THE BENEFICIATION OF STEEL MAKING SLAGS

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SYNOPSIS

The thesis examines the possibilities for the beneficiation of steel making slags by using mineral processing methods. Chemical and Mineralogical investigations have been carried out by SEM and EPMA to determine the most suitable separation methods in terms of crystal size, chemical composition and surface properties.

Magnetic separation was applied in connection with size reductions for the extraction of the metallic iron prills and other iron containing phases and the results were related to the feed size and operating conditions.

The behaviour of the slags in flotation tests was studied with respect to the recovery and grade. It was found that the free lime presence in the slags caused a high acid consumption of both weak and strong acids. It also reacted with acids and consequently produced a white precipitate, ($CaSO_4$ for H_2SO_4). The poor response of the phases to the flotation by different types of collector was found to be due to surface alteration caused by the free lime.

The flocculation tests were carried out at the natural pH of the slags to prevent surface alterations. Settling tests were done to determine the suitable flocculants for the separation tests. The effect of the settling period, flocculant concentration, conditioning period and number of cleaning cycles were determined to optimize the separation tests.

The discussion brings together this study with previous theoretically based work cited in the literature to elucidate the factors governing the utilisation of steel making slags.

KEYWORDS: Chemical and Mineralogical studies of slags by SEM and EPMA, grain size measurements, magnetic separation, flotation, Flocculation.

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CHAPTER 1 INTRODUCTION

The major modern steel making processes in the U.K. are the Electric-ARC and BOS (Basic Oxygen steel making) which cover over 95% steel production in Britain at present. The quantity of slag produced in these processes is approximately one third of the steel output, equivalent to 6 million tonnes in 1976 (1).

This research was initiated to evaluate the potential of these slags (subsequent to the removal of metallic prills) as a source of valuable iron by-products. An increase in the efficiency of the present magnetic demetallising process was attempted by introducing size reduction of the slags.

It is the object of this thesis to examine the application of mineral processing methods for the beneficiation of steel making slags. These investigations involved the determination of the oxide phases present and their properties as well as investigating the amenability of these phases to concentration by specific processing methods.

It was hoped that the results obtained from this study would produce a better understanding of slag utilisation.

CHAPTER 2

PRODUCTION OF SLAGS AND THEIR TREATMENT

2.1 Steel making processes

2.1.1 Basic Oxygen Steel making (BOS)

The first commercial steel was made by this technique at Donawitz and/or Linz in Austria in 1948. In this process hot metal with scrap/ore coolant and suitable fluxes are refined by means of relatively pure oxygen gas blown from a vertical lance into a pear-shaped vessel with a basic lining of tar-bonded dolomite brick.

Control of the process is achieved by the height of the lance above the bath and volume of oxygen blown per unit time. These govern the refining rate, together with the turbulence and droplet formation of the molten metal. The heat required for the process is generated by the oxidation of the metalloids in the metal. The heat is controlled by addition of scrap steel and/or iron ore.

2.1.2 Electric ARC Furnace Steel Making

In this furnace, heating is achieved mainly by radiation from an arc struck between two or three graphite electrodes at very high power inputs.

The charge usually consists of steel scrap, lime and a carburiser (coke, anthracite, etc.). The scrap forms up to 100% of the metallics. The refining is carried out in two stages. The first, which is called the oxidising stage, involves the removal of carbon, silicon, phosphorus and manganese by operating a basic slag rich in oxygen and lime. Oxygen may be blown into the bath by a lance to obtain a temperature of 1700-1800^{0}C. The oxidising slag is black in colour because of the presence of FeO, and is removed by pouring off at an intermediate stage.

In the second reducing stage, new slag making materials consisting of lime, fluorspar, coke and ferro silicon are fed to the bath and the interior of the furnace is then isolated from air. Under these conditions the oxygen content of the slag and metal is reduced to a very low level. The reducing slag is called white slag because of its lack of colour from iron content.

2.2 Slag Formation

2.2.1 In the L.D. process

During refining in top blown converters, oxygen is transferred to the elements dissolved in iron by three mechanisms: Firstly by a direct transfer to the metal by adsorption and absorption within the impact area of oxygen jet; secondly, by an indirect transfer via the slag ferric/ferrous relationship and lastly, from the oxidised metal droplets returning to the bath from the slag-metal emulsion. The final slag produced by this process contains quantities of lime, magnesia, iron oxides, phosphorus pentoxide, silica and manganese oxide.

Q-BOP

In bottom blowing, the oxygen blown through the submerged tuyeres is directly transferred to the metal. The bulk slag remains dry during the major part of the blow and only at the end of the blow does it participate in the refining reactions. However, when powdered lime is injected, microslags are formed at the impact zone of tuyeres and these slags influence the reaction paths.

2.2.2 Arc Process

Melting takes place immediately beneath the electrodes and rotation of the hearth accelerates the melting rate.

During the oxidising stage, carbon, silicon, phosphorus and manganese are removed by basic slag rich in oxygen and lime. According to Mitchell (2) total phosphorus removal is achieved in this stage. The oxidising slag contains oxides of silicon, manganese and phosphorus.

In the reducing stage, after pouring off the first slag, new fluxes are added to the bath and oxygen access is restricted. The oxygen contents of the slag, and subsequently the metal, are reduced to very low levels and sulphur is transferred from metal to slag with a high degree of efficiency. The final reducing slag contains sulphur and calcium based compounds.

2.3 Post Steel Making Treatment of the Slags

At present no special slag cooling or weathering treatment is used. Molten slag is transported to a dumping pit in slag pots and poured out. The cooling rate of slag is influenced by weather conditions and cooling space. In some cases it is accelerated by the application of water jets.

Slag, therefore, has a very heterogeneous texture and structure. It can have particle sizes from a few microns to a few meters and crystal grain sizes from a few micron to several centimeters for the same phase. Differences can also be seen in hardness, colour, density, etc.

2.3.1 Existing Slag Treatments

The excavated slag from the pit is subjected to a sequence of magnetic separations. Prior to treatment no size reduction is applied to the slag. It is divided according to particle size and put through magnetic separators to remove metallic prills. This process is shown in detail in Figure 2.1.

Small quantities of slag are utilised in the production of phosphate slag fertilizer at Port Talbot (3). In some works recyclable grades of slag are obtained to be used in the blast furnace (3).

After a considerable period of weathering, a sufficient amount of slags may be recovered to be used as road aggregates. However, at the present time the bulk of the demetallised slag is dumped (3).

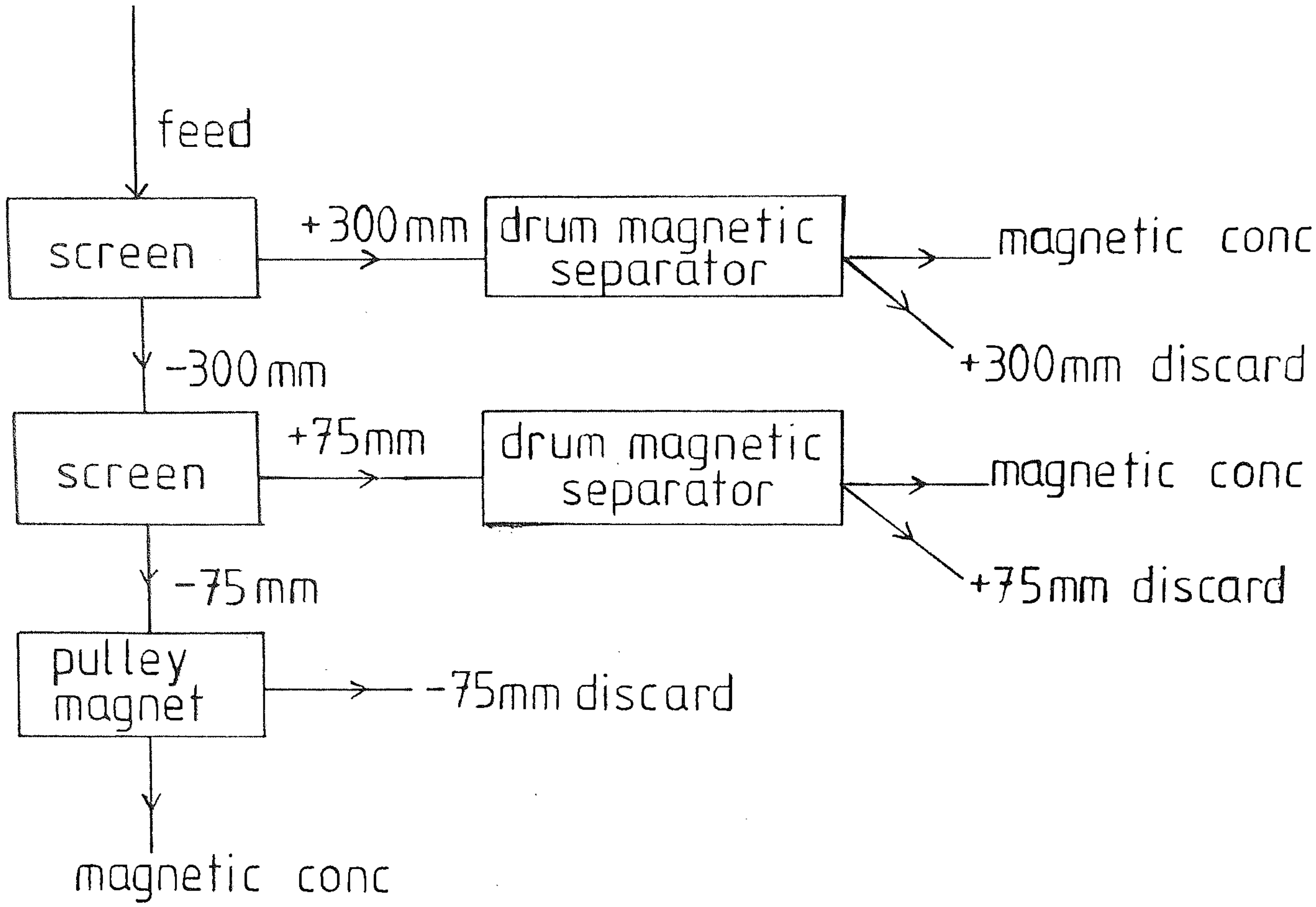


FIG 2,1 SCHEMATIC REPRESENTATION OF SLAG UTILISATION PLANT AT SCUNTHORPE

CHAPTER 3

CHEMISTRY AND MINERALOGY OF THE SLAGS

3.1 Chemical Composition of Slags

3.1.1 Qualitative Analysis of Slags by SEM KEVEX

The samples of BOS ARC and ARC BOS slags for this work were provided by the British Steel Corporation plants from the Sheffield and Scunthorpe works respectively. It was claimed that they had been demetallised by magnetic separation.

Scanning electron microscopy (SEM) employs a beam of electrons which scan the surface of the specimen in a two dimensional raster. X-ray analysis is possible on the SEM as electrons from the electron beam interact with those in the specimen, displacing them from their shells and causing the emission of X-rays which have a wavelength characteristic of the elements in the specimen.

To determine the elements occurring in the slags the X-rays emitted from an area of the specimen were analysed in a multi channel analyser. Thus the most common elements were detected and plotted on chart as shown in Figure 3.1.

By employing spot analysis, elemental composition of the individual phases rich in Fe, Si, Ca, Mn, Al, Ti, were also determined qualitatively. Kevex traces for these elements are shown in Figures 3.2-3.7.

