# FUNDAMENTAL STUDY OF RED MUD BASED FLUXES FOR DESULPHURIZATION AND DEPHOSPHORIZATION OF HOT METAL

by

Abdolkarim Danaei

### **B.Sc. Isfahan University of Technology, Iran, 1985 M.Sc. Sharif University of Technology, Iran, 1993**

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#### Abstract

## FUNDAMENTAL STUDY OF RED MUD BASED FLUXES FOR DESULPHURIZATION AND DEPHOSPHORIZATION OF HOT METAL

Doctor of Philosophy, 2015

Abdolkarim Danaei B.Sc. Isfahan University of Technology, Iran M.Sc. Sharif University of Technology, Iran

Mechanical and Industrial Engineering Ryerson University

Bauxite residue, also known as red mud, is generated during alumina production and is an abundant industrial waste material. Continuously increasing environmental concerns, together with scarcity of traditional mineral resources, have created a thrust to re-use the material. Red mud contains significant amounts of iron oxide and sodium hydroxide, hence a highly basic (pH > 10) slurry. In this research, the use of red mud as starting material for preparation of iron refining fluxes was evaluated.

Red mud based fluxes and hot metal were equilibrated in graphite crucibles at the temperature range of 1300 °C to 1400 °C and oxygen partial pressures range of  $10^{-2}$  atm to  $10^{-6}$  atm. It was found that the sulphide capacity increases with lime addition to a maximum 32 wt% CaO and decreases with increasing Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> content in the fluxes saturated with lime.

An iron foil equilibrium technique was employed to obtain precise measurements of phosphorus distribution between carbon saturated iron and red mud based fluxes. The measurements indicate

that the equilibrium phosphorus distribution ratio initially increases with rise in FeO or CaO concentration of the fluxes and then drops.

The melting behavior of the fluxes was also studied by visualizing the deformation of flux pellets as they were heated using a high temperature microscopy technique. Measurements of characteristic temperature for different fluxes indicated the melting property is a function of slag basicity. Therefore, optical basicity was used to establish a correlation between basicity of the red mud based fluxes and their melting properties.

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Abdolkarim Danaei

Dedication

To my wife, son and daughter

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# Nomenclature

Symbol	Definition	Units
a <sub>i</sub>	The activity of component i	-
a <sub>0</sub>	Activity of oxygen	
Cs	Sulphide capacity of slag	-
$C_{PO_4^{-3}}$	Phosphate capacity of slag	-
ΔG	Gibbs free energy	J/mol
$G_i^{\circ}$	Gibbs free energy of component i in standard state	J/mol
$e_i^j$	Interaction coefficient of <i>i</i> as affected by alloying element <i>j</i>	
f	Henrian activity coefficient, 1wt%	-
K <sub>c</sub>	Equilibrium constant	-
L <sub>P</sub>	Phosphorus distribution ratio (wt%P)/[wt%P]	-
L <sub>S</sub>	Sulphur distribution ratio (wt%S)/[wt%S]	-
М	Molecular weight	g/mol
N	Avogadro's number, $6.022 \times 10^{23}$	atoms mol
N <sub>i</sub>	Compositional fraction	-
n <sub>Oi</sub>	Number of oxygen atoms in component, i,	-

0	Number of oxygen atom in molecule	
Pgas	Partial pressure of gas	atm
R	Gas constant	8.314 J/mol · K
Т	Temperature	Kelvin (K)
x	Pauling's electronegativity	-
X	Equivalent fraction of oxide	
ν	Frequency of light wave	
[P], [S]	Weight percent of sulphur or phosphorus in metal phase	wt%
(P), (S)	Weight percent of sulphur or phosphorus in slag phase	wt%
Λ	Optical basicity of a multicomponent slag	-
$\Lambda_{\rm i}$	Optical basicity of an oxide component	-

# Acronyms

AES	Atomic Emission Spectroscopy
BOF	Basic Oxygen Furnace
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric Analysis
IAI	International Aluminum Institute
ICDD	International Centre for Diffraction Data
ICP	Inductively Coupled Plasma
OB	Optical Basicity
RIR	Reference Intensity Ratio
RM	Red Mud (Bauxite residue)
RMF	Red Mud Flux
SD	Standard Deviation
SE	Standard Error
SEM	Scanning Electron Microscope
SRM	Synthetic Red Mud flux
STA	Simultaneous Thermal Analysis
TGA	Thermal Gravimetric Analysis
UV	Ultraviolet (UV) light
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence Spectroscopy

## Chapter 1

# **1** Introduction

## **1.1** Motivation for the thesis

Aluminum is an abundant element and critical to the daily lives of human beings. However, it can take a long and costly procedure to be extracted from the earth's crust. Aluminum exists primarily as alumina (aluminum oxide), which is extracted from bauxite ore, although other types of ore may also be used as the source of alumina. The Bayer process is the dominant route to extract alumina from Bauxite ore. During the process, a residue amounting to about 120 million tonnes per year is generated. The residue is known as "red mud" – so-called because of its red color resulting from a substantial amount of iron oxide content. It is also quite alkaline and thus harmful to many forms of life. Direct disposal of the material is therefore not possible and it is stored in large pools within the plant's vicinity. Development of solutions for safe disposal or possible development of ways of using this residue for other industrial processes could help to restore polluted locations and eliminate negative impacts on the environment.

Within steelmaking operations, approximately 200 kg (electric furnace route) to 400 kg (blast furnace/ converter route) of slag are produced for making one tonne of liquid steel, resulting in generation of more than 400 million tonnes of iron and steel slag each year. Steelmaking slags are a mixture of silica, calcium oxide, magnesium oxide, aluminum oxide and iron oxides. The amount of discarded slag can be significantly reduced when the steelmaking converter is charged with blast furnace hot metal (also known as pig iron) which has been treated to partially remove phosphorus and sulphur impurities. The focus of the present research is to examine the feasibility of using red mud based fluxes for the refining of blast furnace hot metal. The advantage of this approach is to use the waste material from the aluminum industry to reduce the waste slag produced by the steel industry. Reuse of the red mud prevents landfill waste, helps preserve natural resources and supports the sustainability of the aluminum industry. In addition, it should also generate additional revenues for the aluminum and steelmaking industries. The main thrust of this study is the development of a potential application for red mud – a fluxing agent with high refining capacity – to absorb harmful impurities such as phosphorus and sulphur from hot metal.

## **1.2** Objective of the study

The specific objectives of the research can be defined as follows.

- 1. Physical and chemical characterization of the red mud.
- 2. Design and thermo-chemical evaluation of synthetic fluxes for dephosphorization and desulphurization of hot metal.
- Determination of the melting properties of red mud based fluxes containing additives such as CaO, Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O and SiO<sub>2</sub>.
- 4. Examination of the effect of the above additives on the phosphate and sulphide capacities of molten slag.
- 5. Measurement of the phosphorus and sulphur distribution between carbon saturated iron and red mud based slags.

## **1.3** Organization of the dissertation

This dissertation has been structured in five chapters as follow. **Chapter 2** presents a review of literature pertaining to the present study including a general review of red mud, hot metal treatment, desulphurization and dephosphorization. This chapter also presents the fundamental aspects of desulphurization and dephosphorization. The experimental design is explained in **Chapter 3** along with the experimental conditions and measurement techniques. The experimental results are provided and discussed in **Chapter 4**. **Chapter 5** presents the conclusions arising from this research. **Chapter 6** lists a series of recommendation for future work. An overview of the research is shown schematically in Figure 1-1.



Figure 1-1: Dissertation overview

## Chapter 2

# 2 Literature Review

In this chapter, a literature review is presented to explain the source of red mud and its possible applications (Sections 2.1 and 2.2). Hot metal and refining flux properties are discussed in Sections 2.3 and 2.4 respectively. Theoretical consideration of desulphurization and dephosphorization of hot metal and published results are described in Sections 2.5 and 2.6 respectively.

## 2.1 Aluminum production chain

Alumina (aluminum oxide,  $Al_2O_3$ ) is an essential raw material for aluminum industries. The most significant aluminum ore is bauxite. Bauxite consists mostly of the minerals gibbsite (Al(OH)<sub>3</sub>), boehmite ( $\gamma$ -AlO(OH)), and diaspore ( $\alpha$ -AlO(OH)) in a mixture with the two iron oxides goethite (FeO(OH)) and hematite (Fe<sub>2</sub>O<sub>3</sub>), and small amounts of anatase (TiO<sub>2</sub>)[1].

Extracting aluminum from bauxite involves two processes. First, the ore can be refined by the Bayer process, the lime - soda sintering process, or a combined process to eliminate impurities such as iron oxide, silica and titanium oxide. When the ratio of alumina to silicon oxide in bauxite is higher than 7:10, the Bayer process is used to extract alumina from the bauxite, Figure 2-1a. On the other hand, the lime- soda sintering process is employed for the treatment of low quality bauxite ores, as illustrated in Figure 2-1b. Then, the final product (i.e., high-grade metallurgical alumina [Al<sub>2</sub>O<sub>3</sub>]), is electrolyzed using the Hall-Heroult process to produce primary aluminum [1, 2].

#### 2.1.1 Bayer process

The Bayer process is the main route for alumina production. This process was patented by Bayer in 1892. The process involves four steps: digestion, clarification, precipitation, and calcination as depicted in Figure 2-1a.

#### 2.1.1.1 Digestion

In this step, ground bauxite is mixed with a hot solution of sodium hydroxide at 106°C-240°C, and pumped into large pressure tanks called digesters. The sodium aluminate is formed by the reaction of sodium hydroxide with the aluminous minerals of bauxite. Insoluble impurities remain in suspension and are separated in the clarification step and called bauxite residue. Lime (CaO) is also introduced in the Bayer process to enhance the extraction of alumina[1].

$$Al(OH)_{3(s)} + NaOH_{(aq)} \rightarrow Na^+ + Al(OH)_{4(aq)}^-$$
 2-1

$$AlO(OH)_{(s)} + NaOH_{(aq)} + H_2O \rightarrow Na^+ + Al(OH)_{4(aq)}^- 2-2$$

## 2.1.1.2 Clarification

In this step, the insoluble residue is separated from the sodium aluminate solution. Finer residue is settled by the addition of synthetic coagulants such as polyacrylate and polyamides. The temperature of the clarified solution can be decreased in heat exchangers to change the degree of supersaturation of the dissolved alumina[1].

## 2.1.1.3 Precipitation

The clarified solution is pumped into precipitators and the seed crystals – aluminum hydroxide crystals – are added to the solution in the precipitators to accelerate crystal formation. The agglomerates of aluminum hydroxide crystals are filtered and washed to remove remaining caustic solution[1].

$$Na + Al(OH)_{4(aq)}^{-} \rightarrow Al(OH)_{3(s)} + NaOH_{(aq)}$$
 2-3

#### 2.1.1.4 Calcination

The filtered aluminum hydroxide is calcined in a furnace at 960°C to produce commercially pure alumina[1].

$$2Al(OH)_{3(s)} \rightarrow Al_2O_{3(s)} + 3H_2O_{(g)}$$
 2-4

### 2.1.2 Lime – soda sintering process

This process can be used for bauxite containing diaspore or low quality bauxite ore to produce alumina Figure 2-1b. However, high-energy consumption and environmental pollution are the

drawbacks of this method compared to the Bayer process. In this process, limestone and caustic soda are mixed with crushed bauxite ores, then the mixture is sintered at high temperature to generate sodium aluminate which is dissolved in water or diluted alkaline for further processing.



Figure 2-1: Alumina production flowcharts (a) Bayer process and (b) lime- soda sintering process

## 2.2 Red mud

Extraction of alumina from bauxite ore generates a significant amount of bauxite residue. The high concentration of iron containing minerals in this residue gives its characteristic red color and creates the so-called red mud. The chemical compositions and properties of red mud depend on the chemical and mineralogical composition of bauxite and the bauxite treatment technology used in the alumina production.

As a global average, the production of 1 tonne of aluminum generates 2-3 tonnes of red mud. Presently, according to the global inventory, the accumulation of worldwide bauxite residue is estimated to be over 2.7 billion tonnes as a legacy of nearly 120 years of alumina extraction from bauxite ore and is increasing by more than 90 million tonnes yearly, Figure 2-2 [3].



Figure 2-2: Accumulated bauxite residue (red mud) all over the world for 6 years [3]

## 2.2.1 Chemical and mineralogical characteristics of red mud

The mineralogy and chemical composition of the red mud depends on the quality of the bauxite and the refining process parameters. In general, the red mud consists of iron oxide, aluminum oxide, titanium oxide, sodium oxide, silicon oxide, and calcium oxide [4]. The chemical composition of red mud from selected plants is presented in Table 2–1. Like most ores and soils, bauxite can contain traces of metals such as arsenic, beryllium, cadmium, chromium, lead, manganese, nickel and naturally occurring radioactive materials, such as thorium and uranium. Most of these trace elements stay in the residue [4].

	Australia [5]	Jamaica [6]	Spain [5]	Canada [7]	Germany [5]	Italy [8]	China [9]	China [10]*
Fe <sub>2</sub> O <sub>3</sub>	34.8	49.5	37.5	31.6	44.8	46.1	36.2	12.3
$Al_2O_3$	23.2	16.5	21.2	20.6	16.2	15.3	20.9	6.27
CaO	2.3	5.5	5.5	1.7	5.2	4.4	3.0	37.5
TiO <sub>2</sub>	8.0	7.0	11.5	6.2	12.3	8.8	6.3	3.3
Na <sub>2</sub> O	7.1	7.0	2.3	10.3	4.0	6.4	12.7	2.8
SiO <sub>2</sub>	9.2	3.0	4.4	8.9	5.4	8.3	15.9	17.8

Table 2–1: Chemical composition of red muds from different operations (wt%)

\* Represent the sintering process of red mud

## 2.2.2 Negative effects of red mud

Red mud is categorized as a non-hazardous waste. However, because of the size of this waste stream and its causticity, the red mud disposal leads to important environmental concerns. At present, the red mud is disposed into sealed or unsealed artificial ponds close to the extraction plant, and therefore a considerable amount of land is required. Hence, water with caustic sodium compounds and other toxic materials from the red mud can penetrate to the ground and contaminate ground waters, damage ground cover in large areas, and affect ecosystems. There is also the possibility of leaks and flood, such as red mud spill in 2010 in the Hungarian town of Akja, when the burst of a retaining wall following a period of heavy rain, released one million cubic meters of the toxic red sludge to the surrounding area, killing 10 people and injuring several hundred Figure 2-3.



Figure 2-3: The red mud catastrophe in Hungary, October 2010 (Air photo by Digital Globe)

## 2.2.3 The possible applications of red mud

In spite of the environmental concern of this large waste stream and the exploitation possibilities of red mud for further processing, red mud has never been satisfactorily utilized as a by-product despite 50 years of research and hundreds of related patents and publications. Available potential options for utilization of red mud including the process and final products are summarized in Table 2–2.

In order to successfully convert bauxite residue into a product of value, it will be necessary to overcome the technological and ecological complications. Since red mud contains a significant amount of valuable oxides, a possible application could be in steelmaking industry [11]. Thus, this project is aimed at generating more information and understanding about utilization of red mud as a refining flux in steel manufacturing for desulphurization and dephosphorization of liquid iron during pretreatment of hot metal.

Application	Processes	Product	Reference	
An agricultural modification for	Addition to soil	Improvement of soil properties	[4, 12-14]	
improvement of sandy soils	Neutralization, adsorption	Remediation of soil, re- vegetation		
Material for	Drying, sintering, annealing	Production of cements		
construction purposes (e.g., cement, road fill,	Addition	Production of concrete fillers	[4, 9, 14-18]	
brick making)	Drying, pressing, firing, granulation	Brick production and aggregates of special concretes		
Source of raw	Drying, pelletisation, annealing	Ceramic manufacturing, ceramic glazes	[4, 8, 14, 19-22]	
- ceramic	Addition	Glass manufacturing		
Feedstock for mineral production	Drying, reduction, leaching	Production of Fe <sub>2</sub> O <sub>3</sub> , Al <sub>2</sub> O <sub>3</sub> , TiO <sub>2</sub>	[4, 14, 23-25]	
	Adsorption	Removing of undesirable components		
Applications of red mud in waste water treatment	Chemical treatment	Filtration material	[4, 14, 26-29]	
	Coagulation	Coagulant		
Neutralizing treatment material	Chemical treatment	Filtration material		
for acidic mining wastes	Adsorption	Neutralization of acid mine drainage	[4, 5, 14]	

# Table 2–2: Red mud utilization possibilities

## 2.3 Hot metal

In the steel industry, the blast furnace/converter combination is still the dominant route for making iron. The blast furnace is a metallurgical unit that utilizes coke, limestone and iron ore to produce liquid iron, which is known as hot metal or pig iron. The molten iron is separated from the liquid slag and treated to reduce the content of impurity elements such as sulphur, silicon, and phosphorus.

The chemical composition of hot metal can be varied depending on the composition of the ore charged in the blast furnace, and the method of furnace operation. The chemical compositions of typical hot metal (pig iron) grades are shown in Table 2–3.

Type of hot metal	wt% C	wt% Si	wt% Mn	wt% P	wt% S
Low-phosphorus	4.0-4.5	0.30-0.70	0.20-0.70	0.05-0.12	0.03-0.06
High-phosphorus	3.2-4.0	0.30-0.70	0.25-1.20	1.5-2.20	0.03-0.06
Foundry	3.5-4.2	1.8-2.5	0.70-1.00	0.50-0.70	0.03-0.06

Table 2–3: Typical hot metal composition [30]

Phosphorus and sulphur are the two most deleterious impurity elements found in hot metal. Phosphorus increases the tendency toward cold shortness in steel. It also makes the steel prone to temper embrittlement during heat treatment. Therefore, lowering phosphorus content in steel is a necessary step for all applications requiring steel with high deformability [31].

Sulphur improves machinability, but cannot be used in steel unless there is sufficient manganese to combine with it to form manganese sulphide. If manganese is not present, sulphur forms a low melting iron sulphide network around the austenite grain boundaries. Steel with this structure is very weak and brittle at hot working temperatures (900-1100 °C) and this phenomenon is called hot shortness. Manganese sulphide exist as an isolated phase, rather than network, and acts as an internal lubricant and chip breaker. Internal lubricants reduce friction and wear between tool and work-piece and tool and chip. Table 2–4 shows a summary of the effect of phosphorus and sulphur on steel properties [32].

Property	Effect of phosphorus	Effect of sulphur			
Strength ++					
Bake hardenability	+				
Ductility		Effect of sulphur			
Machinability		MnS: internal lubricant and chip breaker			
Fe-Zn Galvanneal	Can improve resistance to powdering.				
Phosphatability	+				
Fracture toughness					
Weldability	Not harmful up to ~0.1 wt%				
Stress corrosion cracking					

Table 2–4: Typical effects of phosphorus and sulphur in steel [32]

+ Increase + + Strong increase — Decrease — Strong decrease

## 2.3.1 Pretreatment of hot metal

Today, the most common process for steelmaking is the integrated steelmaking process: The blast furnace ironmaking is followed by the hot metal pretreatment, decarburization in a BOF (Basic Oxygen Furnace) and secondary refining. Hot metal pretreatment involves the removal of impurity elements such as silicon, phosphorus and sulphur. Hot metal is then decarburized and converted to steel in the BOF using an oxygen blowing process. The molten steel tapped from BOF is subjected to further refining and degassing in a processing step known as secondary refining.

The hot metal pretreatment process was developed by the Japanese steel industry in the early 1980s. Meanwhile, several similar processes have been adopted within the industry to improve cost-effectiveness by decreasing the amount of disposed slag (as a result of its impact on the environment), lowering the extent of refractory wear and increasing the steel yield [31].

Hot metal pretreatment involves desiliconization, dephosphorization, and desulphurization reactions. The desiliconization step can reduce the silicon content to less than 0.2 wt% to

improve the efficiency of the following stages for phosphorus and sulphur removal. Common procedures for hot metal desiliconization are listed in Table 2–5.

Process	Regent usage	Efficiency %		
Mill scale and lime added to BF runner	15-25 kg t <sup>-1</sup> mill scale, 8-10 kg t <sup>-1</sup> lime	80-90		
Mill scale added to transfer ladle	32 kg t <sup>-1</sup> mill scale	60-80		
Mill scale injection into torpedo car	15-25 kg t <sup>-1</sup> mill scale	40-60		
Oxygen blowing into torpedo car	0.13 Nm <sup>-1</sup> t <sup>-1</sup>	35-40		
Deep oxygen injection into transfer ladle	$0.3 \text{Nm}^{-1} \text{t}^{-1}$	45-55		

Table 2–5: Processes and fluxes for desiliconization [31]

After desiliconization and deslagging, dephosphorization and desulphurization steps are carried out by injection of an oxidizing agent using a carrier gas such as nitrogen or air, and in some cases top or bottom oxygen blowing. Typical fluxes and different processes, which are used in this step, are listed in Table 2–6. Low sulphur steels can be produced by further desulphurization through injection of more reactive agents [31]

Table 2-6: Common processes and fluxes for dephosphorization and desulphurization [31]

			wt% P		wt% S		
Process	Vessel	Flux mixture, wt%	Kg <sup>-1</sup>	Before	After	Before	After
Injection with N <sub>2</sub>	Torpedo car	35 CaO, 55mill scale, 5 CaF <sub>2</sub> , 5 CaCl <sub>2</sub>	52	0.10	0.015	0.025	0.005
Injection with N <sub>2</sub> ,O <sub>2</sub> top blowing	Torpedo car	Na <sub>2</sub> CO <sub>3</sub>	20	0.09	0.020	0.060	0.01
$Na_2CO_3$ top addition $O_2$ top blowing	Ladle	Na <sub>2</sub> CO <sub>3</sub>	20	0.10	0.010	0.030	0.005
Injection with N <sub>2</sub>	Ladle	30 CaO, 62 sinter fine, 4CaF <sub>2</sub> , 4 CaCl <sub>2</sub>	45	0.12	0.010	0.025	0.01
Injection with N <sub>2</sub> ,O <sub>2</sub> top blowing	Ladle	38 CaO, 42 sinter fine, 20 CaF <sub>2</sub>	40	0.10	0.010	0.040	0.02
O <sub>2</sub> top blowing	Q-BOP	39 CaO, 55 sinter fine, 6 CaF <sub>2</sub>	51	0.14	0.010	0.020	0.01

The overall economic benefits of hot metal pretreatment depend on the availability and relative cost of raw materials, steel scrap and hot metal. Today, using fully refined hot metal in BOF charge is neither practical nor cost-effective in most steel plants outside of Japan. Hot metal pretreatment in the European and North American steel plants is confined to desulphurization in the transfer ladle with injection of materials such as lime, calcium carbide, soda ash, magnesium, and fluxes containing these elements and compounds.

