks, whilst this is liquid slag compared to LD slag fines which have been treated. Further analysis will be undertaken on the BOF slag produced at the Port Talbot steelworks to determine the chemical composition of the slag once the demetallization and further treatments have taken place.

Table 4.2: Comparison of XRF analysis of BOF slag sourced from Tata Steel plant, Jamshedpur, India and Tata Steel plant, Port Talbot (86)

	LD slag fines obtained from the waste recycling plant (WRP) at Tata Steel plant, Jamshedpur, India.				**Liquid BOF slag obtained at Tata Steel plant, Port Talbot, UK.**			
Components	**Average (wt%)**	**Min (wt%)**	**Max (wt%)**	**Variance (wt%)**	**Average (wt%)**	**Min (wt%)**	**Max (wt%)**	**Variance (wt%)**
CaO	51.36	37.35	60.06	7.79	44.33	30.14	60.64	9.34
SiO_2	15.71	10.97	26.51	2.1	14.245	7.71	32.67	2.59
MgO	2.09	0.12	6.16	0.58	7.644	3.38	19.85	2.33
Al_2O_3	0.931	0.52	3.76	0.05	2.301	1.03	10.4	0.38
TiO2	1.14	0.6	2.43	0.03	0.748	0.26	1.37	0.02
Fe	18.2	10.1	28.67	7.64	19.13	9.37	33.73	9.66
S	0.016	0.005	0.177	0.01	0.02	0.00	0.29	0.00
MnO	0.446	0.18	4.41	0.03	2.26	1.11	11.23	0.29
Cr_2O_3	0.156	0.04	0.22	0	-	-	-	-
P_2O_5	3.24	2.06	5.65	0.16	1.337	0.44	4.02	0.06
V_2O_5	-	-	-	-	0.68	0.19	1.58	0.05

A graphical view of Table 4.1 can be observed within Figure 4.1. This liquid slag represents the slag which is untreated. The liquid slag is then cooled in the slag pits, producing a crystalline material with grain sizes less than 100 mm. Once the slag has been cooled and weathered, it is then processed (crushing, sieving, and grading) and de-metallised, as observed within Figure 1.17. Once the slag has been processed, it results in applications such as road construction, hydraulic structures, and concrete. A quarter of the liquid slag is represented by the total iron, so when the slag is de-metallised and the chemical composition is acquired, it means that the total iron weight percent will be reduced. Demetallization is the first process of steelmaking slag treatment. The steelworks currently utilise the process of crushing, grinding and electromagnetic separation.

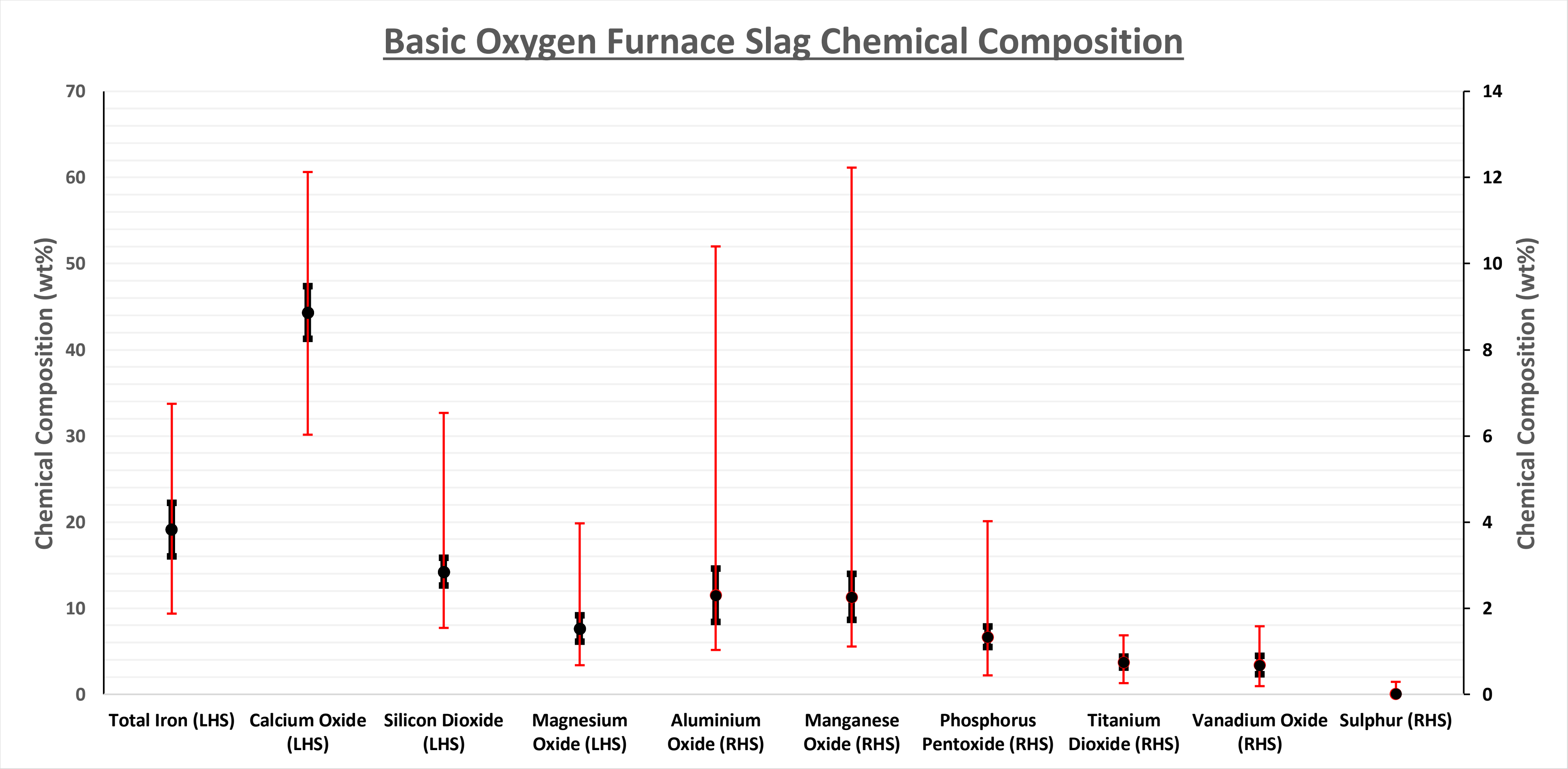

Figure 4.1: Graphical representation of BOF slag of 7325 samples at the Port Talbot steelworks (I represent maximum and minimum value; I represent the standard deviation in the average)

The two sourced slag from the Port Talbot steelworks are defined as ‘Prime’ slag (Figure 4.2) and ‘Recovered’ slag (Figure 4.3). Prime BOF slag has existing purpose and scope, signifying the slag is not readily available. While the recovered BOF slag has no current purpose and scope, signifying the slag is readily available for new recycling opportunities.

At Tata Steel, Port Talbot there is a large stockpile of legacy ‘Recovered’ slag that has no existing recycling applications, which has environmental and economic potential. Both types of BOF slags come in various particle size distributions, the desired particle size distribution from the literature is slag fines of 250 µm or smaller. There will be an economic impact on the process if all slag fines need to be crushed and grinded down to the desired particle size distribution.

Figure 4.2: Prime BOF slag

Figure 4.3: Recovered BOF slag

4.1.1 XRD Chemical composition

The chemical composition of the recovered BOF slag after processing has been identified. These samples were a base where 25 kg of each recovered BOF slag and prime BOF slag were cone and quartered into suitable samples - XRD analysis can then be meaningfully undertaken. The XRD analysis undertaken can be observed in Table 4.3 and Table 4.4 for recovered and prime BOF slag.

Table 4.3: XRD of recovered BOF slag at Port Talbot

Recovered BOF slag chemical composition				
Components	**Sample Weight Percent (wt%)**			
	1	**2**	**3**	**Mean**
Fe	16.12	16.86	16.68	16.553
CaO	35.77	38.37	36.84	36.993
SiO2	14.75	14.23	14.76	14.58
MgO	8.75	8.46	8.72	8.643
Al2O3	13.4	10.76	10.61	11.59
MnO	2.75	2.47	3.63	2.95
P2O5	0.89	1.14	0.95	0.993
S	0.024	0.044	0.024	0.031
TiO2	0.78	0.64	0.81	0.743
V2O5	0.439	0.475	0.475	0.463

Table 4.4: XRD of prime BOF slag at Port Talbot

Prime BOF Slag Chemistry composition				
Components	**Sample Weight Percent (wt%)**			
	1	**2**	**3**	**Mean**
Fe	19.09	18.22	18.75	18.687
CaO	43.43	42.97	43.59	43.33
SiO_2	13.8	14.01	13.7	13.837
MgO	7.4	7.85	7.82	7.69
Al_2O_3	3.44	4.29	3.3	3.677
MnO	7.4	3.03	2.89	4.44
P_2O_5	1.33	1.3	1.37	1.333
S	0.019	0.018	0.017	0.018
TiO_2	0.77	0.76	0.78	0.77
V_2O_5	0.548	0.545	0.595	0.563

As realised in Table 4.3 and Table 4.4 in the prime BOF slag there is a larger weight percent of calcium oxide than the recovered BOF slag, thus having more calcium available to convert from the slag to produce gypsum. From the literature, the LD slag fines taken randomly from waste recycling plant (WRP) at Tata Steel, Jamshedpur, had a calcium oxide weight percentage of 49.15% (87). This was significantly higher than the recovered BOF slag by 12.6% and 5.8% higher than the prime BOF slag, both sourced from Tata Steel, Port Talbot (87). As there is a lower percent of calcium present in the slag from Port Talbot, it is expected that a lower yield of synthetic gypsum would result. Repeating the process, affords neutralisation with calcium hydroxide, which will add additional calcium to the process to produce additional synthetic gypsum. If limes fines are not as readily available as in the patent, monitoring the production of yellow gypsum from the slag sourced from Port Talbot with an alternative neutralising agent will acquire the yellow gypsum produced directly from the slag, calculating the calcium conversion of the process will determine the yield of the process.

Table 4.5 presents a comparison of the two sources of BOF slag sourced from the Port Talbot steelworks compared with the LD slag fines obtained from the waste recycling plant (WRP) at Tata Steel plant, Jamshedpur, India. All data was acquired through XRD analysis. As displayed in Table 4.5, the content of calcium oxide in both slags sourced from the Port Talbot steelworks is lower than that of slag sourced in Jamshedpur. There will be a larger content of calcium present during the leaching stage of the procedure in Jamshedpur, resulting in additional calcium sulphate being produced. There is significantly less calcium oxide present in the recovered BOF slag in comparison to the prime BOF slag, although the availability of both slags will be further discussed.

Table 4.5: Comparison of XRD analysis of BOF slag sourced from Tata Steel plant, Jamshedpur, India and Tata Steel plant, Port Talbot, UK (100)

Components	Weight Percent (wt%)		
	Prime BOF Slag	Recovered BOF slag	LD slag fines taken randomly from WRP at Tata Steel plant, Jamshedpur, India
Fe	18.687	16.553	18.900
CaO	43.330	36.993	49.150
SiO_2	13.837	14.580	11.750
MgO	7.690	8.643	4.210
Al_2O_3	3.677	11.590	1.000
MnO	4.440	2.950	0.397
P_2O_5	1.333	0.993	2.320
S	0.018	0.031	0.190
TiO_2	0.770	0.743	0.934
V_2O_5	0.563	0.463	-
Cr_2O_3	-	-	0.105

4.2 Selection of Slag for Experimental Processing

Two sources of BOF slag were collected from Tata Steel Port Talbot, prime and recovered BOF slag. These two types of BOF slag consist of various particle sizes, both sourced from the production of steel.

Currently, the prime BOF slag is being re-used within the Port Talbot steelworks, and the activity involves the manufacture of a cementitious products. Tarmac Western Limited currently utilise the prime BOF slag at the Port Talbot steelworks (101). The process involves mobile crushing and screening. The equipment is used to process ABS from the "slag mountain" which is subsequently used in the construction industry (Figure 4.4) (102). The "Slag Mountain" refers to a slag heap, which is a man-made mound or heap formed with the waste material. A large legacy "Slag Mountain" has formed within the Port Talbot steelworks, full of recovered BOF slag which currently has no recycling uses.

[redacted]

Figure 4.4: Crushing and screen of Slag at Tarmac Western Limited at Port Talbot Steelworks (102)

Recovered BOF slag is not currently re-used and has a large stockpile of the by-product. A large legacy “slag mountain” stockpile has formed due to there being no-existing recycling process. It was decided to focus on recovered BOF slag moving forward in the research, as it was more readily available, with a large stockpile located at the Port Talbot steelworks.