FIG 3,1 X-RAY MAP FOR GENERAL AREA OF SLAG

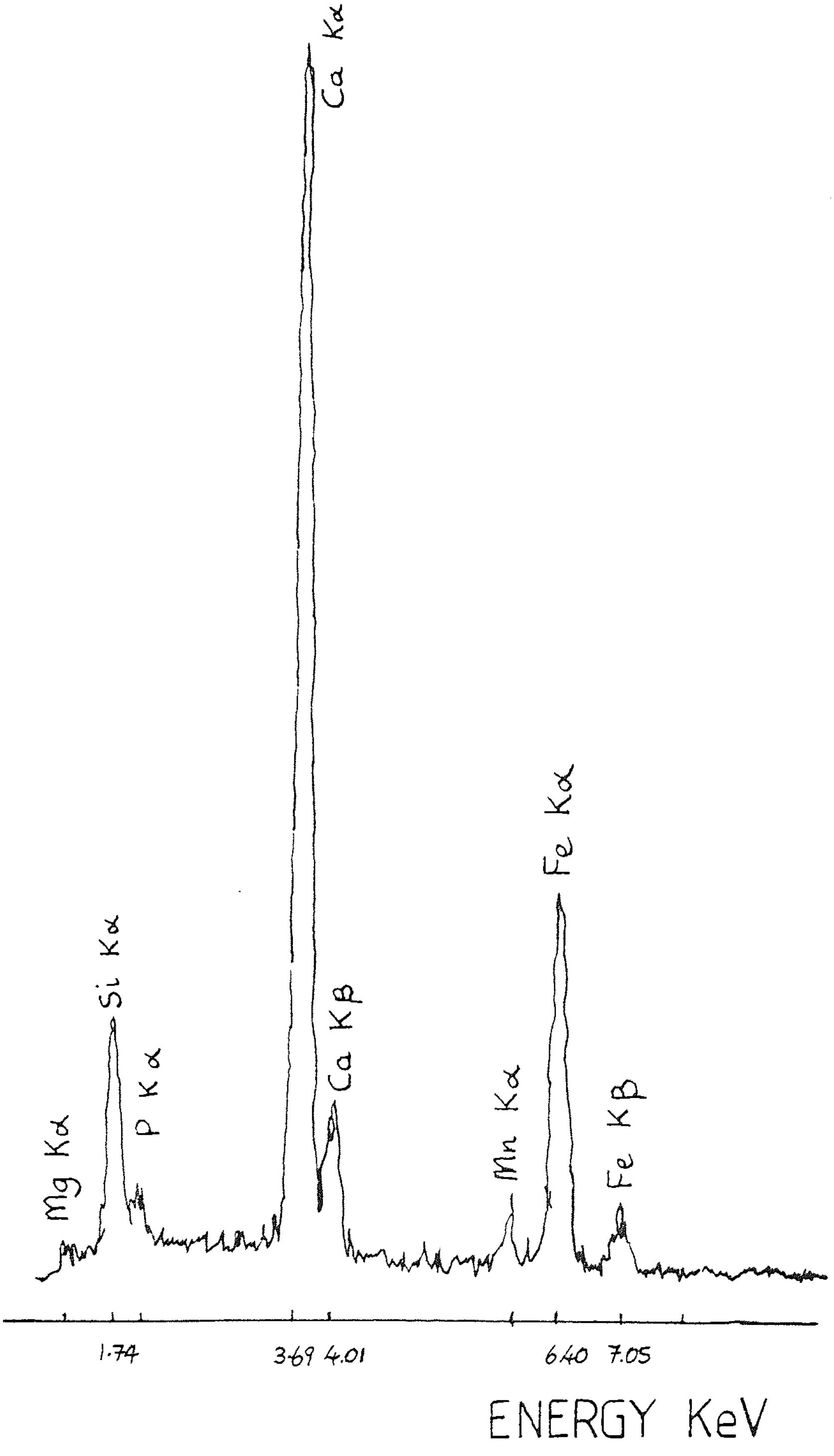


FIG 3,2 X-RAY MAP FOR Fe RICH AREA OF SLAG

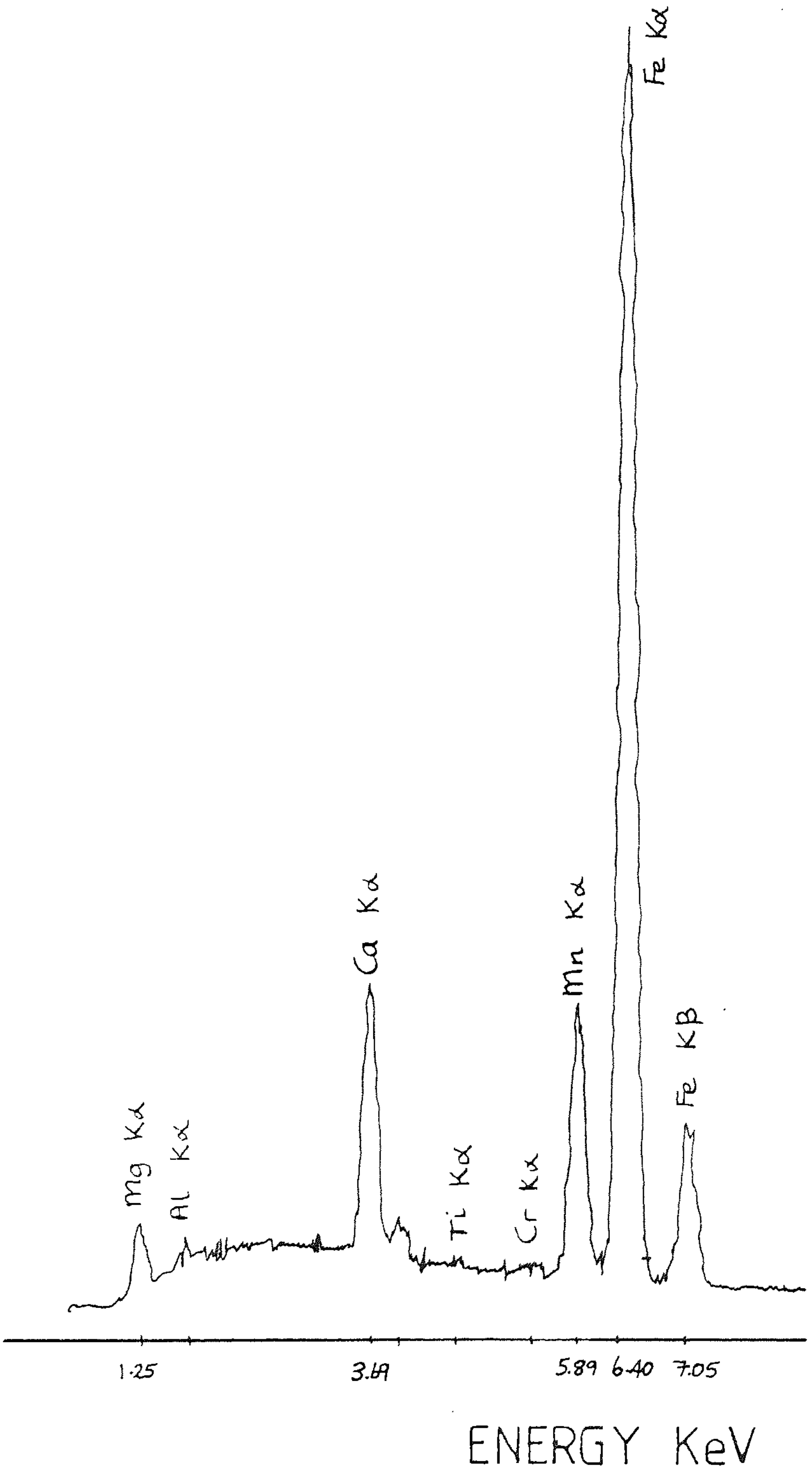


FIG 3,3 X-RAY MAP FOR Si RICH AREA OF SLAG

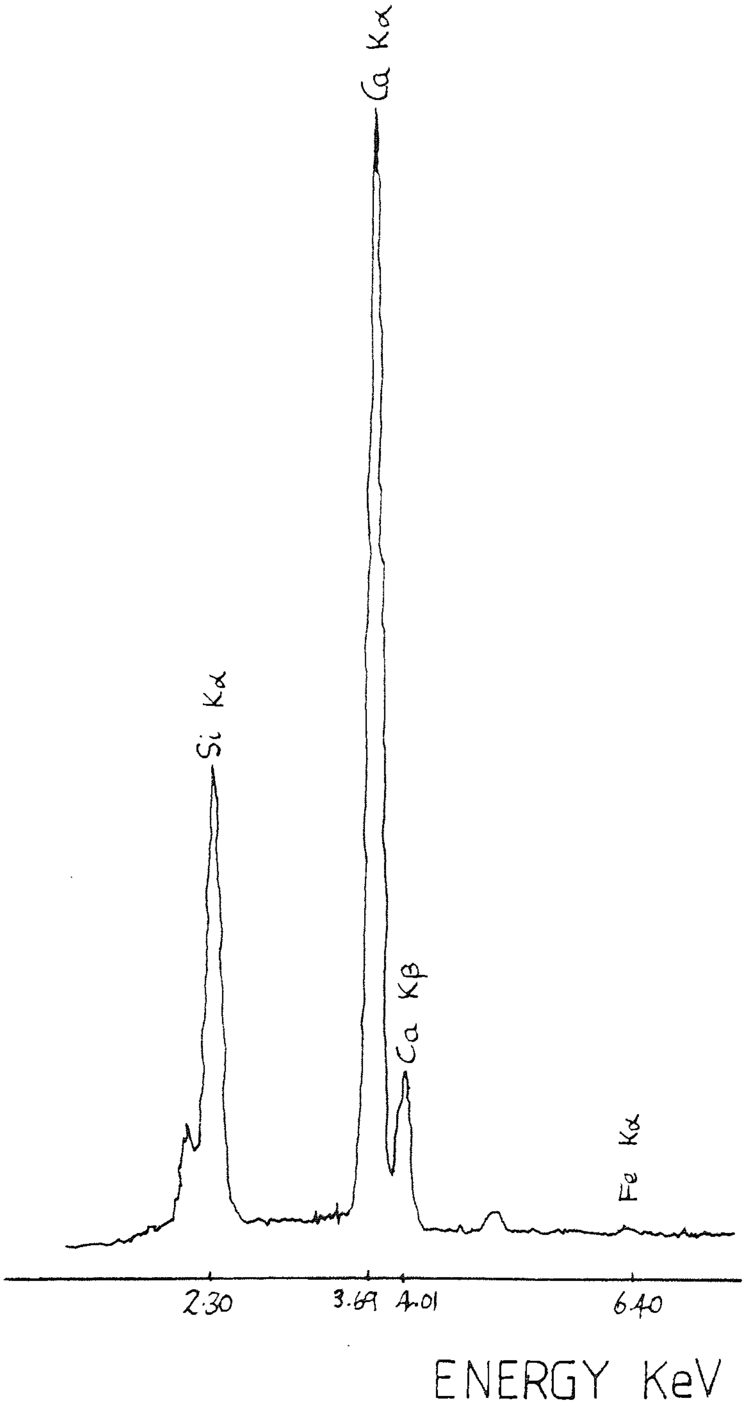


FIG 3,4 X-RAY MAP FOR Ca RICH AREA OF SLAG

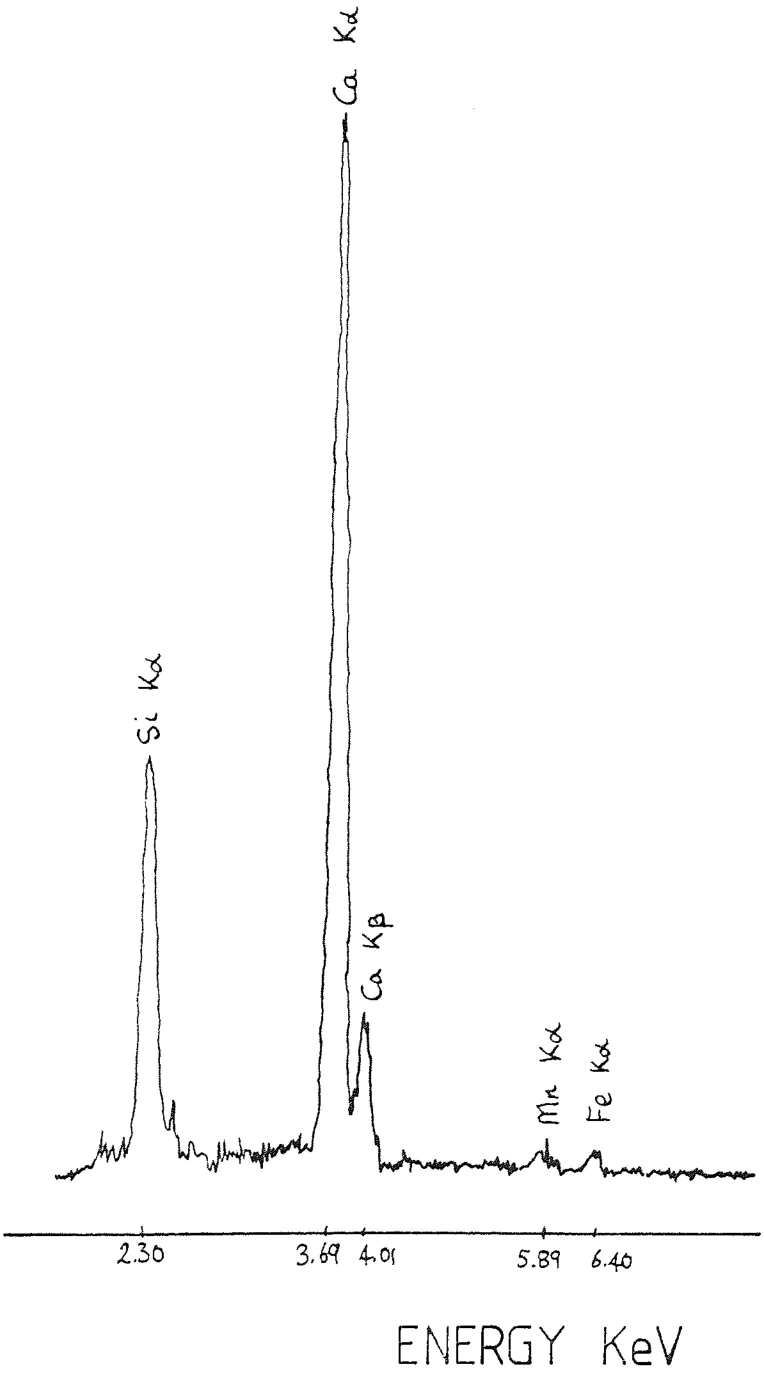


FIG 3,5 X-RAY MAP FOR Mn RICH AREA OF SLAG

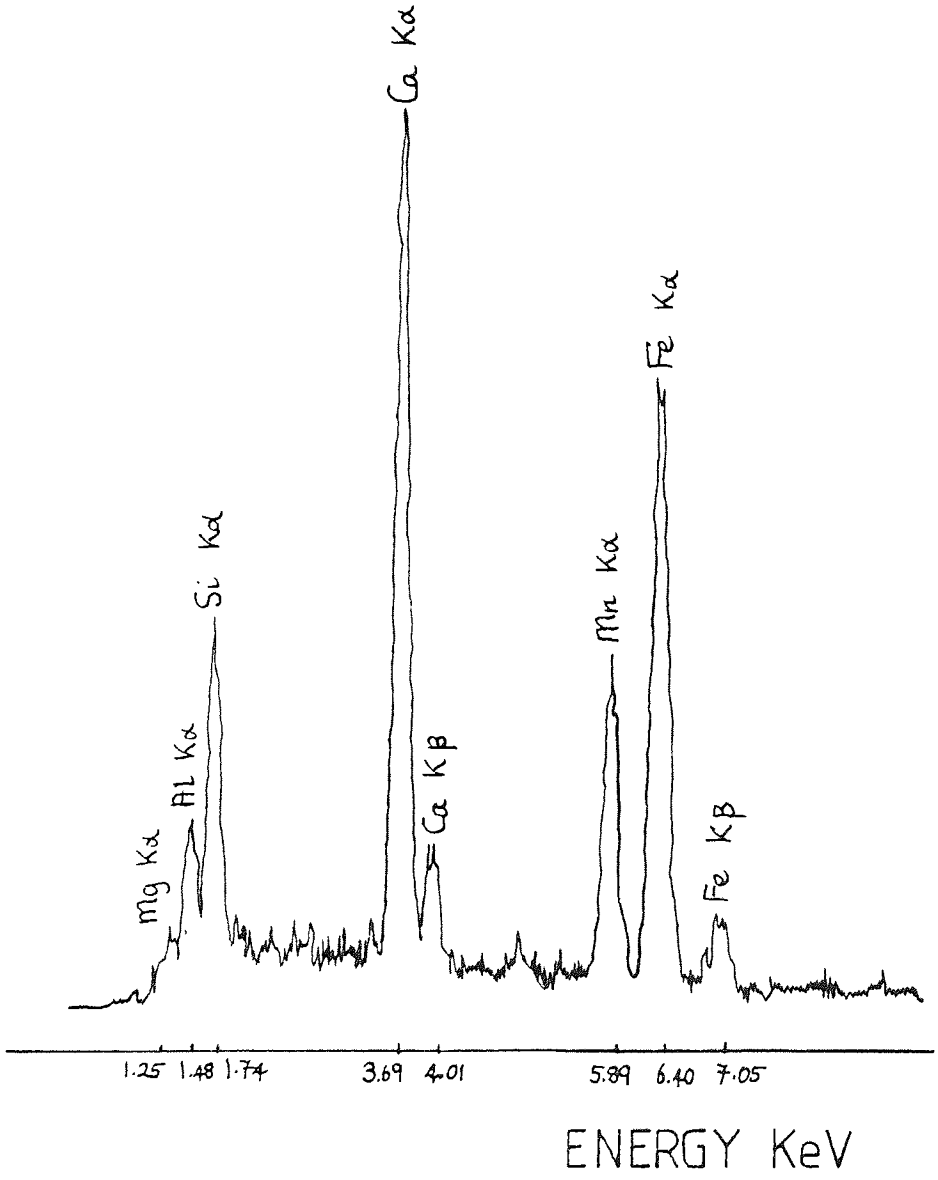


FIG 3,6 X-RAY MAP FOR Al RICH AREA OF SLAG

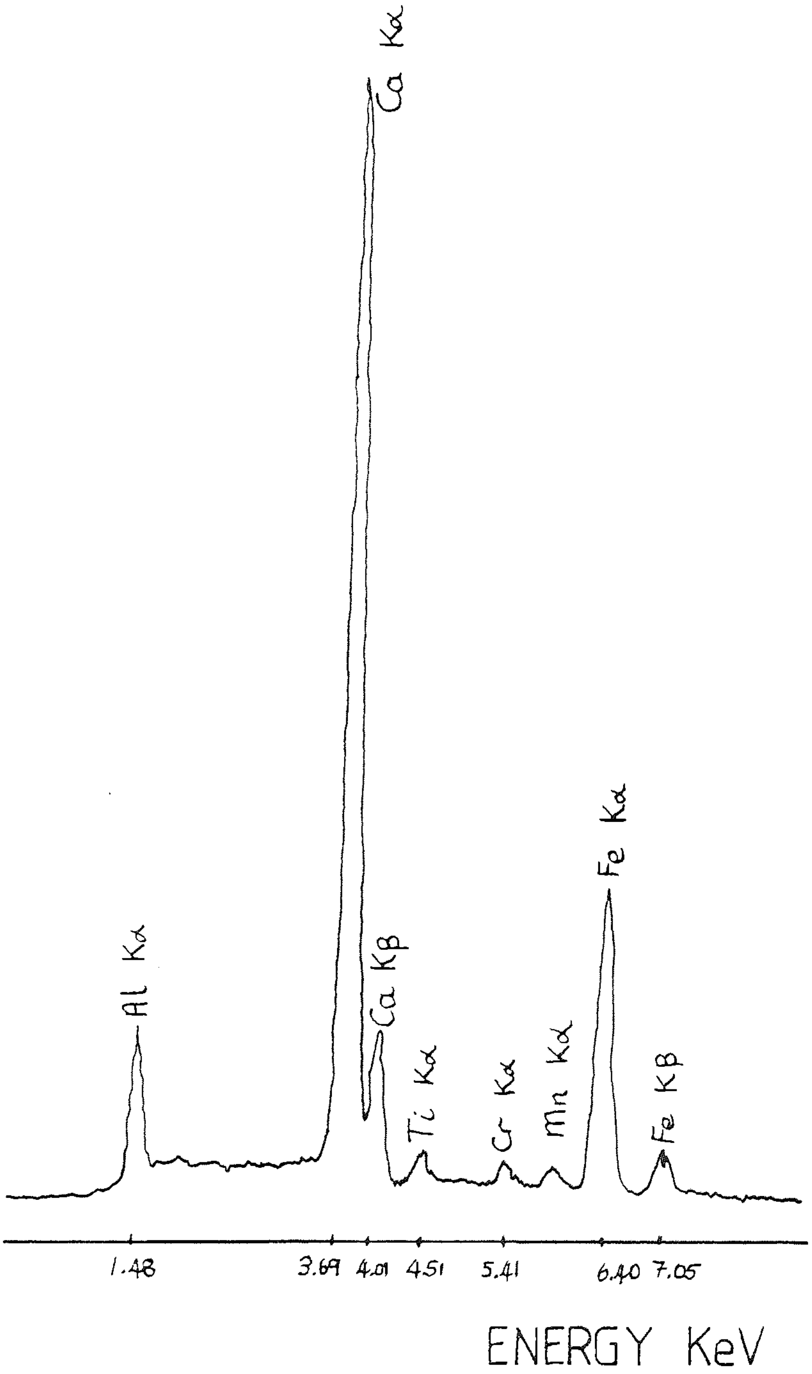
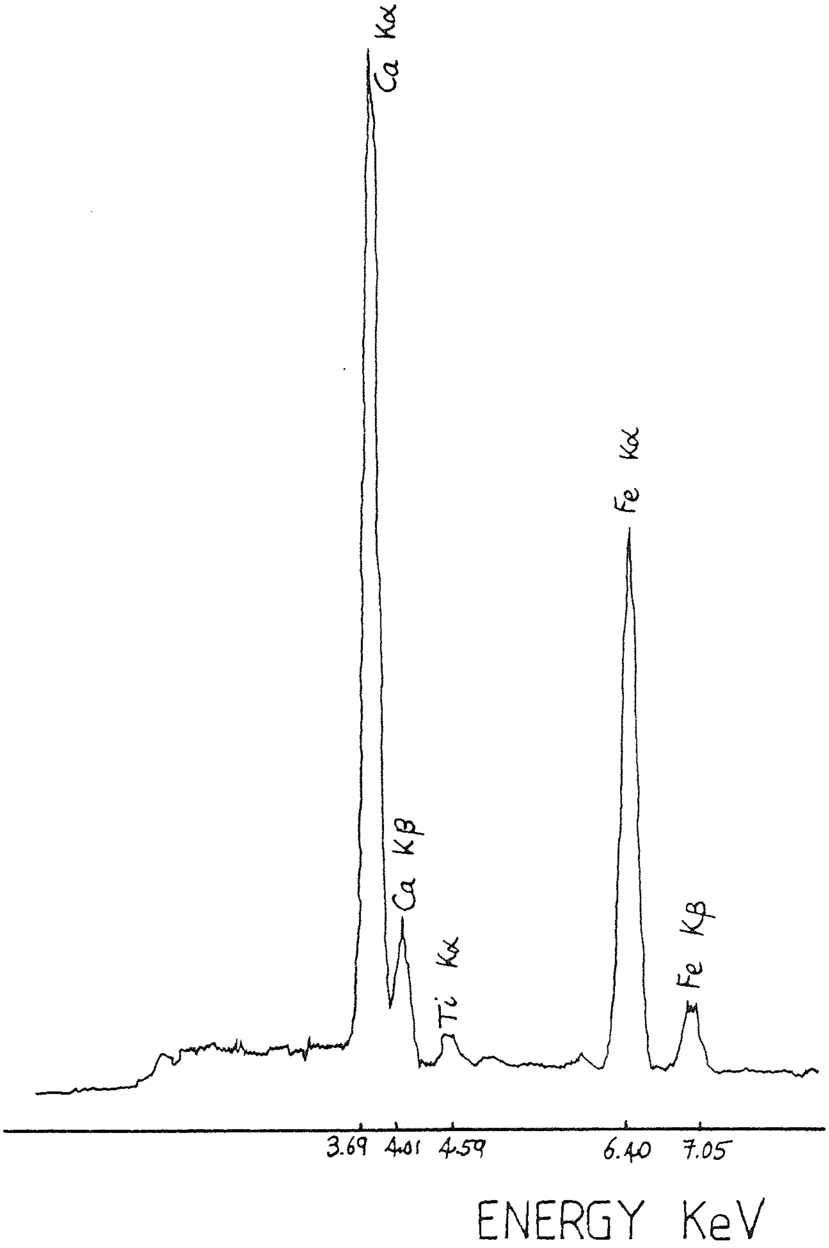


FIG 3,7 X-RAY MAP FOR Ti RICH AREA OF SLAG



3.1.2 Quantitative Chemical Analysis of Slags by Wet Methods

Conventional methods were employed for determining elements in the slags. Dried and finely ground samples were used. The results are shown in table 3.1.

3.1.3 Quantitative Chemical Analysis of the Phases in Slags by EPMA

In the electron probe microanalyser (EPMA) the X-rays are emitted from the surface as in the SEM and are discriminated according to wavelength. The surface composition can be determined by comparing the intensity of the X-rays emitted from the specimen with those of suitable standards.

The spot analytical method was employed throughout the investigations. Analyses were made on iron and silica rich areas for Fe, Ca, Si and Mn which are the major elements in the slags. The results are shown in tables 3.2 and 3.3.