## **2.4** Physicochemical properties of fluxes

In order to understand the efficiency of the treatments of liquid metal under slag, many efforts have been made by researchers to evaluate the physicochemical properties of slags.

Flux, is the substance added to molten metals in order to help separate its bonds with impurities which can then be readily removed (known as slag). "Slag consists mostly of mixed oxides of elements such as silicon, sulphur, phosphorus, and aluminum; ash; and products formed in their reactions with furnace linings and fluxing substances such as limestone" [33]. Slags play an important role in metal production. In metallurgical industries, slags are found in various processing routes and serve different purposes. Metallurgical slags are usually based on the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system. Practically, liquid slags can be used for different purposes such as covering the surface of liquid metal to prevent oxidation, and absorbing undesirable elements and inclusions from the liquid metal.

#### 2.4.1 Structural aspects of molten slags

Essentially, physicochemical properties of molten slag can be controlled by their structure. Many theories of molecular and ionic structure have been suggested to define slag properties[34]. According to the molecular theory, liquid slag is composed of separate oxides such as  $SiO_2$ ,  $Al_2O_3$ , FeO, and CaO. However, electric conductivity behaviours have shown that molten slags are usually ionic conductors [31, 34]. Thus, the molten slags are made up of ions and ions are involved in reactions between metal and slag.

In this definition, liquid slags consist of cations (e.g.,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Fe^{2+}$ ), anions (e.g.,  $O^{2-}$ ,  $F^{2-}$  and  $S^{2-}$ ) and anion complexes such as  $SiO_4^{4-}$ ,  $PO_4^{3-}$ , and  $AlO_3^{3-}$  [34]. Moreover, molten slag contains silica and/or other complex constituents. Silicate slags are three-dimensional

arrangements with  $Si^{4+}$  (cations) surrounded by four oxygen anions (O<sup>2-</sup>) and form a tetrahedron. When each (O<sup>-2</sup>) is connected to two  $Si^{4+}$  ions, (bridging O), this causes the formation of a 3-D array structure.

The silicate tetrahedron  $SiO_4^{4-}$  can be defined as the fundamental building unit in solid silica and molten silicate. The silicate units are joined together in chains to introduce a large polymerized network of silicate anions Figure 2-4.



Figure 2-4: Two dimensional schematic representation of (a) crystalline and (b) molten silica [31]

The addition of basic oxides (e.g., FeO, CaO, MnO) to molten silica results in their dissociation into metallic cations and oxygen anions. This oxygen anion bonds with SiO<sub>2</sub> in the silica structure and brings about a breakdown of the silicate network with an increasing degree of depolymerisation. In fact, some of the oxygen atoms are connected between two silicon atoms (*i.e.*, bridging oxygen  $[O^\circ]$ ), and some to only one silicon atom (*i.e.*, they act as a non-bridging oxygen  $[O^\circ]$ ). The partial depolymerization of the silicate network is shown in Figure 2-5a. The silicate network can be completely depolymerized to single SiO<sub>4</sub><sup>4-</sup> tetrahedra and cation (e.g., Ca, Fe, Mn) and some free oxygen ions (O<sup>2-</sup>) by addition of more basic oxide Figure 2-5b.

The silicate network theory can be applied to explain the physicochemical properties of molten slag such as viscosity. In molten slag the size of the silica and aluminisilicate network increases

with increasing  $Al_2O_3$  and  $SiO_2$  and results in a higher viscosity due to polymerization of the silicate network. The addition of metal oxide brings about a breakdown of the silicate network, resulting in lower viscosity [31].



Figure 2-5: Schematic structural of depolymerization of silicate network with the addition of a basic oxide [31]

## 2.4.2 Basicity definition

Defining basicity is essential to characterize the composition and properties of slags in a simple and practical manner. There are two approaches to defining basicity of slags. One is a simple ratio of concentration of basic to acidic components, and the other is the activity of the free oxygen ions in the slag [35].

#### 2.4.2.1 Common basicity indices

From the first approach, the general equation for slag basicity can be simplified by the following expression:

$$B = \frac{\% CaO}{\% SiO_2}$$
2-5

This ratio is simple, but does not take into account the effect of oxides other than CaO and  $SiO_2$  (MgO, Al<sub>2</sub>O<sub>3</sub>, FeO, etc.) which are often present in slag in large quantities. Many suggestions

have been made to establish more inclusive measures for slag basicity, several of which are listed in Table 2–7.

$\frac{\%(Ca0)}{\%(Si0_2) + \%(Al_20_3)}$
%(CaO)
$\sqrt{(SiO_2) + \%(P_2O_5)}$
%(CaO) + 1.4% (MgO)
$\overline{\%(SiO_2) + 0.84\%(P_2O_5)}$
%(CaO) - 1.86%(SiO <sub>2</sub> ) - 1.19%(P <sub>2</sub> O <sub>5</sub> )
$x(CaO) + \frac{0.5x(MgO)}{x(SiO_2)} + 0.33(Al_2O_3)$

Table 2–7: Typical expressions for basicity [34]

### 2.4.2.2 Optical basicity

The second approach in the ionic theory of slags is the activity of the free oxygen ion, a (O<sup>2-</sup>). Essentially, basicity of a slag can be increased by increasing the quantity of basic oxides. Basic oxides tend to dissociate into a cation and oxygen ion (*i.e.*, when the concentration of free oxygen ion [O<sup>2-</sup>] increases, so does the basicity), although, the thermodynamic activity of the oxygen ion (O<sup>2-</sup>) cannot be determined.

The concept of optical basicity was developed by two glass scientists Duffy and Ingram[36] and introduced to the metallurgical community by Duffy, Ingram and Sommerville in the late seventies [37]. Duffy and Ingram suggested that optical basicity corresponds to the electron donor power of the oxygen ions in glass [36]. They showed experimentally that the shift in frequency of the ultraviolet (UV) spectral of probe ions such as Pb<sup>2+</sup> may be used as a measure of the electron donor power of the oxide ions which is commonly expressed in terms of the optical basicity ( $\Lambda$ ) by using the following equation:

$$\Lambda_{i} = \frac{\nu_{free} - \nu_{slag}}{\nu_{free} - \nu_{CaO}}$$
 2-6

Where:  $v_{free}$ ,  $v_{sample}$ , and  $v_{CaO}$  are shift in peak frequencies for  $Pb^{2+}$ ,  $Pb^{2+}$  in a slag and  $Pb^{2+}$  in CaO, respectively. By definition, the optical basicity value is 1 for pure CaO.
Duffy and Ingram [36] indicated that optical basicity value can be calculated from the Pauling electronegativity number. They introduced a simple formula from the data of materials with known optical basicity, and formulated a relationship between lambda (optical basicity of an oxide  $\Lambda_i$ ) and Pauling's electronegativity of the cation, x, which is shown below in Equation 2-7.

$$\Lambda_{\rm i} = \frac{0.74}{(\rm x - 0.26)}$$

In comparison, the average electron density scale was suggested by Nakamura *et al.* [38, 39] for optical basicity assessment. The obtained optical basicity values for some oxides calculated from Pauling's electronegativities and from average electron density are listed in Table 2–8. Although the two values are in good agreement for most oxides, they do not match for the transition metal oxides. Summerville and Yang [40] proposed that the average electron density gives a more accurate value for the transition metal oxides and suggested a list of recommended optical basicity values as shown in Table 2–8.

For multi-component slags, the optical basicity can be calculated using the following relationships:

$$\Lambda = \sum_{i=1}^{n} \Lambda_i N_i$$

$$N_i = \frac{X_i n_{O_i}}{\sum_{i=1}^{n} X_i n_{O_i}}$$
2-9

Where:

- $\Lambda_i$ : Optical basicity of oxide component "i"
- Λ: Optical basicity of a multicomponent slag
- N<sub>i</sub>: Compositional fraction
- $X_i$ : Mole fraction of component "i" in the slag
- $n_{O_i}$ : Number of oxygen atoms in component "i"

The optical basicity approach has proved to be a valuable tool for designing slags or fluxes which will have the required characteristics with respect to the behavior of different components such as sulphur, phosphorus, hydrogen, magnesia and alkalies [40-43].

Oxide	Optical basicity calculated from Pauling electronegativity*	Optical basicity calculated from electron density**	Recommended optical basicity***
K <sub>2</sub> O	1.04	1.15	1.40
Na <sub>2</sub> O	1.15	1.10	1.20
BaO	1.15	1.08	1.10
CaO	1.00	1.00	1.00
MnO	0.59	0.95	0.95
FeO	0.51	0.93	0.93
MgO	0.78	0.92	0.85
Fe <sub>2</sub> O <sub>3</sub>	0.48	0.69	0.69
$Al_2O_3$	0.61	0.68	0.65
TiO <sub>2</sub>	0.61	0.64	0.65
SiO <sub>2</sub>	0.48	0.47	0.48
$P_2O_5$	0.40	0.38	0.40

Table 2-8: Values of optical basicity of some oxides from different sources [44]

\*: Duffy and Ingram [36] \*\*: Nakamura *et al.* [38, 39] \*\*\*: Summerville and Yang [40]

# 2.5 Desulphurization

Practically, different fluxes can be used to remove sulphur from liquid metal. Sulphur dissolves into molten fluxes as sulphide ions ( $S^{2-}$ ) in reducing conditions ( $P_{O_2}$  less than 10<sup>-6</sup> atm), and as sulphate ions ( $SO_4^-$ ) under highly oxidizing conditions. However, the oxygen potential in the steelmaking process is not high enough for sulphur to dissolve as sulphate ions in molten fluxes[31]. The desulphurization phenomenon occurring in molten fluxes can be evaluated by either the sulphide capacity or sulphur partition ratio. The sulphide capacity is the ability of a liquid flux to hold sulphur in solution at equilibrium conditions with a liquid metal or gas. The sulphur partition ratio shows the ratio of sulphur in flux to sulphur in metal phase.

### 2.5.1 Thermodynamics of desulphurization

### 2.5.1.1 Sulphide capacity and sulphur partition ratio

Fundamentally, the solubility of sulphur in the steelmaking process has two important reactions [45] for the equilibrium in slag-metal and slag-gas systems respectively:

$$[S] + (0^{2^{-}}) = (S^{2^{-}}) + [0]$$
 2-10

$$\frac{1}{2}S_2(g) + (0^{2-}) = (S^{2-}) + \frac{1}{2}O_2(g)$$
 2-11

The equilibrium constant for reactions **2-10** and **2-11** are represented by Equations **2-12** and **2-13** correspondingly:

$$K_{1} = \frac{a_{S^{2-}}}{a_{O^{2-}}} \cdot \frac{h_{O}(1wt\%)}{h_{S}(1wt\%)}$$
2-12

$$K_{2} = \frac{a_{S^{2-}}}{a_{O^{2-}}} \cdot \left(\frac{P_{O_{2}}}{P_{S_{2}}}\right)^{\frac{1}{2}}$$
2-13

Where:  $a_{0^{2-}}$  and  $a_{S^{2-}}$  are the activities of sulphur and oxygen ions in slag phase.

 $P_{O_2}$  and  $P_{S_2}$  are the partial pressures of  $S_2(g)$  and  $O_2(g)$ .

 $h_{s}(1wt\%)$  and  $h_{0}(1wt\%)$  are the activities of sulphur and oxygen in liquid iron according to the one weight percent standard state.

With respect to the one weight percent standard state, the activity of sulphur in iron is defined by:

$$h_{S}(1wt\%) = f_{S}(1wt\%) \cdot [wt\% S]_{metal}$$
 2-14

Where:  $f_{S}(1wt\%)$  is the activity coefficient of sulphur based on the one weight percent standard state.

For infinitely dilute solutions, the activity of sulphur in the slag phase  $(a_{S^{2}})$  is proportional to the concentration and can be defined as:

$$a_{S^{2-}} = N_{S^{2-}} \cdot \gamma_{S^{2-}}$$
 2-15

$$N_{S^{2-}} = \frac{n_{S^{2-}}}{\sum n}$$
 2-16

Where:  $\gamma_{S^{2-}}$  is the activity coefficient of sulphur in the slag and  $n_{S^{2-}}$  is the number of mols of sulphur and n total number of mols.

Since the slag composition is reported in mass percent,  $n_{S^2}$ -per 100g of the substance is given by the ratio:

$$n_{S^{2-}} = \frac{(wt\% S)}{M_S}$$
2-17

With the atomic mass of sulphur being 32g/mol, the activity of sulphur in the slag phase,  $a_{S^{2-}}$ , can be defined by a simplified equation:

$$a_{S^{2-}} = (wt\% S) \cdot C \cdot \gamma_{S^{2-}}$$
 2-18

Where:

$$C = \frac{1}{32\sum n}$$
2-19

Therefore the equilibrium constants in Equations 2-12 and 2-13 can be rewritten as:

$$K_{1} = \frac{(wt\% S)C \gamma_{S^{2-}}}{a_{O^{2-}}} \cdot \frac{h_{O}(1wt\%)}{[wt\% S] \cdot f_{S}(1wt\%)}$$

$$(wt\% S)C \gamma_{S^{2-}} \cdot (P_{O^{2}})^{\frac{1}{2}}$$
2.21

$$K_{2} = \frac{(wt\% S)C \gamma_{S^{2-}}}{a_{0^{2-}}} \cdot \left(\frac{P_{0^{2}}}{P_{S^{2}}}\right)^{\frac{1}{2}}$$
2-21

A new reaction can be constructed by combining Reactions 2-10 and 2-11 as follow:

$$\frac{1}{2}S_2(g) + [0] = \frac{1}{2}O_2(g) + [S]$$
2-22

The equilibrium constant for reaction 2-22 can be expressed as follows:

$$K = \frac{[wt\% S] \cdot f_{s}(1wt\%)}{h_{0}(1wt\%)} \cdot \left(\frac{P_{O_{2}}}{P_{S_{2}}}\right)^{\frac{1}{2}}$$
2-23

The sulphur capacity and the sulphur partition ratio can then be obtained by rearranging Equations 2-20 and 2-21:

$$\frac{(wt\% S)}{[wt\% S]} = \frac{K_1 a_{0^{2-1}} f_s(1wt\%)}{C\gamma_{S^{2-1}} h_0(1wt\%)} = L_S$$
2-24

Where:  $L_S$  is sulphur partition ratio.

Fincham and Richardson [46] defined the sulphide capacity,  $C_S$ , of the slag as follows:

$$(wt\%s)_{slag} = \frac{K_2 a_{0^{2-}}}{C\gamma_{S^{2-}}} \cdot \sqrt{\frac{P_{S_s}}{P_{O_2}}}$$
 2-25

$$C_{S} = \frac{K_{2}a_{0^{2^{-}}}}{C\gamma_{S^{2^{-}}}} = (wt\% S)_{slag} \cdot \left(\frac{P_{0_{2}}}{P_{S_{2}}}\right)^{\frac{1}{2}}$$
2-26

Where (wt% S) is the concentration of sulphur in the slag, while  $P_{O2}$  and  $P_{S2}$  are partial pressures of oxygen and sulphur in the gas phase from the slag-gas exchange reaction [46].

The value of  $C_S$  the sulphide capacity of the slag is a directly measurable quantity that can be used as a property which depends on temperature and composition of slag. This is a valuable parameter to compare the desulphurization ability of different slags.

The relationship between sulphur partition ratio ( $L_s$ ) and sulphide capacity ( $C_s$ ) can be obtained by combining Equations 2-23 and 2-26:

$$C_{s} = (wt\%S) \cdot \frac{K \cdot h_{0}(1wt\%)}{[wt\%S] \cdot f_{s}(1wt\%)}$$
2-27

$$\log_{C_{S}} = \log(wt\% S) + \log K + \log h_{0}(1wt\%) - \log[wt\% s] - \log f_{s}(1wt\%)$$
2-28

$$\log C_{s} = \log \frac{(wt\% S)}{[wt\% S]} + \log K - \log f_{s}(1wt\%) + \log h_{0}(1wt\%)$$
 2-29

The equilibrium constant K can be derived from the standard free energy.

The standard free energy and equilibrium constant for reaction 2-22 are:

$$\Delta G^{\circ} = -17907.96 + 26.36 \text{ T} \quad \text{J. mol}^{-1}$$
 2-30

$$\log K = \frac{935.45}{T} - 1.375$$
 2-31

By substituting log K as  $\left(\frac{935.45}{T} - 1.375\right)$  and  $\frac{(wt\% S)}{[wt\% S]}$  as (L<sub>S</sub>), Equation **2-29** can be re-written as:

$$\log C_{s} = \log L_{s} + \log h_{0}(1wt\%) - \log f_{s}(1wt\%) + \frac{935.45}{T} - 1.375$$
 2-32

Considering the dissolution of oxygen into liquid iron, the equation is:

$$\frac{1}{2}O_2(g) = [0] \quad \Delta G^\circ = -115750 - 4.63 \text{ T} \qquad \text{J.mol}^{-1} \qquad 2-33$$

$$K = \frac{h_0(1wt\%)}{p_{0_2}^{\frac{1}{2}}}$$
 2-34

$$\log K = \log h_0(1wt\%) - \frac{1}{2} \ln P_{O_2} = \frac{6121}{T} + 0.15$$
 2-35

$$\log h_0(1 \text{wt\%}) = \frac{1}{2} \ln P_{O_2} + \frac{6121}{T} + 0.15$$
2-36

By substituting  $\log h_0(1wt\%)$  into Equation 2-32, the following equation can be presented:

$$\log C_{\rm S} = \log L_{\rm S} + \frac{1}{2} \log P_{\rm O_2} - \log f_{\rm S} + \frac{7055}{\rm T} - 1.224$$
 2-37

where  $f_S$ , the activity coefficient for low solute content, can be obtained by using the following formulation:

$$\log f_i = e_i^i [\%i] + \sum e_i^j [\%j]$$
 2-38

In this equation, i represents the dissolved element in the liquid metal and  $e_i^j$  is the interaction coefficient of *i* as affected by alloying element *j*.

The dependence of final sulphur content  $[S]_f$  and initial sulphur content  $[S]_i$  in liquid steel, the sulphur distribution ratio,  $L_S$ , and the ratio of slag to metal quantities, Q, is given here:

$$[S]_{f} = \frac{[S]_{i}}{1 + L_{s} \cdot Q}$$
2-39

Equation 2-39 and Equation 2-37 are important for evaluation of the desulphurization in the steelmaking process.

#### 2.5.2 Composition and temperature dependence of sulphide capacity

Many efforts have been made to determine the composition and temperature dependence of sulphide capacity [41, 47-50]. The basicity has traditionally been considered as being a function of composition. Nevertheless, it may vary with temperature due to thermally activated polymerization or depolymerization of the complex ions in the slag melt [41, 51].

### 2.5.3 Relationship between optical basicity and sulphide capacity

An empirical model was developed by Sommerville and Sosinsky [51] where sulphide capacity was related to the composition through optical basicity as shown in Figure 2-6. The resulting relationship that they obtained for a temperature of 1500 °C is given as:

$$\log C_{\rm S} = 12.6 \, \Lambda - 12.3$$
 2-40

Sosinsky and Sommerville [41] also investigated temperature dependence of sulphide capacity based on previously measured data for melts free of transition metal oxides. Their results are shown in Figure 2-7.



Figure 2-6: Relationship between sulphide capacity and optical basicity of slags at 1500 °C [41]



Figure 2-7: Plot of the logarithm of the sulphide capacity vs. 1/T for various iso-optical basicities [41]

Taniguchi *et al.* [52] studied the relationship between  $\log C_S$  and temperature. Their results are shown in Figure 2-8 along with other published data. It can be seen that the slope of  $\log C_S$  vs.  $10^4/T$  from Taniguchi *et al.* work [52] is in very good agreement with that of Hayakawa *et al.* [50]. The relationship is linear with slight increase of the slope at higher optical basicity.



Figure 2-8: Relationship between log C<sub>S</sub> and temperature in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO slags, numerical values show optical basicity [52]

Equation 2-40 is useful only for a fixed temperature of 1500 °C. Therefore, Sosinsky and Sommerville [41] derived an empirical correlation between sulphide capacity, optical basicity and temperature in the range 1400 °C  $\leq$  T  $\leq$  1700 °C which is appropriate for ironmaking, external treatment of hot metal and steelmaking. The relation is shown by the following equation:

$$\log C_{\rm S} = \frac{22690 - 54640\,\Lambda}{\rm T} + 43.6\Lambda - 25.2$$
 2-41

where: T is the temperature in K and

 $\Lambda$  is the optical basicity.