Commercialisation of patent 572/KOL/2014 within the Port Talbot steelworks, would provide a recycling opportunity for recovered BOF slag, where there is a large legacy “slag mountain” which could be utilised as an input for this process. Steel is continuously being produced at the Port Talbot steelworks, which ensures that a constant supply of recovered BOF slag is available as an input for the process.

4.3 Particle Size Characterisation

Particle size distribution will significantly impact the cost associated with this process at the Port Talbot steelworks. To note, the desired particle size distribution from the patent is 250 μm or smaller. If the slag is not the desired particle size, grinding is undertaken, which will increase the cost of the process. Sieving the recovered BOF slag will determine the percentage of slag of the desired particle size distribution. The percentage of slag fines of 250 µm or smaller will not need to undertake any grinding, but anything larger will have been grinded down. Sieving the recovered BOF slag, obtaining the particle size distribution, and then undertaking the process at different particle size fractions will determine how the yield of calcium fluctuates in parallel to increasing the particle size.

The recovered BOF slag was then sieved into seven different particle size distributions. The smallest particle size fraction was 250 µm or smaller and the largest particle size fraction was 2360 µm or greater. Each particle size distribution can be identified within Figure 4.5.

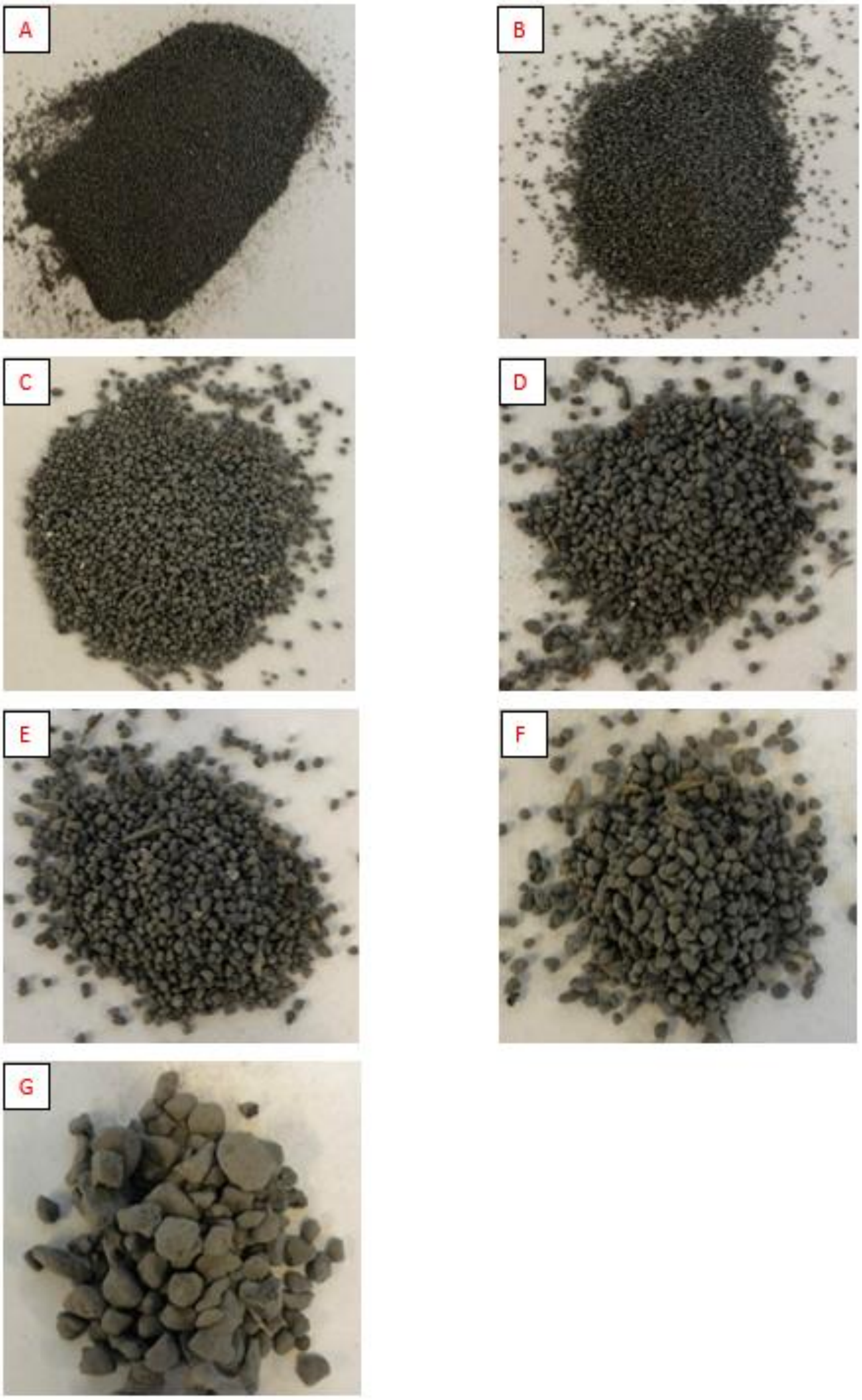

Figure 4.5: Recovered BOF Slag in particle size fractions; A)250 µm or smaller B)250-500 µm C)500-710 µm D)710-1000 µm E)1000-1400 µm F)1400-2360 µm E)2360 µm or greater

The granularity of the various particle size distribution of the recovered BOF slag is observed in Figure 4.5 and represent a sub-sample cone and quartered from Port Talbot steelworks. The desired particle size from the literature is 250 µm or smaller, only 3.2% of the sub-sample represents the desired particle size for the optimum process. This means that 96.8% of the recovered BOF will be required to be grinded and crushed in accordance with the process invented in Jamshedpur, India. Grinding will increase the costs associated with the process, as the tool required for the process is expensive, particularly tool maintenance. The costs associated with crushing and grinding will need to be further evaluated, to accurately determine an estimated cost to acquire the particle size distribution required.

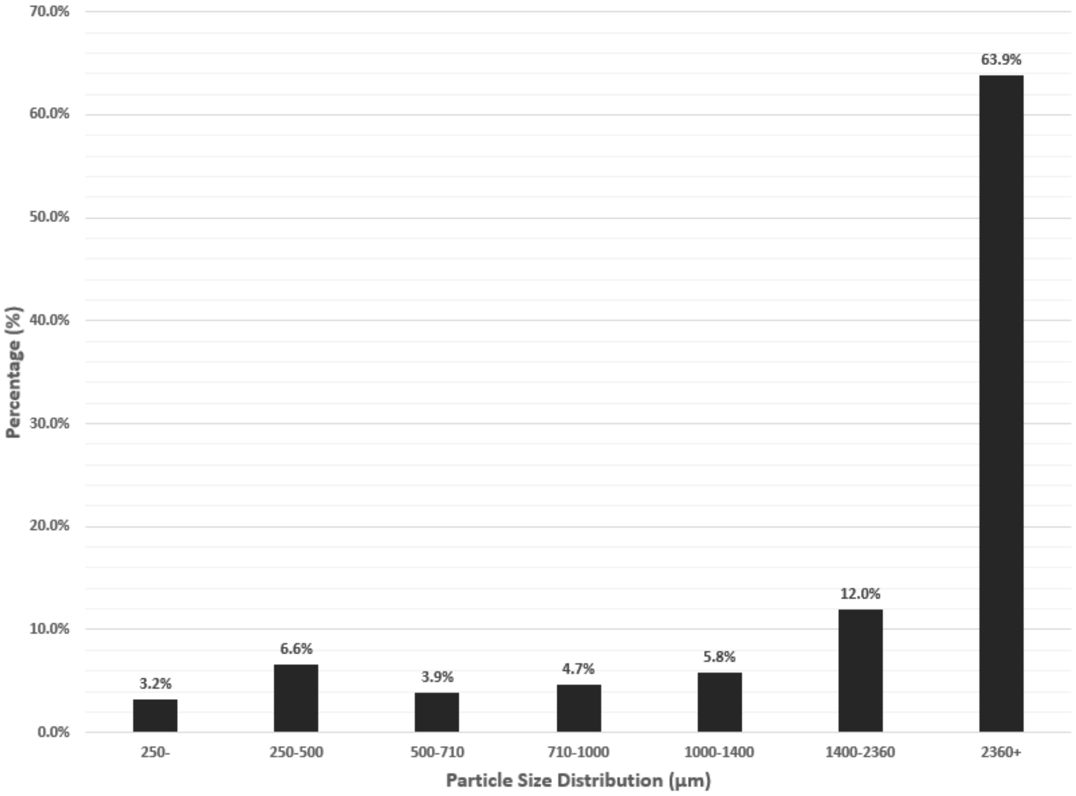

Figure 4.6: Recovered BOF slag particle size distribution

In light of this analysis, it was determined that only 3.2% of the recovered BOF slag particles meet the specified 250 µm or smaller particle size distribution within the literature (87). Crushing and grinding the recovered BOF slag particles to the desired particle sizes will increase the processing associated with this process. To determine the impact particle size distribution has on the commercialisation of this process, analysis is critical to determine an optimum particle size distribution. This optimum particle size distribution will need to consider the associated costs, which will be added through crushing and grinding, while monitoring the calcium conversion at larger particle size distributions

4.4 Repeating the Procedure

To assess the impact of the recovered BOF slag acquired from the Port Talbot steelworks, the process was repeated using cone and quartered samples of slag fines that were 250 µm or smaller. Repeating this process will enable comparison to the literature, whilst determining if the results obtained in the literature are repeatable (87).

4.4.1 Calcium Hydroxide

For comparison with the literature, the first experiment that was conducted was to repeat the process from the Indian Patent 572/KOL/2014. The experiment used slag fines of 250 µm or smaller, and utilised the same conditions and quantities as the literature (87). The process was repeated to check process reliability, experimenting with recovered BOF slag sourced from Tata Steel Port Talbot rather than the literature, where the slag is sourced from Tata Steel plant, Jamshedpur.

Figure 4.7: Input (Recovered BOF slag 250 µm or smaller)

The experiment was carried out on a laboratory scale at Swansea University. The process will be repeated three times and averaged, to ensure the experimental results gained are reliable and the results repeatable. The recovered BOF slag 250 µm or smaller (Figure 4.7), sulphuric acid (ACS Reagent, 95-98%) and distilled water were taken in the ratio 1:1.4:7.6. This mixture is then atmospheric leached for two hours, the resultant slurry formed after this two-hour period can be observed in Figure 4.8.

Figure 4.8: Slurry created

This slurry is then neutralised to pH 7 using Calcium Hydroxide (ACS Reagent ≥95%) mixed with distilled water. The lime fines (CaO) are mixed with water, as specified within the literature (87). Calcium hydroxide ($Ca(OH)_2$) is obtained by the action of water on calcium oxide. When mixed with water, a small proportion of it dissolves, forming a limewater, and the rest remains as a suspension called milk of lime.

Table 4.6: Comparison between the literature and averaged experimental results (87)

Materials	**Unit**	**Literature (Jamshedpur)**	**Average Experimental Results (Port Talbot)**
Input (LD Slag fines 250 µm or smaller)	g	10	10
Sulphuric Acid (ACS Reagent, 95-98%)	g	25.76	25.76
Distilled Water	g	86	86
Temperature	°C	105-110	105-110
Duration	Minutes	120	120
Lime fines	g	10	-
Calcium Hydroxide (ACS Reagent ≥95%)	g	-	10
Water Used for mixing lime fines	g	50	50
Output (Yellow Gypsum)	g	45	35.5

It can clearly be seen from Table 4.6, 9.5 g that less yellow gypsum was produced when repeating the process with slag sourced from Tata Steel, Port Talbot. The average experimental results only achieved a 76.51% process efficiency, compared to the 98.33% that was achieved in the literature. Although this is significantly less this was expected, as when comparing the chemical composition of the slag produced in Jamshedpur and Port Talbot, there was significantly less calcium oxide present in the slag. For future experimental analysis, elemental analysis was undertaken on the input and output of the process. The input of the process is defined as recovered BOF slag, and the output of the process is defined as the synthetic yellow gypsum produced. Observing the elemental analysis will permit the calcium yield to be calculated, calculating the quantity of synthetic yellow gypsum being produced from reacting the calcium hydroxide with the excess sulphuric acid. Observed within Figure 4.9, the output of the procedure can be visually seen after neutralisation and drying for 24 hours.

As previously summarised, when comparing the chemical composition of the slag fines of 250 µm or smaller used within Indian Patent 572/KOL/2014, the slag fines sourced from Tata Steel plant, Jamshedpur, India contained 12.6% more calcium oxide in comparison to the recovered BOF slag from the Port Talbot steelworks (87). More calcium sulphate will be produced during the leaching stage of the experiment, when more calcium is contained in the input of the process.