The X-ray resolution of the microanalyser is approximately equivalent to the optical resolution of the best microscope (i.e. $\sim$1 μm). It provides, in addition to details of shape and size, information about the chemical composition and spatial position of various phases in the specimens.

In Figures 3.8-3.27 the elemental distribution of ARC and BOS slags are shown using the X-ray resolution of the microanalyser.

TABLE 3.1

CHEMICAL ANALYSIS OF THE SLAGS

Compound	BOS % Slag	ARC % Slag
CaO	46.4	41.0
SiO_2	13.8	14.3
MnO	2.8	4.2
FeO	24.2	22.2
MgO	2.8	3.1
Al_2O_3	4.0	8.8
TiO_2	0.7	0.9
P_2O_5	2.4	1.6
TOTAL	97.1	96.1

Trace elements are Cr, V, Ni, S and the balance could be O.

TABLE 3.2

CHEMICAL ANALYSIS OF IRON-RICH AREAS

	BOS Slag		ARC Slag	
Compound	% Range	% Average	% Range	% Average
CaO	4.2-52.0	18.8	2.4-38.0	11.4
FeO	38.8-72.9	59.5	27.5-49.6	41.7
SiO_2	0.1-6.7	1.7	0.1-8.5	2.0
MnO	6.6-13.9	10.7	2.8-33.2	21.6
MgO	4.3-19.6	8.4	14.5-22.4	18.7

TABLE 3.3

CHEMICAL ANALYSIS OF SILICA-RICH AREAS

	BOS Slag		ARC Slag	
Compound	% Range	% Average	% Range	% Average
CaO	28.0-83.9	59.9	45.7-77.8	60.5
FeO	1.0-3.1	2.0	0.5-9.5	4.7
SiO_2	9.1-64.2	31.9	24.0-38.4	32.6
MnO	0.1<	0.1<	0.4-5.2	2.2

MICROANALYSER X-RAY PHOTOGRAPHS OF BOS SLAG

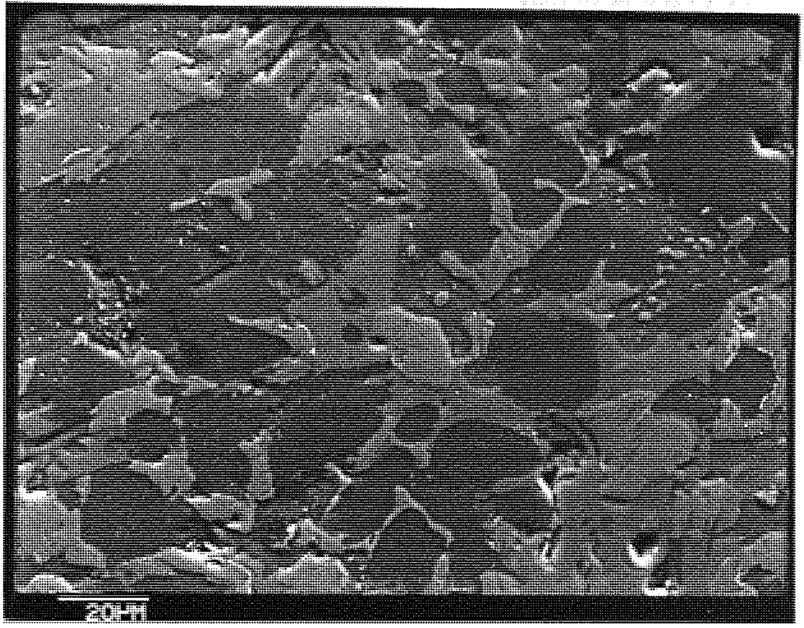


FIGURE 3.8   Electron Image

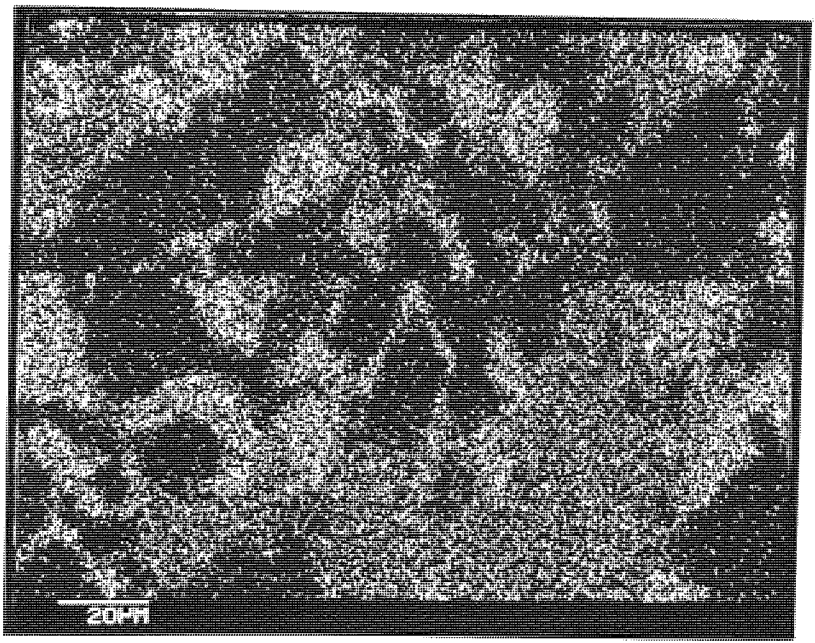


FIGURE 3.9   Iron X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF BOS SLAG

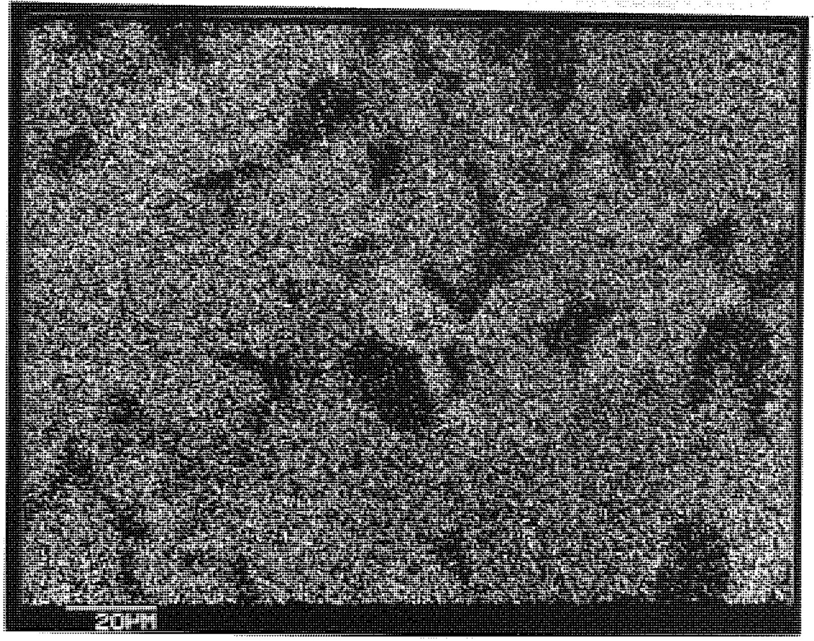


FIGURE 3.10 Calcium X-rays

FIGURE 3.11 Manganese X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF BOS SLAG