Young *et al.* [53] showed that Equation **2-41** can be applied for higher sulphide capacity. Therefore, Young *et al.* modified the Sosinsky's expression and suggested the following relationships:

For 
$$\Lambda \leq 0.8$$

$$\log C_{\rm S} = -13.913 + 42.84\Lambda - 23.82\Lambda^2 - \left(\frac{11710}{\rm T}\right) - 0.02223(\% {\rm SiO}_2) - 0.02275(\% {\rm Al}_2 {\rm O}_3)$$
2-42

For  $\Lambda \ge 0.8$ 

$$\log C_{\rm S} = -0.6261 + 0.4808\Lambda + 0.7917\Lambda^2 - \left(\frac{1697}{\rm T}\right) + \frac{2587\Lambda}{\rm T} - 5.144$$
× 10<sup>-4</sup>(%FeO)
2-43

# 2.5.4 Sulphide capacity measurement techniques

According to different literature [32, 47, 48, 54] two types of experiments can be performed to obtain the sulphide capacity of a slag under equilibrium conditions. The first technique [32, 54] involves equilibrating slag and metal in a controlled atmosphere. Then sulphide capacity can be calculated from the sulphur distribution ratio, temperature, and the oxygen potential of the system according to Equation 2-37. In the second method [47, 48] the sulphide capacity is defined from the slag-gas equilibrium reaction with a gas mixture of known oxygen and sulphur partial pressures to describe the absorption potential of sulphur from the gas phase to form sulphide in the slag phase.

#### 2.5.5 Slags in desulphurization

External desulphurization is a common practice in hot metal pretreatment. The desulphurization of hot metal is often achieved using fluxes based on either sodium carbonate or lime.

#### 2.5.5.1 Sodium carbonate based fluxes

Sodium carbonate or soda ash is a common desulphurization agent in the steelmaking process. Upon injection into liquid iron, sodium carbonate decomposes to Na<sub>2</sub>O and CO<sub>2</sub>. Silicon in the melt is oxidized by CO<sub>2</sub> and together with Na<sub>2</sub>O forms a Na<sub>2</sub>O-SiO<sub>2</sub> slag.

The thermodynamics of sulphur in binary  $Na_2O-SiO_2$  slags has been measured by Nagashima and Katsura [55] using slag-gas techniques under various oxygen partial pressures at 1100 °C, 1250 °C, and 1300 °C. The results of their study indicate that the solubility of sulphur in slag

reaches a minimum at a specific oxygen partial pressure while the temperature,  $Na_2O/SiO_2$  ratio, and the total amount of sulphur in the gas phase are constant.

They also found that the dissolved sulphur in the melts generally appears as sulphate ions at high oxygen partial pressure ( $P_{O_2} > 10^{-10}$  atm), whereas the sulphur dissolved commonly as sulphide ions at lower oxygen partial pressure [55].

Chan and Fruehan [56] studied the sulphur partition ratios and sulphide capacity between carbon saturated iron and Na<sub>2</sub>O-SiO<sub>2</sub>. Their study was undertaken using both the slag-metal and the gasslag techniques for sulphur partition ratio and sulphide capacity respectively. The results of the two measurements are shown in Figure 2-9. They also found these slags with high sulphide capacity could absorb 5 wt% S at 0.4 mole fraction Na<sub>2</sub>O.

Inoue and Suito [54] carried out similar experiments on the sulphur partition ratio between carbon saturated iron and Na<sub>2</sub>O-SiO<sub>2</sub> slags at 1250 °C and 1350 °C. The results of Chan and Fruehan's [56] investigation are shown in Figure 2-10 along with Inoue and Suito's [54] data.



Figure 2-9: Correlation between Na<sub>2</sub>O mole fraction and sulphide capacities at 1200 °C as measured by the gas-slag method and partition ratio data from slag-metal converted to sulphide capacity via the C-CO equilibrium with P<sub>CO</sub>= 1 atm



Figure 2-10: Measured sulphur partition ratio data from Chan and Fruehan [56] and Inoue and Suito [54]

Kunisada and Iwai [57] investigated the effect of CaO, MnO, MgO and  $Al_2O_3$  on the sulphide capacity of  $Na_2O$ -SiO<sub>2</sub> slags at 1500 °C using a slag-gas equilibrium technique in a platinum crucible. They showed that for these binary slags, the sulphide capacity can be related to the basicity as follows:

$$\log C_{\rm S} = 4.64 \text{B} - 6.88$$
 (1500 °C) 2-44

$$B = \frac{Na_2O}{SiO_2} \qquad [mole ratio] \qquad 2-45$$

In addition, they found that the sulphide capacity of the  $Na_2O-SiO_2$  slags increases with adding basic oxides such as CaO, MnO and MgO and decreases with  $Al_2O_3$  addition as shown in Figure 2-11.



Figure 2-11: Effect of CaO, MnO, MgO and Al<sub>2</sub>O<sub>3</sub> on the sulphide capacity of Na<sub>2</sub>O-SiO<sub>2</sub> slags [57]

### 2.5.5.2 Calcium oxide based fluxes

The desulphurization of hot metal by calcium oxide (lime) based fluxes is an efficient and inexpensive method for hot metal treatment.

These slags contain other oxides such as  $Al_2O_3$ ,  $SiO_2$ , MnO, MgO and FeO. In a multicomponent slag system, the MgO and CaO are considered as basic oxides, whereas the  $SiO_2$  and  $Al_2O_3$  are known as acidic components. Also, the oxygen potential of the system has a large effect on the sulphide capacity which can be dictated by the FeO and MnO contents of the flux. One further component found in most of these CaO based slags is calcium fluoride, CaF<sub>2</sub>, which primarily decreases the melting point of the slag.

The significant properties of CaO based slags and sulphur removal can be illustrated by the following equation:

$$CaO + S = CaS + O$$
 2-46

This reaction shows lime in the slag phase reacts with sulphur in the metal phase to form calcium sulphide in the slag and oxygen in the metal. Clearly, desulphurization of the metal will be favored by slag containing high concentrations of lime and low oxygen content in the metal.

The sulphide capacities of lime based slags such as CaO-SiO<sub>2</sub> and CaO-Al<sub>2</sub>O<sub>3</sub> systems have been extensively investigated by others as presented in Table 2–9 and Figure 2-12. Based on the results in Figure 2-12, the sulphide capacities of CaO-SiO<sub>2</sub> slags are lower than the CaO-Al<sub>2</sub>O<sub>3</sub> slags, although the data obtained by different researchers do not completely agree with each other due to the fact that sulphur is not only present in slag as sulphide ions [58].



Figure 2-12: Sulphide capacity of CaO based slags [59]

System	Temperature, °C	Experimental method	Ref.
CaO-SiO <sub>2</sub>	1500-1600	Slag-gas	Fincham and Richardson [46]
CaO-SiO <sub>2</sub>	1500	Slag-gas	Carter and Mcfarlane [60]
CaO-Al <sub>2</sub> O <sub>3</sub>	1500	Slag-gas	Carter and Mcfarlane [60]
CaO-Al <sub>2</sub> O <sub>3</sub>	1500	Slag-gas	Sharma and Richardson [61]
CaO-Al <sub>2</sub> O <sub>3</sub>	1500	Slag-gas	Kor and Richardson [62]
CaO-Al <sub>2</sub> O <sub>3</sub>	1650	Slag-gas	Fincham and Richardson [46]
CaO-Al <sub>2</sub> O <sub>3</sub>	1650	Slag-gas	Cameron, Gibbons and Tylor [63]
CaO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> ( <10% )	1500	Slag-gas	Fincham and Richardson [46]
CaO-Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> ( <10% )	1550	Slag- gas	Cameron, Gibbons and Tylor [63]
CaO-CaCl <sub>2</sub>	1175-1350	Slag -metal	Yang and McLean [64]
CaO-Na <sub>2</sub> O-SiO <sub>2</sub>	1400	Slag-gas	Chan and Fruehan [59]

Table 2–9: Sulphide capacity measurement in CaO based slags

Yang *et al.* [64] calculated the sulphide capacity of CaO-CaCl<sub>2</sub> slags using phosphate capacity data at 1175 °C-1350 °C in a graphite crucible by the slag-metal technique. The plot of the sulphide capacity vs. optical basicity shows that slag sulphide capacity increases with optical basicity and temperature. The relationship between the sulphide capacity of CaO-CaCl<sub>2</sub> slags and optical basicity is shown in Figure 2-13.

The efficiency of lime based slags can be increased by the addition of Na<sub>2</sub>O. Chan and Fruehan [59] investigated CaO-SiO<sub>2</sub>-Na<sub>2</sub>O-(Al<sub>2</sub>O<sub>3</sub>) slags at 1400 °C and measured the sulphur partition ratio using the slag-metal method with carbon saturated iron melt and determined the sulphide capacity value by slag-gas techniques in graphite crucibles respectively. They concluded that the addition of 10 to 15 wt% Na<sub>2</sub>O to CaO-SiO<sub>2</sub> slags increases the sulphide capacity and partition ratio by a factor of about 10 Figure 2-14. However, adding Na<sub>2</sub>O at low

concentration to CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags did not have a significant effect on the sulphide capacity due to the high sulphide capacity of the slag without Na<sub>2</sub>O [59].



Figure 2-13: Relationship between sulphide capacity and optical basicity of CaO-CaCl<sub>2</sub> slags [64]



Figure 2-14: Sulphur partition ratio of CaO-Na<sub>2</sub>O-SiO<sub>2</sub> slags at 1400 °C plotted at different Na<sub>2</sub>O levels [59]

# 2.6 Dephosphorization

The hot metal dephosphorization process has been developed to meet increasing demands for low phosphorus steel and also treating high phosphorus ores. Dephosphorization success depends on basic and oxidizing slags, low temperature, and high fluidity of slag to achieve favorable thermodynamic and kinetic conditions. This review will concentrate on the literature related to hot metal treatment, rather than that concerning steelmaking.

# 2.6.1 Thermodynamics of dephosphorization

Phosphorus is introduced into liquid iron from the blast furnace raw materials such as iron ore, coke, and limestone, as well as from scrap during steelmaking. Phosphorus can be removed in a hot metal pretreatment process or during the steelmaking operation [31].

## 2.6.2 Phosphate capacity

Dephosphorization of hot metal is an important treatment during iron and steelmaking. Therefore, there has been a substantial interest in measuring the ability of fluxes and slags to remove phosphorus. The phosphorus distribution ratio (between slag and metal) and phosphate capacity of slags are important parameters to compare dephosphorization properties of different slags.

According to Wagner [65] and others, the equilibrium reaction for phosphorus distribution between liquid iron and slag can be written as:

$$\frac{1}{2}P_2(g) + \frac{5}{4}O_2(g) + \frac{3}{2}O^{2-}(slag) = PO_4^{3-}(slag)$$
2-47

Where the equilibrium constant is:

$$K = \frac{a_{PO_4^{-3}}}{P_{P2}^{1/2} \cdot P_{O2}^{5/4} \cdot a_{O^{-2}}^{\frac{3}{2}}}$$
2-48

The phosphate capacity of the slag was suggested by Wagner [65] as follows:

$$C_{PO_4^{3-}} = \frac{(wt\% PO_4^{3-})_{slag}}{P_{P2}^{1/2} \cdot P_{O2}^{5/4}} = K_{PO_4^{3-}} \cdot \frac{a_{O^{2-}}^{3/2}}{f_{PO_4^{3-}}}$$
2-49

Where:

wt pct 
$$PO_4^{3-}$$
: Weight percent of  $PO_4^{3-}$  dissolved in slag

 $f_{PO_4^{3-}}$ : Activity coefficient at infinite dilution concentration

 $P_{O_2}$ : Oxygen partial pressure at the slag-metal interface

 $P_{P_2}$ : Phosphorus partial pressure in equilibrium with the liquid metal

The phosphate capacity can be revised to expand its ease of application by considering as following [66]:

$$\frac{1}{2}P_2(g) = [P]_{(1wt\% \text{ in Fe})}$$
2-50

$$\Delta G^{\circ} = -122352 - 19T (J)$$
 2-51

The equilibrium constant of this reaction is given by:

$$K = \frac{a_{\rm P}}{P_{\rm P_2}^{\frac{1}{2}}}$$
 2-52

The numerical value of *K* can be expressed as follows:

$$\log K = \frac{6392}{T} + 0.99$$
 2-53

By substitution of Equations 2-52 and 2-53 into Equation 2-49, Equation 2-54 can be established in logarithmic form:

$$\log C_{PO_4^{3-}} = \log(wt\% P)_{(slag)} + \log(MM_{PO_4^{3-}}/MM_P) - \log f_P [P]_{(1wt\% in Fe)} - \log P_{O_2}^{\frac{5}{4}} + \frac{6392}{T} + 0.99$$
2-54

Where:

- $f_P$ : The activity coefficient of phosphorus at 1wt% standard state in liquid iron.
- $MM_{PO_4^{3-}}/MM_P$ : The ratio of the molar mass of phosphate and phosphorus in slag and metal, respectively, which is equal to 3.06.

The phosphorus distribution ratio between the slag and metal at equilibrium,  $L_P$ , can be experimentally determined, and is defined as:

$$L_{\rm P} = \frac{(\rm wt\%P)}{[\rm wt\%P]}$$
2-55

Thus, the relationship between phosphate capacity and the phosphorus distribution ratio can be written as:

$$\log L_{\rm P} = \log C_{\rm PO_4^{3-}} + \log f_{\rm P} + \log P_{\rm O_2}^{\frac{5}{4}} - \frac{6392}{\rm T} - 1.475$$
 2-56

For carbon saturated iron, partial pressure of oxygen in equilibrium with carbon is obtained via:

$$C(gr) + \frac{1}{2}O_2(g) = CO(g)$$
  $\Delta G^\circ = -114391 - 85.77T (J/mol)$  2-57

$$\frac{1}{2}\log PO_2 = \log a_{\rm C} + \log P_{\rm CO} - (\frac{5976}{\rm T} + 4.48)$$
2-58

and the activity coefficient  $f_P$  can be expressed as follows [67]:

$$\log f_{P} = e_{P}^{C} \cdot wt\% C + e_{P}^{P} \cdot wt\% P$$
2-59

By replacement of  $e_P^C = 0.145$ ,  $e_P^P = 0.062$  [68] the following relationship is obtained at  $1350^{\circ}C$ :

$$\log f_{\rm P} = 0.145 \cdot \text{wt \% C} + 0.062 \cdot \text{wt \% P}$$
 2-60

# 2.6.3 Relationship between phosphate capacity and optical basicity

Although the phosphate capacity  $(C_{PO_4^{3-}})$  is usually defined by Equation 2-54, various other expressions have been defined to show a relationship between optical basicity and phosphate capacity. Gaskell [69] analyzed phosphorus distribution from data by Suito *et al.* [70] and established a relationship between the dephosphorization equilibrium, optical basicity, and temperature as follows :

$$\ln\left(\frac{X_{PO_4^{3^-}}}{[\%P][\%0]^{2.5}}\right) = \left(-558.874 + \frac{2.176 \times 10^6}{T} - 1.93 \times \frac{10^9}{T^2}\right)\Lambda - 28.78$$
2-61

Mori [71] studied the dephosphorization equilibrium by use of optical basicity and showed that a linear relationship between  $\log C_P$  and optical basicity exists at 1600 °C:

$$\log C_{PO_4^{3-}} = 17.55\Lambda + 5.72$$
 2-62



Mori's experimental results are shown in Figure 2-15 for different slag systems.

Figure 2-15: Relationship between  $\log C_{PO4}^{3-}$  and optical basicity [71]

Bergman [72] also analyzed Suito *et al.*'s [70] experimental data in terms of phosphate monomer ( $PO_4^{3-}$ ) and dimer ( $P_2O_7^{4-}$ ) and showed log  $C_{PM}^{(3)}$  for phosphate monomer correlated linearly with the optical basicity as follows:

$$\log C_{\rm PM}^{(3)} = 21.30\Lambda + \frac{32912}{\rm T} - 27.90$$
 2-63

Yang *et al.* [44] studied slag-metal equilibrium with different lime based slags under CO gas atmosphere in a graphite crucible at various temperatures. Their results in Figure 2-16 show the linear relationship between optical basicity and the phosphate capacity of a number of slags. It can be seen that for all slags, phosphate capacity increases with increasing optical basicity.



Figure 2-16: Comparison of the phosphate capacity of slags from different studies [44]

In the slags saturated with CaO, further addition of CaO does not change the basicity of the liquid phase of the slag, whereas the apparent value of the optical basicity increases with CaO addition, hence the constant value after a certain optical basicity for these slags. It can further be seen that the phosphate capacity of slags decreases with an increase in temperature. The authors suggested the data in Figure 2-16 can be represented by a regression equation as follows:

$$\log C_{PO_4^{3-}} = \left(-\frac{36412}{T} + 37\right)\Lambda + \frac{71493}{T} - 30.08$$
 2-64

### 2.6.4 Hot metal dephosphorization fluxes

The dephosphorization fluxes often contain alkali metal oxide and carbonates, most commonly sodium carbonate, and the alkaline earth metal oxides, commonly calcium oxide [73, 74].

#### 2.6.5 Sodium carbonate based slags

Sodium carbonate is one of the most effective additives to dephosphorization fluxes. Pak and Fruehan [75] reported that the earliest work with a sodium carbonate system as a dephosphorizer was done by Eaton in 1877 who performed dephosphorization of hot metal prior to decarburizing it in a converter. Afterward, Maddocks and Turkdogan [74, 76] and Oelsen [77] investigated the use of a sodium carbonate based flux for dephosphorization of hot metal. Their results show that although the slag and metal did not reach equilibrium, very high degrees of dephosphorization were achieved.

It should be noted that, upon injection of carbonate reagents into the hot metal,  $Na_2CO_3$  decomposes into  $Na_2O$  and  $CO_2$ . The  $Na_2O$  can react with other oxides, such as SiO<sub>2</sub>, to form a  $Na_2O$ -SiO<sub>2</sub> slag. Various studies have been done to investigate the phosphate capacity and phosphorus distribution ratio of  $Na_2O$ -SiO<sub>2</sub> slags.

Inoue and Suito [78-80] and their coworkers investigated the dephosphorization of carbon saturated iron using sodium carbonate and/or sodium sulphate fluxes in the temperature range of 1250 °C to 1350 °C. They studied the time dependent behavior of phosphorus, sulphur, and manganese in carbon saturated iron after the addition of sodium based fluxes [80]. In addition they investigated the phosphorus distribution ratio between carbon saturated iron and sodium based fluxes in a graphite crucible under a CO gas flow [78]. Also, they studied the reaction of sodium based fluxes with iron, carbon, and phosphorus dissolved in iron by the use of iron, graphite, and magnesia crucibles [79].

Niekerk and Dippenaar [67] studied the phosphorus distribution between carbon saturated iron and slags containing Na<sub>2</sub>O and SiO<sub>2</sub> at 1350°C in a graphite crucible under CO gas atmosphere. The phosphate capacity was calculated by assuming  $P_{CO} =1$  atm and considering the activity of carbon based on the actual carbon content in the iron melt. They found a significant increase in the phosphate capacity of Na<sub>2</sub>O-SiO<sub>2</sub> slags by the addition of Na<sub>2</sub>O. The results of Niekerk and Dippenaar [67] are in good agreement with those of Inoue and Suito [78] who performed similar experiments on the phosphorus distribution between Na<sub>2</sub>O-SiO<sub>2</sub> slags and hot metal at 1250 °C and 1350 °C. A graph of Niekerk and Dippenaar's work is shown in Figure 2-17 together with the data previously reported by Inoue and Suito [78].



Figure 2-17: Phosphate capacity of Na<sub>2</sub>O-SiO<sub>2</sub> slags at 1350 °C [78]

Pak and Fruehan [81] investigated the equilibrium phosphorus partition ratio and phosphate capacity between Na<sub>2</sub>O-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> slags and carbon saturated iron using a graphite crucible under CO or Ar-CO at 1200 °C. Their results showed that the equilibrium phosphorus partition ratio increases as the basicity increases and  $L_P$  is independent of the P level in slag. The phosphate capacities for these slags were calculated from the measured phosphorus partition ratio and available thermodynamic data. The phosphate capacities are plotted as a function of basicity in Figure 2-18.



Figure 2-18: Phosphate capacity of Na<sub>2</sub>O-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> slags at 1200 °C [81] (Open symbol, P transfer from metal to slag and solid symbol, P transfer from slag to metal)

The C-CO reaction ( $P_{CO} = 1$  atm) sets the oxygen pressure ( $P_{O_2} = 8.45 \times 10^{-18}$  atm). It can be observed that the phosphate capacity has a linear correlation with basicity and is independent of the P level in slag.

Borode [82] studied the equilibrium phosphorus partition ratio and phosphate capacity between  $Na_2O-SiO_2$  melts and carbon saturated iron using a slag-metal equilibrium technique in graphite crucibles at 1400 °C. The phosphate capacity data obtained in Borode's work was related to the optical basicity, Figure 2-19.



Figure 2-19: Relationship between phosphate capacity and optical basicity at 1400 °C [82]

### 2.6.6 Lime based fluxes

Environmental considerations over disposal of sodium containing slags and evolution of alkali fumes have enhanced the use of limestone-based reagents, which are often mixed with iron ore or sinter fines. Sasaki *et al.* [83] performed hot metal dephosphorization with a combination of a lime based flux and an oxidizing agent. Their experiments concentrated on BOF (basic oxygen furnace) and CaO-CaF<sub>2</sub>-FeO<sub>x</sub> slags.