Figure 4.9: Output produced (Synthetic yellow gypsum)

SEM analysis is a powerful investigative tool which uses a focused beam of electrons to produce complex, high magnification images of a sample's surface topography. SEM images were taken of the recovered BOF slag at the start of the process, and once the synthesis of yellow gypsum has concluded. SEM was used to observe the microstructure of the input and output of the synthesis, Figure 4.10 through to Figure 4.13 exhibit the microstructure of the recovered BOF slag and synthesised yellow calcium sulphate produced at two different magnifications. SEM images of the resultant synthesised yellow calcium sulphate produced were captured, to subsequently compare to the SEM analysis undertaken at the Tata Steel plant at Jamshedpur.

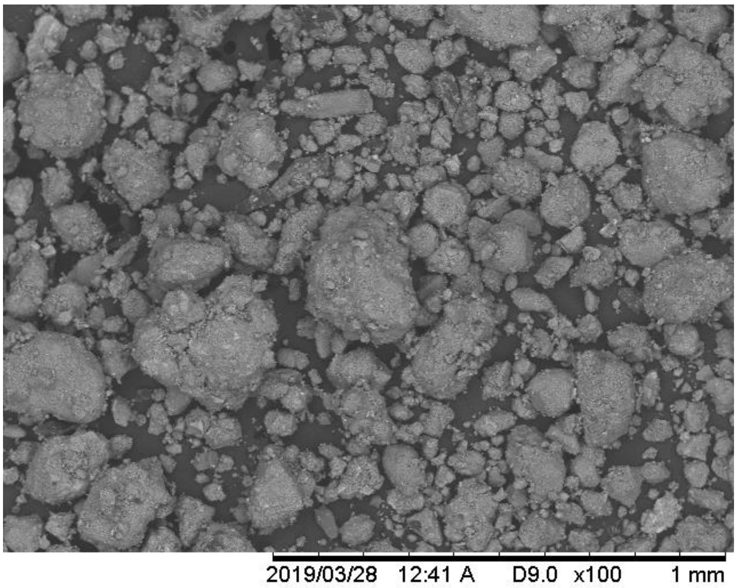

Figure 4.10: Recovered BOF Slag at 100X magnification

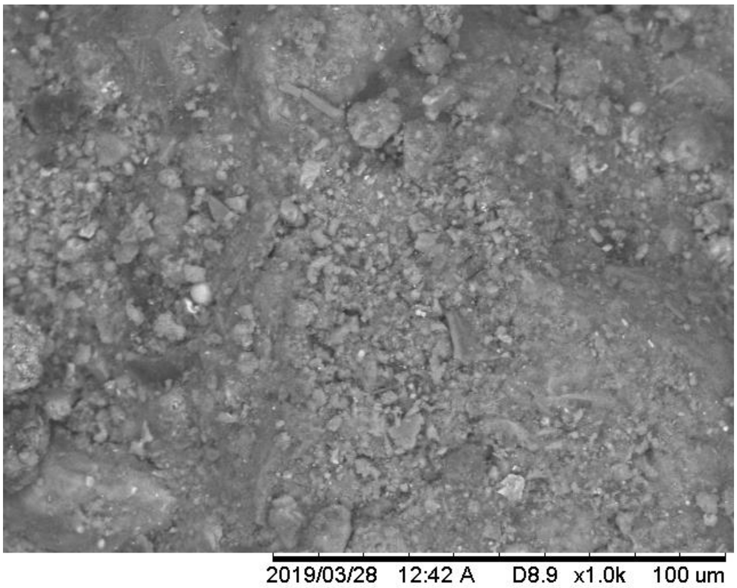

Figure 4.11: Recovered BOF Slag at 1000X magnification

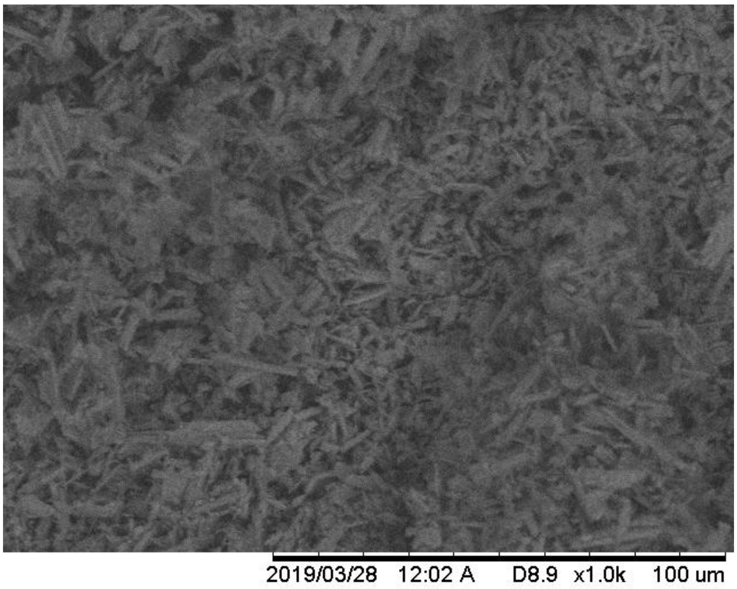

Figure 4.12: Gypsum product after synthesis at 1000X magnification

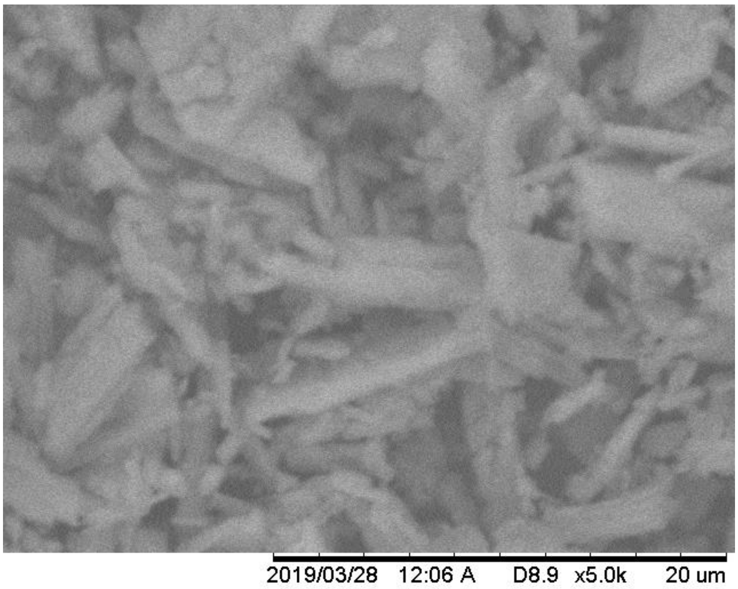

Figure 4.13: Gypsum product after synthesis at 5000X magnification

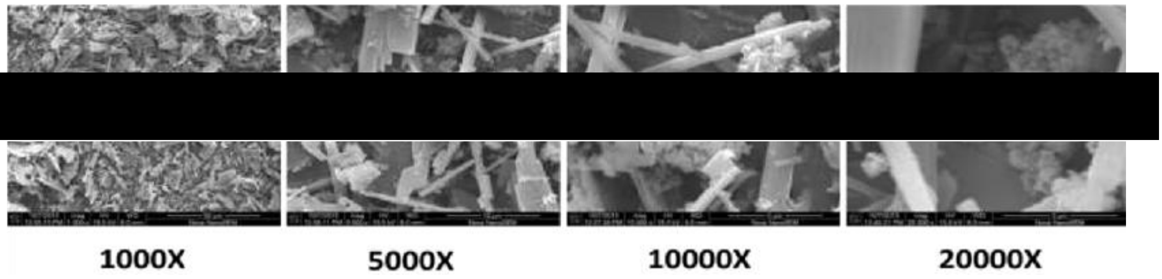
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Figure 4.14: SEM photographs of yellow gypsum at different magnifications obtained from chemical reagent H_2SO_4 & LD Slag fines (87).

Figure 4.14 represents the SEM micrographs of the synthesised yellow gypsum produced from the Tata Steel plant at Jamshedpur under different magnifications (87). The morphology of the material was found to be like tabular crystals, along with the presence of intermittent needle-like and rod like structures as observed from the SEM micrographs captured within the literature (88). This can be observed when comparing the SEM images captured within this research. It was observed that gypsum was present as tubular and radiating elongated crystals. Within this research there was a lack of characterisation of the synthetic gypsum produced beyond the SEM analysis, this is a limitation of this study.

4.4.2 **Sodium Hydroxide**

Aim: to determine the quantity of synthetic yellow gypsum produced from the process with neutralisation with sodium hydroxide. This experiment was undertaken using the same conditions as the Indian Patent 572/KOL/2014 using slag fines of 250 μm or smaller, using the same conditions, same quantities as the literature but using an alternative neutralising agent.

This experiment was undertaken to determine how much calcium sulphate is produced from neutralising the remaining sulphuric acid with calcium hydroxide. Sodium hydroxide was selected as an alternative inorganic compound for neutralisation, as the only source of calcium in the experiment is the recovered BOF slag. The calcium sulphate produced when neutralising with Sodium Hydroxide (ACS reagent, ≥97.0%, pellets) will be provided from the recovered BOF slag alone. The averaged experimental results obtained can be seen in Table 4.7: -

Table 4.7: Comparison of the process with Calcium Hydroxide and Sodium Hydroxide

Materials	Unit	Average Experimental Results (Calcium Hydroxide)	Average Experimental Results (Sodium Hydroxide)
Input (Recovered BOF slag 250 µm or smaller)	g	10.00	10.00
Sulphuric Acid (ACS Reagent, 95-98%)	g	25.76	25.76
Distilled Water	g	86.00	86.00
Temperature	°C	105-110	105-110
Duration	Minutes	120.00	120.00
Calcium Hydroxide (ACS reagent ≥95.0%)	g	10.00	-
Sodium Hydroxide (ACS reagent, ≥97.0%, pellets)	g	-	10.00
Water Used for mixing lime fines	g	50.00	50.00
Output (Yellow Gypsum)	g	35.50	20.00

Undertaking this experiment, the quantity of calcium sulphate produced from the recovered BOF slag fines was obtained as 20.0 g. It can clearly be seen in Table 4.7, that 15.5 g extra synthetic yellow gypsum is produced from the process when calcium hydroxide is used to neutralise the remaining sulphuric acid, this represents a 77.75% increase of synthetic yellow gypsum. Neutralising with calcium hydroxide, produces more calcium sulphate. But if other sources of neutralising agent are more readily available, this could also an alternative option when undertaking IS. Utilising available calcium hydroxide through collaboration between companies, would significantly impact the commercialisation of this process.

4.5 Assessment of Impact of Particle Size Distribution on the Process

4.5.1 Chemical Composition

Analysis on the process of producing synthetic gypsum was undertaken to identify the impact that particle size distribution has on the leaching of recovered BOF slag and production of synthetic gypsum. This analysis was undertaken using the same experimental condition as patent 572/KOL/2014, and the same experimental conditions are applied to determine the impact that particle size distribution has on the process. Cost-saving analysis is afforded to determine the optimum particle size distribution for use on the BOF slag produced at the Port Talbot steelworks.

Elemental composition was identified through XRD analysis of each particle size distribution range. The elemental composition of each particle size distribution range was undertaken to see how each chemical composition varied depending on the particle size distribution. The main elemental compositions comprise iron (III) oxide, calcium oxide, silicon dioxide, aluminium oxide, magnesium oxide, sulphur, and zinc.

XRD analysis was undertaken on the recovered BOF Slag sieved to particle sized from 2360 µm or greater to 250 µm or smaller. The averaged XRD analysis of recovered BOF slag at different particle size ranges can be seen in Table 4.8: -

Table 4.8: Averaged XRD analysis of recovered BOF Slag (Input) at different particle size ranges

Particle Size Range (µm)	**Average Weight Percent (wt%)**						
	Fe_2O_3	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**S**	**Zn**
250-	22.347	29.57	15.86	5.44	9.41	0.197	0.032
250-510	26.101	29.09	17.94	6.49	9.04	0.247	0.026
510-710	25.906	30.87	14.57	7.53	9.66	0.248	0.036
710-1000	26.818	31.66	14.34	8.17	9.65	0.211	0.031
1000-1400	26.381	32.58	15.25	8.49	9.03	0.209	0.019
1400-2360	25.081	34.02	14.45	8.59	9.52	0.356	0.017
2360+	25.498	39.56	14.78	6.82	8.82	0.1	0.005

The chemical compositions were determined for each particle size distribution acquired. From the results obtained, observe that the weight percentage calcium oxide increases as the particle size distributions increase. The amount of iron (III) oxide weight percent is consistent, except for 250 µm or smaller. The experiment highlighted that the larger particle size distributions will take longer to leach than the smaller particles, resulting in an expected lower percent calcium yield, as the experimental conditions utilised are the same as the literature. The patent in this study used optimised process conditions for slag fines 250 μm or smaller. Further process optimisation could be undertaken for larger particle size distributions. The optimum process conditions from the patent were utilised throughout this study, due to time constraints.