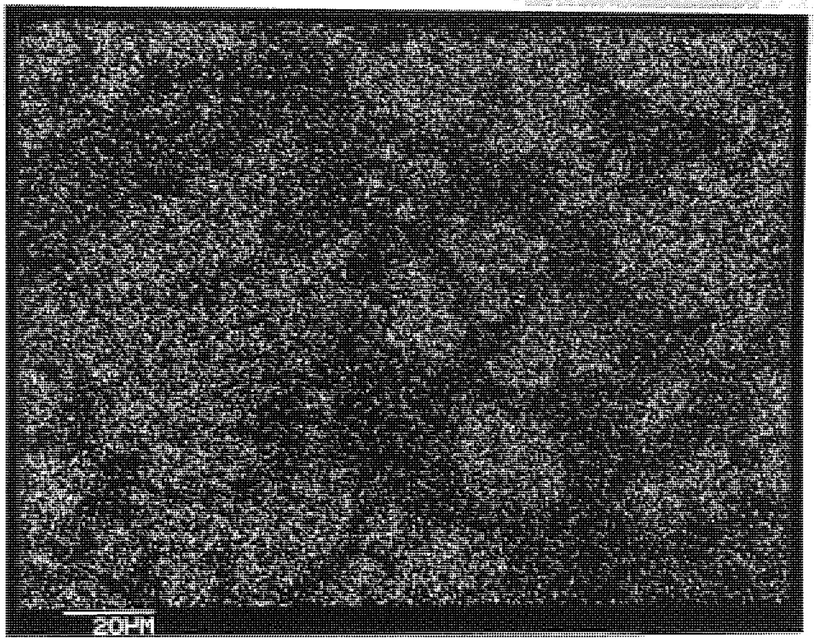


FIGURE 3.12 Silicon X-rays

FIGURE 3.13 Magnesium X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF BOS SLAG

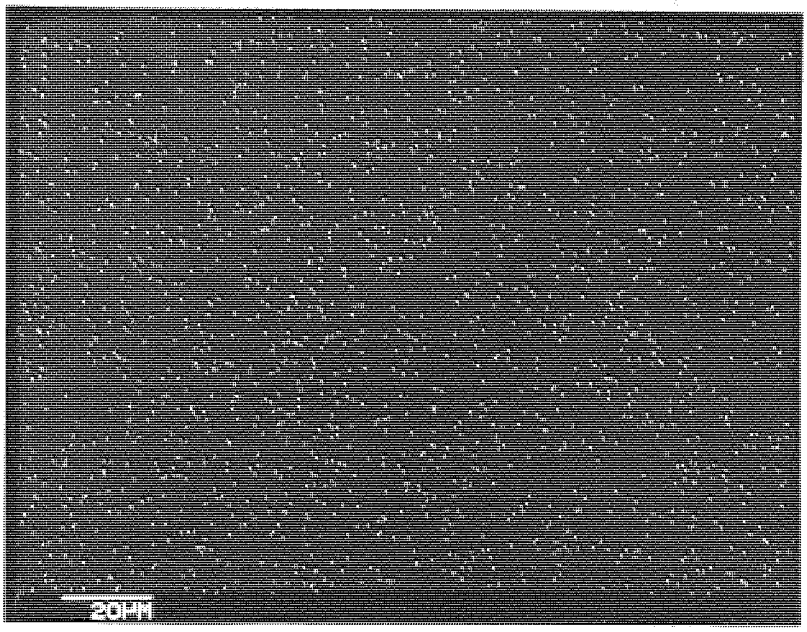


FIGURE 3.14 Aluminium X-rays

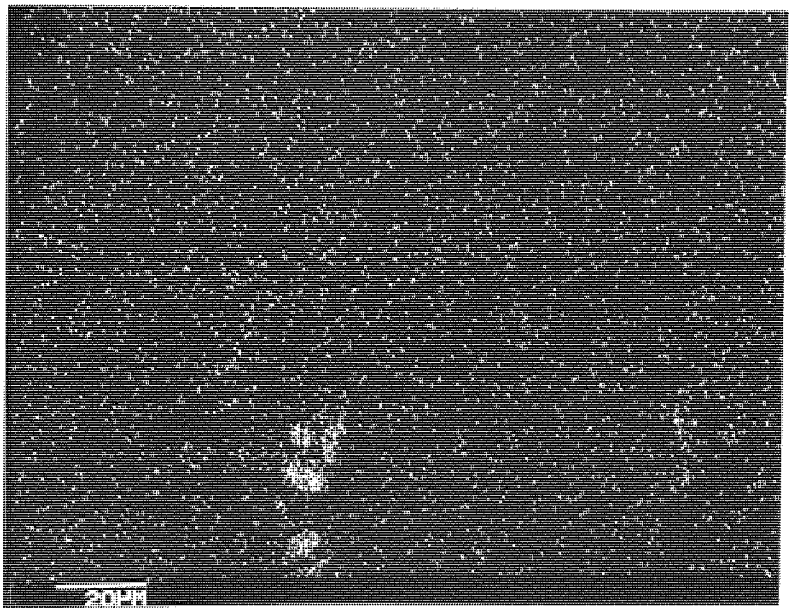


FIGURE 3.15 Sulphur X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF BOS SLAG

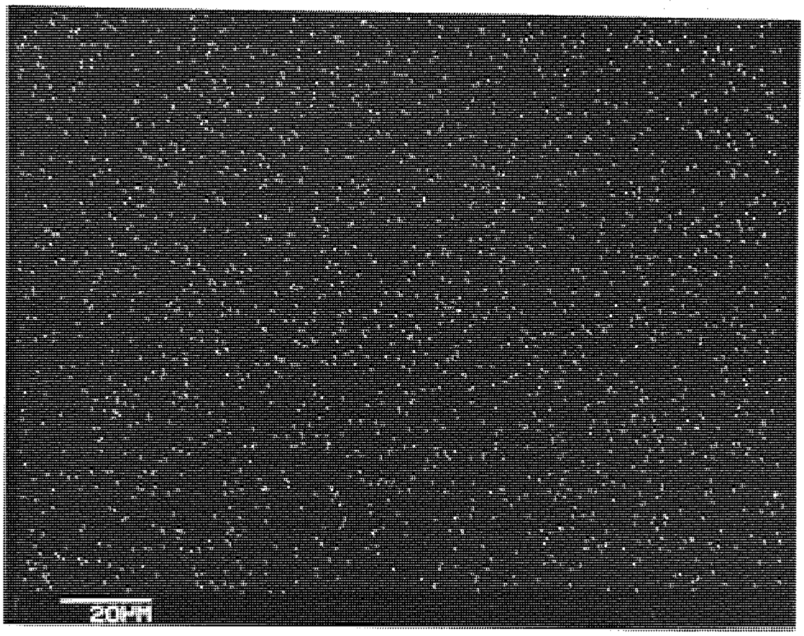


FIGURE 3.16 Chromium X-rays

FIGURE 3.17 Titanium X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF ARC SLAG

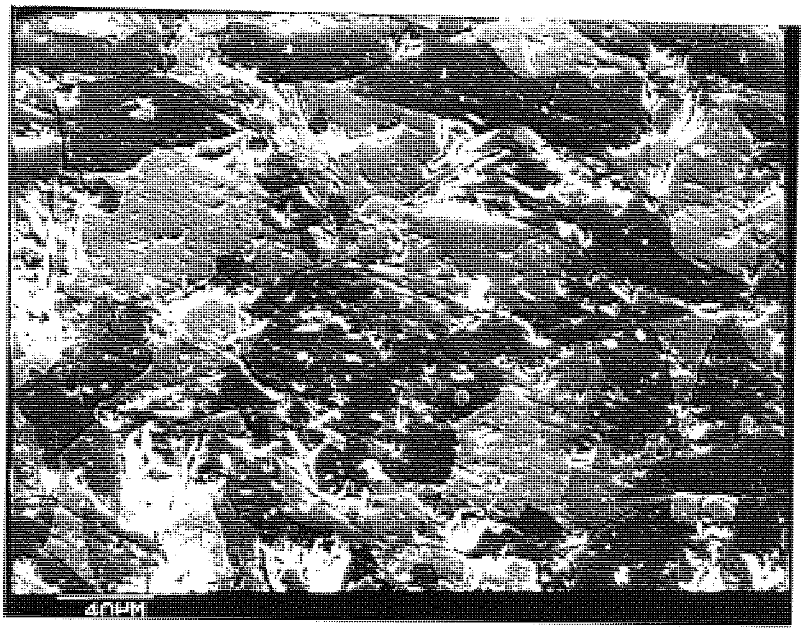


FIGURE 3.18 Electron Image

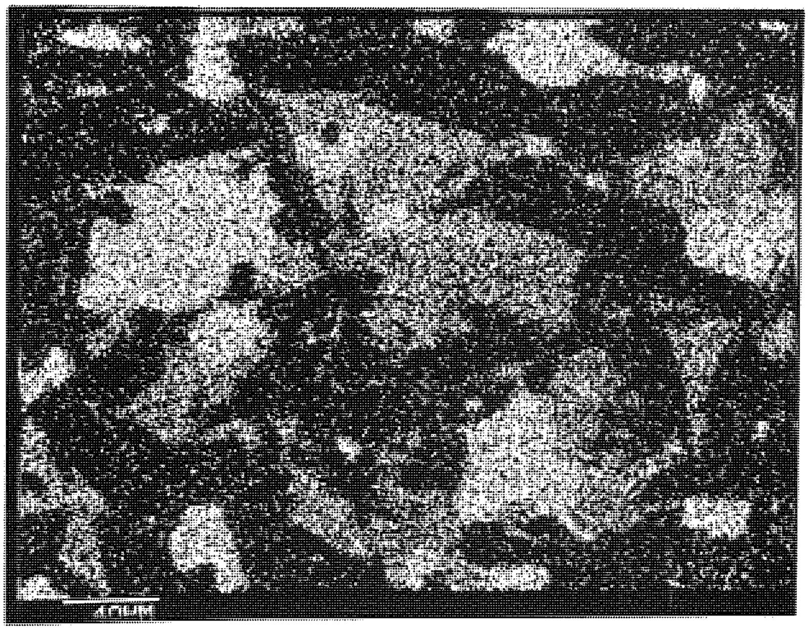


FIGURE 3.19 Iron X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF ARC SLAG

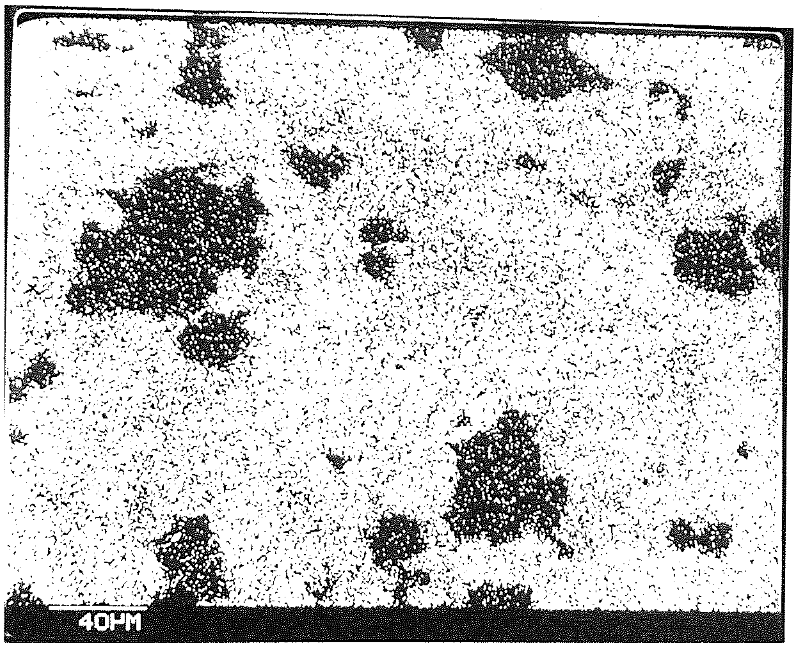


FIGURE 3.20 Calcium X-rays

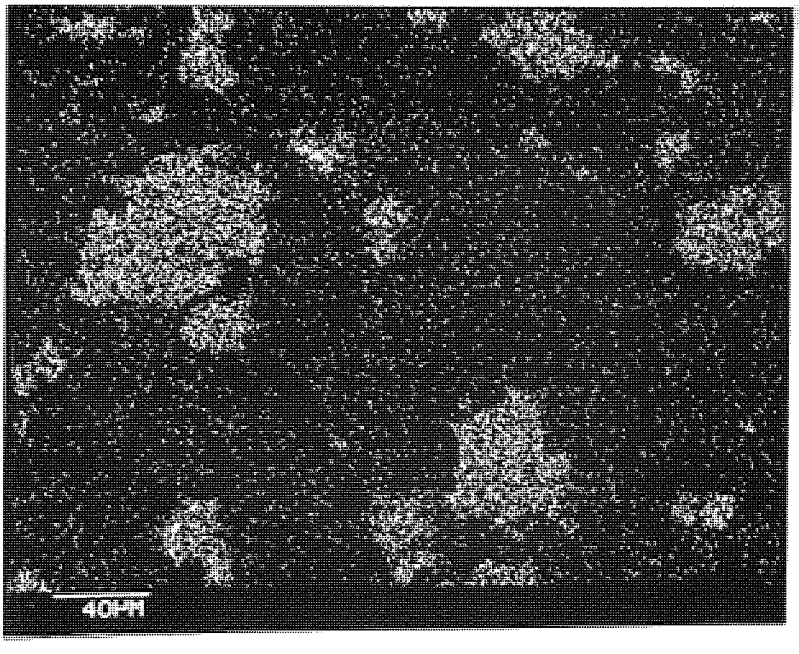


FIGURE 3.21 Manganese X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF ARC SLAG