Essentially, slag-metal reactions during hot metal dephosphorization do not reach the equilibrium state. This is because the involved slags are usually highly oxidizing, containing high levels of iron and/or manganese oxides, which can be reacted with carbon dissolved in the hot metal and result in a violent CO evolution. It should be noted that the phosphorus distribution ratio is affected by oxygen potential in the slag-metal system and the oxygen potential can be

represented by the FeO content in the slag system. Consequently, Iwasaki and Sano [84] developed a technique to indirectly measure the phosphorus distribution ratios between CaO-FeO-SiO<sub>2</sub> slag and carbon saturated iron using an iron crucible in the temperature range of 1300 °C to 1380 °C. They suggested the equilibrium distribution of phosphorus between a solid iron foil and a slag can be experimentally determined and then converted to distribution of phosphorus for carbon saturated iron using available thermodynamic data. In fact, the slag in equilibrium with solid iron could be equilibrated with the carbon saturated iron, as the chemical potential of phosphorus in solid iron is the same as that in carbon saturated iron [84].

Ito and Sano [85] employed a similar technique to investigate the phosphate capacity between basic slags and carbon saturated iron at 1300 °C. They found the CaO-SiO<sub>2</sub>-FeO system shows high dephosphorization capacity when it is saturated with 2CaO.SiO<sub>2</sub> and the addition of iron oxide to the basic slags decreases the phosphate capacity values (Figure 2-20). It can be seen that phosphate capacity for the CaO-SiO<sub>2</sub>-FeO system (with CaO/SiO<sub>2</sub>=0.7 or 0.8) increases from 19 to 20.5 with increasing FeO. On the other hand, phosphate capacity for the slag saturated with 2CaO.SiO<sub>2</sub> is close to 22 and slightly decreases with the increasing FeO content [85]. This can be explained by iron oxide slightly increasing or even decreasing the activity of oxygen ion ( $a_0^{-2}$ ) in basic slags due to the amphoteric property of FeO and because of the quite repulsive interaction with phosphate ion which increases activity coefficient of phosphate ion ( $f_{PO_4^{-3}}$ ) [85].



Figure 2-20: Relationship between the phosphate capacity and FeO (wt%) for the CaO-SiO<sub>2</sub>-FeO system at 1300 °C [85]

Muraki *et al.* [86] measured the composition and temperature dependence of the phosphate capacity of CaO-CaF<sub>2</sub>-SiO<sub>2</sub> slags by performing a slag metal equilibrium technique at temperatures of 1200 °C to 1400 °C. Muraki *et al.* stated that in liquid slag as an ionic solution, dephosphorization is facilitated by increasing the activity of oxygen ion and decreasing the activity coefficient of phosphate ion at constant temperature. They showed that fluxes with CaCl<sub>2</sub> or CaF<sub>2</sub> without FeO have higher  $C_{PO_4^{3-}}$  compared to fluxes that contain a large amount of FeO. As a result, FeO in highly basic slags behaves like as an acidic oxide. The results of Muraki *et al.* are shown in Figure 2-21, which are in good agreement with those reported earlier by others [85].



Figure 2-21: Phosphate capacity of various slag system containing CaO [86]

Werme *et al.* [87] also used the Iwasaki and Sano [84] technique to measure distribution of phosphorus between CaO-FeO-SiO<sub>2</sub>-P<sub>2</sub>O<sub>5</sub> slag containing 10% P<sub>2</sub>O<sub>5</sub> and carbon saturated iron at 1300°C. Their results indicated that for slags saturated with (C2S-C3P) the highest distribution ratio was at 35 wt% FeO. On the other hand, Werme *et al.* [87] showed that the maximum distribution shifted to higher FeO levels for unsaturated slags Figure 2-22.



Figure 2-22: Variation in phosphorus distribution with FeO content at different basicities [87]

They stated that the behavior is a result of the combined effects of CaO and FeO concentration in the slag. With increasing the FeO concentration beyond a certain level (corresponding to maximum  $L_P$ ), the positive effect of the increase in oxygen potential on the  $L_P$  cannot be balanced against the negative effect of the decrease in CaO activity and vice versa [87]. A graph of their data along with of the results Ito and Sano [85] is plotted in Figure 2-23. It can be seen that the maximum distribution ratio is lower for the CaO-FeO-SiO<sub>2</sub> slags with low phosphorus content [87].



Figure 2-23: Equilibrium phosphorus distribution between (C<sub>2</sub>S-C<sub>3</sub>P)<sub>SS</sub> saturated slags and carbon saturated iron at 1300 °C [87]

Yang *et al.* [64] and coworkers investigated the effect of temperature on the phosphate capacity of CaO-CaCl<sub>2</sub> slags at 1175 °C - 1350 °C. Figure 2-24 shows the logarithm of slag phosphate capacity against the reciprocal of the absolute temperature for the slags containing CaO and CaCl<sub>2</sub>. They found that the slag phosphate capacity decreases with increasing temperature and increases with increasing CaO content.



Figure 2-24: Effect of temperature on phosphate capacity of CaO-CaCl<sub>2</sub> slags [64]

As explained earlier (Sec. 2.2.3) the proposed research is aimed at an investigating of the fundamental aspects of using a waste material that is high in iron oxide, for the refining treatment of hot metal as well as molten steel. This will require physical and chemical characterization of the waste components as well as design and thermo-chemical evaluation of synthetic fluxes for desulphurization and dephosphorization.

# Chapter 3

# **3** Experimental Aspects

This chapter presents details of the experimental work related to the research. The first section concentrates on the red mud characterization techniques. The second section describes experiments involving measurements of the sulphide capacity of red mud based fluxes. The third section provides details on the measurements of the phosphorus partition ratio between synthetic red mud based fluxes and carbon saturated iron. The final section describes the experiments, methods and materials for studying the melting behavior of red mud based fluxes.

# 3.1 Characterization of red mud

In order to characterize red mud, fresh alkaline suspension ( $\approx$ 30% water content) from Alcoa Inc. (Aluminum Company of America) was used, Figure 3-1 (a). This red mud was produced through the Bayer process for extraction of alumina. The slurry was placed in a Pyrex container and dried in an electric oven at 105 °C for 75 hr. The dried red mud Figure 3-1 (b) was crushed and sieved to pass a 250 mesh sieve, and then a combination of XRF (X-Ray Fluorescence Spectroscopy), XRD (X-Ray Diffraction), TGA (Thermal Gravimetric Analysis), DSC (Differential Scanning Calorimetry) and SEM (Scanning Electron Microscope) techniques were used to characterize the structure and determine the concentrations of various impurities present in the red mud.

### 3.1.1 X-Ray diffraction analysis

The phase analysis of the red mud was studied using a Philips diffractometer PW3710 with a nickel filter to produce a monochromatic copper  $k_{\alpha 1}$  radiation ( $\lambda = 1.54A$ ) and a proportional detector to capture the scattered copper X-rays. The voltage and current were 40 kV and 40 mA respectively. The step size of  $2\theta = 0.03$  degree and time per step of 5 second were adjusted to obtain diffraction peaks with highest intensity. The 2 $\theta$  diffraction angle range of 5°- 90° was covered. The results were compared with the International Centre for Diffraction Data (ICDD) databases using X' High Score software for peak identification.



(a) (b)

Figure 3-1: Red mud from Bayer process; (a) Fresh red mud; (b) Dried red mud

# 3.1.2 XRF analysis

The qualitative chemical analysis of the red mud was performed with a Philips 2440 X-ray fluorescence spectrometer. Each sample was pressed into a disk with the addition of a binder (boric acid) and using a hydraulic press operating at a pressure of 70 MPa. The XRF data were analyzed using a Philips software package which is capable of detecting all elements between fluorine (N = 9) and uranium (N = 92).

### 3.1.3 TGA and DSC

The thermal behavior of red mud was evaluated using a Netzsch Simultaneous Thermal Analyzer STA 449 F3 Jupiter System for high quality TGA and DSC measurements. This simultaneous thermal analysis (STA) apparatus can be used for determining mass change with thermogravimetric analysis and transformation temperatures and enthalpies with differential scanning calorimetry. Dried red mud (15 mg) was placed into an alumina pan and situated on a special pedestal which was attached to the thermobalance assembly. The resolution of this low drift microbalance was 1 µg.

The STA 449 F3 Jupiter system continuously measured changes in sample weight as heat was supplied to the sample. The experimental conditions employed were heating rate of 10 °C/min and temperature range of 25 °C to 1400 °C under a 99.999% Argon (Grade 5) atmosphere. The collected data were analyzed by the Proteus Software package.

### 3.1.4 Particle size analysis

A Horiba LA-950 unit was used to analyze the particle size distribution of red mud. With this method, a powder sample was suspended in water with the aid of a stirrer and ultrasonic waves, and then exposed to a laser beam which scatters as it strikes the particles. The results were analyzed with appropriate software to give the size distribution of the particles within the suspension.

### 3.1.5 ICP analysis

Optima 7300 ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) was used to analyze the minor elements of red mud. Samples for analysis by ICP were prepared by acid digestion with nitro-hydrochloric acid ( $HNO_3+3$  HCl). The ICP experimental details are given in Appendix 1.

# **3.2** Desulphurization experiments

Sulphur partition studies of a set of red mud based fluxes were conducted under reducing conditions. The slag-metal equilibrium technique was adapted to assess the effect of chemical composition and temperature on the sulphur partition between red mud based fluxes and hot metal from 1300 °C to 1400 °C in a carbon monoxide atmosphere. Graphite crucibles were used as containers of molten slag and hot metal.

### 3.2.1 Materials

The chemicals used and their purity grades for desulphurization studies are shown in Appendix 2 (Table. A2-1).

### 3.2.2 Carbon saturated iron preparation

Reducing conditions and high operating temperature are favorable for sulphur removal in hot metal pretreatment. The hot metal (carbon saturated iron) was prepared by melting 500 g of electrolytic iron pieces and 20 g of graphite powder and iron sulphide (FeS) in a graphite crucible at 1450 °C using a 30 kW induction furnace. After melting, the liquid metal was poured into cold water for rapid solidification in order to prevent any sulphur segregation during solidification. The solidified carbon saturated iron was analyzed using the LECO C/S

combustion analyzer as well as Inductively Coupled Plasma (ICP) methods. The sample was digested by adding nitric acid (HNO<sub>3</sub>) and deionized water. A more detail is presented in Appendix 1(Sec. A1.1). The solidified carbon saturated iron lumps were used for desulphurization experiments. The composition of the electrolytic iron and the final carbon saturated iron is given in Table 3-1.

Table 3–1: Chemical composition of electrolytic iron and prepared carbon saturated iron (wt %)

Material	Carbon	Manganese	Silicon	Sulphur	Phosphorus	Iron
Electrolytic iron*	0.0007	0.0016	0.001	0.002	0.0006	Balance
Carbon saturated iron	4.31-4.65	0.21-0.38	0.33-0.40	0.18-0.20	0.001-0.005	Balance

\* Based on supplier information



(a) (b) Figure 3-2: Electrolytic iron and carbon saturated iron

# 3.2.3 Flux components

The synthetic fluxes were prepared from the dried red mud and additives of reagent grade calcium oxide, titanium oxide, silicon oxide, and alumina. The oxides were calcined at 800 °C for 2 hr. The target flux compositions and their optical basicities are listed in Table 3–2. These compositions were designed to examine the influence of various oxides on the desulphurization. Fluxes RMF1 to RMF6 containing increasing amounts of lime were used to establish the effect of lime content in the flux. Fluxes RMF7 to RMF10 will show the effect of alumina, and fluxes RMF11 to RMF14 and RMF15 to RMF18 are meant to establish the effects of titania and silica respectively on the desulphurization properties.

### 3.2.4 Furnace

A schematic diagram of the experimental arrangement is given in Figure 3-3. As seen, the furnace used in this work was a vertical tube furnace with  $MoSi_2$  heating elements and a gastight alumina 69.85 mm (OD) 63.5 mm (ID) working tube. The tube was sealed by two water cooled aluminum caps on both ends to maintain a reducing atmosphere by purging carbon monoxide through the tube. The temperature was controlled using a proportional integral derivative (PID) controller and B-type (Pt30%Rh - Pt/6%Rh) thermocouple. A separate R-type (Pt/Pt-13%Rh) thermocouple was inserted from the bottom of the furnace and placed in contact with the bottom of the graphite crucible during the experiment. Accuracy of temperature control was obtained using a USB data acquisition device. The maximum observed variation from the set point was recorded ( $\pm 1$  °C) at 1400 °C. The temperature profile inside the tube is plotted in Figure 3-4 to ensure that the crucible was located in the hot and uniform-temperature zone of the furnace. The thermocouples were tested with a FLUKE 814 temperature calibrator which was also used to measure the response of the temperature data acquisition system. The calibration error for B-type and R-type thermocouples was  $\pm 3$  °C and  $\pm 2.5$  °C, respectively.

		Basicity	Optical basicity
Heat No.	Flux Composition	(B)	$(\Lambda)$
RMF1	100RM	0.34	0.72
RMF2	90RM+10 CaO	1.3	0.73
RMF3	80RM+20CaO	2.5	0.75
RMF4*	70RM+30CaO	4.1	0.76
RMF5	60RM+40CaO	6.1	0.78
RMF6	50RM+50CaO	9.0	0.80
RMF7	90RMF4+10 Al <sub>2</sub> O <sub>3</sub>	4.1	0.74
RMF8	85RMF4+15 Al <sub>2</sub> O <sub>3</sub>	4.1	0.74
RMF9	80RMF4+20 Al <sub>2</sub> O <sub>3</sub>	4.1	0.73
RMF10	75RMF4+25 Al <sub>2</sub> O <sub>3</sub>	4.1	0.72
RMF11	95RMF4+5TiO <sub>2</sub>	4.1	0.76
RMF12	92RMF4+8TiO <sub>2</sub>	4.1	0.76
RMF13	88RMF4+12TiO <sub>2</sub>	4.1	0.76
RMF14	85RMF4+15TiO <sub>2</sub>	4.1	0.76
RMF15	90RMF4+10 SiO <sub>2</sub>	1.8	0.74
RMF16	85RMF4+15 SiO <sub>2</sub>	1.4	0.73
RMF17	80RMF4+20 SiO <sub>2</sub>	1.2	0.72
RMF18	75RMF4+25 SiO <sub>2</sub>	1.0	0.70

Table 3–2: Flux compositions used in the desulphurization study

RMF4<sup>\*</sup>: Flux composition contains 70RMF+30CaO



(1) Alumina tube, (2) Alumina pedestal, (3) Thermocouple, (4) Water cooled aluminum caps, (5) Graphite crucible, (6) Carbon monoxide gas, (7-8) Gas purifier units, (9) Gas bubbling indicator, (10) Exhaust with burner

Figure 3-3: Schematic diagram of the experimental set up for the vertical furnace



Figure 3-4: Temperature profile in the vertical tube furnace

### 3.2.5 Experimental procedure

The experiments were carried out on all compositions which are listed in Table 3–2 at various temperatures from 1300 °C to 1400 °C. The values for the flux basicity, defined as  $B = \frac{\%CaO}{\%SiO_2}$  or optical basicity are also listed in Table 3–2. Preliminary experiments were performed to obtain the time required to reach equilibrium.

Before running each experiment, four holes (diameter 17 mm and depth 60 mm) were made in a cylindrical graphite block (Diameter: 50 mm) so that each hole acted as one crucible and in each run, four samples were examined. Each hole contained 10 g of carbon saturated iron and 5 g of slag materials that were weighed and mixed and then added in the crucible. The graphite crucible was then placed on an alumina pedestal and lifted into the furnace.

Subsequently, the furnace was sealed and argon was passed through the furnace at 250 mL/min for 10 min to flush air out of the furnace. At this point, CO purge started and the furnace was heated to the desired temperature. Holding time for achieving equilibrium was 30 hr. The flow rate of CO was maintained constant at 60 mL/min in all runs. The crucible containing the molten slag and metal was then taken out from the furnace and submerged in water to the level of the molten material inside the crucible.

After quenching, the graphite crucible was cut and the slag and solid metal were removed from the crucible. Any metallic particles were manually removed from the slag with a magnet.

Slag samples were then crushed and ground to a fine powder using a puck mill and were kept in sealed glass containers. The metal and slag phases were analyzed using the LECO C/S combustion analyzer as well as X-ray fluorescence and Inductively Coupled Plasma (ICP) methods Appendix 1 (Sec. A1.1 - Sec. A1.2).

# **3.3** Dephosphorization experiments

The objective of this part of the work was to investigate the effect of temperature and slag composition on the phosphorus partition ratio.

The slag-metal equilibrium technique was employed to evaluate the effect of temperature, iron oxide and other common oxides on the distribution of phosphorus between synthetic red mud and hot metal from 1300 °C to 1400 °C. Fundamentally, red mud based fluxes that contain high amounts of iron oxide cannot reach equilibrium with carbon saturated hot metal at high temperatures as iron oxide will react with the dissolved carbon, rendering the flux essentially free of iron oxide. To avoid such difficulty, it is possible to measure the phosphorus distribution of fluxes containing iron oxide indirectly using the solid iron foil technique [84]. This method involves equilibration between synthetic red mud fluxes and a solid iron foil in an ARMCO iron crucible under the inert atmosphere of argon. After equilibration, the slags were quenched, dried, crushed and analyzed using XRF and ICP techniques. The equilibrium phosphorus distribution was then determined and the results were converted to the equilibrium phosphorus distribution for the carbon saturated system, using the thermodynamic data.

#### 3.3.1 Materials

The characteristics of the materials used in dephosphorization experiments are listed in Appendix 2 (Table A2-2).

### 3.3.2 Iron oxide preparation

The primary component, 100 g  $Fe_2O_3$  and 15 g reagent grade Fe powder were first heated at 1400 °C for 15 h in ARMCO soft iron crucibles under argon atmosphere to obtain FeO:
The crucible was quickly taken out of the furnace and quenched in cold water. After cooling, the solid material inside the crucible was removed and then ground to a fine powder and stored in an airtight glass container for secondary experiments as the iron oxide phase of the flux. XRD analysis on the solid material was performed and confirmed that FeO was the dominant phase.

#### **3.3.3** Flux components

Different compositions were designed to investigate the influence of various oxides and temperature on the dephosphorization ability of the flux. The flux components are listed in Table 3–3. Fluxes SRM1 to SRM6 containing increasing amounts of lime were used to establish the influence of lime and iron oxide content. Fluxes SRM7 to SRM10 represent different levels of alumina. Fluxes SRM11 to SRM14 and SRM15 to SRM18 were used to evaluate the effect of titania and silica respectively on the dephosphorization properties.

#### 3.3.4 Furnace

The furnace used in this work was a horizontal tube furnace with 6 MoSi<sub>2</sub> heating elements and a gas tight alumina tube, 69.85 mm (OD) and 63.5 mm (ID), which was supplied by the McDaniel Refractory Co. A schematic diagram of the experimental arrangement is given in Figure 3-5. The temperature was controlled using two thermocouples, similar to the desulphurization experiments (Sec 3.2.4). The atmosphere in the alumina tube was controlled by introducing high purity argon by passing the gas first through a gas train and an oxygen getter furnace to remove moisture, oxygen, and carbon dioxide.

The temperature profile along the length of the furnace was obtained to determine the hot zone of the furnace (Figure 3-6). During this procedure, both ends of the heating tube were covered by water cooled aluminum caps. The accuracy of the data acquisition system was measured by the FLUKE 814 temperature calibrator. The maximum discrepancy between the FLUKE 814 temperature calibrator and the temperature recorded by the data acquisition system was  $\pm 1$  °C. The total measurement error for B-type and R-type thermocouples was evaluated  $\pm 3$  °C and  $\pm 2.5$  °C, respectively.

Heat No.	Flux Composition
SRM-1	90RM+10P <sub>2</sub> O <sub>5</sub>
SRM-2	80RM+10P2O5+10CaO
SRM-3	70RM+10P2O5+20CaO
SRM-4	60RM+10P2O5+30CaO
SRM-5 <sup>*</sup>	50RM+10P2O5+40CaO
SRM-6	40RM+10P <sub>2</sub> O <sub>5</sub> +50CaO
SRM-7	90SRM5+10 Al <sub>2</sub> O <sub>3</sub>
SRM-8	85SRM5+15 Al <sub>2</sub> O <sub>3</sub>
SRM-9	80SRM5+20 Al <sub>2</sub> O <sub>3</sub>
SRM-10	75SRM5+25 Al <sub>2</sub> O <sub>3</sub>
SRM-11	95SRM5+5 TiO <sub>2</sub>
SRM-12	92SRM5+8 TiO <sub>2</sub>
SRM-13	88SRM5+12 TiO <sub>2</sub>
SRM-14	85SRM5+15 TiO <sub>2</sub>
SRM-15	90SRM5+10 SiO <sub>2</sub>
SRM-16	84SRM5+15 SiO <sub>2</sub>
SRM-17	80SRM5+20 SiO <sub>2</sub>
SRM-18	75SRM5+25 SiO <sub>2</sub>

Table 3–3: Flux compositions used in the dephosphorization study

SRM5<sup>\*</sup>: Flux composition contains 50RM+10P<sub>2</sub>O<sub>5</sub>+40CaO



(1) Alumina tube, (2) Alumina holder, (3) Ziconia substrate, (4) Iron crucible, (5) Thermocouple, (6) Water cooled aluminum caps, (7) Gas drying column, (8) Gas purifier column, (9) Getter furnace, (10) Argon gas, (11) Gas bubbling indicators, (12) Exhaust

Figure 3-5: Schematic diagram of the experimental set up for the horizontal furnace



Figure 3-6: Temperature profile and hot zone of the horizontal tube furnace

#### 3.3.5 Experimental procedure

A series of experiments were carried out to determine the required time to achieve equilibrium. According to the results, the holding time of 32 h at the target temperature was chosen in the subsequent experiments.