The same chemical composition analysis was undertaken on the calcium sulphate produced (Table 4.9). As expected, the calcium oxide at each particle size distribution range was significantly reduced when comparing the XRD analysis undertaken on the slag.

Table 4.9: XRD analysis of Gypsum (Output) produced from different particle size distributions

Particle Size Range (μm)	**Average Weight Percent (wt%)**						
	Fe_2O_3	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**S**	**Zn**
250-	8.545	13.48	7.35	2.72	1.47	10	0.015
250-510	10.908	13.36	8.93	3.32	2.32	10.4	0.016
510-710	9.817	14.99	7.73	3.64	1.52	11.8	0.012
710-1000	12.24	16.88	8.13	4.25	1.55	9.82	0.012
1000-1400	9.017	15.3	7.09	3.46	1.24	11.8	0.035
1400-2360	6.02	15.88	7.23	2.44	1.5	11.9	0.005
2360+	9.178	11.04	4.61	3.41	3.32	14.1	0.004

4.5.2 Calcium Conversion

The results obtained through XRD analysis were utilised to determine the mass of calcium in the recovered BOF slag at each particle size distribution range and determining the mass of calcium converted to calcium sulphate produced as observed in Table 4.10.

Table 4.10: Calculation of Calcium in input and output of the process

Input						
Particle Size Distribution (µm)	**Slag (g)**	**Average Calcium (wt%)**	**Error (±)**	**Percentage Error (%)**	**Mass of Calcium (g)**	**Error (±)**
250-	10.0005	21.1334	0.2812	1.3304	2.1134	0.0281
250-510	10.0013	20.7903	0.6298	3.0295	2.0793	0.0630
510-710	10.0042	22.0625	0.5161	2.3391	2.2072	0.0516
710-1000	10.0021	22.6271	1.0948	4.8383	2.2632	0.1095
1000-1400	10.0172	23.2846	1.7747	7.6219	2.3325	0.1778
1400-2360	10.0046	24.3138	0.7137	2.9353	2.4325	0.0714
2360+	10.0921	28.2731	0.8589	3.0378	2.8534	0.0867
Output						
Particle Size Distribution (µm)	**Gypsum (g)**	**Average Calcium (wt%)**	**Error (±)**	**Percentage Error (%)**	**Mass of Calcium (g)**	**Error (±)**
250-	19.9984	9.6340	0.5441	5.6479	1.9267	0.1088
250-510	18.5443	9.5483	0.3030	3.1736	1.7707	0.0562
510-710	16.5528	10.7132	0.3211	2.9971	1.7733	0.0531
710-1000	14.4034	12.0640	0.4785	3.9663	1.7376	0.0689
1000-1400	14.0819	10.9348	0.4523	4.1359	1.5398	0.0637
1400-2360	13.0342	11.3493	0.4667	4.1122	1.4793	0.0608
2360+	9.1188	8.3233	0.8163	9.8075	0.7590	0.0744

Utilising the XRD analysis undertaken on the recovered BOF slag (input) and synthetic gypsum (output) for each associated particle size distribution, enabled calculations to be undertaken to determine the mass of calcium present in the input and output of the process. Observed within Table 4.10 the calcium conversion reduces as the particle size distribution increases. Although this is expected, through cost analysis an optimum particle size distribution can be identified for positive utilisation of the process in Wales. Through use of Calculation 3.1, the calcium content was calculated for the recovered BOF slag and synthetic yellow gypsum produced as each particle size distribution can be observed within Table 4.11, this calculation enabled the yield of calcium to be identified.

Table 4.11: Mass of Calcium in input and output

Particle Size Distribution (µm)	**Mass of Calcium (g)**	
	Recovered BOF Slag	**Synthetic Yellow Gypsum**
250-	2.1134	1.9267
250-510	2.0793	1.7707
510-710	2.2072	1.7733
710-1000	2.2632	1.7376
1000-1400	2.3325	1.5398
1400-2360	2.4325	1.4793
2360+	2.8534	0.7590

Leaching is the process of a solute becoming detached or extracted from its carrier substance by way of a solvent. During the experimental analysis, the larger particle size distribution ranges, the slag was not completely “leached”, meaning that some of the calcium within the slag had not completely conversed. The leaching process was undertaken for 2 hours with continuous stirring, further research could be undertaken to determine the required optimum atmospheric leaching duration for each particle size distribution.

The slag that is not converted during the atmospheric leaching could be re-used in a latter process, as the larger sized particles will take longer to detach and extract. Longer atmospheric leaching could be undertaken for higher particle size distribution, but this would increase the costs associated with processing and maintaining 105-110 °C within the reactor for longer periods. Process optimisation was undertaken in the literature, this analysis utilised the same experimental conditions (87). Undertaking the process on larger size particle distributions may have a lower calcium conversion but would reduce the cost associated with crushing and grinding. Utilisation in latter processing could offer potential cost-benefits when offering recommendations, if the process is feasible for commercialisation in Wales.

The associated error from the results has been obtained, to determine the accuracy of the results. Through these calculations, the yield of calcium was obtained and displayed in Figure 4.15. From the results obtained in Figure 4.15, the yield of calcium for slag fines 250 μm or smaller, was 91.2%, which differs to 76.8% for slag fines 710-1000 μm and for slag greater than 2360 μm the yield is a mere 26.6%. Undertaking leaching of particles 1000 μm or smaller could be possible where the yield would be 76.8% or greater, although this only represents 18.4% of the particle size distribution. The remaining 81.6% would need to be crushed and ground to achieve a particle size distribution of 1000 μm or smaller.

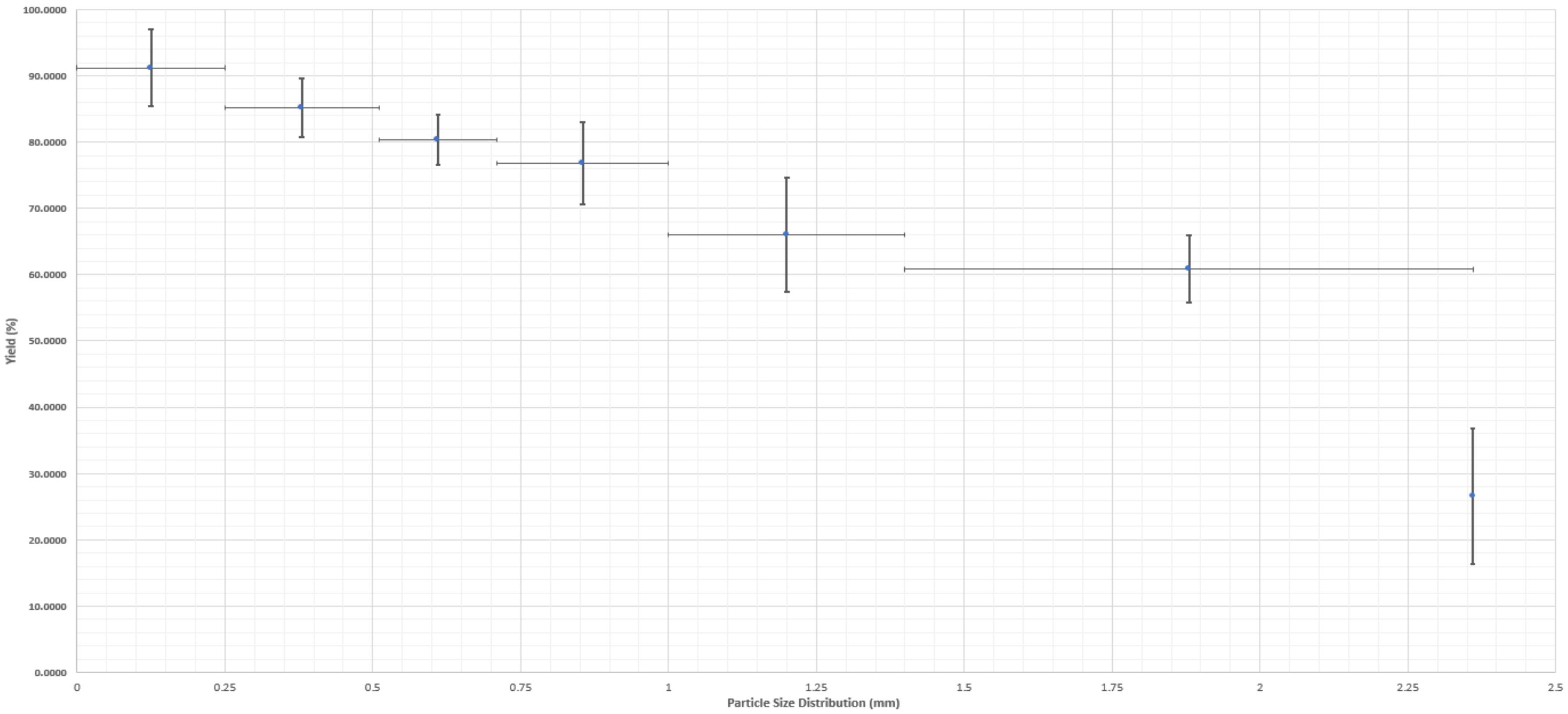

Figure 4.15: Yield of calcium at various particle size distribution ranges

(Horizontal Error bars represent particle size distribution range and Vertical Error bars represent Percentage Error)

4.6 Filtrate

Assessment of the contents of the filtrate was undertaken to determine if there was any worth being discarded in the filtrate. The filtrate was captured during the repeating of the Indian Patent 572/KOL/2014 process, using slag fines of 250 µm or smaller and analysis was undertaken (87). The filtrate was reused in this patent, the filtrate was neutral and was added at the reactor, meaning that the process was designated a zero-discharge process. Although re-use of the filtrate provides a zero-discharge process, assessing the filtrate for any worth was undertaken. The weight percent calcium, iron and zinc were examined when undertaking MP-AES analysis on the filtrate.

Table 4.12: Weight percent of Calcium, iron, and zinc within 200 ml of filtrate produced through synthesis of yellow gypsum from 250 µm or smaller recovered BOF Slag fines

Filtrate	**Analyte Weight Percent (wt%)** Ca (393.366nm)	Fe (371.993nm)	Zn (213.857nm)
1	0.0007	1.0170	0.0000
3	0.0006	0.7930	0.0000
4	0.0005	2.0600	0.0000
Average	0.0006	1.2900	0.0000

The weight percent calcium was analysed to see if any calcium was not converted to calcium sulphate during the process. The calcium is being fully converted to the synthetic yellow gypsum (Table 4.12). Zinc was not detected in the filtrate when analysis was undertaken. While there is iron that resides in the filtrate, it only represents 1.29% of the filtrate. The filtrate can be reused within the process in the reactor when the recovered BOF slag, sulphuric acid and water are mixed in ratio 1:1.4:7.6.

There is no worth in the filtrate as only 1.29% of the filtrate is iron - reuse in the process can reduce the quantity of water required. Reuse in the process will ensure that there is no waste produced during the process and reduces the quantity of water required for the processing in the reactor.

4.7 Conclusion

This chapter has outlined the historic data for the chemical compositions of slag acquired at the Port Talbot steelworks. The recovered BOF slag will be further investigated within this study, as it is readily available and has no existing recycling opportunities. The calcium content reduces as observed from the liquid slag in comparison to the recovered BOF slag.

The overwhelming weight percent of the recovered BOF slag equates to a particle size distribution greater than the specified particle size distribution in Patent 572/KOL/2014. This results in additional crushing and grinding required or investigating the impact of increased particle size distribution on yield of calcium.

The process was repeated, applying the same conditions as Patent 572/KOL/2014, the process efficiency dropped due to a reduction in calcium oxide in comparison to the literature. It still obtained a calcium conversion yield of 91.1%. For commercialisation of this process, neutralisation with a calcium compound such as lime, will provide a 77.5% increase in synthetic yellow gypsum produced. The additional synthetic gypsum will significantly reduce the price associated with the process.

The analysis undertaken identified that the calcium yield is only significantly impacted for the largest particle size distribution. However, this represents the majority of recovered BOF slag. Grinding to a particle size of 1000 µm or smaller could be undertaken to achieve a calcium yield of 76.8%, any additional recovered BOF slag that is not fully leached could be recycled within the process. For the commercialisation of this process, crushing and grinding must be undertaken due to the impact on calcium conversion at the largest particle size distribution (this represents an overwhelming weight percent of recovered BOF slag). Further process optimisation for all particle size distributions defined could eliminate the crushing and grinding associated costs, through identification of sufficient leaching processing periods for larger particle size distributions. Further analysis must be undertaken to evaluate how the calcium conversion deviates at each defined particle size distribution and the cost associated is impacted.