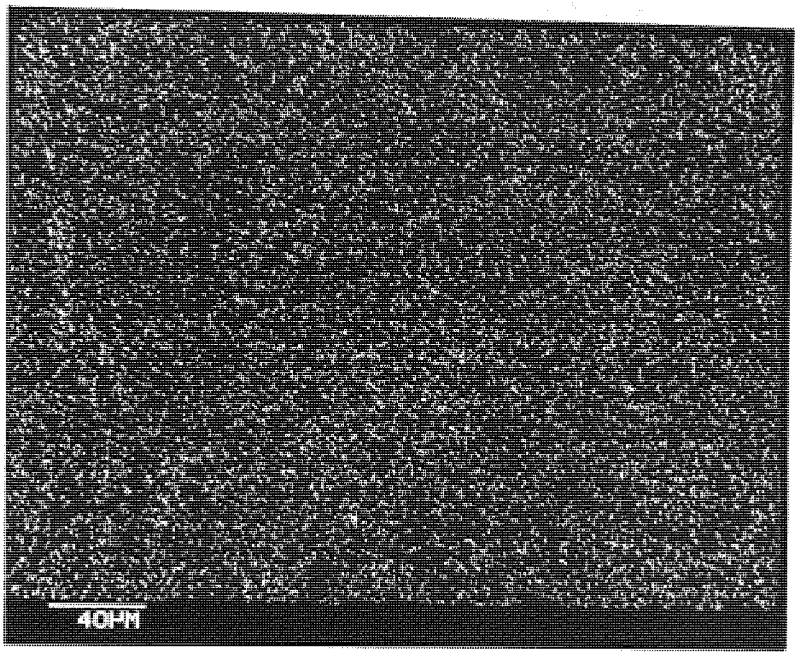


FIGURE 3.22 Silicon X-rays

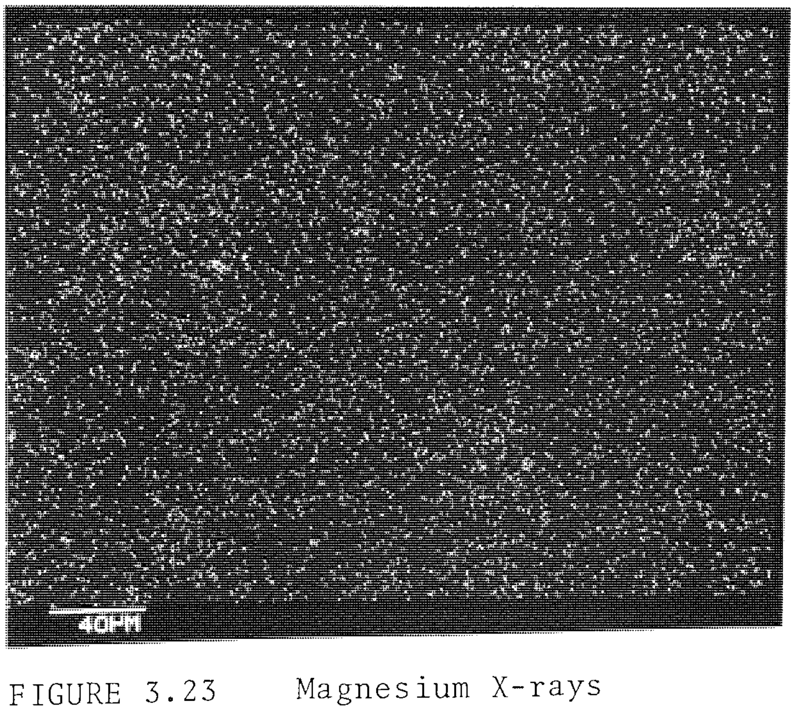


FIGURE 3.23 Magnesium X-rays

MICROANALYSER X-RAY PHOTOGRAPHS OF ARC SLAG

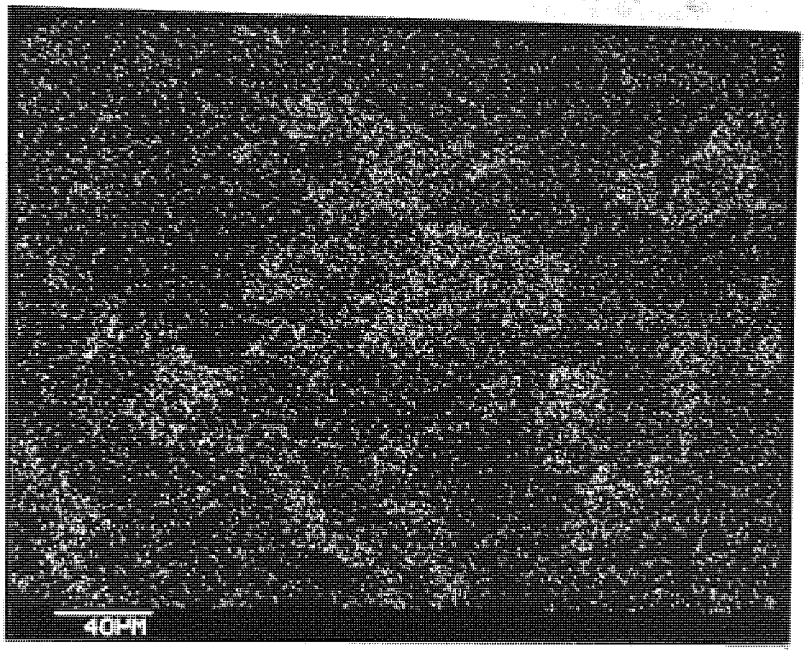


FIGURE 3.24 Aluminium X-rays

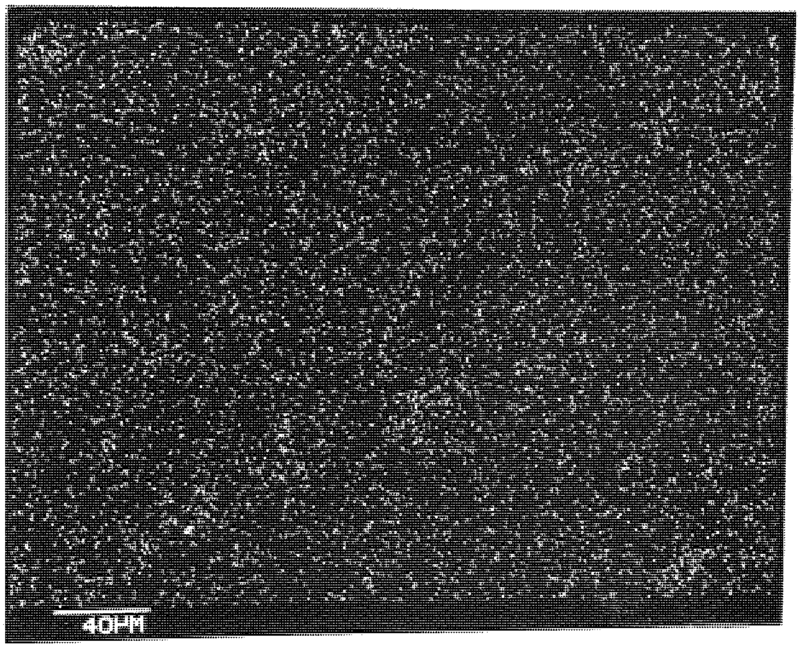


FIGURE 3.25 Sulphur X.rays

MICROANALYSER X-RAY PHOTOGRAPHS OF ARC SLAG

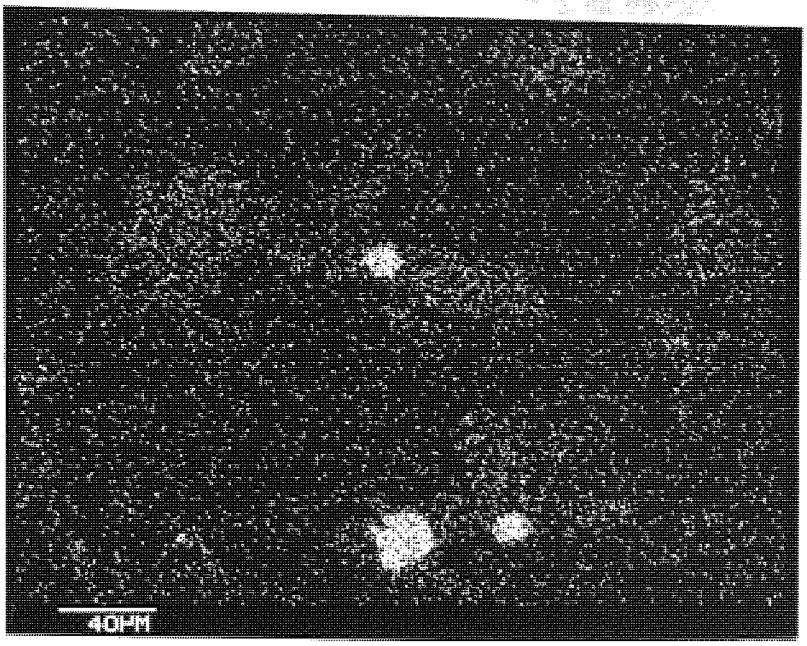


FIGURE 3.26 Chromium X-rays

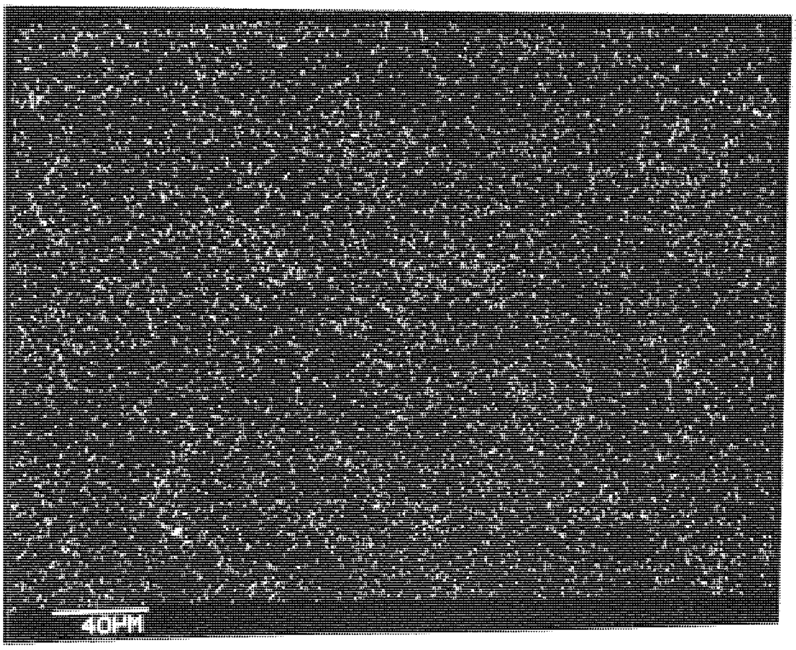


FIGURE 3.27 Titanium X-rays

3.2 Mineralogical Composition of the Slags

In addition to the results obtained by using SEM and EPMA (3.1) further investigations were carried out on the projection microscope to study the mineralogy of the slags.

The samples were etched with various solutions (4) to reveal the characteristics of the phases. These can be classified as follows:

1 - Tricalcium silicate $3CaO\ SiO_2$, C_3S
2 - Dicalcium silicate $2CaO\ SiO_2$, C_2S
3 - An "RO" phase, based on wustite (Mn, Ca, Mg, Fe)O
4 - A ferrite phase, based on C_2F, $2CaO\ Fe_2O_3$, and C_4AF $4CaO\ Al_2O_3\ Fe_2O_3$
5 - Free lime
6 - Metallic iron prills

The silicates and "RO" phase were found to be the most abundant phases (see figures 3.28 and 3.29).

3.2.1 Tricalcium Silicate or Alite (C_3S)

This is one of the highest melting point phases and consequently, solidified early during slag cooling and it invariably took the form of large laths up to 500 μm in length, Figure 3.28.

Tricalcium silicate is not only unstable above 1900°C, but it is also unstable below 1250°C, slowly decompos~~it~~ing into C_2S and CaO. This change is accelerated by the

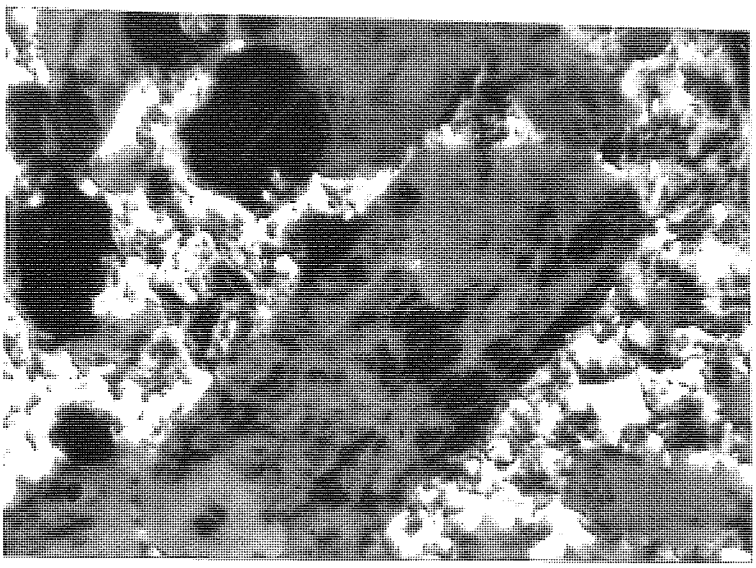


FIGURE 3.28 300 x The long crystal is Tricalcium Silicate partially being converted to CaO and Dicalcium Silicate

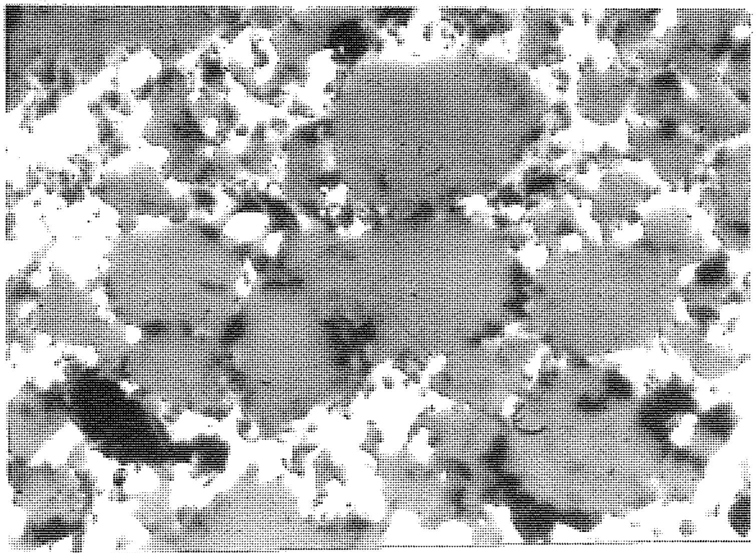


FIGURE 3.29 300 x Grey rounded grains are Dicalcium Silicates. Light Patches are RO phases

by the presence in the compound of either of the decomposition products C_2S and CaO and/or of calcium sulphate and certain other salts (4). The breakdown is more rapid when the material is exposed to moist air, since $Ca(OH)_2$ is formed in this way.