For preparation of each sample, flux components from Table 3–3 were weighed (10 g), mixed and pressed into a custom made ARMCO iron crucible (H: 35 mm, OD: 30 mm, ID: 27 mm), Figure 3-7(a) together with 0.3 g of iron foil, Figure 3-7(b) and the crucible sealed with an iron lid which was made with the same material as the crucible. The crucible was then placed on the zirconia substrate and positioned horizontally in the tube on an alumina sample base. Afterward, the furnace was sealed and argon was purged at 250 mL/min for 15 min to flush air out of the furnace. The argon flow was then decreased to 60 mL/min and the furnace heated to the desired temperature and held for 32 h to reach equilibrium. After equilibrium, the iron crucible with its contents was taken out of the furnace and quenched in cold water.

After each experiment, the iron crucible was cut and the metal and slag phases were removed from the crucible. The metal part was carefully separated, Figure 3-7(c). The slag was cleaned and any metallic pieces removed using a magnet, then crushed and ground to a fine powder using

a laboratory mill to a size of  $110 - 200 \mu m$ . A few grams (4 - 6 g) of slag powder were analyzed using XRF for high concentration components and 0.15 gram of slag was dissolved in aqua regia and analyzed by ICP for low concentration elements as explained earlier (Sec. 3.2.5). The iron foil, after cleaning in citric acid and an ultrasonic machine, was analyzed by ICP to determine the amount of phosphorus.



Figure 3-7: (a) ARMCO iron crucible; (b) Pure iron foil before experiment; (c) Iron foil after experiment

# 3.4 Melting behavior experiments

The study of the melting behavior of flux materials during the heating process is one of the most critical steps in the flux design. The physical and chemical properties of the flux determine its effectiveness in providing a cover and removing of inclusions. In the past, a few investigations have been done on the effect of chemical composition on the melting behavior of some fluxes [88-93]. However, there are no available data pertaining to the melting behavior of red mud based fluxes. Practically all the methods used to obtain the melting properties of fluxes rely on visual observation of the flux behavior during heating [94]. A custom made high temperature optical microscope system was assembled to measure the linear dimensional variation of flux compacts up to 1400 °C according to the German Industrial Standard 51730 [95].

## 3.4.1 Materials

The raw materials used in the melting behavior experiments are shown in Appendix 2 (Table A2-4).

#### **3.4.2** Flux components

The flux samples with different optical basicity ranging from 0.7 to 0.8 were prepared using a mixture of dried red mud and high purity reagent CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub> to obtain the compositions shown in Table 3–2. Fluxes RMF1 to RMF6 are meant to show the effect of lime content in the flux on its melting behavior. Fluxes RMF7 to RMF10, RMF11 to RMF14, and RMF15 to RMF18 were designed to examine the effects of alumina, titania, and silica respectively.

#### 3.4.3 Apparatus

A schematic diagram of the experimental apparatus is shown in Figure 3-8. The equipment consists of two main parts: a horizontal tube furnace with  $MoSi_2$  heating elements and a 69.85 mm (OD) × 3 mm (Wall) alumina work tube (McDaniel Refractory Co.), and a Zeiss optical tube with CCD video camera which was controlled by Vision Gauge software. The temperature of the furnace was controlled by a B-type thermocouple (Pt30%Rh - Pt/6%Rh) and PID controller, and argon was passed through the heating tube at a flow rate of 60 mL/min. Accuracy of temperature measurement was checked using a separate R-type (Pt/Pt-13%Rh) thermocouple placed close to the holder and a USB data acquisition recorded the temperature which was assumed to be the same as the sample.

The accuracy of the thermocouple was confirmed by measuring the temperature at the melting point of tin (232 °C) and copper (1085 °C) Table 3–4.

Material	Measured melting point (°C)	Reference melting point (°C) [96]
Tin	235	232
Copper	1087	1085

Table 3–4: Validation of thermocouple accuracy

#### 3.4.4 Experimental procedure

The sample, weighing approximately 17 g, was pressed into a cylindrical pellet (D = 15 mm and H = 15 mm) using a hydraulic press die. Before placing the sample compact into the furnace, temperature was raised to 1100 °C which is a minimum of 150 °C below the target temperature [95], at the rate of 4 °C per minute. The compact was then placed on a sample holder made of alumina and positioned into the heated tube furnace at 1100 °C; the furnace glass cover was mounted and argon purge began. The temperature was then increased to the final temperature at the rate of 10 °C per minute. During heating, the dimensional variations of the sample were constantly recorded using the camera placed in front of a transparent window of the tube furnace. The characteristic temperatures of the sample were evaluated from optical images taken during heating according to German Industrial Standard 51730.

#### **3.4.4.1** Characteristic temperatures

The following are defined according to the German Industrial Standard 51730 (Figure 3-9) [95].

- 1) Deformation temperature (DT): The temperature at which the outline of the sample starts to change.
- Hemispherical temperature (HT): The temperature at which the specimen assumes hemispherical shape and is measured as the temperature at which the ratio of the final height (H<sub>h</sub>) to the initial height (H<sub>i</sub>) of the specimen is ~0.6.
- 3) Flowing temperature (FT): The temperature at which the ratio of the final height (H<sub>f</sub>) to the initial height (H<sub>i</sub>) of the specimen is ~0.3. The final height of the specimen is half of the height of the test piece at the hemisphere temperature



(1) Alumina tube, (2) Alumina holder, (3) Pellet sample, (4) Thermocouple, (5) Water cooled aluminum caps, (6) Quartz window, (7) Optical tube, (8) CCD camera, (9) Computer, (10) Argon gas, (11) Getter furnace, (12) Gas drying unit, (13) Gas purifier unit, (14) Gas bubbling indicator, (15) Exhaust



Figure 3-8: Schematic diagram of high temperature microscopy facility

Figure 3-9: Definition of characteristic temperatures

# Chapter 4

# 4 **Results and Discussion**

This chapter presents the experimental results in four sections: red mud characterization in Section 4-1, equilibrium studies on the desulphurization and dephosphorization including the effect of composition and temperature on the sulphide capacity and phosphorus distribution in Sections 4-2 and 4-3 respectively, and melting behaviour of the synthetic fluxes and the effect of composition on characteristic temperatures in Section 4-4.

## 4.1 Red mud characterization

## 4.1.1 Phase identification and quantitative analysis

The X-ray diffraction pattern of the dried red mud sample that was used in the current study is given in Figure 4-1. The main crystalline constituents are iron oxide as hematite, aluminum hydroxide, titanium oxide, calcium titanate, and sodium aluminum silicate. The evaluated phases of RM in this study agree with those phases reported in the literature[97, 98].



Figure 4-1: XRD pattern of red mud (RM)

The chemical composition of the red mud determined by X-ray fluorescence (XRF) analysis is given in Table 4–1. It confirms that the chemical composition of this material is in accord with reported compositions of red mud from different sources, Table 4–2. The differences are because of the quality of bauxite ore and operational parameters of the upgrading process such as pressure, temperature and the additives used.

Compounds	wt%	Compounds	wt%
A12O3	19.60	Fe2O3	45.12
SiO2	10.95	TiO2	7.07
Na2O	9.37	CaO	3.9
$P_2O_5$	0.18	$SO_3$	0.25
Other	3.5	-	

Table 4–1: Quantitative analysis of the red mud

Table 4–2: Major chemical	composition of rec	I muds from different	locations	(wt%) [98	81
				· · · ·	

	Current study	China	Australia	Jamaica	Spain	Hungary	Germany	Italy	IAI*
Fe <sub>2</sub> O <sub>3</sub>	45.12	36.22	34.05	51.50	47.85	37.08	43.94	46.12	30-60
$Al_2O_3$	19.60	20.85	25.45	15	20.20	13.64	14.08	15.34	10-20
CaO	3.90	3.04	3.69	7	6.22	9.37	4.36	4.39	2-8
TiO <sub>2</sub>	7.07	6.26	4.90	6.70	9.91	3.50	7.27	8.82	Trace- 10
Na <sub>2</sub> O	9.37	12.7	2.74	6.97	8.40	8.76	8.15	6.36	2-10
SiO <sub>2</sub>	10.95	15.89	17.06	1.70	7.5	12.41	10.34	8.32	3-50
$P_2O_5$	0.18	N/A	N/A	N/A	0.46	0.08	0.11	0.20	N/A
$SO_3$	0.25	N/A	N/A	N/A	0.15	1.37	0.57	0.3	N/A

\* International Aluminum Institute

#### 4.1.2 TGA analysis of red mud

Thermal analysis was performed in a Netzsch STA 449 F3 simultaneous thermal analyzer to characterize red mud samples with respect to weight change between room temperature and 1400 °C. The results of the thermal analysis of red mud sample at the heating rate of 10 C.min<sup>-1</sup> under argon atmosphere (flow = 20 mL/min) are plotted in Figure 4-2.

The TGA diagram shows a continuous weight loss distributed in the range of 25 °C -1400 °C with a total mass loss of 15.08% up to 1400 °C and a significant weight loss before 330 °C. The first derivative of mass change with temperature (DTG) and Differential Scanning Calorimetry (DSC) are plotted on the same figure to show the critical temperatures more clearly. There is no sharp mass or phase change above 900 °C.

Three separate peaks are evident from DTG graph: at 280, 315 and 685°C. The first and major mass loss (5.95%) occurs around 280 °C. This can be related to water evaporation, gibbsite decomposition and formation of  $\gamma - Al_2O_3$ . The following reaction is suggested by Atasoy [99] and Mehta et al. [100] at this temperature:

$$2\text{Al}(\text{OH})_3 \rightarrow \gamma - \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$$
4-1

A second mass loss (3.03%) around 315 °C may be associated with the decomposition of goethite into hematite, according to the following reaction:

$$2FeO(OH) \rightarrow Fe_2O_3 + H_2O$$
 goethite  $\rightarrow$  hematite + water 4-2

The mass loss at 685 °C can be attributed to the decomposition of calcite [100, 101].

Considering DSC curve in Figure 4-2, one can identify different endothermic peaks at 280, 315, 685 and 1220 °C. It is likely that the first two endothermic peaks between 280 °C and 312 °C can be correlated to the gibbsite and goethite dehydroxylation. The difference in their decomposition temperature is related to the difference in the dehydroxylation temperature of Al-OH and Fe-OH

groups [98]. The endothermic peak observed at 685 °C is likely due to decomposition of calcite. Similar experimental observations have been reported by Alp and Coral [102]. They described an endothermic peak for this reaction that starts at about 680 °C and ends at 776 °C.

The endothermic peak at 1220 °C on the DSC curve which is accompanied by a small mass loss on the DTG curve can be attributed to decomposition of sodium oxide that results in loss of Na vapor and  $O_2$  to the gas. Since sodium is primarily tied in the aluminosilicates, the extent of this reaction is limited.



Figure 4-2: TGA, DSC and DTG curves obtained from thermal analysis of red mud

After thermal analysis, XRD analysis was conducted on the products to examine the effect on a change in mineralogical make of the red mud. Figure 4-3 shows the XRD pattern, indicating that

the main phases are hematite, nepheline, perovskite, dicalcium aluminum and gehlenite. It appears that the thermal treatment has resulted in formation of multi-component oxides.



Figure 4-3: XRD pattern of red mud after thermal treatment at 1400 °C

## 4.1.3 Particle size analysis

The results of particle size analysis are shown in Figure 4-4. As seen, the range is relatively wide, from 0.3 to 200  $\mu$ m. The cumulative particle size distribution in Figure 4-4 shows that approximately 90 vol% (D<sub>90</sub>) of the dried red mud is  $\leq 55 \mu$ m, 50 vol% (D<sub>50</sub>)  $\leq 6.75 \mu$ m and 10 vol % (D<sub>10</sub>) is  $\leq 1.5 \mu$ m. These are in agreement with other studies. Roach [103] and Grafe [1] for example have reported that the particle size of bauxite residue is typically in the range of 100 nm to 200  $\mu$ m while their measurements on some samples yielded 2-100  $\mu$ m. The scanning electron microscopy (SEM) image of red mud is shown in Appendix 3 (Figure A3-1).



Figure 4-4: Particle size analysis of the red mud

# 4.2 Desulphurization studies

In the present work the effect of different additives on the sulphide capacity of the red mud based fluxes was studied using flux-metal equilibrium technique in the temperature range of 1300-1400 °C using graphite crucibles under reducing atmosphere. Table 3–2 presents the chemical composition of the initial fluxes, which were prepared using the dried red mud from Bayer process and reagent grade CaO,  $Al_2O_3$ , TiO<sub>2</sub> and SiO<sub>2</sub> as additives.

**4.2.1** Sulphide capacity measurement between red mud based fluxes and hot metal The sulphide capacity for each experiment was calculated in terms of the sulphur distribution ratio,  $L_S = \frac{(wt\%S)}{[wt\%S]}$ , by considering the change of Gibb's free energy for the dissolution of gaseous sulphur into liquid iron as follows [44]:

$$\log C_{\rm S} = \log L_{\rm S} + \frac{1}{2} \log P_{\rm O_2} - \log f_{\rm S} + \frac{7055}{\rm T} - 1.224$$
4-3

where  $C_s$  is the sulphide capacity of slag,  $f_s$  is the activity coefficient of sulphur in liquid iron based on 1 wt% standard sate,  $P_{O_2}$  is the partial pressure of O<sub>2</sub>, and T is the absolute temperature of the system. Equation **4-3** indicates that for effective desulphurization, slag must have a large sulphide capacity, activity coefficient of sulphur in liquid iron needs to be high, also high temperature and low oxygen partial pressure, *i.e.* reducing conditions are desired.

The oxygen partial pressure was calculated based on the equilibrium between the applied atmosphere (CO = 1 atm) and the graphite crucible, according to:

$$C(gr) + \frac{1}{2}O_2(g) = CO(g)$$
 4-4

$$\Delta G^{\circ} = -114391 - 85.77T \text{ (J/mol)}$$
4-5

$$\frac{1}{2}\log PO_2 = \log a_{\rm C} + \log P_{\rm CO} - (\frac{5976}{\rm T} + 4.48)$$
4-6

where in the present study:  $a_C = 1_{a}$ ,  $P_{CO} = 1$  atm

#### Table 4-3: Partial pressure of oxygen at different temperatures

Temperature, °C	logP <sub>O2</sub>	P <sub>O2</sub> (atm.)
1300	-16.56	2.77×10 <sup>-17</sup>
1350	-16.32	4.74×10 <sup>-17</sup>
1400	-16.10	7.87×10 <sup>-17</sup>

The value of  $f_s$ , sulphur activity coefficient in liquid iron was calculated using the interaction coefficients at 1600 °C as given by Sigworth and Elliot [104] ( $e_S^C = 0.11$ ,  $e_S^O = -0.27$ ,  $e_S^S = -0.028$ ). Since  $P_{O_2}$  is small, only  $e_S^C$  and  $e_S^S$  are considered.

$$\log f_{\rm S} = e_{\rm S}^{\rm C} \cdot \rm{wt\%} \, \rm C + e_{\rm S}^{\rm S} \cdot \rm{wt\%} \, \rm S$$
4-7

$$logf_{S(1873K)} = 0.11 \times wt\% C - 0.028 \times wt\% S$$
 4-8

The activity coefficient is extrapolated from 1873 to 1473K assuming it is inversely proportional to temperature [56].

$$\log f_{S(T)} = \log f_{S(1873K)} \times \left(\frac{1873}{T}\right)$$
 4-9

## 4.2.2 Optical basicity

The optical basicity of a multi component slag with given composition was calculated using the following relationship [41] in which X is the equivalent cation fraction calculated from Equation 4-11 [41] and  $\Lambda$  is the optical basicity value of the slag component, taken from the recommended values provided in Table 4–4.

$$\Lambda = X_A \Lambda_A + X_B \Lambda_B + \cdots$$
 4-10

$$X = \frac{x_i n_i}{\sum x_i n_i}$$
 4-11

In Eq. 4-11,  $x_i$  and  $n_i$  are the mole fraction and number of oxygen atoms in the oxide molecule *i* respectively.

Compound	Optical basicity value, $\Lambda$
CaO	1
$Al_2O_3$	0.65
$SiO_2$	0.48
$SO_3$	0.33
FeO	0.93
$TiO_2$	0.65
Na <sub>2</sub> O	1.15
$P_2O_5$	0.4

Table 4–4: Optical basicity values used in the calculations [41]

The calculated values for the flux basicity, defined as  $B = \% CaO/SiO_2$  or optical basicity are listed in Table 3–2.

# 4.2.3 Equilibrium time

Preliminary experiments were performed to determine the time required to reach equilibrium. Ranges of holding time from 5 to 35 hours were examined at 1350 °C (Table 4–6). Figure 4-5 shows the variation with time of sulphur partition ratio for flux composition RMF1, RMF2 and RMF4. As seen, the sulphur partition ratio reaches a steady state value, here defined as equilibrium concentration, after ~ 25 hours Therefore, for subsequent experiments the holding time was set to 30 hr to ensure equilibrium is reached under various conditions.

Flux		С	ompositi	Basicity	Optical basicity			
No.	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	Na <sub>2</sub> O	SiO <sub>2</sub>	(B)	(Λ)
RMF1	46.5	20	8	4	10	11.5	0.34	0.72
RMF2	41.9	18.0	7.2	13.6	9.0	10.4	1.3	0.73
RMF3	37.2	16.0	6.4	23.2	8.0	9.2	2.5	0.75
RMF4	32.6	14.0	5.6	32.8	7.0	8.1	4.1	0.76
RMF5	27.9	12.0	4.8	42.4	6.0	6.9	6.1	0.78
RMF6	23.3	10.0	4.0	52.0	5.0	5.8	9.0	0.80
RMF7	29.6	21.8	5.1	29.8	6.4	7.3	4.1	0.74
RMF8	28.3	25.2	4.9	28.5	6.1	7.0	4.1	0.74
RMF9	27.1	28.3	4.7	27.3	5.8	6.7	4.1	0.73
RMF10	26.0	31.2	4.5	26.2	5.6	6.4	4.1	0.72
RMF11	31.0	13.3	10.1	31.2	6.7	7.7	4.1	0.76
RMF12	30.1	13.0	12.6	30.4	6.5	7.5	4.1	0.76
RMF13	29.1	12.5	15.7	29.3	6.3	7.2	4.1	0.76
RMF14	28.3	12.2	17.9	28.5	6.1	7.0	4.1	0.76
RMF15	29.6	12.7	5.1	29.8	6.4	16.4	1.8	0.74
RMF16	28.3	12.2	4.9	28.5	6.1	20.0	1.4	0.73
RMF17	27.1	11.7	4.7	27.3	5.8	23.4	1.2	0.72
RMF18	26.0	11.2	4.5	26.2	5.6	26.4	1.0	0.70

Table 4–5: Initial chemical compositions of red mud based fluxes used in the experiments



Figure 4-5: Variation of sulphur partition ratio with time at 1350 °C

## 4.2.4 Desulphurization results

Table 4–7 presents the composition of metal and flux after equilibrium, along with the calculated sulphide capacity and optical basicity in the temperature range of 1300 -1400 °C. The flux composition is comparable with the original blend, except the Na<sub>2</sub>O content that has dropped significantly. In addition, iron oxide in the flux was reduced to metal with the carbon of hot metal and graphite crucible.