5 Cost Analysis

Cost analysis is the act of breaking down a cost summary into its constituents and studying and reporting on each factor. Cost analysis is the comparison of costs for the purpose of disclosing and reporting on conditions related to improvement. Cost analysis is undertaken to assess the potential impact of yellow gypsum synthesis at the Port Talbot steelworks.

5.1 Crushing and Grinding

As the bulk of the recovered BOF slag from Port Talbot steelworks is not within the desired particle size distribution, this needs an investigation to identify the impact of larger size particle distributions on the process. This was undertaken due to the increased costs associated with crushing and grinding slag to the desired particle size of 250 µm or smaller. In order to calculate the impact of the cost of crushing and grinding, Darlow Lloyd and Sons Ltd were contacted for estimations (103). The cost estimations from Darlow Lloyd and Sons Ltd can be clearly seen in Table 5.1: -

Table 5.1: Price estimations for crushing and grinding

Method	**Particle Size Distribution (µm)**	**Price per tonne (£)**
Crushing	2000 or smaller	10
Grinding	250 or smaller	30

Any recovered BOF slag that has a greater particle size distribution than the 2360 µm will firstly have to be crushed (this represents 63.9% of the slag obtained). This will add additional costs, because crushed slag needs to be ground down to achieve the desired particle size distribution. This will increase the starting cost to achieve a particle size distribution of 250 µm. The cost to achieve the desire particle size distribution can be seen in Table 5.2.

Table 5.2: Price estimations to desired particle size distribution of 250 µm per tonne of recovered BOF slag estimated by DLS (103)

Particle Size Distribution (µm)	**Quantity (kg)**	**Price to desired Particle Size Distribution (£)**
250-	31.8	0.00
250-500	66.1	1.98
500-710	39.0	1.17
710-1000	46.9	1.41
1000-1400	57.8	1.74
1400-2360	119.8	4.79
2360+	638.6	25.54

As there is a large initial cost associated with particle size of 2360 µm or greater, this will significantly affect the overall cost associated with the synthesis of yellow gypsum from steelmaking slag. The prices estimated in Table 5.2 are for grinding and crushing, utilising the industrial grinder and for the crusher at DLS disposal.

Without IS, the costs associated with this process could significantly improve. The total costs of owning an industrial grinder and crusher includes the operating and fixed costs. Operating costs include fuel, lubrication, maintenance, repairs, and labour. Fixed costs include ownership, and expenses incurred (regardless of being in or out of use). The fixed costs also include the price of the machine, duration of ownership, value at end of ownership, insurance, and taxes. Without IS, the costs associated in crushing and grinding alone could significantly impact the process costs.

5.2 Chemical Sources

The costs associated with the sourced chemicals were identified. These are base costs associated with laboratory scale operation to produce synthetic gypsum. These initial prices allow comparison to be made to identify optimum particle size for BOF slag fines. This in turn will render the production of synthetic gypsum potentially more feasible while providing potential IS. The prices of each chemical per gram are recorded, this is due to the process being scaled to laboratory scale. The costs associated with the sourced chemicals from Sigma-Aldrich are presented within Table 5.3 (104).

Table 5.3: Cost associated with the sourced chemicals from Sigma-Aldrich (104)

Materials	**Quantity (g)**	**Price (£)**	**Price per gram**
Sulphuric Acid (ACS Reagent, 95-98%)	4566.75	114	0.02
Calcium Hydroxide (ACS reagent ≥95.0%)	2500	142	0.06
Sodium Hydroxide (ACS reagent, ≥97.0%, pellets)	12000	370	0.03

The chemical costs are sourced based on the chemicals used – from the literature, lime fines are readily available in Jamshedpur, generated from the lime making process, while calcium hydroxide was sourced for experimental analysis to be undertaken (87). Moreover, in the patent, sulphuric acid is re-used from copper concentrate smelting industries. If these chemicals are not as readily available in Wales, and recycled chemicals are not an option, we must estimate the cost of the process including all chemical costs. The expenses are sourced from Sigma-Aldrich, who supply chemical and biochemical products and kits used in scientific research (104). These expenses are based off a one-off purchase, and do not reflect bulk purchase, which would significantly reduce this price.

The costs acquired in this chapter do not consider large scale operations, where bulk chemical purchases could be undertaken. Bulk purchasing will enable negotiations to be undertaken to acquire the best price. Buying in bulk can provide many advantages, including less frequent refill change-outs and fewer opportunities for subsequent chemical spills. This results in safer and more efficient laboratory environments. Buying in bulk can also mean fewer shipping costs, and less packaging disposal, which contributes to sustainability. Bulk purchase will reduce the costs associated will the process, meaning the synthetic yellow gypsum can be produced at a lower cost at large scale production. Table 5.4 presents approximate bulk purchase prices for Tata Steel from sources at the Port Talbot steelworks. Prices could be reduced further for larger bulk purchases. The sulphuric acid quoted in Table 5.4 is supplied at a lower concentration than the experiments undertaken in this research, this will impact the process efficiency. Further experimentation would need to be undertaken utilising samples of the bulk products to determine the impact on the process. The significant reduction in value can be observed in Table 5.4, the price of calcium hydroxide reduced by 99.85%, while the sulphuric acid price reduced by 99.45% respectively. Unfortunately, the bulk purchase cost of sodium hydroxide could not be sourced.

Table 5.4 Approximate Bulk Purchase cost of Sulphuric Acid and Calcium Hydroxide from Tata Steel

Materials	**Quantity (t)**	**Price (£)**	**Price per gram (£/g)**
Sulphuric Acid (77%)	1	105	0.00011
Calcium Hydroxide	1	90	0.00009

5.3 Comparison with Patent 572/KOL/2014

In comparison with the literature, cost-analysis was undertaken to identify the price associated with repeating this process and additional costs for acquiring the desired particle size distribution. The experimental findings were scaled 1:100 to determine the associated costs on a large-scale operation. The chemicals acquired for the process to produce 3.55 kg of synthetic gypsum are identified in Table 5.5. The cost associated with 1 kg of recovered BOF slag is obtained with prices to crush and grind the slag provided from Tata Steel, Port Talbot to the desired 250 μm or smaller from the patent. The price of the recovered BOF slag itself would be free of charge, because the large legacy stockpile can be used. The costs acquired for the chemicals do not also consider the bulk chemical purchase if changed to large scale production in Wales. The chemical price was scaled based on Sigma-Aldrich, from whom the chemicals were sourced for the experimental analysis. The price associated with water is utilised from the literature, to ensure consistency (87).

Table 5.5: Cost associated with the process sourcing chemicals from Sigma-Aldrich

Materials	**Unit**	Quantity	Price (£)
Recovered BOF Slag (250µm or smaller)	kg	1.00	0.04
Sulphuric Acid (ACS Reagent, 95-98%)	kg	2.58	51.52
Water	kg	8.60	109.48
Calcium Hydroxide (ACS reagent ≥95.0%)	kg	1.00	60.00
Water Used for mixing lime fines	kg	5.00	63.65
Total Input			284.68

The costs of chemicals stand at £80.19 per kg of synthetic yellow gypsum produced. In the literature, the invention relates to alternative utilisation of sulphuric acid and lime fines generated during the production of lime from limestone. The IS will reduce the costs associated with the process in Jamshedpur. The costs associated in producing synthetic yellow gypsum could be significantly reduced through IS.

Table 5.6: Cost associated with the process through bulk purchase

Materials	**Unit**	Quantity	Price (£)
Recovered BOF Slag (250µm or smaller)	kg	1.00	0.04
Sulphuric Acid (ACS Reagent, 95-98%)	kg	2.58	0.28
Water	kg	8.60	109.48
Calcium Hydroxide (ACS reagent ≥95.0%)	kg	1.00	0.09
Water Used for mixing lime fines	kg	5.00	63.65
Total Input			173.54

The costs of chemicals stand at £48.88 per kg of synthetic yellow gypsum produced, through bulk purchase an 39.04% reduction in price is observed.

5.4 Particle Size Distribution

Cost analysis was undertaken for each particle size distribution. Each particle size distribution range used sodium hydroxide as the neutralising agent. This was undertaken to determine the price per kg of synthetic yellow gypsum produced at each particle size range. Using sodium hydroxide as the neutralising agent reduced the quantity of yellow gypsum produced as anticipated but reduced the price of the inputs of the process (see Table 5.7).

Table 5.7: Cost associated with process neutralising with sodium hydroxide

Materials	**Unit**	**Quantity**	**Price (£)**
Recovered BOF Slag	kg	1.00	0.00
Sulphuric Acid (ACS Reagent, 95-98%)	kg	2.58	51.52
Water	kg	8.60	109.48
Sodium Hydroxide (ACS reagent, ≥97.0%, pellets)	kg	1.00	30.00
Water Used for mixing lime fines	kg	5.00	63.65
Total Input			254.65

The costs of chemicals stand at £127.33 per kg of synthetic yellow gypsum produced utilsing sodium hydroxide. The total input was the same at each particle size distribution, although the recovered BOF slag was not completely leached for the bigger particle size ranges. This resulted in higher costs per kg as the particle size distribution increases. Also neutralising with sodium hydroxide increases the cost per kg of synthetic yellow gypsum produced as compared to using calcium hydroxide. Using sodium hydroxide as the neutralising agent, instead of calcium hydroxide, increased the associated price per kg by £47.14 for particle sizes of 250 µm or smaller. This is due to the additional calcium sulphate produced when excess sulphuric acid is neutralised with calcium hydroxide.

The overall cost for this process could be significantly reduced through collaboration and IS opportunities. The costs associated with the neutralising agents (calcium hydroxide or sodium hydroxide) and the sulphuric acid for leaching, could be utilised as a by-product from another industrial process, within Wales and the surrounding areas. Sulphuric acid and sodium hydroxide represent 32% of the total input associated with the process. Outsourcing these products has a major commercial potential, and results in economic and environmental benefits to both parties. The calculated price per kg of synthetic yellow gypsum produced at defined particle size distributions can be observed in Figure 5.1.

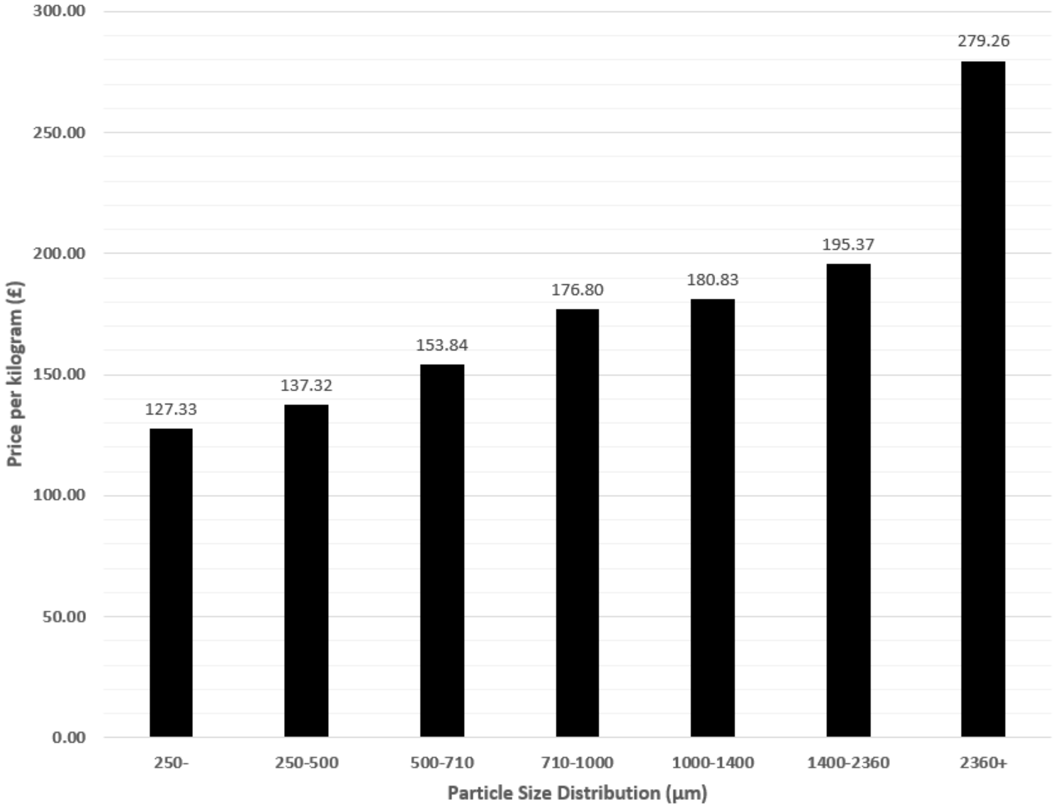

Figure 5.1: Price per kg of synthetic yellow gypsum produced at defined particle size distributions

The price per kg of synthetic yellow gypsum produced increases significantly for larger particle size distributions - for particles bigger than 2360 μm costs equate to £279.26. This is significantly larger than the particle size range of 1400-2360 μm, which costs £195.37 per kg of synthetic yellow gypsum produced. In Figure 5.2, the yield of calcium can be seen alongside the price per kg of synthetic gypsum produced. It is observed that as the yield of calcium reduces, the price per kg of synthetic gypsum produced increases. With the use of Figure 5.2, the yield of calcium drops below 70% for particle size distributions of 1000 µm or bigger, and the price per kg of synthetic gypsum produced achieves £176.80.