The alite crystals may comprise up to 25% of the slag content by volume, but generally it was much lower than this. Electron microprobe studies have confirmed that the alite crystals contain small amounts of phosphorus, manganese, iron and these probably have a stabilising effect.

3.2.2. Dicalcium silicate (C_2S)

This calcium silicate was the major phase in the slags, contributing between 35-85% of the total volume. Dicalcium silicate grains were smaller than alite grains and varied from about 10 - 100 μm. It appeared that they were formed as a primary 'phase' during cooling.

In the pure state, C_2S undergoes a complex series of phase transformations during heating and cooling. C_2S occurs mainly as larnite, the β polymorph, although in some cases it exists wholly or partially as bredigite, the α^1 form.

3.2.3 The "RO" phase or wustite (Mn, Mg, Ca, Fe)O

RO is the term used to describe a phase which is based on wustite, a cubic form of FeO with small amounts of MnO, CaO and MgO in solid solution. This phase, together with the ferrite phase, solidified at lower temperatures than the calcium silicates and formed an interstitial phase with a grain size of 10 - 50 µm. It constituted some 8 to 35% of the total volume.

Pure wustite is thermodynamically unstable under normal atmospheric conditions and should oxidise first to magnetite, "Fe_3O_4" and then to hematite "Fe_2O_3" at low temperatures. However, it is normally accepted that wustite is stable in these slags for all practical purposes.

3.2.4 The ferrite phases C_2F, C_4AF

These phases like the RO phase occupied some 8 to 35% by volume and occurred interstitially under similar cooling conditions. They cover a solid solution range of composition between the two extremes of dicalcium ferrite, C_2F, and brown millerite, C_4AF, in which half the iron was replaced by aluminium. In most cases the ferrite phases were associated with the RO phase and it was very difficult to detect them under the microscope.

3.2.5 Free Lime

The free lime content of the slags varied widely from less than 1 to almost 20% by weight, although it was usually less than 10 percent.

Three types of free lime are found in the slags:

1 - Unassimilated lime

2 - Precipitated lime

3 - Alite-derived lime

Unassimilated lime arises in steel making processes when lime is added beyond the saturation limit or is added too late or with a too large size to complete assimilation. In the present work unassimilated lime occurred as nodules up to 2 mm diameter, or even larger in some cases.

Precipitated lime is produced during the early stages of cooling as grains of up to 100 μm diameter in localised agglomerations.

Alite-derived lime is produced at lower temperatures, as previously described, and occurs in a very finely divided state in association with β - C_2S.

3.2.6 Metallic iron prills

They are formed during the cooling stage as trapped molten metal coalesces and is solidified intergranularly but as spherical prills. Their sizes and shapes vary considerably according to the solidification environment. They occupy some 0.5 - 1% by volume of the total for the demetallised slags (i.e. 1.5 - 3.0 wt%).

3.3 Grain Size measurements

3.3.1 Measurement procedure

Hand picked samples of the slags were sliced by a disc saw to give a flat surface and the sliced chips were then mounted in bakelite. The mounted specimens were ground down on various sizes of abrasive papers. This process was followed by polishing on diamond cloths until a clear view of the phases was obtained on the projection microscope. Six specimens were prepared for each type of slag.

By using suitable adjustments to the magnification the grain sizes of each phase (as silicates and 'RO' phase) were determined by measuring the width of the grains and the readings were tabulated. After recording a large number (∿1450) of measurements, a new area on the specimen was examined. The same procedure was done for each specimen to give an approximate estimate of the grain size distribution of each phase for BOS and ARC slags.

3.3.2 Results

The grain sizes of the phases were determined in size groups instead of single sizes. The number of grains in the same size group are shown in tables 3.4 - 3.7.

The results were also plotted as a function of grain size versus % of grain numbers (frequency curves), Figures 3.30 and 3.31.

3.4 Discussion

It can be seen that the difference between the slags is not in the chemical composition, but in the distribution of compounds (table 3.2). Since physical properties of the slags are mainly influenced by cooling conditions, which vary from melt to melt, the differences in these properties cannot be related to the actual steel making processes. (Physical properties of the phases in the slags are shown in table 3.8).

TABLE 3.4

GRAIN SIZE DISTRIBUTION OF SILICATE PHASES IN BOS SLAG

Grain size interval micron	Average size micron	No.of grains in size range	% of grains	Cumulative % undersize
200 - 167	183.5	-	-	100.00
167 - 150	158.5	1	0.07	99.93
150 - 133	141.5	4	0.28	99.65
133 - 117	125.0	5	0.36	99.29
117 - 100	108.5	15	1.08	96.21
100 - 83	91.5	24	1.73	96.48
83 - 67	75.0	56	4.05	92.43
67 - 50	58.5	164	11.86	80.57
50 - 40	45.0	221	15.98	64.59
40 - 33	36.5	184	13.34	51.25
33 - 30	31.5	191	13.81	37.44
30 - 27	28.5	117	8.46	28.98
27 - 23	25.0	97	7.01	21.97
23 - 20	21.5	107	7.74	14.23
20 - 17	18.5	97	7.01	7.22
17 - 13	15.0	64	4.62	2.60
13 - 10	11.5	27	1.95	0.65
10 - 7	8.5	7	0.51	0.14
7 - 3	5.0	2	0.14	-
3 - 1	2.0	-	-	-
TOTAL		1383	100.00	

TABLE 3.5

GRAIN SIZE DISTRIBUTION OF "RO" PHASE IN BOS SLAG

Grain size interval micron	Average size micron	No.of grains in size	% of grains	Cumulative % undersize
200 - 167	183.5	-	-	-
167 - 150	158.5	-	-	-
150 - 133	141.5	-	-	-
133 - 117	125.0	-	-	100.00
117 - 100	108.5	1	0.07	99.93
100 - 83	91.5	5	0.35	99.58
83 - 67	75.0	11	0.76	98.82
67 - 50	58.5	26	1.81	97.01
50 - 40	45.0	46	3.21	93.80
40 - 33	36.5	66	4.60	89.20
33 - 30	31.5	135	9.42	79.78
30 - 27	28.5	126	8.79	70.99
27 - 23	25.0	123	8.58	62.41
23 - 20	21.5	138	9.63	52.78
20 - 17	18.5	172	12.03	40.75
17 - 13	15.0	187	13.05	27.70
13 - 10	11.5	155	10.82	16.88
10 - 7	8.5	128	8.93	7.95
7 - 3	5.0	88	6.14	1.81
3 - 1	2.0	26	1.81	-
TOTAL		1433	100.00	

TABLE 3.6

GRAIN SIZE DISTRIBUTION OF SILICATE PHASES IN ARC SLAG

Grain size interval micron	Average size micron	No.of grains in size range	% of grains	Cumulative % undersize
200 - 167	183.5	-	-	-
167 - 150	158.5	-	-	100.00
150 - 133	141.5	2	0.14	99.86
133 - 117	125.0	3	0.15	99.71
117 - 100	108.5	8	0.57	99.14
100 - 83	91.5	21	1.51	97.63
83 - 67	75.0	34	2.44	95.19
67 - 50	58.5	93	6.67	88.52
50 - 40	45.0	187	13.42	75.10
40 - 33	36.5	216	15.52	59.58
33 - 30	31.5	251	18.12	41.46
30 - 27	28.5	138	9.91	31.55
27 - 23	25.0	124	8 .90	22.65
23 - 20	21.5	104	7.43	15.22
20 - 17	18.5	95	6.82	8.40
17 - 13	15.0	61	4.38	4.02
13 - 10	11.5	28	2.01	2.01
10 - 7	8.5	12	0.86	1.15
7 - 3	5.0	10	0.72	0.43
3 - 1	2.0	6	0.43	-
TOTAL		1393	100.00	

TABLE 3.7

GRAIN SIZE DISTRIBUTION OF "RO" PHASE IN ARC SLAG

Grain size interval micron	Average size micron	No.of grains in size range	% of grains	Cumulative % undersize
200 - 167	183.5	-	-	-
167 - 150	158.5	-	-	-
150 - 133	141.5	-	-	100.00
133 - 117	125.0	1	0.07	99.93
117 - 100	108.5	1	0.07	99.86
100 - 83	91.5	5	0.35	99.51
83 - 67	75.0	7	0.48	99.03
67 - 50	58.5	17	1.18	97.85
50 - 40	45.0	40	2.78	95.07
40 - 33	36.5	52	3.62	91.45
33 - 30	31.5	93	6.47	84.98
30 - 27	28.5	103	7.17	77.81
27 - 23	25.0	119	8.28	69.53
23 - 20	21.5	155	10.78	58.75
20 - 17	18.5	192	13.39	45.36
17 - 13	15.0	213	14.82	30.54
13 - 10	11.5	171	11.90	18.64
10 - 7	8.5	136	9.46	9.18
7 - 3	5.0	86	5.98	3.20
3 - 1	2.0	46	3.20	-
TOTAL		1437	100.00	