Flux No.	Time (h)	[S], wt.%	(S), wt.%	L <sub>s</sub>
RMF1	5	0.12	0.754	6.28
RMF1	10	0.09	0.894	9.93
RMF1	15	0.077	1.421	18.45
RMF1	25	0.035	1.522	43.49
RMF1	30	0.0225	1.51	67.11
RMF1	35	0.0225	1.49	66.22
RMF2	5	0.14	0.721	5.15
RMF2	10	0.077	0.9555	12.41
RMF2	15	0.0525	1.4455	27.53
RMF2	25	0.021	1.606	76.48
RMF2	30	0.02	1.742	87
RMF2	35	0.021	1.785	85
RMF4	5	0.15	0.688	4.59
RMF4	10	0.055	1.017	18.49
RMF4	15	0.012	1.47	122
RMF4	25	0.008	1.69	211
RMF4	30	0.007	1.7	242
RMF4	35	0.007	1.68	240

# Table 4–6: Results of the equilibrium time study

Elux No Tomporatura $(^{\circ}C)$		Flux co	ompositio	ons in m	ole fract	tion afte	r equilit	orium	Metal pha	.se, wt%	log Co	Optical basicity
FIUX INO.	Temperature (C)	CaO	$Al_2O_3$	SiO <sub>2</sub>	FeO	TiO <sub>2</sub>	Na <sub>2</sub> O	S	S	С	log Cs	Optical basicity
RMF1	1300	0.139	0.323	0.286	0.055	0.160	0.029	0.009	0.121	4.61	-4.72	0.62
RMF2	1300	0.367	0.239	0.204	0.055	0.102	0.024	0.009	0.113	4.90	-4.65	0.68
RMF3	1300	0.535	0.175	0.151	0.039	0.067	0.020	0.014	0.097	4.20	-4.30	0.73
RMF4	1300	0.621	0.140	0.113	0.045	0.052	0.016	0.014	0.034	4.98	-3.90	0.77
RMF5	1300	0.682	0.105	0.103	0.046	0.049	0.0	0.014	0.029	4.90	-3.85	0.79
RMF6	1300	0.765	0.065	0.076	0.050	0.031	0.0	0.013	0.032	4.70	-3.88	0.84
RMF7	1300	0.599	0.206	0.093	0.049	0.044	0.016	0.009	0.027	4.62	-3.99	0.75
RMF8	1300	0.582	0.228	0.087	0.053	0.042	0.014	0.010	0.034	4.77	-4.08	0.74
RMF9	1300	0.544	0.245	0.088	0.061	0.039	0.016	0.008	0.062	4.78	-4.41	0.74
RMF10	1300	0.544	0.274	0.078	0.049	0.038	0.011	0.006	0.068	4.76	-4.59	0.74
RMF11	1300	0.594	0.141	0.109	0.036	0.097	0.014	0.007	0.015	5.65	-3.90	0.76
RMF12	1300	0.573	0.128	0.107	0.048	0.122	0.015	0.007	0.026	5.25	-4.13	0.76
RMF13	1300	0.551	0.133	0.106	0.038	0.151	0.013	0.007	0.049	5.02	-4.40	0.75
RMF14	1300	0.537	0.121	0.095	0.047	0.178	0.013	0.006	0.048	4.87	-4.38	0.75
RMF15	1300	0.515	0.125	0.244	0.054	0.043	0.013	0.006	0.028	4.81	-4.14	0.71
RMF16	1300	0.492	0.104	0.300	0.048	0.038	0.013	0.006	0.033	4.8	-4.24	0.70
RMF17	1300	0.492	0.104	0.300	0.048	0.038	0.013	0.006	0.045	4.73	-4.37	0.70
RMF18	1300	0.455	0.104	0.363	0.050	0.037	0.014	0.005	0.075	4.55	-4.60	0.67
RMF1	1350	0.135	0.326	0.288	0.059	0.158	0.026	0.008	0.110	4.52	-4.71	0.62
RMF2	1350	0.362	0.236	0.198	0.069	0.103	0.022	0.010	0.077	4.89	-4.48	0.68
RMF3	1350	0.525	0.176	0.151	0.051	0.066	0.018	0.014	0.063	4.98	-4.22	0.73
RMF4	1350	0.612	0.121	0.136	0.052	0.051	0.014	0.014	0.021	4.90	-3.69	0.77
RMF5	1350	0.716	0.086	0.103	0.036	0.045	0.0	0.014	0.019	4.45	-3.64	0.80
RMF6	1350	0.782	0.060	0.072	0.037	0.035	0.0	0.014	0.017	4.25	-3.54	0.84
RMF7	1350	0.581	0.200	0.097	0.057	0.044	0.014	0.008	0.022	4.45	-3.96	0.75
RMF8	1350	0.587	0.237	0.095	0.041	0.043	0.016	0.008	0.032	4.39	-4.12	0.74

Table 4–7- Experimental results of sulphur equilibrium between flux and metal

					Table	4 <b>–</b> 7- Co	ntinued	•				
RMF9	1350	0.542	0.249	0.088	0.062	0.040	0.013	0.007	0.050	4.51	-4.40	0.74
RMF10	1350	0.531	0.279	0.082	0.051	0.037	0.014	0.005	0.040	4.88	-4.46	0.73
RMF11	1350	0.580	0.135	0.115	0.054	0.096	0.012	0.008	0.017	5.11	-3.87	0.76
RMF12	1350	0.580	0.130	0.112	0.037	0.122	0.013	0.007	0.025	4.90	-4.07	0.76
RMF13	1350	0.556	0.129	0.103	0.047	0.145	0.013	0.007	0.059	4.74	-4.42	0.75
RMF14	1350	0.557	0.118	0.097	0.046	0.163	0.012	0.007	0.060	4.66	-4.43	0.76
RMF15	1350	0.527	0.122	0.256	0.034	0.042	0.013	0.006	0.020	4.68	-4.01	0.71
RMF16	1350	0.498	0.100	0.293	0.054	0.037	0.012	0.006	0.034	4.61	-4.25	0.70
RMF17	1350	0.481	0.092	0.329	0.046	0.035	0.011	0.005	0.049	4.62	-4.45	0.69
RMF18	1350	0.462	0.089	0.349	0.052	0.032	0.010	0.006	0.048	4.46	-4.38	0.68
RMF1	1400	0.143	0.324	0.301	0.050	0.154	0.019	0.688	0.095	4.08	-4.64	0.62
RMF2	1400	0.370	0.240	0.199	0.053	0.108	0.019	1.017	0.025	4.90	-3.99	0.68
RMF3	1400	0.531	0.182	0.156	0.037	0.068	0.012	1.47	0.010	4.80	-3.42	0.72
RMF4	1400	0.622	0.106	0.163	0.031	0.051	0.013	1.69	0.008	4.74	-3.25	0.76
RMF5	1400	0.717	0.087	0.109	0.025	0.050	0.0	0.012	0.007	4.68	-3.27	0.80
RMF6	1400	0.779	0.066	0.074	0.031	0.037	0.0	0.012	0.008	4.90	-3.32	0.84
RMF7	1400	0.594	0.209	0.108	0.035	0.047	0.013	0.678	0.012	4.27	-3.77	0.74
RMF8	1400	0.560	0.234	0.099	0.050	0.043	0.009	0.646	0.015	4.01	-3.86	0.74
RMF9	1400	0.546	0.262	0.092	0.044	0.042	0.009	0.525	0.019	4.24	-4.08	0.73
RMF10	1400	0.534	0.278	0.085	0.052	0.036	0.011	0.451	0.025	4.99	-4.35	0.73
RMF11	1400	0.599	0.130	0.122	0.033	0.096	0.013	1.006	0.015	4.56	-3.73	0.76
RMF12	1400	0.580	0.130	0.115	0.037	0.120	0.011	0.868	0.036	4.55	-4.17	0.75
RMF13	1400	0.546	0.132	0.107	0.048	0.148	0.011	0.849	0.049	4.45	-4.31	0.75
RMF14	1400	0.565	0.124	0.106	0.028	0.161	0.009	0.893	0.078	4.44	-4.48	0.75
RMF15	1400	0.530	0.117	0.262	0.034	0.040	0.011	0.744	0.021	4.55	-4.01	0.71
RMF16	1400	0.516	0.099	0.292	0.041	0.037	0.009	0.616	0.029	4.42	-4.22	0.70
RMF17	1400	0.495	0.088	0.335	0.037	0.031	0.009	0.584	0.028	4.51	-4.23	0.69
RMF18	1400	0.478	0.081	0.359	0.038	0.030	0.009	0.583	0.032	4.37	-4.28	0.68

#### 4.2.5 Effect of the basicity on the sulphide capacity of red mud based fluxes

The relationship between the sulphide capacity and the optical basicity, as a unified measure of the flux basicity, is shown in Figure 4-6 for the temperature range of 1300 - 1400 °C. The results show the sulphide capacity increases with increasing optical basicity and temperature. The effect of temperature is more evident at higher optical basicity. The sulphide capacity reaches a maximum at optical basicity of 0.76–0.77 for all the temperatures, indicating this as the optimum value, beyond which the sulphide capacity does not increase. As will be discussed later, this is the point where the flux is saturated with CaO. In order to investigate the effect of individual flux components on sulphide capacity, flux RMF4 was chosen as the basis, as it corresponds to the composition with optical basicity of ~0.77.



Figure 4-6: Relationship between sulphide capacity and optical basicity

# **4.2.6** Effect of CaO on the optical basicity and the sulphide capacity of the red mud based fluxes

The degree of the silicate network polymerization can dictate the sulphur absorption capacity of the liquid flux. Lime, as a basic component, is known to contribute to depolymerisation of the

silicate network and increases the activity of the oxygen ion  $(O^{2-})$  leading to higher optical basicity, Figure 4-7.

The relationship between sulphide capacity and the CaO content is shown in Figure 4-8. The sulphide capacity increases with increasing lime for all temperatures. The trend appears to change at  $X_{CaO} \sim 0.6$ , above which addition of lime does not improve the sulphide capacity (RMF4 through RMF6). XRD analysis was carried out on the samples RMF3, RMF4, RMF5 and RMF6, with the results provided in Appendix 4 (Figure A4-1 – Figure A4-4).

The obtained results revealed peaks for free lime in the sample RMF5 and RMF6 but not for samples RMF3 and RMF4. Therefore, RMF4 sample containing ~ 32.8% CaO was considered as the point where the flux is just saturated with CaO. This is well consistent with the trend of sulphide capacity that reaches a plateau at the same concentration. Addition of lime over the saturation concentration results in undissolved lime that does not contribute to desulphurization, as the activity of CaO and  $O^{2-}$  and the extent of flux depolymerisation remain unchanged. In fact, due to the formation of solid phases in the molten flux, the kinetics of the desulphurization is slowed as the flux viscosity is increased.



Figure 4-7: Relationship between optical basicity and mole fraction of lime in the red mud based fluxes

As a result of the high temperature nature of experiments and the long hours needed for achieving equilibrium condition, it is not customary to repeat all the experiments in the high temperature equilibrium studies. Thus, in this study samples (RMF1 through RMF6) with different CaO concentration were chosen to test the repeatability of the experiments. These samples were treated three times at the 1350 °C. The resulting measurement of these treatments had a standard deviation about  $\pm 5\%$  of the calculated sulphide capacity values at 1350 °C for each sample.



Figure 4-8: Effect of CaO on the sulphide capacity at different temperatures *Error bars were determined for 1350 °C only.* 

# **4.2.7** Effect of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> on the optical basicity and sulphide capacity of the red mud fluxes

In order to investigate the effect of other oxide additives on the sulphide capacity, different amounts of  $Al_2O_3$ ,  $TiO_2$  and  $SiO_2$  were added to the flux RMF4 which was found to exhibit the highest sulphide capacity. The final compositions and sulphide capacities for new composition are shown in Table 4–7.

The results in Figure 4-9 (RMF7 through RMF10) and Figure 4-10 (RMF11 through RMF14) show the effect of  $Al_2O_3$  and TiO<sub>2</sub> on the sulphide capacity of the red mud based fluxes in the temperature range of 1300 °C to 1400 °C respectively. It can be seen that the sulphide capacity decreases with increasing the concentration of both components. Alumina and titanium oxide are known as amphoteric oxides that depending on the total flux composition can perform as either network modifiers or network formers. In highly basic fluxes used here (RMF4), these oxides behave as network former [34].

 $Ti_4^+$  and  $Al_3^+$  form tetrahedra and can be incorporated into the silicate network as  $TiO_4^{4-}$  and  $AlO_4^{5-}$  species. The charge balance can be maintained by other ions such as Na<sup>+</sup> or Ca<sup>2+</sup> so that these cations do not participate in depolymerization of the silicate network [34], thus the "effective" concentration of basic components decreases. In other words,  $Al_2O_3$  and  $TiO_2$  promote polymerization of the flux structures and decrease mole fraction of the free oxygen ion  $(O^{2-})$ .

Figure 4-11 and Figure 4-12 show the effect of alumina and titania addition respectively on the optical basicity of the fluxes in the temperature range of 1300 °C- 1400 °C. It is clear that both oxides decrease the optical basicity, in accordance with their effect on the sulphide capacity.



Figure 4-9: Effect of Al<sub>2</sub>O<sub>3</sub> on the sulphide capacity at different temperatures



Figure 4-10: Effect of TiO<sub>2</sub> on the sulphide capacity at different temperatures



Figure 4-11: Effect of Al<sub>2</sub>O<sub>3</sub> on the optical basicity at different temperatures



Figure 4-12: Effect of TiO<sub>2</sub> on the optical basicity at different temperatures

The effect of SiO<sub>2</sub> on the sulphide capacity of the flux (RMF15 through RMF18) in the in the range of 1300 - 1400 °C is plotted in Figure 4-13. It can be seen that the sulphide capacity decreases with increasing SiO<sub>2</sub> content regardless of the temperature. SiO<sub>2</sub> is a network former and increases the degree of the polymerization in the flux structure, which is evidenced by a decrease in the availability of the free oxygen ions (O<sup>2-</sup>) Figure 4-14 [105]. The effect would then obviously be a drop in sulphide capacity as the SiO<sub>2</sub> content increases.



Figure 4-13: Effect of SiO<sub>2</sub> on the sulphide capacity at different temperatures



Figure 4-14: Effect of SiO<sub>2</sub> on the different oxygen bondings [105]



Figure 4-15- Effect of SiO<sub>2</sub> on optical basicity at different temperatures

## 4.2.8 Effect of temperature on the sulphide capacity of red mud based fluxes

Temperature should have a positive effect on the sulphide capacity as described earlier. The obtained sulphide capacity data are plotted against reciprocal temperature in Figure 4-16, confirming that an increase in temperature results in higher sulphide capacity which would be in accordance with the increase of free oxygen ions due to the breaking of the bonds [47]. Separate lines for fluxes with approximately equal optical basicity have been plotted. The difference in the slope of the lines is believed to be because of the effect of the optical basicity as discussed below. Values are shown using separate lines. It should be noted that the variation of line slopes is correlated to the optical basicity values and hence with flux composition.

The equilibrium constant (K) for the sulphur removal reaction can be related to temperature through a form of Van't Hoff's equation [41, 47, 106] where  $\Delta H$  is the reaction enthalpy.

dln K _	ΔH		
$\overline{d(1/T)}$ –	R		4-12

In the presence of lime as the main basic component of slag, the desulphurization reaction can be expressed as follows:

$$CaO(s) + \frac{1}{2}S_2(g) = CaS(s) + \frac{1}{2}O_2(g) \Delta G^\circ = 92000 - 2.55T \left(\frac{J}{mol}\right)$$
4-13

From the equilibrium constant of Reaction **4-13** and Equation **4-12** the relation between flux sulphide capacity and temperature can be simplified as:

$$\frac{d(\log C_{\rm S})}{d(\frac{1}{T})} = \frac{-\Delta H}{2.303R}$$
4-14

Therefore, the slope of the lines in Figure 4-16 can be correlated to the enthalpy of the desulphurization reactions, which could be a combination of Reaction 4-13 together with dissolution of oxygen and sulphur into metal and CaO/CaS into slag. The enthalpy of the overall sulphur pick up process was calculated and plotted against the optical basicity in Figure 4-17, which increases from 99.8 kJ/mole at an optical basicity of 0.62 to 338.9 kJ/mole at an optical basicity of 0.77.

The present results are in good agreement with the temperature dependence of the sulphide capacities reported by previous researchers for different compositions [47, 48, 50, 52]. Hence, the obtained results are plotted in Figure 4-18 with other published data [47, 48, 50, 52]. Although previous findings are in different slag systems and temperatures, the trends are similar. It also can be seen that the slope slightly increased with increasing optical basicity in all systems.



Figure 4-16: Relationship between sulphide capacity and temperature



Figure 4-17- Relationship between the enthalpy of sulphur transfer to flux and optical basicity



Figure 4-18: Relationship between log C<sub>s</sub> and temperature (data from this study and literatures)

# 4.3 Dephosphorization studies

Red mud based fluxes with high iron oxide content cannot be equilibrated with carbon-saturated iron as the iron oxide is reduced. Thus, in this study, the phosphorus distribution ratio in the temperature range of 1300- 1400 °C is experimentally determined between the synthetic red mud based flux and a strip of pure solid iron. The results can then be extended to calculate the distribution of phosphorous between slag and liquid iron, considering the thermodynamics of fusion of iron [85, 87]. This method was developed by Sano and his coworkers [84, 85].

Table 4–8 presents the chemical composition of the initial fluxes, which were prepared using reagent grade CaO,  $Al_2O_3$ ,  $TiO_2$ ,  $SiO_2$ ,  $CaHPO_4$ ,  $Na_2CO_3$  and synthetic FeO (wustite) as additives.

	Composition wt %							
Flux No.	FeO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	Na <sub>2</sub> O	SiO <sub>2</sub>	$P_2O_5$	
SRM-1	41.9	18.0	7.2	3.6	9.0	10.4	10.0	
SRM-2	37.2	16.0	6.4	13.2	8.0	9.2	10.0	
SRM-3	32.6	14.0	5.6	22.8	7.0	8.1	10.0	
SRM-4	27.9	12.0	4.8	32.4	6.0	6.9	10.0	
SRM-5	23.3	10.0	4.0	42.0	5.0	5.8	10.0	
SRM-6	18.6	8.0	3.2	51.6	4.0	4.6	10.0	
SRM-7	25.4	20.0	4.4	29.5	5.5	6.3	9.1	
SRM-8	24.3	23.5	4.2	28.2	5.2	6.0	8.7	
SRM-9	23.3	26.7	4.0	27.0	5.0	5.8	8.3	
SRM-10	22.3	29.6	3.8	25.9	4.8	5.5	8.0	
SRM-11	26.6	11.4	9.3	30.9	5.7	6.6	9.5	
SRM-12	25.8	11.1	11.9	30.0	5.6	6.4	9.3	
SRM-13	24.9	10.7	15.0	28.9	5.4	6.2	8.9	
SRM-14	24.3	10.4	17.2	28.2	5.2	6.0	8.7	
SRM-15	25.4	10.9	4.4	29.5	5.5	15.4	9.1	
SRM-16	24.3	10.4	4.2	28.2	5.2	19.0	8.7	
SRM-17	23.3	10.0	4.0	27.0	5.0	22.4	8.3	
SRM-18	22.3	9.6	3.8	25.9	4.8	25.5	8.0	

 Table 4–8: Initial chemical compositions of synthetic red mud based fluxes used in the experiments

## 4.3.1 Synthetic iron (II) oxide preparation

In this study, synthetic FeO (wustite) was prepared by equilibrating iron (III) oxide (hematite) and pure iron powders at high temperature. Then X-ray diffraction examination was performed to verify transformation of hematite to wustite, as seen in Figure 4-19 for a typical experiment. In

this figure, a small peak for metallic iron is identified at around  $2\theta = 42^{\circ}$ . Automatic semiquantitative analysis based on RIR (Reference Intensity Ratio) method was performed using PDXL software to determine the approximate amount of this phase. It was found that 99.8 wt pct of the product is wustite.



Figure 4-19: Diffraction pattern of synthetic wustite

## 4.3.2 Phosphorus distribution ratio between red mud based fluxes and hot metal

## 4.3.2.1 Principles of Calculation

The phosphorus distribution was measured by analyzing the flux, (%P), and iron foil,  $[%P]^{Fe-\gamma}$ .

$$L_{\rm P}^{\rm Fe-\gamma} = \frac{(\% P)}{[\% P]^{\rm Fe-\gamma}}$$
4-15

Im *et al.* [107] reported that in dilute solution of phosphorus and temperature of 1300 °C the equilibrium between carbon saturated iron and solid iron dictates the following distribution of P:

$$\frac{[\%P]^{Fe-\gamma}}{[\%P]^{Fe-C}} = 0.413$$
**4-16**

Consequently, the phosphorus distribution between red mud based fluxes and carbon saturated iron can be obtained as follows:

$$L_{P}^{Fe-C} = \frac{(^{\%}P)}{[^{\%}P]^{Fe-C}} = L_{P}^{Fe-\gamma} \cdot \frac{[^{\%}P]^{Fe-\gamma}}{[^{\%}P]^{Fe-C}} = L_{P}^{Fe-\gamma} \times 0.413$$
4-17

Details of the method of calculation of phosphorus partition ratio are provided in Appendix 5.

## 4.3.2.2 Equilibrium time

Preliminary experiments were performed to determine the time required to reach equilibrium. A range of dwelling time from 10 to 35 hrs was applied to similar samples at 1350 °C. Table 4–9 shows the variation with time of phosphorus distribution in carbon saturated iron for flux composition SRM-3. As seen in Figure 4-5, the phosphorus distribution reaches a steady state value, here defined as equilibrium holding time after ~ 30 hours. Therefore, for subsequent experiments the holding time was set to 35 h to ensure equilibrium is reached under various conditions for all fluxes in Table 4–11.

Flux	Temperature (°C)	Time (h)	[P], wt.%	(P), wt.%	L <sub>P</sub>
SRM-3	1350	10	0.003	5.56	765
SRM-3	1350	15	0.006	5.53	380
SRM-3	1350	25	0.007	5.09	300
SRM-3	1350	30	0.008	5.29	272
SRM-3	1350	35	0.006	4.21	271

Table 4–9: Results of the equilibrium time study



Figure 4-20: Time required to reach equilibrium at 1350 °C

## 4.3.2.3 Phosphate capacity of red mud based fluxes

A convenient measure for comparing dephosphorization properties of different fluxes is phosphate capacity as mentioned previously in Chapter 2. The phosphate capacity of the slags used in this study was calculated using Equation 2-56 and can be expressed as a function of temperature, distribution ratio, oxygen potential, and activity coefficient of phosphorus as follows:

$$\log C_{PO_4^{3-}} = \log L_P - \log f_P - \frac{5}{4} \log P_{O_2} + \frac{6392}{T} + 1.475$$
4-18

where  $L_P$  can be obtained from the slag-metal equilibrium results (experimental) and the oxygen partial pressure is calculated from iron oxide activity data by considering the reaction of  $\gamma$ -Fe (gamma iron) and liquid iron oxide as follows:

$$Fe_{(S)} + \frac{1}{2}O_2 = FeO_{(L)}$$

$$\frac{1}{2}logP_{O_2} = loga_{FeO} - loga_{Fe} + \frac{\Delta G}{19.44 \times T}$$
4-19
4-20

where  $a_{Fe} = 1$  for the pure solid iron strip.
The Gibbs free energy of formation of FeO, which was extracted from FactSage®, thermodynamic database for different temperatures is provided in Table 4–10.

Temperature, °C	$\Delta G^{o}$ J/mol
1300	-161653
1350	-159442
1400	-157245

Table 4-10: Estimated energy of formation of FeO from FactSage

Activity of FeO was also calculated using appropriate slag models of FactSage®.