The costs associated with grinding and crushing the recovered BOF slag may be a determining factor when it is cost-effective to produce the synthetic gypsum. If available sources calcium hydroxide and sulphuric acid can be identified, particle size distribution will become a significant factor in acquiring a cost-effective process. Determining the yield of calcium at the defined particle size distributions allow further evaluation of an optimum particle size distribution for a break-even point for cost-effective processing.

The prices identified in Figure 5.2 are obtained using sodium hydroxide, which will produce significantly less calcium sulphate, than with neutralisation with calcium hydroxide. As previously indicated, the increased cost for particle sizes of 250 µm or smaller is increased due to less synthetic gypsum being produced from the neutralisation process. The yield of calcium combined with price per kg of synthetic gypsum produced, offers an indication of how the conversion of recovered BOF slag is impacted by the larger particle size distributions. A clear correlation arises for the yield of calcium which decreases the price per kg of synthetic gypsum increases.

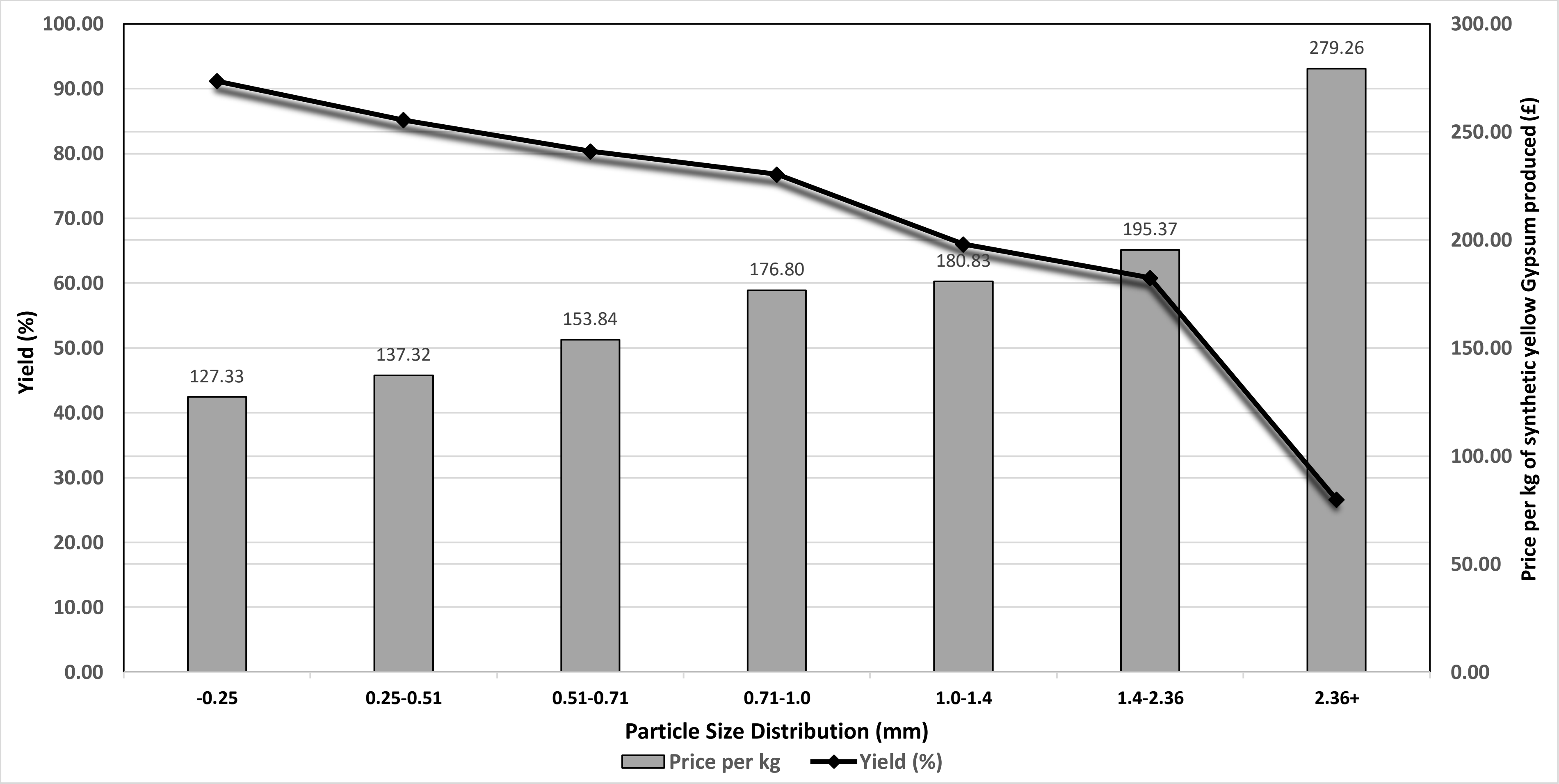

Figure 5.2:Yield of Calcium combined with Price per kg of synthetic yellow gypsum produced at each particle size distribution range

5.5 Market Analysis

The market price of synthetic gypsum is the current price at which the product can be effectively traded. The market price of synthetic gypsum will impact the commercialisation of yellow synthetic gypsum production from recovered BOF slag, ensuring the market price can shield the price associated with the production process.

The global synthetic gypsum market is expected to reach £1.457 Billion by 2026 compared to £1.041 Billion in 2018, a compound annual growth rate of 4.2% according to a report by Reports and Data (105). The increasing demand for end-user applications of synthetic gypsum (for instance plaster of Paris), due to the recyclable nature of the product is expected to drive the market in the upcoming years.

The literature points to the process efficiency, estimated around 98.33% and average cost worked out around £99.47 per tonne of synthetic gypsum produced. This was considerably less when compared to the cost of £239.80 per ton for commercial calcium sulphate product used as soil conditioner (87). The price cited in the literature excludes the further processing/pelletizing cost, which needs to be included to compare with commercial calcium sulphate products in construction and agriculture industries.

Contained within Table 5.8 is a summary of the various alternative gypsum products and the associated price per ton. When undertaking cost analysis for gypsum products, it was discovered that the mass of products price could be significantly reduced through mass purchase, even though some product prices were associated with a minimum order for purchase.

Table 5.8: Price of gypsum products per ton

Product	**Price (£)/Ton**
FGD Gypsum (106)	6.17-19.28
Gypsum Board Ceiling Plaster Powder Used for Making Moulding Gypsum Board Stone and Wall (107)	104.09-173.49
Gypsum Powder (107)	154.21
Good quality plaster of Paris gypsum powder for building materials (107)	77.11-154.21
Factory direct Gypsum used for Cement Gypsum (107)	10.64-14.5
Construction Application and Powder Calcium Sulphate Dihydrate (106)	138.79-231.32
Natural Gypsum (107)	92.53-100.24
Pelleted Gypsum (108)	325.36

For products at the lower price ranges within Table 5.8 such as FGD gypsum and factory direct gypsum, there is a minimum bulk order of 3000 Tons. Additionally, some products require shipping from China, which will have a negative impact on the environment, as all trade involves transport, adding considerably to overall emissions. Most of the higher valued end products have uses in industry, and once the yellow synthetic gypsum is produced, further processing will create feasible commercialisation. The synthetic gypsum produced through this method could be used in construction and agriculture industries as discussed within the applications of gypsum. Per Table 5.8 FGD gypsum and desulphurisation gypsum can be sourced at a much lower rate. Pelleted gypsum is primarily used for agricultural crops, lawn and garden, soil stabilisation and remediation and water clarifier. Pelleted gypsum priced as observed in Table 5.8 has the greatest market value. The processing costs would need to be identified for pelletization for agricultural or processing for construction purposes. But the final product would have a higher market value than being sold as powdered synthetic gypsum.

5.6 Conclusion

The overwhelming weight percent of the recovered BOF slag will require crushing and grinding, but this price can be reduced through collaboration. It has been strongly demonstrated within this chapter that purchasing chemicals such as sulphuric acid and calcium hydroxide for this process would significantly reduce the prospect of commercialisation. Through collaboration and IS, the prospect of commercialisation of this process increases due to a reduction in chemical expenses. Large scale production would enable bulk purchase of chemicals, and this significantly reduces the costs associated with the process as identified in Table 5.4, where the price is significantly reduced.

Additional processing on the final product would significantly improve the worth of output, where natural gypsum and FGD gypsum can be obtained at a lower price than final product of this process. Further processing to products in industries such as agriculture and construction will aid the commercialisation of this process, thus increasing final product value. Through the market analysis, pelletizing the synthetic gypsum produced presents a more valuable final product compared with other products identified. Although characterisation of the synthetic gypsum would need to be conducted to identify the purity of the calcium sulphate produced.

6 Industrial Symbiosis and Collaboration

Identifying organizations within this section to offer potential IS and collaboration opportunities will ultimately assist in the commercialisation of this process at the Port Talbot steelworks. The major costs associated with this process, through the cost analysis undertaken, is sulphuric acid for the leaching process and the neutralising agent, which must be carefully selected.

6.1 Local Availability of Resources

The local availability of resources of metals and energy played a crucial role in Britain's development during the industrial revolution. Sulphuric acid is the most used leaching agent and is a common acid in electrolyte solutions. Within the literature, sulphuric acid, which is a hazardous by-product in copper concentrate smelting industries, is utilised as a by-product for the process in Jamshedpur where copper smelters produce approximately one ton of sulphuric acid per one ton of copper concentrate.

Determining the availability of sulphuric acid as a by-product for IS within the UK, will aid the commercialisation of this process. Figure 6.1 represents the Locations of prospects, historic mining fields, metal smelters and steel mills in the UK, identifying potential industrial processes of which by-products can be utilised (109).

As represented in Figure 6.1, there are no copper concentrate smelting industries in the UK to supply sulphuric acid as a by-product. There are multiple potential prospects for mining copper, but none currently in use to assist this process. Sulphuric acid is produced as a by-product during the lead smelting process, and this could be utilised within this process. Nickel concentrates may be leached with sulphuric acid or ammonia, or they may be dried and smelted in flash and bath processes. This is the case with copper potentially providing sulphuric acid as a by-product (110). This is dependent on the company and processing methods. Finding any alternative processes across the UK and Europe, where by-products could provide IS, would have environmental and economic benefits to both organizations.

Finding by-products for use in the commercialisation of this project is not limited to sources within the UK. Tata steel's aim is to maintain their position as one of world's leading steel companies, constantly exploring new ways of working with others and identifying the best ideas and technologies, wherever they may be located. Although finding by-products outside of the UK would increase the related costs because of shipping logistics; this has a negative environmental impact. Outsourcing sulphuric acid from Europe and other countries could offer their products at a competitive price, reducing the price associated with this process.