FIG3,30 GRAIN SIZE DISTRIBUTION OF PHASES IN BOS SLAG

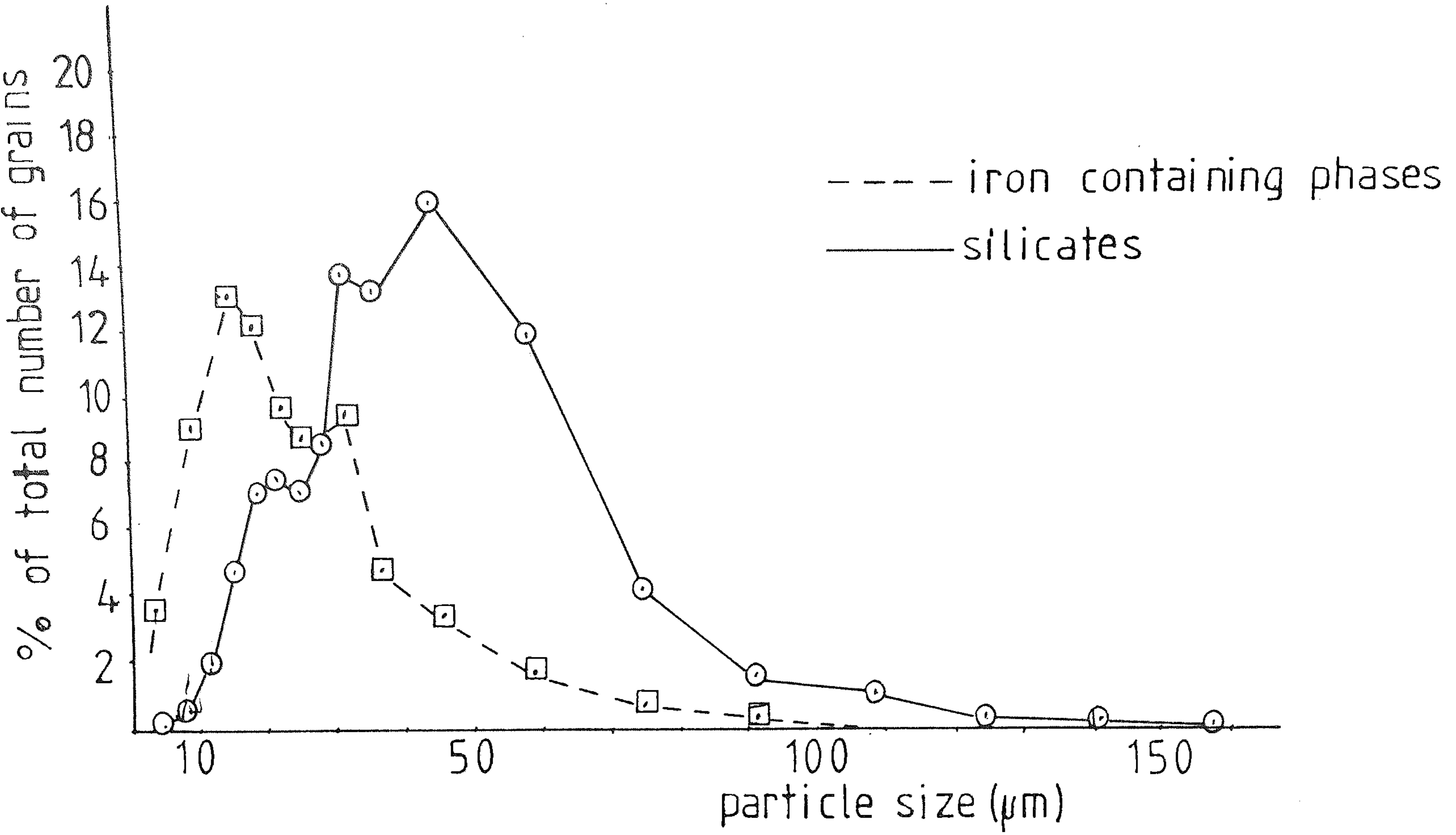


FIG 3,31 GRAIN SIZE DISTRIBUTION OF PHASES IN ARC SLAG

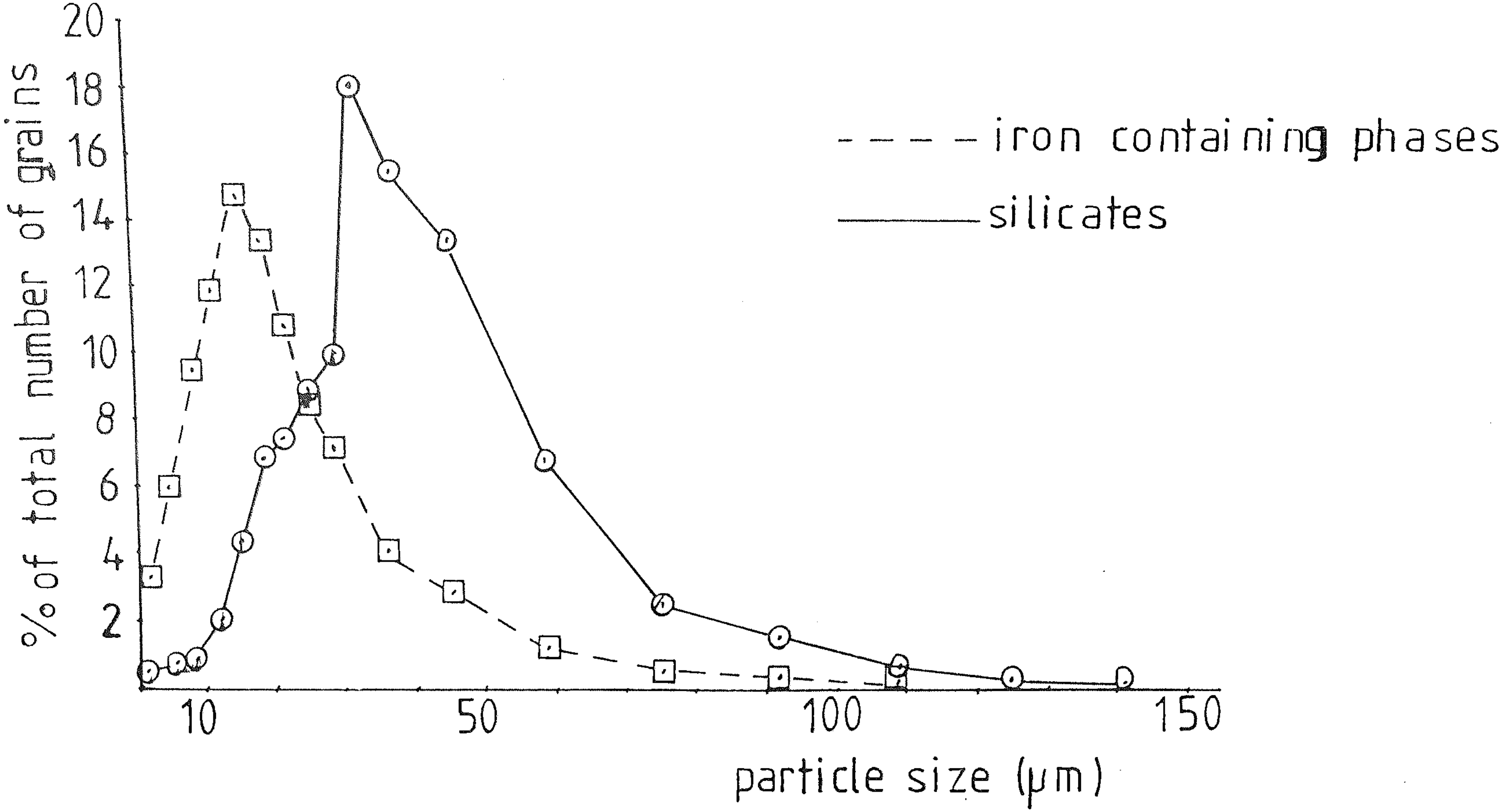


TABLE 3.8

PROPERTIES OF MAJOR PHASES IN SLAGS

	C_3S	C_2S	RO	C_2AF	C_4AF	Typical BOS Slag	Typical Blast Furnace Slag
Melting Point C	1900	2130	1420*	1435**	1415	-	-
Density $Mgm^{-3}x10^{-3}$	3.22	3.28	5.70	3.84	3.77	3.68	3.00
Hardness Mohs	5-6	5-6	6-7	6-7	6-7	5-7***	5-7***

* Wustite

** Ferrite

*** Mohs hardness values strictly apply to pure minerals only.

The slag values are estimates based on the constituents phases.

The slags, both BOS and ARC, were heterogeneous chemically and mineralogically. As it can be seen from EPMA results, a definite chemical composition cannot be found for a particular phase even within the same steel making process slags. The silicate phases are non-stoichiometric, especially tricalcium silicates which generally contain excessive amounts of CaO. This excess varies widely and unfortunately, is true for other phases.

Two distinctive areas can be seen for the elemental electron distribution maps (see Figures 3.8 - 3.27), those which are iron rich and those which are calcium rich. They directly correspond to the "RO" and ferrite phases for iron rich areas, and to the calcium silicate phases for the other.

There is a wide grain-size range for the two major phases, but generally they are less than 100 μm. The silicate phases have a greater grain-size for both slags and the majority of these grains are in the 20-80 μm range. The metallic oxide phases have relatively smaller sizes and 80% of the grains are less than 40 μm.

It would seem that enrichment of the phases, which contain silicate and iron, should be done by separation techniques which are suitably applied to the grain-sizes similar to those above such as magnetic separation, flotation and flocculation.

CHAPTER 4

MAGNETIC SEPARATION OF SLAGS

4.1 Literature Review

4.1.1 Introduction

A definition of a magnetic separator has been given as a device used to separate magnetic materials from less or non-magnetic materials (5). It is used chiefly in three ways

(a) The recovery of iron oxides from iron ores.

(b) The removal of the magnetic mineral portion from a stream of ore or refined feed.

(c) Removal of tramp iron from run of mine ore.

The first reference of the application of magnetic principles to the separation of minerals was made by Agricola in 1556 (6).

The first patent applicable to magnetic separation was issued to William Fullarton in 1792 (7), for a device used to separate iron ore from its gangue.

It was not until the 1890's that commercial machines came into widespread use, developed by such men as Wenström (1887) (8), Edison (1888) (9), Ball (1890 (10), Wetherill (1896) (11) and others. The magnetic drum of Wenström was designed for the treatment of iron ores with a wide size range.

The early machines were "low intensity" types and were mainly developed for the concentration of iron ores. It is only recently that the identification of the salient parameters of magnetic separation have caused separators to be developed which maximise the magnetic forces involved. As a result of these developments minerals which were previously considered non-magnetic may now be separated by "high intensity" separators.

4.1.2 Theoretical Aspects of Magnetic Separation

4.1.2.1 Theory of magnetism

The full physical theory of magnetism is one of the more complex aspects of modern physics. A simple model is developed to explain the basic properties of magnetism.

Most magnetic effects in substances arise from the behaviour of their electrons. Electrons give rise to magnetism in two ways.

1 - By revolving around the atomic nucleus

2 - By their angular momentum about their own axis (called spin).

In each case the electrical charge of the electron maybe thought of as moving round in a closed path and, therefore, acting as a current loop. The current loop (the current multiplied by the area) gives rise to the magnetic moment in the same way as a single turn coil, and this is a measure of the turning force the loop experiences in a magnetic field.

4.1.2.2 Types of magnetism

In 1845 Faraday showed that all substances may be classified as magnetic (14), although the relative value of the magnetism induced in a substance when it is placed in a magnetic field may be very small.

Substances can be classified in three groups according to their permeabilities.

1 - Ferromagnetic substances, having magnetic properties similar to iron (e.g. nickel, cobalt)

2 - Paramagnetic substances, permeabilities slightly greater than unity (1.000 - 1.001) (e.g. salts of iron and rare earths)

3 - Diamagnetic substances, permeabilities slightly less than unity (up to 0.999) (e.g. copper and bismuth).

4.1.2.3 Magnetic units and quantities

At least 29 systems of units have been used in electricity and magnetism (12), most of which are now forgotten. The important units and quantities are shown in table 4.1.

4.1.3 Mineralogical Considerations for Magnetic Separation

4.1.3.1 Susceptibilities and permeabilities

The first attempt to categorise the properties of minerals was made in 1849 (16) by Plücker. He compared the susceptibilities of five minerals with that of iron.

TABLE 4.1

MAGNETISM UNITS

Term	Symbol	Practical rationalised M.K.S. system	Practical unrationalised C.G.S. system
Force	F	Newton	Dyne
Charge	Q	Coulomb	Coulomb
Pole strength	m	-	Maxwell
Magnetic field strength	H	Ampere-turn/ metre	Oersted
Magnetic flux	Ø	Weber	Maxwell
Magnetic flux density	B	Weber/metre^2	Gauss
Magnetisation	I,M.J	Weber/metre^2	Gauss
Permeability of free space	μo	Henries/metre	UNITY
Permitivity of free space	Ko	Farads/metre	UNITY

In 1902 Crane (17) measured the permeabilities of some 55 minerals and metal powders and noted that the physical condition of the sample was an important parameter in the final measurements.

Dean and Davis (18) have modified Crane's results by comparing the minerals' susceptibilities with that of iron, taking the value for iron 100.

This data presented in table 4.2 relates to the susceptibilities of pure compounds or of geological samples from particular localities. In practice each mineral will have a range of susceptibilities which depend on several factors (19), these include:

(a) The inclusion of an impurity, e.g. discrete particles of magnetite

(b) The presence of iron in the crystal lattice of a non-magnetic mineral, e.g. cassiterite can contain up to 4% iron and sphalerite up to 11% iron

(c) The solid solution of a ferromagnetic component within a non-magnetic mineral, e.g. series of ferberite/wolframite/huebnerite ($FeWO_4$/$(Fe,Mn)WO_4$/$MnWO_4$)

(d) The locality, e.g. hematite from Brazil is more susceptible than hematite from the U.S.A. (19).

TABLE 4.2

THE SUSCEPTIBILITIES OF SOME MINERALS COMPARED WITH THAT OF IRON

Mineral	k(r)	Mineral	k(r)
Iron Fe	100.00	Corundum Al_2O_3	0.83
Magnetite Fe_3O_4	40.18	Pyrolusite MnO	0.71
Franklinite $(Zn,Fe,Mn)O_4$ $(FeMn)_2$	35.38	Manganite $MnO(OH)$	0.52
Ilmenite $FeTiO_3$	24.70	Hemimorphite $Zn_4(SiO_7)$ $(OH)_2.H_2O$	0.81
Pyrrhotite FeS	6.69	Quartz SiO_2	0.37
Siderite $FeCO_3$	1.82	Rutile TiO_2	0.37
Hematite Fe_2O_3	1.32	Pyrite FeS_2	0.23
Zircon $ZrSiO_4$	1.01	Sphalerite ZnS	0.23
Limonite $FeO.\ OH_A.H_2O$	0.84	Dolomite $CaMg(O_3)_2$	0.22

4.1.3.2 Hysteresis curves of ferromagnetic minerals

The magnetization curves and full hysteresis loops of ferromagnetic mineral powders were first produced by Gottschalk in 1935 (20).

Dean and Davis (21) showed the effect of decreasing particle size on the coercive force and remanence for a slag magnetite and a naturally occurring magnetite. The coercive force and remanence for both magnetites increased with decreasing mean particle size, the coercive force was found to be directly proportional to the specific surface.

4.1.3.3 The time factor in magnetization of mineral particles

The existence of a time factor was first described in 1885 by Ewing (22), who investigated the behaviour of soft iron bars placed in magnetic fields.

The time factor, also mentioned by Truscott (23) and Davis in 1941 (21), has been clearly demonstrated by Fraas in 1963 (24). In his experiments the time of magnetization for various particles in the non-uniform separating field was investigated and found to be decreased by the action of a preliminary uniform field.

A simple test showed that the selectivity of separation (at the same feed rate) was increased by the action of the preliminary uniform field.

4.1.4 Magnetic Separation

4.1.4.1 Physical considerations for magnetic separation

4.1.4.1.1 The concept of field gradient

The field gradient at any point in the field of a magnet is defined as the rate of change of intensity at that point. The same concept applies in any magnetic field no matter how it has been produced. The rate of change of the gradient is greater at one millimetre distance from the pole face than it is at 60 millimetres from the face.

It is this gradient that is incorporated in all magnetic separators, and is the most important single factor in the design of magnetic separators.

4.1.4.1.2 Forces on a body in a magnetic field

When a body is placed into the field of a magnet it becomes polarized, developing induced north and south poles. Magnetic attraction or repulsion is an example of the force which in any system possessing potential energy works the body towards the position of equilibrium where the potential energy is least.

When a small, spherical body is placed in a uniform magnetic field (the lines of force being parallel and equally spaced) the attractions for the induced poles, body and magnet balance each other with the result that the body will align itself along the lines of force, but will neither be attracted nor repelled, even though the body may have become strongly magnetized (25-28).

In the case of a ferromagnetic body in a uniform field the forces of attraction from each pole do not balance each other, since the field gradient is greater nearer the near poles, with the result that attraction will take place towards the nearest pole (the localised field gradients around the body are non-symmetrical).

If the body in the magnetic field is a point dipole (the smallest magnetic particle possible), the forces acting on the body may be determined by the straightforward application of Coulomb's Law (21).

$$F = \frac{Q_1 \; Q_2}{k_o r^2}$$

where, F is measured in dynes

Q_1 and Q_2 are the charge strengths (e.s.u.)

r is the distance between the charges and poles (cm)

k_o is the permittivity of free space in which the charges and poles lie.

However, in most practical situations (e.g. for mineral particles) the body is not a point dipole and the solution of Coulomb's Law becomes complex.

4.1.4.2 Particle capture in magnetic separators

The field and its associated gradient in magnetic separators are provided either, as in all types of electromagnets, by magnetizing coils via the pole pieces, or by powerful permanent magnets.

It is the design of the pole pieces that largely determines the magnitude of the field gradient across the gap. There are several basic designs of magnetic separators that cover the range of magnetic separation equipment. The most important types may be summarised:

(a) Belt

(b) Induced roll

(c) Drum

(d) Wet high intensity

All magnetic separators at present in commercial use are variations of these four types, the differences being in the manner in which the material to be separated is presented to the magnetic fields and the manner of its subsequent removal after separation.

4.1.4.3 Forces present in magnetic separators

(a) The force of gravity is present in every mechanical separator and may or may not act against the magnetic force. The presence of gravity, however is a necessity for separation and even if gravity acts against the magnetic force it actually assists the separation.

(b) Friction is present in every system that involves particle-particle, particle-belt or particle-drum contact. If a closely sized mixture of magnetic and non-magnetic particles are spread over the belt in a single, closely packed layer the vertical magnetic force acting on a certain magnetic particle surrounded by non-magnetic particles will be opposed not only by its gravitational force, but also by a frictional force due to contact with neighbouring particles and the belt.

(c) Fluid resistance is important in wet separators particularly with small particles, as the particle size becomes smaller the magnetic force required to overcome drag and gravitational forces becomes larger.

(d) Rotational forces and angular momentum will be acting on the particles in some types of separators, especially where the particles are fed on to a revolving drum. When magnetic particles enter rotating magnetic fields they can form elongated stringers or clusters, which rotate with the movement of the drum.

(e) Electrostatic attractions between particles increases as the size of the particles decreases. The electrostatic force between two particles is given by Coulomb's Law. As particle size decreases the electrostatic force increases as $1/r^2$

As the practical situation is reached, the complexity of the mechanics of particle separation increases. In practice the feed is never presented as a monolayer to the separating zone because the throughput would be far too slow. In addition, the feed in practice varies from day to day. For example, the moisture content and degree of liberation affect the efficiency of separation, and these are both likely to vary.

4.1.5 Classification of magnetic separators

Magnetic separators may be classified on the basis of three criteria

(a) magnetic field production
(b) mechanical separation
(c) field intensity (29).

(a) The magnetic attraction may be induced by
  (i) a permanent magnet
  (ii) D.C. electromagnet
  (iii) A.C. electromagnet

  and the separation affected by
  (1) movement of the particles in a moving (multiphase) magnetic field
  (2) movement of the diamagnetic particles out of the field
  (3) remanent magnetism

(b) These include the following types - drum, cross belt disc, reciprocators, centrifugal, drag, falling stream, etc.