The activity coefficient of phosphorus was calculated using interaction parameters, considering a binary Fe-P alloy as following.

$$\log f_{\rm P} = e_{\rm P}^{\rm P} \cdot {\rm wt\%} \, {\rm P} \qquad e_{\rm P}^{\rm P} = 0.062 \, [104]$$
 4-21

## 4.3.3 Dephosphorization results and discussion

Table 4–11 shows the composition of each flux after equilibrium and phosphorus content in iron strip, along with the measured phosphorus distribution ratio between synthetic red mud flux and iron strip and the calculated ratio for hot metal. In addition, the calculated phosphate capacity and optical basicity values in the temperature range of 1300-1400 °C are listed in Table 4–11. The final flux composition is comparable with the original blend, except Na<sub>2</sub>O content that has dropped noticeably.

Heat No T °C		Flux compositions in after equilibrium (wt%)							(%P) [	[%P]	OB	τ Fe-γ	L Fe-C	(I=	
neat no.	IC	CaO	$Al_2O_3$	SiO <sub>2</sub>	$P_2O_5$	FeO	TiO <sub>2</sub>	Na <sub>2</sub> O	(wt%)	(wt%)	OB	Lp	Lp	$u_{\rm FeO}$	$10g C_{PO_4^{3-}}$
SRM-1	1300	8.77	17.03	9.19	9.89	42.42	7.95	4.76	4.30	0.022	0.71	199.02	82.20	0.79	21.31
SRM-2	1300	14.92	15.20	7.88	11.64	38.54	6.34	4.48	5.06	0.022	0.71	234.30	96.76	0.68	21.54
SRM-3	1300	24.08	14.13	6.73	12.31	33.50	5.19	4.07	5.35	0.020	0.73	270.25	111.61	0.54	21.84
SRM-4	1300	31.59	10.59	6.26	11.51	31.49	5.31	3.26	5.00	0.018	0.75	277.93	114.78	0.39	22.22
SRM-5	1300	39.39	8.98	6.10	10.84	26.67	4.77	3.25	4.72	0.016	0.77	291.05	120.20	0.27	22.65
SRM-6	1300	47.08	8.15	5.26	10.77	21.34	4.09	2.32	4.68	0.018	0.78	260.03	107.39	0.24	22.71
SRM-7	1300	39.12	15.10	5.13	10.27	23.39	4.62	2.37	4.46	0.021	0.76	215.68	89.08	0.24	22.61
SRM-8	1300	38.59	19.29	5.08	10.69	22.35	3.02	1.97	4.65	0.023	0.76	202.14	83.48	0.26	22.51
SRM-9	1300	36.37	22.95	4.98	9.55	21.51	2.77	1.88	4.15	0.023	0.75	180.46	74.53	0.39	22.04
SRM-10	1300	36.56	24.03	3.76	9.65	20.27	3.11	2.62	4.20	0.023	0.75	182.45	75.35	0.36	22.13
SRM-11	1300	39.51	8.12	5.15	11.40	25.71	6.90	3.22	4.95	0.018	0.77	275.27	113.69	0.25	22.68
SRM-12	1300	38.09	7.80	4.10	11.47	26.67	9.73	2.13	4.99	0.018	0.76	277.01	114.41	0.27	22.60
SRM-13	1300	38.39	8.46	5.43	10.90	23.49	11.04	2.30	4.74	0.024	0.76	197.38	81.52	0.26	22.51
<b>SRM-14</b>	1300	37.90	6.21	4.22	9.97	24.93	14.00	2.77	4.33	0.024	0.77	180.62	74.60	0.28	22.41
SRM-15	1300	39.97	6.29	11.11	10.78	24.08	3.55	2.21	4.69	0.023	0.74	208.31	86.03	0.27	22.48
SRM-16	1300	38.93	7.57	13.33	10.62	22.52	3.19	2.83	4.62	0.025	0.73	184.74	76.30	0.38	22.06
SRM-17	1300	37.98	5.94	18.62	11.22	21.25	2.86	2.14	4.88	0.028	0.71	177.35	73.25	0.56	21.63

Table 4–11: Experimental results of phosphorus equilibrium between synthetic red mud flux and pure iron

SRM-18	1300	37.13	6.07	21.50	10.42	20.20	3.51	1.17	4.53	0.030	0.70	151.06	62.39	0.52	21.64
SRM-1	1350	7.79	18.78	7.01	10.51	43.67	8.27	3.97	4.57	0.025	0.71	180.12	74.39	0.69	20.87
SRM-2	1350	15.95	16.58	6.06	11.33	38.54	7.28	4.27	4.94	0.022	0.72	224.73	92.81	0.62	21.09
SRM-3	1350	24.23	14.50	6.15	11.70	33.71	5.80	3.89	5.10	0.020	0.73	257.13	106.20	0.53	21.31
SRM-4	1350	31.91	12.43	6.43	11.50	28.90	5.12	3.71	5.01	0.018	0.75	284.86	117.65	0.41	21.64
SRM-5	1350	41.18	10.45	6.51	9.66	24.30	4.80	3.10	4.21	0.015	0.77	273.55	112.97	0.23	22.23
SRM-6	1350	49.40	8.59	5.00	10.04	19.97	4.20	2.79	4.38	0.018	0.79	241.13	99.59	0.22	22.24
SRM-7	1350	39.60	13.71	5.06	11.87	22.39	3.68	1.69	5.18	0.024	0.74	215.43	88.97	0.22	22.22
SRM-8	1350	38.89	15.27	5.75	10.27	22.39	3.31	2.13	4.48	0.024	0.74	186.49	77.02	0.23	22.10
SRM-9	1350	38.65	17.90	4.95	11.82	21.20	3.34	2.15	5.15	0.029	0.75	179.90	74.30	0.24	22.02
SRM-10	1350	37.18	22.27	4.92	11.30	19.22	3.36	1.75	4.93	0.031	0.74	160.77	66.40	0.32	21.66
SRM-11	1350	39.16	10.04	5.46	11.39	23.73	8.04	2.17	4.97	0.020	0.75	243.10	100.40	0.23	22.20
SRM-12	1350	40.11	9.11	4.46	11.22	23.83	9.38	1.89	4.89	0.024	0.76	207.91	85.87	0.24	22.08
SRM-13	1350	39.22	7.99	5.42	11.13	23.70	11.49	1.06	4.85	0.024	0.75	202.11	83.47	0.25	22.03
SRM-14	1350	38.71	7.62	4.16	9.95	22.74	14.76	2.05	4.34	0.026	0.76	166.23	68.65	0.25	21.96
SRM-15	1350	40.01	9.42	13.10	10.59	22.30	2.15	2.42	4.62	0.026	0.74	175.51	72.48	0.35	21.61
SRM-16	1350	37.69	9.33	16.02	10.13	21.12	2.85	2.86	4.42	0.027	0.72	165.83	68.49	0.47	21.25
SRM-17	1350	38.64	8.47	19.15	9.47	19.55	2.89	1.84	4.13	0.031	0.71	134.09	55.38	0.48	21.14
SRM-18	1350	37.85	7.70	21.50	10.00	19.82	2.78	1.35	4.36	0.036	0.70	121.73	50.28	0.50	21.06
SRM-1	1400	8.86	17.62	11.67	9.69	41.96	6.42	3.78	4.21	0.023	0.70	184.86	76.35	0.849	20.16

SRM-2	1400	15.19	16.50	7.53	10.53	40.35	6.46	3.43	4.59	0.025	0.72	185.89	76.77	0.645	20.46
SRM-3	1400	23.62	14.99	7.19	10.78	34.80	5.50	3.11	4.70	0.021	0.73	224.95	92.90	0.555	20.71
SRM-4	1400	32.15	10.68	6.12	11.17	31.81	5.18	2.89	4.87	0.019	0.75	256.35	105.87	0.37	21.20
SRM-5	1400	41.99	8.00	6.40	11.04	25.28	4.92	2.37	4.81	0.019	0.77	253.23	104.59	0.229	21.72
SRM-6	1400	49.32	8.01	3.54	11.05	21.76	3.37	2.96	4.82	0.023	0.80	211.27	87.25	0.216	21.70
SRM-7	1400	40.66	12.51	6.44	10.05	23.93	3.59	2.82	4.38	0.024	0.77	180.30	74.46	0.214	21.65
SRM-8	1400	39.24	16.32	5.19	10.30	23.32	2.85	2.78	4.49	0.027	0.76	166.40	68.72	0.209	21.64
SRM-9	1400	37.89	19.34	4.68	9.79	22.66	3.72	1.93	4.27	0.024	0.75	175.57	72.51	0.257	21.43
SRM-10	1400	37.55	23.15	3.62	10.24	20.85	2.66	1.94	4.46	0.030	0.75	150.26	62.06	0.258	21.36
SRM-11	1400	40.79	9.98	5.83	10.50	22.84	8.16	1.91	4.58	0.027	0.76	171.39	70.78	0.214	21.62
SRM-12	1400	39.53	9.22	4.78	10.66	22.45	10.77	2.60	4.65	0.030	0.76	154.91	63.98	0.214	21.58
SRM-13	1400	37.80	8.76	4.99	9.65	23.04	13.82	1.94	4.21	0.030	0.76	140.25	57.92	0.263	21.31
SRM-14	1400	39.43	7.60	4.35	8.81	21.39	16.47	1.97	3.84	0.039	0.77	98.47	40.67	0.23	21.30
SRM-15	1400	40.60	8.94	12.05	10.07	22.55	3.80	1.98	4.39	0.027	0.74	162.58	67.15	0.308	21.20
SRM-16	1400	39.76	7.50	14.61	10.33	22.28	3.79	1.73	4.50	0.030	0.73	150.09	61.99	0.373	20.96
SRM-17	1400	37.83	8.34	17.62	9.28	22.29	3.02	1.62	4.04	0.033	0.72	122.57	50.62	0.499	20.56
SRM-18	1400	38.31	7.10	19.80	9.96	20.12	3.72	0.98	4.34	0.036	0.71	120.65	49.83	0.469	20.62

# 4.3.3.1 Effect of iron oxide on the phosphorus distribution ratio and phosphate capacity

The effect of iron oxide content on the phosphorus distribution ratio and the phosphate capacity of the synthetic red mud based fluxes (SRM-1 through SRM-6) at different temperatures from 1300 to 1400 °C are plotted in Figure 4-21 and Figure 4-23.It can be seen that the phosphorus distribution ratio first increases with increasing iron oxide concentration to reach a maximum around 30 wt pct FeO and then drops. In term of repeatability of the experiments samples (SRM-1 through SRM-6) were chosen to repeat the experiment three times at 1400 °C. The resulting experiments had a standard deviation approximately  $\pm$ 7% of the calculated phosphorus distribution ratios at 1400 °C for each sample.



Figure 4-21: Effect of iron oxide content on the phosphorus distribution ratio  $(L_P^{Fe-C})$ Error bars were determined for 1400 °C only.

The results show similar variation in the temperature range of 1300 °C – 1400 °C. The maximum distribution ratios are  $L_P^{Fe-C} = 288$ ,  $L_P^{Fe-C} = 281$  and  $L_P^{Fe-C} = 251$  corresponding to 26.6wt%, 28.9 wt% and 31.8 wt% iron oxide at 1300 °C, 1350 °C and 1400 °C respectively.

Mohassab *et al.*[108] reported the same tendency between FeO concentration and phosphorus distribution, Figure 4-22. As seen,  $L_P$  increases with FeO content up to 20-30 wt pct, and then begins to decrease as FeO content is raised. They attributed this trend to the variation of the

activity coefficient of P<sub>2</sub>O<sub>5</sub> ( $\gamma_{P_2O_5}$ ) with FeO content;  $\gamma_{P_2O_5}$  was decreased with increasing FeO when FeO < 20–30 wt% and increased afterwards.



Figure 4-22: Effect of FeO content on L<sub>P</sub> at different basicity [108]

Figure 4-23 shows the effect of FeO content on the phosphate capacity. It can be seen that  $\log C_{PO_4^{3-}}$  increases when the FeO concentration decreases to ~ 25–28 wt pct for different temperatures and then becomes more or less stable at lower FeO contents.



Figure 4-23: Effect of iron oxide content on the phosphate capacity

The variations in phosphate capacity or phosphorus distribution can be explained by looking into the reaction of dephosphorization as follows:

$$[P] + \frac{5}{4}O_2(g) + \frac{3}{2}(O^{2-}) = (PO_4^{3-})$$
4-22

Increasing FeO content leads to higher FeO activity and consequently increases the oxygen partial pressure of the system, shifting the reaction to the right side; the effect is larger P incorporation in the slag phase. Even though the phosphorus removal is favored with increase in oxygen partial pressure, high iron oxide content would reduce the distribution ratio or dephosphorization capacity due to decreasing the CaO content or basicity.

Equation 4-22 suggests that both oxygen potential and basicity  $(0^{2-})$  are desired for dephosphorization. Larger FeO on one hand leads to higher oxygen potential and on the other hand results in lower CaO concentration, hence the reduced basicity. One therefore expects that maximum L<sub>P</sub> is obtained at certain FeO content, as Figure 4-21 demonstrates.

Figure 4-24 compares the calculated distribution ratio in this study along with other results [85, 87]. The trend of experimental results in the present study is similar to that reported by Werme and Lundh [85, 87] even though the absolute values are different. In the present study iron oxide concentration higher than 44 wt% or below ~ 20 wt% were not investigated because of the limited range of iron oxide content in the original red mud based slag. The reason for not seeing a maximum clearly in the results of this study is that lower iron oxide contents (< 20 wt% ) would be required to drive the curve down.

Phosphorus oxidation is strongly exothermic and is favored at lower temperature. The effect of temperature on the phosphorus distribution ratio and phosphate capacity is shown in Figure 4-21 and Figure 4-23, respectively. It can be noticed that both  $L_P$  and  $C_{PO_4^{3-}}$  decrease with increasing temperature in the range of 1300-1400 °C. This finding is consistent with the previously reported results by Mohassab *et al.* [108] Figure 4-25.



Figure 4-24: Equilibrium phosphorus distribution between various fluxes and carbon-saturated iron at 1300 °C



Figure 4-25: Effect of temperature on L<sub>P</sub> at different basicities [108]

#### 4.3.3.2 Effect of CaO content on the phosphorus distribution ratio

Lime is a very effective fluxing agent for dephosphorization of liquid iron due to the strong interaction and formation of stable compounds between the CaO and  $P_2O_5$ , namely  $3CaO.P_2O_5$ . It is of significant interest to understand the optimum amount of lime required to make red mud an effective flux, because the initial CaO content of red mud is not large, and the lime addition affects the flux cost. The dependence of phosphorus distribution ratio and phosphate capacity on CaO content in the synthetic red mud fluxes are shown in Figure 4-26 and Figure 4-27, respectively. As seen, the phosphorus distribution ratio reaches a maximum at about 32wt% CaO for all temperatures. Larger CaO amounts show a negative impact on L<sub>P</sub>. Again, it can be explained that an optimum balance of oxygen potential (determined by FeO activity) and basicity is required for maximum L<sub>P</sub>. Clearly, the above CaO content is where this balance is maintained for the current fluxes.



Figure 4-26: Relationship between the phosphorus distribution ratio (L<sub>P</sub><sup>Fe-C</sup>) and lime content



Figure 4-27: Effect of lime content on the phosphate capacity

# 4.3.4 Optical basicity

The optical basicities of synthetic red mud based fluxes were calculated using the method and values discussed earlier, Table 4–4. The results are provided in Table 4–11.

Figure 4-28 and Figure 4-29 show the relationship between the phosphorus distribution ratio and phosphate capacities with the optical basicity of synthetic red mud based fluxes (fluxes SRM-1 through SRM-6) at different temperature.

It is evident from Figure 4-28 that the phosphorus distribution ratio increased when the optical basicity was increased to ~0.75 in the temperature range of 1300  $^{\circ}$ C – 1400  $^{\circ}$ C and decreases with further increase in the optical basicity. An increase in the basicity is generally expected to increase the phosphorus distribution ratio and phosphate capacity [31, 109], unless as stated earlier it operates against oxygen potential, which is the case here, hence a maximum in the curves.

Figure 4-30 shows the variation of the phosphate capacity with optical basicity, obtained by Yang *et al.* [44] along with the results of the present study.



Figure 4-28: Correlation between the phosphorus distribution ratio  $(L_P^{Fe-C})$  and optical basicity



Figure 4-29: Correlation between phosphate capacity and optical basicity



Figure 4-30: Comparison of the phosphate capacities of different slags and present study

# **4.3.5** Effect of acidic oxides on the phosphorus distribution ratio and phosphate capacity of the synthetic red mud based fluxes

The results presented earlier showed that fixed flux SRM-5 offers the highest P absorption when FeO is varied and the composition of the remaining flux is fixed. Red mud is essentially the alumina-free bauxite ore and its composition widely varies, particularly the amounts of acidic oxides Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>. In order to investigate the effect of these oxides different amounts of each were added to flux SRM-5. Table 4–11 shows the final compositions, distribution ratio, and phosphate capacity for the new compositions (SRM-7 through SRM-18).

The obtained results are plotted versus  $Al_2O_3$  (SRM-7 through SRM-10) and TiO<sub>2</sub> (SRM-11 through SRM-14) content in the range of 1300 °C -1400 °C in Figure 4-31 - Figure 4-34.

The results indicate that phosphorus partition ratio and phosphate capacity decrease with increasing  $Al_2O_3$  and  $TiO_2$  contents. This is expected as addition of these oxides decreases both the basicity and oxygen potential (due to the decrease in FeO).



Figure 4-31: Relationship between the phosphorus distribution ratio  $(L_P^{Fe-C})$  and wt% Al<sub>2</sub>O<sub>3</sub>



Figure 4-32: Relationship between the phosphate capacity and wt% Al<sub>2</sub>O<sub>3</sub>



Figure 4-33: Relationship between the phosphorus distribution ratio  $(L_P^{Fe-C})$  and wt% TiO<sub>2</sub>



Figure 4-34: Relationship between the phosphate capacity and wt% TiO<sub>2</sub>

It is well known that during dephosphorization, phosphate ions  $PO_4^{3-}$  replace  $SiO_4^{4-}$  and participate in 2CaO.SiO<sub>2</sub> solid solution[87]. On the other hand, in the network structure of silicate slag some cations such as  $AI^{3+}$  and  $Ti^{4+}$  can form tetrahedral units that are incorporated into the silicate network like  $AIO_4^{5-}$  and  $TiO_4^{4-}$  [34]. Thus increasing  $AI_2O_3$  or  $TiO_2$  content prevents the ions  $PO_4^{3-}$  to participate in 2CaO.SiO<sub>2</sub> and decreases the holding capacity of slag for

phosphorus or in other words decreasing the phosphate capacity. Consequently, increasing  $Al_2O_3$  and  $TiO_2$  content show a decreasing effect on dephosphorization. The same tendency was observed by Jiang [110] as depicted in Figure 4-35 and Figure 4-36.



Figure 4-35: Effect of Al<sub>2</sub>O<sub>3</sub> on the phosphorus distribution ratio at 1350 °C [110]



Figure 4-36: Effect of Al<sub>2</sub>O<sub>3</sub> on the phosphate capacity at 1350 °C [110]

The activity coefficient of  $P_2O_5$  ( $\gamma_{P_2O_5}$ ) in slag is an important thermodynamic parameter that affects its behavior in hot metal pre-treatment [81, 111, 112]. According to Jiang, [110] Al<sub>2</sub>O<sub>3</sub> addition increases the activity coefficient of  $P_2O_5$  (Figure 4-37), which increases the activity of  $P_2O_5$  at constant mole fraction and consequently gives rise to lower phosphate capacity.



Figure 4-37: Effect of Al<sub>2</sub>O<sub>3</sub> on the activity coefficient of P<sub>2</sub>O<sub>5</sub> at 1350 °C [110]

**4.3.6** Effect of SiO<sub>2</sub> on the phosphorus distribution ratio and phosphate capacity The effect of SiO<sub>2</sub> on the phosphorus partition ratio and phosphate capacity of synthetic red mud based fluxes (SRM-15 through SRM-18) in the range of 1300 – 1400 °C are plotted in Figure 4-38 and Figure 4-39. It can be observed that  $L_P$  and  $C_{PO_4^{3-}}$  decreases with increasing SiO<sub>2</sub> content.

This tendency can be attributed to the variation of basicity with the addition of an acidic oxide such as SiO<sub>2</sub>. The activity coefficient of  $P_2O_5$  is increased with the addition of acidic oxides, resulting in reduced phosphate capacity of slag [81, 111, 112].



Figure 4-38: Relationship between the Phosphorus distribution ratio  $(L_P^{Fe-C})$  and wt% SiO<sub>2</sub>



Figure 4-39: Relationship between the Phosphate capacity and wt% SiO<sub>2</sub>

# 4.4 Melting behaviour

The melting behaviour of the red mud samples RMF1-RMF18 (Table 3–2) was determined using a high temperature microscopy method, and the average values of the characteristic temperatures, standard deviations and standard errors based on three repeats for each composition are presented in Table 4–12. The typical recorded image of the sample RMF4 corresponding to the characteristic temperatures are illustrated in Figure 4-40.





Upon heating the compacts, a slight expansion was observed in some samples. This can be due to the release of water vapor and other gases formed during the decomposition of goethite, gibbsite, and calcite. This early swelling was followed by shrinkage and corresponds to the deformation temperature and initial melting of the flux. Subsequently, the sample melted partially with the formation of a cap on top of the compact (hemispherical temperature). Finally, on full melting, the flux became fluid and spread over the sample holder (flowing temperature).