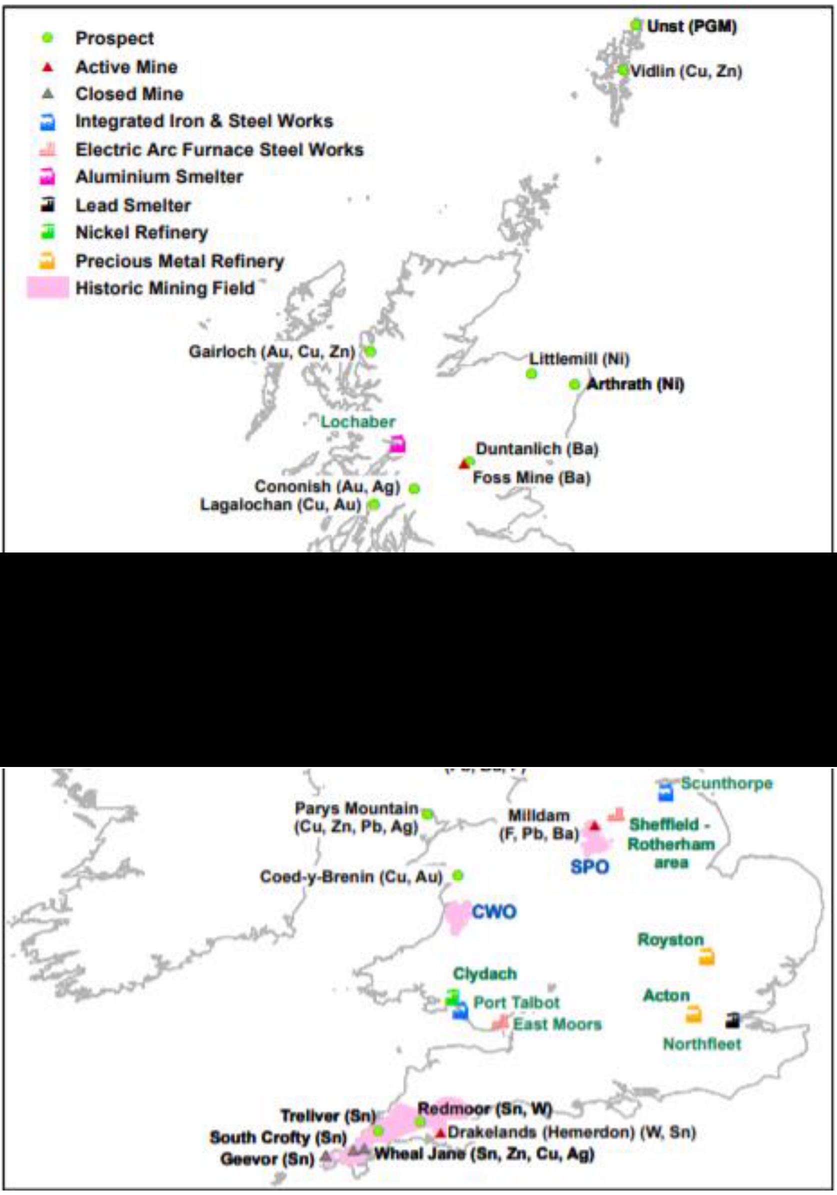

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Figure 6.1: Locations of prospects, historic mining fields, metal smelters and steel mills. (NPO, Northern Pennine Orefield; SPO, Southern Pennine Orefield; CWO, Central Wales Orefield; Ag, silver; Au, gold; Ba, barytes; Cr, chromium; Cu, copper; F, fluorspar; Ni, nickel; Pb, lead; PGM, platinum group metals; Sn, tin; W, tungsten; Zn, zinc) (109)**.**

6.2 **Boliden**

Boliden are one of the smelting industries major producers of high-quality sulphuric acid. Sulphuric acid is a by-product of the smelting process. Boliden boasts an annual production capacity of 1.7milion tonnes of sulphuric acid within their smelting plants at Rönnskär, Harjavalta, Kokkola and Odda (111). Bulk purchase of sulphuric acid from Boliden would reduce the price per kg of synthetic gypsum previously stated. Figure 6.2 illustrates Boliden's sites within Europe (111). Collaboration between Boliden and Tata steel, utilising sulphuric acid as a by-product, would aid the commercialisation of this process in Wales. Finding potential collaborations within Europe and not only UK is possible, with a company of the scale of Tata Steel.


[redacted]

Figure 6.2: Boliden's European Sites including smelters, mines and marketing offices (111)

6.3 **Darlow Lloyd and Sons**

Darlow Lloyd and Sons (DLS) and the waste management services have provided Tata Steel with environmental and cost-associated benefits. This is a successful collaborative relationship between DLS, and Tata Steel, which has helped to create

CE for by-products. Through exploring and innovative processes DLS were able to recycle products which may have been previously sent to landfill, providing CE.

DLS offer the complete industrial waste management solution for their five-point strategy plan towards "Zero-waste" (103): -

1. Patented Binders for sludge recycle & reuse
2. Bi-Product upgrading (Millscale)
3. Waste / aggregate recycling
4. Landfill Management
    a. Transfer sorting station management
    b. Landfill site construction & mining
5. Water recycling

DLS has an existing relationship with Tata Steel, Port Talbot and utilises their knowledge to determine estimated costs associated for crushing and grinding, which allows for collaboration possibilities to acquire suitable particle size distributions for processing. Through collaboration with DLS, the recovered BOF slag could be ground and crushed using their expertise and resources already at their disposal. This would significantly reduce the associated fixed costs. With their existing projects in Tata Steel, collaboration would be benefit both parties.

6.4 Tarmac Buxton Lime

Tarmac Buxton Lime (TBL) is a global leader in the supply of lime and limestone solutions. TBL is the UK's leading supplier of High Purity Limestone for FGD (112). Utilising the limestone will no longer be applied in FGD processing with the closure of all Britain's coal power plants by 2025. Limestone reacting with sulphuric acid can be seen in Equation 6.1.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2CO_3 \qquad \textbf{Equation 6.1}$$

$$H_2CO_3 \rightarrow CO_2 + H_2O \qquad \textbf{Equation 6.2}$$

Additional calcium sulphate can be provided in the process through neutralisation with limestone as calcium hydroxide (see Equation 6.1 and 6.2). As a result of closure of all Britain's coal power plants, a market opportunity has been created for the commercialisation of synthetic yellow gypsum, utilising the limestone previously used in FGD processing.

TBL also provide products such as hydrated lime also referred to as calcium hydroxide or slaked lime. This could also be utilised through collaboration. Bulk purchase of products with Tarmac Buxton Lime could be made with Tata Steel, with Tarmac having existing IS with use of the granulated slag from the Port Talbot steelworks.

6.5 Pelletized synthetic Gypsum

Through collaboration with existing companies, the synthetic gypsum produced from this process could be used to produce pelletized synthetic gypsum for the agriculture industry within the UK.

6.5.1 Fertilizer Engineering and Equipment Company (FEECO) International

Fertilizer Engineering and Equipment Company (FEECO) International, Inc. was founded in 1951, as an engineering and equipment manufacturer. FEECO is recognised globally as an expert in providing industry-leading process design, a range of engineering capabilities, including everything from process development and sample generation, feasibility studies, to detailed plant engineering. Additionally, it includes manufacturing to a variety of industries, including (113): -

- Fertilizer and agriculture
- Mining and minerals
- Power/utility
- Paper
- Chemical processing
- Forest products

FEECO has been providing the best in high-quality, custom gypsum equipment and process solutions for decades. They frequently help their customers with pelletizing gypsum for use as a soil amendment, drying gypsum ore, processing FGD gypsum (synthetic gypsum), and more.

Synthetic gypsum, like natural gypsum, is also processed into a fine powder before it undergoes pelletization. It even provides the same soil amending benefits as natural gypsum. However, synthetic gypsum as a class, is somewhat more challenging to pelletize in comparison to natural gypsum. Consequently, testing is necessary to evaluate each synthetic variation and ultimately determine the best pelletization process for each synthetic gypsum type. FEECO International provides a comprehensive testing services in four categories (114): -

- Feasibility/Proof of Concept: An initial, non-witnessed batch testing phase in which the possibility of creating a product is explored.
- Proof of Product: A more in-depth batch testing phase in which more time is spent determining whether a product can be made to desired specifications.
- Proof of Process: A continuous testing phase that aims to establish the equipment set-up and parameters required for continuous production of your specific material.
- Process/Product Optimization: An in-depth study to optimize your specific material’s characteristics and/or production parameters in an industrial setting.

Utilising FEECO International’s experience in processing synthetic gypsum could aid the commercialisation through providing the UK with pelletized synthetic gypsum to the agricultural industry. Figure 6.3 represents pelletized synthetic gypsum which has been manufactured utilising FEECO experience within this sector.

[redacted]

Figure 6.3: Pelletized Synthetic Gypsum (114)

6.5.2 Charah Solutions

Charah solution provides synthetic gypsum marketing and management services for utilities and industrial customers (115). Charah performs all aspects of managing and recovering the resource value, from by-products generated during the combustion of coal in the production of electricity.

The company has filed a patent successfully in 2018 that pertain to methods and systems for producing pelletized synthetic gypsum, this patent produces synthetic gypsum fertilizer product and the method for making it (116). While synthetic gypsum and natural gypsum generally have similar chemical properties (i.e., calcium and sulphur percentage compositions), synthetic gypsum cannot be effectively utilised. The patents clarify that synthetic gypsum cannot effectively be utilised in the agriculture industry due to its difficult material handling properties. This is due to the small particle sizes of synthetic gypsum, along with its moisture retention and difficulty in handling. Agricultural applicability is reduced due to difficulties of feeding synthetic gypsum through spreading equipment onto or into the soil. The company claim that it is the first to pelletize synthetic gypsum (FGD gypsum) and commercialised its patented fertilizer SUL4R-PLUS in 2014.

Charah Solutions supports synthetic gypsum marketing and management services for utilities and industrial customers to reduce or eradicate the costs associated with the management of this product (115). Whether providing operational support for onsite management or implementing innovative transportation and marketing solutions, Charah Solutions prides itself on delivering cost savings to its customers. Utilising a company’s knowledge and professionalism, such as Charah Solutions, to market and manage the synthetic gypsum produced, would have significant advantages for further processing.

6.5.3 Gypsoil

Gypsoil works with many leading coal-fired utility companies and other processing plants which produce co-product gypsum to establish safe and reliable supplies for farmers in the Midwest, Southeast and Mid-South regions of the USA (117). Gypsoil brand gypsum has the exact same chemical composition as mined gypsum, but it is typically purer than mined gypsum. Gypsoil is a co-product of the process that cleans the air from coal-fired plants and is sometimes called FGD gypsum.

Embodiments of this invention overcome deficiencies of the prior art by using an innovative manufacturing and production process to produce an improved FGD gypsum which has superior durability and desirable solubility properties (118). In one embodiment, FGD gypsum products are engineered to maintain its integrity well past its initial contact with water, dissolving at a significantly slower rate which is more comparable to potash than to all other gypsum granules. This property is desirable and advantageous over the prior uses because this keeps the nutrients where they can be absorbed by the crop, without creating unwanted run-off into watersheds. Gypsoil provides benefits such as improved water quality, water conservation, enhanced crop yield, reduced toxicity, and soil nutrient retention.

Gypsoil's parent company, Beneficial Reuse Management (BRM) is in the business of identifying opportunities to utilise by-products of various manufacturing processes. They are identifying safe and effective ways, that can ultimately benefit the agricultural industry to efficiently use these materials.

6.6 Conclusion

It has been demonstrated that by utilising by-products from the smelting industries with large scale operation and collaboration with lime and limestone suppliers, that IS and collaboration can significantly improve the prospects of commercialisation. Through IS and collaboration with these organizations, it will afford a reduction in the chemical expense associated with this process assisting commercialisation.

Processing synthetic yellow gypsum into pelletized synthetic yellow gypsum, would increase the value of the final product, and organizations with existing patents and knowledge have been outlined. These organizations would assist in the commercialisation of large-scale operations, providing the UK's agricultural industry with pelletized synthetic gypsum produced utilising a by-product of the steel industry.

IS has been undertaken in this research but has been limited due to time constraints. Potential IS opportunities have been outlined, but existing sulphuric acid and calcium hydroxide sources have not been specifically identified. More detailed IS could utilise the resources available to a company the scale of Tata Steel, to determine potential by-product supplies. Communication with Government bodies, such as Natural Resources Wales, can also aid identification of by-product supplies.

7 Conclusion

7.1 Limitations

This research was limited due to the time constraints of a master's by Research. This research focussed on the deliverables identified and all research undertaken was influenced by these deliverables. The deliverables were established at the start of this research project, to ensure the research was worthwhile to Tata Steel. The deliverables were also established considering the time constraints of this study, although this study has laid a foundation for which further work can be conducted.

One limitation to this research is lack of characterisation of the synthetic yellow gypsum produced beyond the SEM micrographs captured in this study. Determining the purity of the product would allow further comparison with the literature, where they achieved 86.12% calcium sulphate by estimation of sulphur trioxide content. The purity of the synthetic gypsum produced will determine the final product solutions.

The IS conducted within this research only offers potential sources for sulphuric acid and neutralising agents. A detailed IS study is required to further aid commercialisation of this process, identifying sulphuric acid and neutralising agent supplies would significantly reduce the processing costs. Communication with bodies, such as Natural Resources Wales, could help acquire detailed information of potential supplies. Unfortunately, due to time constraints of this research this was not able to be undertaken. The IS and collaboration undertaken in this study identifies pelletized synthetic gypsum as a potential final product, but further research could explore alternative products that are more cost effective.