Sample	Deformati	on Temp (DT)	erature	Hemispher	ical Temp (HT)	Flowing Temperature (FT)			
1	°C	SD*	SE**	℃ SD* SE**			°C	SD*	SE**
RMF1	1264	10	6	1274	6	3	1280	9	5
RMF2	1227	6	3	1234	9	5	1257	7	4
RMF3	1163	11	7	1172	13	7	1176	12	7
RMF4	1154	9	5	1163	9	5	1170	8	5
RMF5	1214	9	5	1224	10	6	1232	8	5
RMF6	1235	11	6	1259	10	6	1288	8	4
RMF7	1147	8	5	1174	11	6	1193	11	6
RMF8	1156	10	6	1184	14	8	1207	13	8
RMF9	1172	9	5	1193	11	6	1222	11	6
RMF10	1184	9	5	1223	10	6	1237	11	6
RMF11	1164	13	8	1212	13	7	1250	11	6
RMF12	1224	10	6	1276	9	5	1293	7	4
RMF13	1263	9	5	1308	8	5	1350	8	5
RMF14	1288	9	5	1349	15	8	1411	12	7
RMF15	1218	12	7	1235	9	5	1250	7	4
RMF16	1214	9	5	1223	8	5	1233	7	4
RMF17	1205	9	5	1212	9	5	1225	10	6
RMF18	1200	12	7	1211	9	5	1221		5

red mud based fluxes

Table 4–12: The average characteristic temperatures, standard deviations and standard errors for

SD\*: Standard deviation

SE\*\*: Standard error

4.4.1 The relationship between flux components and melting behavior

## 4.4.1.1 Effect of CaO on the melting behavior

The effect of lime content on the characteristic temperatures of fluxes RMF1 through RMF6 is shown in Figure 4-41 with increasing lime content all three temperatures decrease to a minimum, corresponding to a mass content of 33 wt% CaO. The phase diagram of CaO-SiO<sub>2</sub> system is shown in Figure 4-42.



Figure 4-41: Effect of lime on characteristic temperatures of fluxes RMF1 through RMF6

As seen, addition of lime, a basic component, to an acidic flux such as silica leads to the formation of phases with melting point lower than the melting point of individual components. Addition of excess lime, over 33% in this case, results in over-saturating the liquid and formation of undissolved lime that raises the characteristic temperatures. Although the flux system here is more complex than the binary CaO-SiO<sub>2</sub> system, the same trends can take place, as commonly seen in ternary or higher order systems.

A secondary reason for the variations of the characteristic temperatures, the FT in particular, is the change in slag structure with composition. From a fundamental point of view, the building unit in molten silicates is the tetrahedron  $SiO_4^{4-}$ . The  $SiO_4^{4-}$  tetrahedra are joined together in three

dimensional silicate networks. The addition of a basic oxide such as lime breaks down the silicate structure and depolymerizes the network, lowering the characteristic temperatures.



Figure 4-42: Phase diagram of CaO-SiO<sub>2</sub> system [113]

# 4.4.1.2 Effect of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> on the melting behavior

In order to investigate the effect of chemical composition on the characteristic temperatures, different amounts of Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and SiO<sub>2</sub> were added to the flux RMF4 (Table 3–2) which was found to exhibit the lowest characteristic temperatures. The results in Figure 4-43 (RMF7 through RMF10) and Figure 4-44 (RMF11 through RMF14) indicate that the characteristic temperatures of the fluxes all increase with the addition of alumina and titania, an indication that they act as network formers for the composition range covered.



Figure 4-43: Effect of alumina on characteristic temperatures of fluxes RMF7 through RMF10



Figure 4-44: Effect of titanium oxide on characteristic temperatures of fluxes RMF11 through RMF14

The relationship between characteristic temperatures of fluxes RMF15 through RMF18 and silica content is presented in Figure 4-45. As seen, the characteristic temperatures gradually decrease with increasing the silica content. Again, the trend can be explained by the phase diagram of CaO-SiO<sub>2</sub>, in which addition of silica to a highly basic system should decrease the melting point.



Figure 4-45: Effect of silica on characteristic temperatures of fluxes RMF15 through RMF18

FactSage<sup>™</sup> thermodynamic package was used to determine the amount of liquid phase at high temperatures for different compositions (RMF7 through RMF18). The mass percentage of liquid phase as a function alumina, titanium oxide and silicon oxide at different temperatures is plotted in Figure 4-46, Figure 4-47 and Figure 4-48 respectively. It can be seen that the experimental findings are in agreement with the results of the calculations.

In Figure 4-46 and Figure 4-47 with increasing alumina and titanium oxide, the amount of high melting point phases such as Gehlenite ( $Ca_2Al_2SiO_7$ ) and perovskite ( $CaTiO_3$ ) increases respectively. As a result, the portion of liquid slag at a constant temperature decreases, raising the characteristic temperatures that were observed in Figure 4-43 and Figure 4-44.



Figure 4-46: Mass percentage of liquid phase in slag vs. alumina content at different temperatures



Figure 4-47: Mass percentage of liquid phase in slag vs. titania content at different temperatures

In Figure 4-48 with increasing  $SiO_2$  the percentage of the liquid phase increases. This can be related to forming low melting point phases and decreasing the high melting point phase such as Gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>).



Figure 4-48: Mass percentage of liquid phase in slag vs. silica content at different temperatures

### 4.4.1.3 Effect of Basicity

Traditionally, the ratio of basic oxides to acidic oxides is used as a measure of slag basicity. The effect of basicity on the characteristic temperatures of mold fluxes for continuous casting is illustrated in Figure 4-49 [114]. Basicity ratios between 1.0 and 1.1 correspond to the lowest characteristic temperatures. Increasing the CaO or  $SiO_2$  contents beyond this optimum ratio results in higher temperatures. Thus, to have a flux with relatively low characteristic temperatures, basic and acidic components should be mixed in appropriate amounts.

For multi-component fluxes with constituents that possess different basic strengths, the simple  $(CaO/SiO_2)$  ratio does not provide a true measure of the flux basicity. In this work, the optical basicity is used as a more appropriate indicator to correlate different flux compositions with the corresponding melting characteristics.



Figure 4-49: Characteristic temperatures of mold fluxes as a function of the CaO/SiO<sub>2</sub> ratio[114]

Table 3–2 presents the values of optical basicity for the flux compositions studied here. The variation in the characteristic temperatures of fluxes RMF1 through RMF6 as a function of the optical basicity is shown in Figure 4-50. It can be seen that with an increase in optical basicity, the characteristic temperatures approach a minimum, indicating optimum flux composition for better fluidity. The minimum appears to occur at optical basicity of ~ 0.77, corresponding to a mass content of 33 wt% CaO. This is expected as discussed earlier based on the effect of lime content on the melting properties.



Figure 4-50: Characteristic temperatures as a function of the optical basicity for RMF1 through RMF6 fluxes

# Chapter 5

# 5 Conclusions and Impact of Research

# 5.1 Conclusions

The overall objective of this work was to evaluate the potential use of red mud, a waste material, as a refining flux with high capacity for removal of sulphur and phosphorus from hot metal in the steel manufacturing process. This section summarizes the major findings.

### 1- Characterization of red mud

The results from XRD and XRF analyses of red mud show that it contains a number of different constituents in the form of oxides or hydroxides of iron, aluminum, silicon, sodium, and titanium.

The thermal events observed by TGA-DSC curves up to 1400 °C were explained in detail. Mass loss up to  $\sim$ 720 °C indicated decomposition of various hydrated phases including gibbsite, goethite and calcite. This was consistent with DSC results, showing the endothermic nature of these reactions.

#### 2- Sulphide capacity of red mud based fluxes

Desulphurization experiments were carried out using a slag – metal equilibrium technique in graphite crucibles under carbon monoxide atmosphere in the temperature range 1300 to 1400°C to investigate the capability of the red mud based fluxes as a desulphurization refining agent in hot metal pretreatment. The results indicate that the sulphide capacity is influenced by the chemical composition and temperature. The sulphide capacity is found to increase with lime content for all temperatures, and reaches a maximum at ~ 46 - 49% CaO. Further increase in lime did not improve the sulphide capacity. Addition of  $Al_2O_3$ ,  $TiO_2$  and  $SiO_2$  showed a continuous decrease in the sulphide capacity. The effect of various oxides on the sulphide capacity was attributed to the nature (acid vs base) of the oxide so that basic oxides favour S removal. Oversaturating the slag with CaO however offers no benefit as it precipitates as solid phases that have little to no effect on S absorption.

It was shown that the sulphide capacity increases with increasing temperature from 1300  $^{\circ}$ C to 1400  $^{\circ}$ C at fixed slag basicity (*i.e.* optical basicity). An optimum flux composition could be determined for maximum sulphide capacity with the aid of the optical basicity concept.

#### **3-** Phosphate capacity of red mud based fluxes

The phosphorus distribution ratios and phosphate capacity were measured by equilibrating the synthetic red mud fluxes with solid iron foil under an argon atmosphere at temperatures ranging from 1300 to 1400 °C. The results led to the following conclusions.

The equilibrium phosphorus distribution ratio initially increases with increasing FeO or CaO concentration in fluxes then change to a negative trend at higher concentrations of FeO or CaO.

The maximum phosphorus distribution ratios were obtained at 26 % FeO (39% CaO), 28 wt% FeO (32 wt% CaO) and 25 % FeO (41 wt% CaO) at 1300 °C, 1350 °C and 1400 °C respectively.

The phosphate capacity was found to decrease with increasing Al<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>, and SiO<sub>2</sub>.

#### 4- Melting behaviour study

A high temperature microscopy technique was applied to investigate the melting behavior of red mud based fluxes. The results indicate that additions of lime from 10% to 32%, lowered the characteristic melting/softening temperatures of red mud based fluxes while additions of  $Al_2O_3$  and  $TiO_2$  had an opposite effect. Addition of lime over 32%, corresponding to the saturation limit, increased the melting temperature of the flux. It was found that the flux has the lowest softening and flowing temperatures when the optical basicity is around 0.73. This provides a foundation for engineering a flux which exhibits optimum melting characteristics as well as appropriate refining capabilities for the removal of impurities such as sulphur and phosphorus during metal processing operations.

# 5.2 Major contributions and potential impact

The scientific significance of the present research lies in the generation of fundamental knowledge of the physical and chemical properties of red mud. The obtained results on refining characteristics of slags/fluxes provide a basis for not only utilization of red mud as the base material for a flux, but also improving current hot metal treatment practices.

This research can enable development of laboratory models that can be scaled up for red mud applications.

From a practical point of view, as the utilization of red mud based fluxes is implemented, significant benefits can be realized; reduced environmental footprint of aluminum production, effective utilization of a waste thereby reducing demand on the earth's resources, and economic benefits for the aluminum and steel industries.

# Chapter 6

# 6 Future work

The results of this study indicated that a suitable hot metal refining flux can be prepared based on the use of red mud. However, the following aspects are also of importance from both fundamental and practical viewpoints and need to be studied.

1- Kinetic study of S and P pick-up by slag

The present study was conducted from a thermodynamic perspective. It would be worthwhile to study the kinetics of desulphurization and dephosphorization of hot metal using the red mud based flux. The results would be particularly interesting as they would show the variation of the flux performance with time, as the composition changes due to decomposition of sodium oxide.

2- Effect of sodium oxide on refractory and off-gas

Since red mud contains a considerable amount of sodium oxide, the impact on the degradation of refractory materials should be investigated. Further, the rate of sodium oxide loss from slag, and possible complications in the off–gas handling system, such as condensation on the duct walls need to be evaluated.

3- Viscosity of red mud fluxes

The effectiveness of any flux under the limited treatment time of industrial processes is highly dependent on the rate of the reactions, which in part is determined by the viscosity ( $\mu$ ) and hence mass transport within the slag phase. Also, tapping of the slag and refractory erosion are strongly dependent on the viscosity. These aspects need to be quantified.

4- Melting rate

It is known that fluidity of the flux is important for good desulphurization and dephosphorization kinetics. Therefore, additional work could be conducted with different

slag systems to examine the relationship between the desulphurization and dephosphorization rates and the melting rate of the slag.

## 5- Characteristics of post–refining flux

The chemical composition, mineralogy, microstructure (phases and their segregation), and leaching behavior of the constituents are of interest for determining the fate of the slag after its use in hot metal treatment. The information is essential in order to determine potential applications (e.g. cement feedstock, construction material, etc) or safe disposal strategies for the material.

## **Appendices**

#### Appendix 1: Inductively coupled plasma (ICP)

Inductively Coupled Plasma Optical Emission Spectroscopy ICP-OES is one of the common methods for analysis of trace elements and impurities in a variety of different sample materials. With this technique, an aqueous sample is converted to aerosol using a nebulizer and injected into to the inductively coupled plasma which sustains a temperature of approximately (8000-10000 K), so the sample mist reaching the plasma is quickly vaporized. The plasma source dissociates the sample into its constituent atoms and promoting them to excited states. The atoms emit photons of characteristic wavelength while returning to their original state.

These emissions are separated based on their intensities and wavelength and a spectrometer records the light and quantification is achieved by comparing the intensity of emission from an unknown sample with that of a standard sample. Thus the wavelength of the photons can be used to identify the elements from which they originated. Up to 70 elements can be determined simultaneously in a single analysis. Even though, inter element interferences are possible if the wavelength of the element of interest is near the wavelength of another element. The internal standard such as yttrium (Y) is most widely used to manage interferences in ICP.

#### A1 Sample Preparation

The ICP-OES samples require acid digestion for the most analysis. The solid sample is dissolved in the appropriate medium and injected into the instrument.

#### A1.1 Carbon saturated iron digestion

A 0.15 gram sample of the carbon saturated iron was digested in a glass beaker with 15 ml of concentrated nitric acid (HNO<sub>3</sub>, 70 wt%) and deionized water in the volume ratio of 2:1 respectively.

The glass beaker and content was heated to a temperature of 60-80 °C for half an hour. The digested solution was filtered through a filter. The filtrate was made up to the 50 ml into a volumetric flask by adding deionized water. A 50 ml blank sample was also prepared with the exact same ratios of the acids used for digestion.

## A1.2 Flux sample digestion

Aqua regia (royal water) or nitro-hydrochloric acid was used for red mud/flux digestion. The mixture is prepared by mixing concentrated nitric acid and hydrochloric acid in a volume ratio of 1:3. A 0.1 gram of flux sample was digested into 20 ml of the acid mixture. The digestion was carried out at 90 °C for 60 minutes. The solution was filtered and diluted to volume with deionized water.

## **Appendix 2: Raw materials for research**

The chemicals used and their purity grades for desulphurization, dephosphorization and melting behaviour experiments are shown in Table A2-1, Table A2-2 and Table A-2-4 respectively. Lime, alumina, titania, silica and dicalcium phosphate were calcined at 800 °C for 3 h to remove any moisture.

Material	Purity, wt%	Supplier
Red mud (RM)	NA	Alcoa Co.
Calcium oxide (CaO)	99.98	Alfa Aesar
Silicon oxide (SiO <sub>2</sub> )	99.95	Alfa Aesar
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )	99.98	Alfa Aesar
Titanium oxide (TiO <sub>2</sub> )	99.95	Sigma Aldrich
Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )	99.98	Sigma Aldrich
Ferrous sulphide (FeS)	99.95	Sigma Aldrich
Electrolytic iron	99.90	Allied Metals Corporation
Graphite powder	99.99	GraphiteStore.com
Purified graphite rod	99.99	GraphiteStore.com
Alumina tube	99.80	McDaniel Refractory Co
Carbon monoxide (CO)	99.99	Linde

 Table A2- 1: Characteristics of the materials used for desulphurization experiments

Material	Purity wt%	Supplier
Calcium oxide (CaO)	99.98	Alfa Aesar
Silicon oxide (SiO <sub>2</sub> )	99.95	Alfa Aesar
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )	99.98	Alfa Aesar
Titanium oxide (TiO <sub>2</sub> )	99.95	Sigma Aldrich
Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )	99.98	Sigma Aldrich
Iron (III) oxide (Fe2O3)	99.98	Sigma Aldrich
Fe powder (Fe)	99.99	Alfa Aesar
Dicalcium phosphate (CaHPO <sub>4</sub> )	99.98	Sigma Aldrich
High purity iron foil thickness 100µm	≥99.98	Sigma Aldrich
Armco iron	99.95	Goodfellow
Alumina tube	99.80	McDaniel Refractory Co
Zirconium dioxide rod	99.20	Goodfellow
Argon gas	99.99	Linde

 Table A2- 2: Characteristics of the materials used in dephosphorization experiments

Table A2- 3: Composition of Armco iron and iron foil

Material	С	Mn	Si	Cu	Р	S	Fe
Armco iron	0.013	0.009	0.009	0.01	0.006	0.005	99.95
High purity iron foil	0.005	0.006	0.001	0.001	0.002	0.005	99.98

Material	Purity, %	Supplier
Red mud	NA	Alcoa Co.
Calcium oxide (CaO)	99.98	Alfa Aesar
Silicon oxide (SiO <sub>2</sub> )	99.95	Alfa Aesar
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )	99.98	Alfa Aesar
Titanium oxide (TiO <sub>2</sub> )	99.95	Sigma Aldrich
Sodium carbonate (Na <sub>2</sub> CO <sub>3</sub> )	99.98	Sigma Aldrich

Table A2- 4: Characteristics of the materials used for the melting behavior experiments
## Appendix 3: Scanning electron microscopy of red mud

The Hitachi S2500 scanning electron microscope was used to characterize the particle morphologies of the red mud sample.

The scanning electron microscopy image Figure A3-1(A) shows red mud powder is constituted by agglomerates which formed by very fine particles of different sizes. The presence of agglomerated particles can be seen in Figure A3-1(B). The results indicate that the red mud particles are polygonal in shape and 90% of the particles are  $55\mu m$  or smaller.



(A) (B) Figure A3- 1: Scanning electron microscopy of red mud









Figure A4- 3: XRD pattern of RMF4



Figure A4- 4: XRD pattern of RMF5



Figure A4- 5: XRD pattern of RMF6

## **Appendix 5: Calculation of phosphorus partition ratio**

Spencer and Kubaschewski [115] stated the chemical potential of phosphorus in  $\mathbf{Fe} - \mathbf{\gamma}$  relative to a standard state of superheated liquid phosphorus can be defined as follow:

$$\mu_{P}^{\gamma} = \mu_{P(l)}^{\circ} + RTln\gamma_{P}^{\gamma} X_{P}^{\gamma}$$
1

where:

RTln
$$\gamma_{\rm P}^{\gamma} = -128519 + 32.67T$$
 (1184 to 1665 K, J. mol<sup>-1</sup>) 2

On the other hand, the chemical potential of phosphorus in carbon saturated liquid iron relative to a standard state of 1% solution of phosphorus in liquid iron can be determined [116]

$$\mu_{P}^{Fe-C} = \mu_{P(1\%)}^{\circ} + RTln\gamma_{P}^{Fe-C}.X_{P}^{Fe-C}$$
3

$$\mathring{\mu}_{P(1\%)}^{\circ} = (\frac{1}{2})\mathring{\mu}_{P2(g)}^{\circ} - 122172 - 19.25T$$
 J. mol<sup>-1</sup> 4

By substituting Equation 4 into Equation 3:

$$\mu_{P}^{Fe-C} = \left(\frac{1}{2}\right) \mu_{P2(g)}^{\circ} - 122172 - 19.25T + RT \ln \gamma_{P}^{Fe-C} \cdot X_{P}^{Fe-C} \quad J. \text{ mol}^{-1} \qquad 5$$

Barin *et al.* [117] suggested the term  $\mu_{P(1)}^{\circ}$  in Equations 1 and 3 and  $\mu_{P2(g)}^{\circ}$  in Equation 7 can be rewritten relative to a standard state of white phosphorus at 298.15K as follows:

$$\hat{\mu}_{P(l)} = -7238 + 133.30T - 26.33TlnT$$
 J. mol<sup>-1</sup> 6

$$\hat{\mu}_{P2(g)}^{\circ} = 131428 + 27.75T - 39.96 \cdot 10^{-5}T^2 + 20.79 \cdot \frac{10^4}{T} - 18.15T \ln T$$
 J. mol<sup>-1</sup> 7

The quotient of the phosphorus concentration in solid iron ( $Fe - \gamma$ ) and liquid Fe-C (carbon saturated iron whereas  $a_C = 1$ ) can be explained in term of %P. The following relation is given for dilute solutions of phosphorus in iron:

$$X_{\rm P} \approx \frac{[\%{\rm P}] \cdot M_{\rm Fe}}{M_{\rm p} \cdot 100}$$
8

Therefore when a solid iron has the same chemical potential for phosphorus as that of a carbon saturated iron the following quotients can be constructed by combining Equations 6 and 1 and Equations 7 with 5 as follow:

$$\ln \frac{[\%P]^{Fe-\gamma}}{[\%P]^{Fe-C}} = -69.43 - 10.05 \cdot 10^{-5}T + \frac{39906}{T} + \frac{52320}{T^2} + 4.12\ln T + \ln \gamma_P^{Fe-C}$$

Activity coefficient of phosphorus in carbon saturated iron at 1600 °C is given by [68]:

$$\ln \gamma_{\rm P}^{\rm Fe-C} = 1.8 + 3.5 X_{\rm P}$$
 10

In dilute solution while  $X_P \rightarrow 0~~\text{thus}~~ ln\gamma_P^{Fe-C} = 1.8$ 

By considering the regular solution model the value of the activity coefficient cab be corrected to 1300 °C instead of 1600 °C as follow :

$$\ln \gamma_{\rm P}^{\rm Fe-C} = 1.8 \times \frac{1873}{1573} = 2.14$$
 11

Consequently, Im et al. [107] reported that in dilute solution of phosphorus at 1300 °C:

$$\frac{[\%P]^{\gamma}}{[\%P]^{\text{Fe}-\text{C}}} = 0.413$$
12

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