Whilst a comprehensive cost analysis has been undertaken in this study, a more detailed cost analysis would obtain a more accurate processing cost. The experimental findings were scaled 1:100 to determine the associated costs on a large-scale operation. The results obtained through scaling may not be reflective of large-scale operation but were acquired to obtain recommendations. Within this study the cost associated with heating the mixture to 105-110 °C for two hours in the reactor with continuous stirring has not been considering. The costs associated with water supply for these experiments have utilised the literature to allow comparison. Although comprehensive analysis has been undertaken to commercialise this process, only recommendations have been presented through laboratory scale operation.

7.2 Recommendations

The dissertation has allowed us to develop several recommendations for Tata Steel to consider, when further examining commercialisation of yellow gypsum synthesis from recovered BOF slag at the Port Talbot steelworks. These recommendations will further support commercialisation of this process at the Port Talbot steelworks, the recommendations are discussed below: -

- **A more in-depth IS study must be conducted**. This will further aid commercialisation of the process at the Port Talbot steelworks, identifying sulphuric acid and calcium hydroxide supplies local to the steelworks would significantly reduce the processing cost. Re-use of sulphuric acid waste in this process would have significant environmental and economic benefits for both Tata Steel and any potential partners through IS.
- **Analytical study to characterise synthetic yellow gypsum produced**. Characterisation of product will enable further discovery of what manufactured goods can be produced from the synthetic yellow gypsum. This will also determine what purity of the product and what phases of gypsum are produced. This will also aid commercialisation of the process, determining a market value for which a detailed cost analysis can be conducted. Further analysis can also be conducted if further processing is required for commercialisation of this product.
- **Determine optimum processing for various particle size distributions identified within this research**. Throughout this research the process identified within the literature has been repeated for all particle size distributions, due to process optimisation being undertaken at Jamshedpur steelworks. As 96.8% of the recovered BOF slag has larger particle size distribution than that defined within the literature, undertaking process optimisations for the defined particle size distributions would reduce the crushing and grinding costs associated, which could further enable commercialisation.

- **Analytical study using EDS.** This should be conducted to characterise the recovered BOF slag, the large legacy “slag mountain” and other by-products produced at the Port Talbot steelworks. This would allow identification of potential alternative recycling opportunities at the Port Talbot steelworks whilst determining the calcium content of the legacy stockpile.
- **A detailed cost analysis must be undertaken by Tata Steel.** This should be conducted to determine accurate processing costs associated with the industrial scale production. This would include the costs associated with heating the mixture to 105-110 °C for two hours in the reactor with continuous stirring and the energy required. The equipment required for industrial scale processing would need to be examined and the costs associated with these products.

7.3 General Conclusion

In this study, an assessment of efficiency of yellow gypsum synthesis utilising BOF slag and commercial potential of this process has been undertaken. Recovered BOF slag is readily available at the Port Talbot steelworks, with an existing legacy “slag mountain” formed due to the lack of existing recycling capacity. The recovered BOF slag was utilised throughout this research, because of its availability and legacy stockpile. Production of gypsum from a by-product of the steelmaking process has been outlined. Once Britain’s coal power plants close, a shortage of gypsum within the UK will provide a potential market opportunity for synthesis of yellow gypsum at the Port Talbot steelworks.

An assessment has been undertaken determining the efficiency of yellow gypsum synthesis from BOF slag sourced from the Port Talbot steelworks, exploiting the Indian patent 572/KOL/2014. The chemical compositions of liquid, prime and recovered BOF slag have been summarised, the recovered BOF calcium oxide content was 12.6% less in comparison to slag produced at the Tata Steel plant, Jamshedpur. A method was determined to investigate calcium conversion throughout this process, neutralisation with sodium hydroxide was undertaken to determine the calcium converted from the recovered BOF slag to the synthetic gypsum produced. This method determined the quantity of gypsum produced directly from the recovered BOF slag. The particle size distribution from the readily available recovered BOF slag has been identified, 63.9% of the BOF slag represented particle size distribution of 2360 μm or greater. Calcium conversion from the slag to synthetic gypsum has been determined at each particle size distribution. A particle size distribution of 1000 μm or smaller was assessed as desirable for efficient calcium conversion. Crushing and grinding is required for 81.7% of recovered BOF slag obtained for desired particle size distribution, larger particle sized slag that are not fully leached could be recycled and reused within the process.

Neutralising the excess sulphuric acid within the process with a calcium neutralising agent, will produce up to an additional 77.5% synthetic gypsum. Lime and limestone suppliers have been identified through collaboration and replacing existing FGD processes in UK to fill a market hole. Sulphuric acid suppliers have been identified, where bulk purchase would significantly reduce chemical expenses, or alternatively uncover a by-product of an industrial process that can be utilised. Reducing the chemical expenses associated with this processing, significantly improves the commercialisation of this process through large scale operation. Large scale operation and neutralising with calcium hydroxide would significantly reduce the £176.80 per kg of gypsum produced for particle size distribution of 1000 μm or smaller. This is due to additional synthetic gypsum produced and a decrease in chemical expenses. When neutralising with calcium hydroxide at a particle size distribution of 250 μm or smaller, the price reduced to £80.19 per kg of synthetic yellow gypsum produced, due to the additional synthetic gypsum produced through neutralisation with sulphuric acid and an increased calcium yield. Concluding, that large scale production and bulk purchase of chemicals would significantly reduce the price cited if IS was unavailable.

This study, therefore confirmed commercialisation of this process in the Port Talbot steelworks is feasible, but it would require a large-scale operation and the synthetic yellow gypsum produced would potentially require further processing. Through market analysis and comparing the existing market - DSG is available at a lower rate compared to this process. However, further processing the synthetic yellow gypsum produced to products within the agriculture and construction industry would provide a higher valued final product. Pelletized synthetic gypsum is a workable solution that is currently applied in the United States, where FGD gypsum is pelletized and vastly used in agricultural across the United States. Utilising this process in the UK would further aid commercialisation of this process.

Appendices

Appendix A: Results for comparison with Patent 572/KOL/2014 (Calcium Hydroxide)

Sample	**Recovered slag fines (250-µm)**		
Experiment	1	2	3
Weighing boat (g)	2.8524	2.8984	2.847
Weighing boat + Slag (g)	12.8566	12.8931	12.8509
Slag Sample (g)	10.0042	9.9947	10.0039
Water (ml)	76.0319	75.9597	76.0296
Sulphuric Acid (96% Concentration) (g)	25.7708	25.7463	25.77
Weighing boat (g)	2.6036	2.8425	2.7505
Weighing boat + Calcium Hydroxide (g)	12.6037	12.8433	12.751
Calcium Hydroxide (g)	10.0001	10.0008	10.0005
Water Used for mixing lime fines	50	50	50
Watch Glass (g)	2.8447	2.8456	2.8409
Watch glass+ Product (g)	38.0861	39.0479	37.9276
Product (g)	35.2414	36.2023	35.0867
Process Efficiency			
Slag Sample (g)	10.0042	9.9947	10.0039
Sulphuric Acid (g)	25.7708	25.7463	25.77
Lime used (g)	10.0001	10.0008	10.0005
Input of Process	45.7751	46.5311	45.9066
Output (Synthetic Yellow Gypsum) (g)	35.2414	36.2023	35.0867
Process Efficiency	76.9881	77.8024	76.4306

Appendix B: Sodium Hydroxide results for comparison with Calcium Hydroxide

Sample	**Recovered slag fines (250-µm)**		
Experiment	1	2	3
Weighing boat (g)	2.8453	2.7904	2.9035
Weighing boat + Slag (g)	12.8454	12.7904	12.9049
Slag Sample (g)	10.0001	10	10.0014
Water (ml)	86.00086	86	86.01204
Sulphuric Acid (96% Concentration) (g)	25.7708	25.7463	25.77
Weighing boat (g)	2.6036	2.8425	2.7505
Weighing boat + Sodium Hydroxide (g)	12.6037	12.8433	12.751
Sodium Hydroxide (g)	10.0001	10.0008	10.0005
Watch Glass (g)	36.9511	36.9485	36.7419
Watch glass+ Product (g)	56.8918	56.5667	57.1783
Product (Synthetic Gypsum) (g)	19.9407	19.6182	20.4364

Appendix C: XRD Analysis on particle size distribution on the process of BOF slag and synthetic yellow gypsum

		Average Weight Percent (wt%)						
Particle Size Range (µm)	**Product**	**Fe_2O_3**	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**S**	**Zn**
250-	**Slag**	22.347	29.57	15.86	5.44	9.41	0.197	0.032
	Gypsum	8.545	13.48	7.35	2.72	1.47	10	0.015
250-510	**Slag**	26.101	29.09	17.94	6.49	9.04	0.247	0.026
	Gypsum	10.908	13.36	8.93	3.32	2.32	10.4	0.016
510-710	**Slag**	25.906	30.87	14.57	7.53	9.66	0.248	0.036
	Gypsum	9.817	14.99	7.73	3.64	1.52	11.8	0.012
710-1000	**Slag**	26.818	31.66	14.34	8.17	9.65	0.211	0.031
	Gypsum	12.24	16.88	8.13	4.25	1.55	9.82	0.012
1000-1400	**Slag**	26.381	32.58	15.25	8.49	9.03	0.209	0.019
	Gypsum	9.017	15.3	7.09	3.46	1.24	11.8	0.035
1400-2360	**Slag**	25.081	34.02	14.45	8.59	9.52	0.356	0.017
	Gypsum	6.02	15.88	7.23	2.44	1.5	11.9	0.005
2360+	**Slag**	25.498	39.56	14.78	6.82	8.82	0.1	0.005
	Gypsum	9.178	11.04	4.61	3.41	3.32	14.1	0.004

Appendix D: Assessment of impact of particle size distribution on the process neutralising with sodium hydroxide

Sieve Size (µm)	**250-**				**250-500**			**500-710**		
Experiment	1	2	3	Average	1	2	Average	1	2	Average
Weighing boat (g)	2.8453	2.7904	2.9035	2.8464	2.9177	2.9159	2.9168	2.9499	2.9195	2.9347
Weighing boat + Slag (g)	12.8454	12.7904	12.9049	12.8469	12.9194	12.9167	12.9181	12.9511	12.9267	12.9389
Slag Sample (g)	10.0001	10.0000	10.0014	10.0005	10.0017	10.0008	10.0013	10.0012	10.0072	10.0042
Water (ml)	86.0009	86.0000	86.0120	86.0043	86.0146	86.0069	86.0108	86.0103	86.0619	86.0361
Sulphuric Acid (g)	25.7603	25.7600	25.7636	25.7613	25.7644	25.7621	25.7632	25.7631	25.7785	25.7708
Watch Glass (g)	36.9511	36.9485	36.7419	36.8805	3.0654	3.0654	3.0654	3.0630	3.0544	3.0587
Watch glass + Product (g)	56.8918	56.5667	57.1783	56.8789	21.5685	21.6508	21.6097	19.6697	19.5533	19.6115
Product (g)	19.9407	19.6182	20.4364	19.9984	18.5031	18.5854	18.5443	16.6067	16.4989	16.5528

<u>Sieve Size (µm)</u>	**710-1000**			**1000-1400**			**1400-2360**			**2360+**			
Experiment	1	2	Average	1	2	Average	1	2	Average	1	2	3	Average
Weighing boat (g)	2.9525	2.9545	2.9535	2.9227	2.9223	2.9225	3.0647	3.0844	3.0746	2.9221	2.9245	3.0866	2.9777
Weighing boat + Slag (g)	12.9598	12.9514	12.9556	12.9263	12.9530	12.9397	13.0866	13.0923	13.0895	13.0151	12.8942	13.3002	13.0698
Slag Sample (g)	10.0073	9.9969	10.0021	10.0036	10.0307	10.0172	10.0012	10.0079	10.0046	10.0930	9.9697	10.2136	10.0921
Water (ml)	86.0628	85.9733	86.0181	86.0310	86.2640	86.1475	86.0103	86.0679	86.0391	86.7998	85.7394	87.8370	86.7921
Sulphuric Acid (g)	25.7788	25.7520	25.7654	25.7693	25.8391	25.8042	25.7631	25.7804	25.7717	25.9996	25.6819	26.3102	25.9972
Watch Glass (g)	3.0588	3.0575	3.0582	3.0694	3.0685	3.0690	3.0819	3.1631	3.1225	3.0978	3.0971	3.0810	3.0920
Watch glass + Product (g)	17.4827	17.4403	17.4615	17.1255	17.1762	17.1509	16.2377	16.0756	16.1567	11.8461	12.6652	12.1210	12.2108
Product (g)	14.4239	14.3828	14.4034	14.0561	14.1077	14.0819	13.1558	12.9125	13.0342	8.7483	9.5681	9.0400	9.1188

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