(c) Classification based on field intensities:

  1 - low intensity separators (a) dry
  (b) wet

  field strength of up to 1200 gauss

  2 - medium intensity separators (a) dry
  (b) wet

  field strength of 1200-5000 gauss

3 - high intensity separators (a) dry
(b) wet
field strength of 5000-24000 gauss

4 - super high intensity separators
field strength of above 24000 gauss

These latter fields are available through the use of super conducting magnets (and special solenoid electromagnets). So far as is known there is only one commercial type of superconducting separator being used (in the clay industry (30) and only one prototype separator (31) being used in pilot plant tests. Both these types of separators are operated wet.

4.1.6 Application of magnetic separations

The applications of magnetic separation are extremely diverse, and may be discussed under three headings:

1 - Mineral beneficiation
2 - Tramp-iron removal
3 - Industrial water treatment

4.1.6.1 Mineral beneficiation

The commonest minerals to have been separated magnetically in large quantities have been for obvious reasons, the magnetic iron minerals. The first attempts to recover magnetite as a by-product were made at Mineville, New York in 1853 (32).

Heavy medium separator (sink and float operations) are particularly used in coal processing plants and the medium (usually magnetite) of S.G. 1.5 - 1.7 is recovered by magnetic means before being recirculated to the separation bath.

Many paramagnetic minerals are commercially concentrated ranging from chromite ($FeCr_2O_4$) to wolframite ($Fe\ Mn\ WO_4$). The high-intensity separators used for the concentration of paramagnetic minerals are of two types: induced roll types for dry separations and high-intensity wet types for wet separations.

Refractory minerals are also cleaned by magnetic means in two ways

1 - ferromagnetic scalping

2 - removal of iron and iron-bearing minerals from refractory or ceramic minerals, or metalliferrous non-magnetic minerals.

4.1.6.2 Tramp iron removal

The main purpose of tramp iron (nuts, bolts, nails, drill bits, wire, cable - in fact, general iron scrap - which has fallen into the feed) removal is the protection of subsequent processes which would be damaged by such material.

4.1.6.3 Industrial water treatment

This is a relatively new application which is still in the pilot plant stage, but is increasing in the United States. The basic idea is to use high-intensity wet separator which acts as a high-rate magnetic filter to remove the pollutant particles.

There are several applications of this process reported to date:

(a) steel-mill waste water cleaning
(b) refinery waste waters
(c) sewage water

4.2 Experimental Work

4.2.1 Preparation of samples

All slag samples of BOS and ARC used in these experiments were reduced in a jaw crusher prior to the grinding in a batch rod mill (diameter is 250 mm). 250 g of representative batches were prepared for metallic recovery and magnetic separation tests.

For the recovery tests the samples were ground in the mill, which had rods with various diameters weighing about 6000 g and was rotated at 60 rpm, for 7, 10, 15, 20, 30, 40, 60, 90 and 120 minutes. The products were then screened on a wide range of sieves using a sieve shaker.

The samples for the magnetic separation tests were ground in the same manner but the grinding time was kept constant at 10 minutes. They were screened to give the following fractions; + 3350, 3350-2800, 2800-1003, 1003-600, 600-295, 295-180, 180-125, 125-53 and -53 μm. Each fraction was stored for the experiments.

4.2.1.1 Results

The particle size distributions of each run for BOS and ARC slags are shown in figures 4.1 and 4.2 respectively as a function of cumulative percentage undersize (also see tables 4.3-4.6).

In figure 4.3 the grindability of the slags is shown as a function of grinding time against the amount of material passing 53 μm sieve. The plus 53 μm fractions of the ground samples for different grinding periods were collected separately in polyethylene bags for metallic iron recovery tests.

4.2.2 Magnetic separation tests

4.2.2.1 Description of the equipment

A disc magnetic separator (Rapid Co. Ltd.) was used in these experiments. The magnetic fraction removal with this separator can be achieved in a direction perpendicular to that of feed. The magnetic particles are picked up and removed from the zone of high magnetic field by the rotating disc. Once outside the magnetic field the particles are released into suitable collection bins. This is shown schematically in figure 4.4

FIG 4,1 PARTICLE SIZE DISTRIBUTION OF BOS SLAG FOR DIFFERENT GRINDING PERIODS

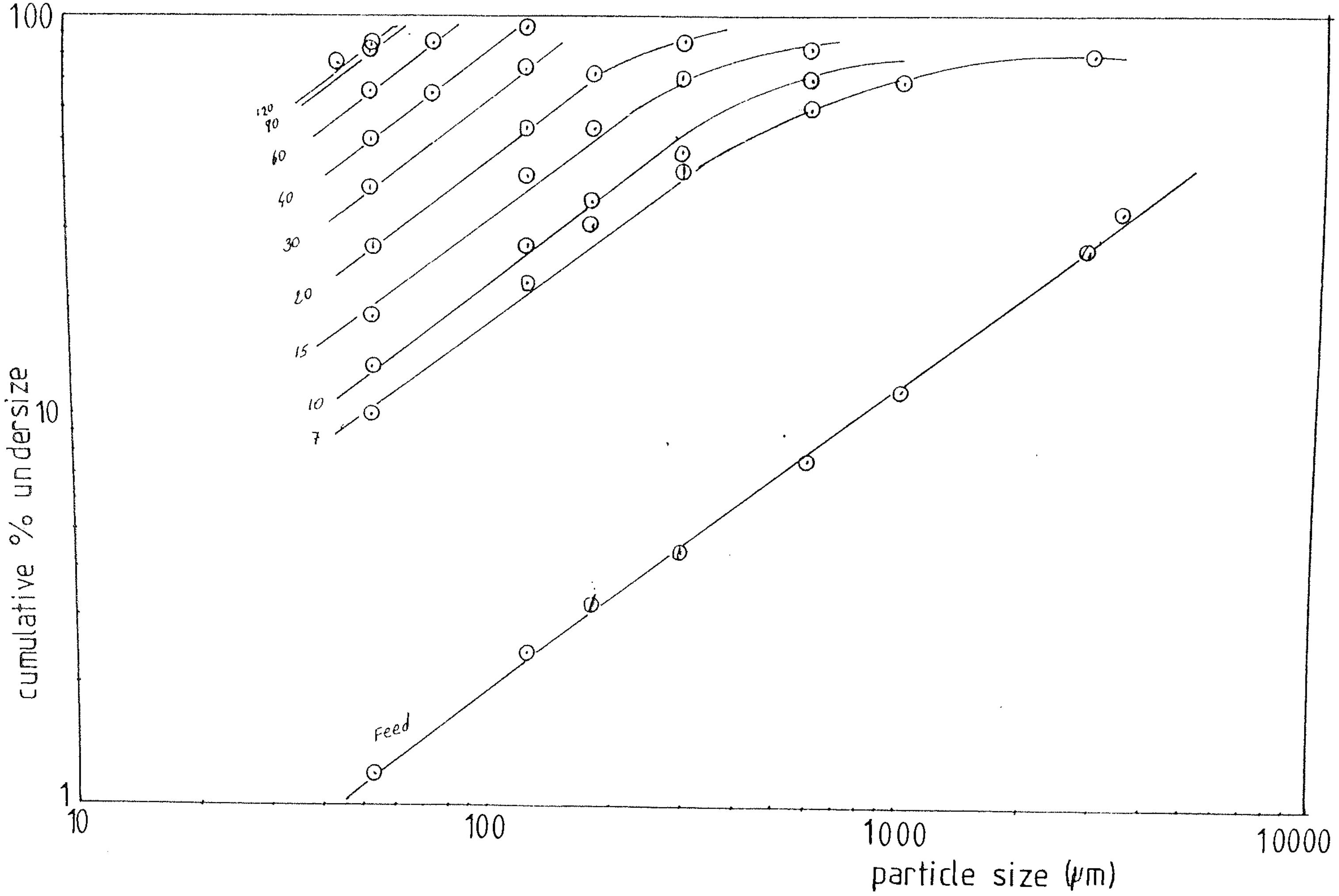


FIG 4,2 PARTICLE SIZE DISTRIBUTION OF ARC SLAG FOR DIFFERENT GRINDING PERIODS

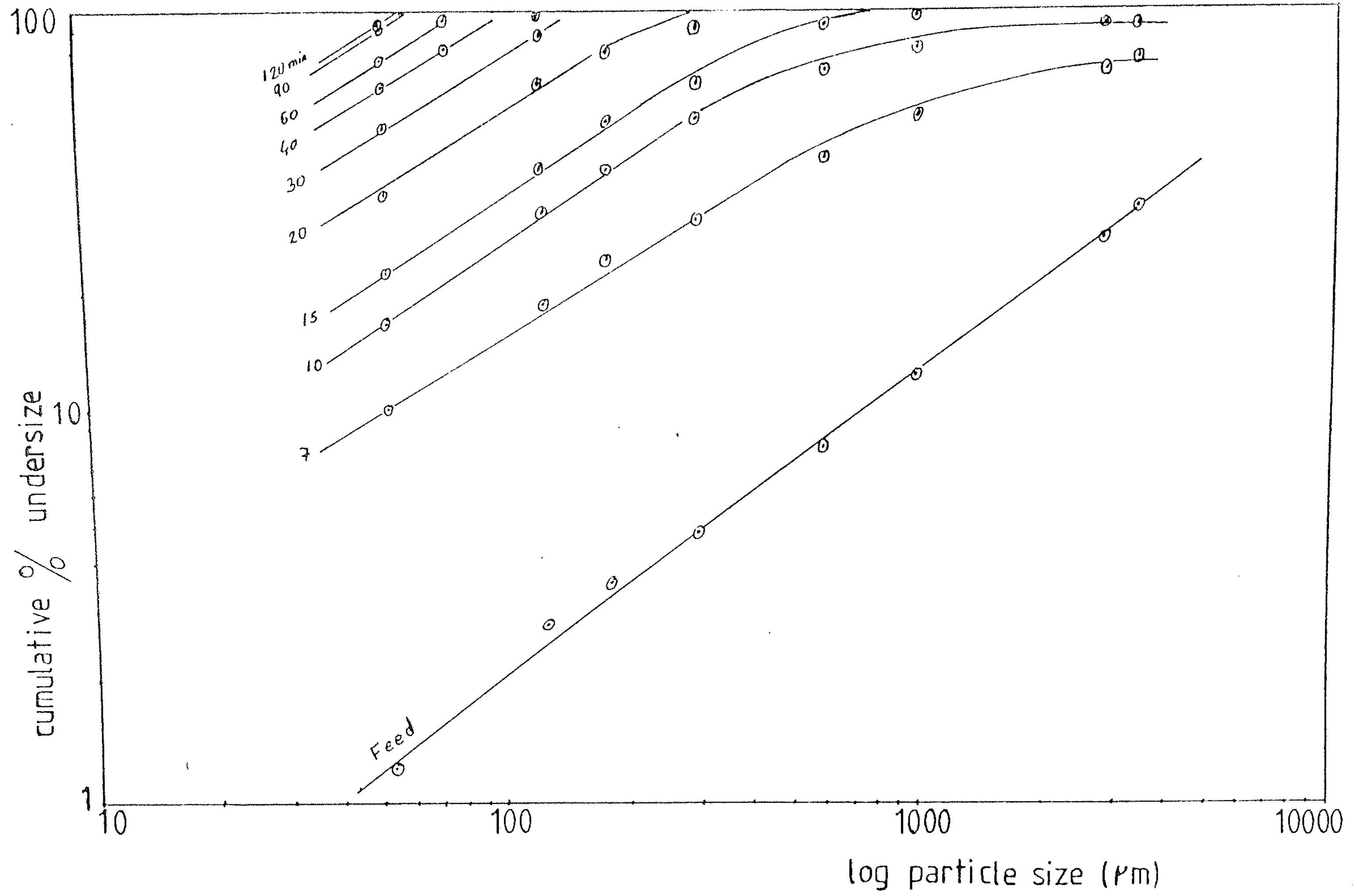


TABLE 4.3

GRINDING TEST FOR BOS SLAG

Grinding Time	Feed			7 minutes			10 minutes			15 minutes			20 minutes		
Fraction size µm	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer
+3350	164	66.8	33.2	41	16.4	83.6	56	22.5	77.5	25	10.1	89.9	20	7.9	92.1
-3350+2800	15	6.1	27.1	7	2.8	80.8	6	2.4	75.1	2	0.8	89.1	1	0.4	91.7
-2800+1003	38	15.5	11.6	28	11.2	69.6	22	8.7	66.4	5	2.0	87.1	2	0.8	90.9
-1003+600	10	4.0	7.6	27	10.8	58.8	16	6.4	60.0	6	2.4	84.7	1	0.4	90.5
-600 +295	8	3.2	4.6	40	16.0	42.8	34	13.5	46.5	34	13.7	71.0	9	3.6	86.9
-295 +180	3	1.2	3.2	29	11.6	31.2	29	11.5	35.0	40	16.2	54.8	36	14.3	72.6
-180 +125	2	0.8	2.4	23	9.2	22.0	20	7.9	27.1	33	13.4	41.4	47	18.6	54.0
-125 + 53	4	1.6	0.8	30	12.0	10.0	37	14.8	12.3	58	23.6	17.8	68	27.0	27.0
-53	2	0.8		25	10.0		31	12.3		44	17.8		68	27.0	
TOTAL	246	100.0		250	100.0		251	100.0		247	100.0		252	100.0	

TABLE 4.4

GRINDING TEST FOR BOS SLAG

Grinding Time	30 minutes			40 minutes			60 minutes			90 minutes			120 minutes		
Fraction size µm	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer
+3350	3	1.2	98.8	3	1.2	98.8	2	0.8	99.2	-	-	-	-	-	-
-3350+2800	-	-	98.9	-	-	98.8	0.5	0.2	99.0	0.5	0.2	98.8	-	-	-
-2800+1003	1	0.4	98.5	1	0.4	98.4	1	0.4	98.6	0.5	0.2	99.6	0.5	0.2	99.8
-1003+600	1	0.4	98.1	1	0.4	98.0	0.5	0.2	98.4	0.5	0.2	99.4	0.5	0.2	99.6
-600 +295	1	0.4	97.7	1	0.4	97.6	0.5	0.2	98.2	1	0.4	99.0	0.5	0.2	98.4
-295 +180	11	4.5	93.2	2	0.8	96.8	0.5	0.2	98.0	0.5	0.2	98.8	0.5	0.2	99.2
-180 +125	44	17.8	75.4	8	3.2	93.6	1	0.4	97.6	1	0.4	98.4	1	0.4	98.8
-125 +53	92	37.4	38.0	100	39.8	53.8	76	30.7	66.9	44	17.6	80.8	37	14.8	84
-53	94	38.0	-	135	53.8	-	165	66.8	-	202	80.8	-	210	84.0	-
TOTAL	247	100.0		251	100.0		247	100.0		250	100.0		250	100.0	

TABLE 4.5

GRINDING TESTS FOR ARC SLAG

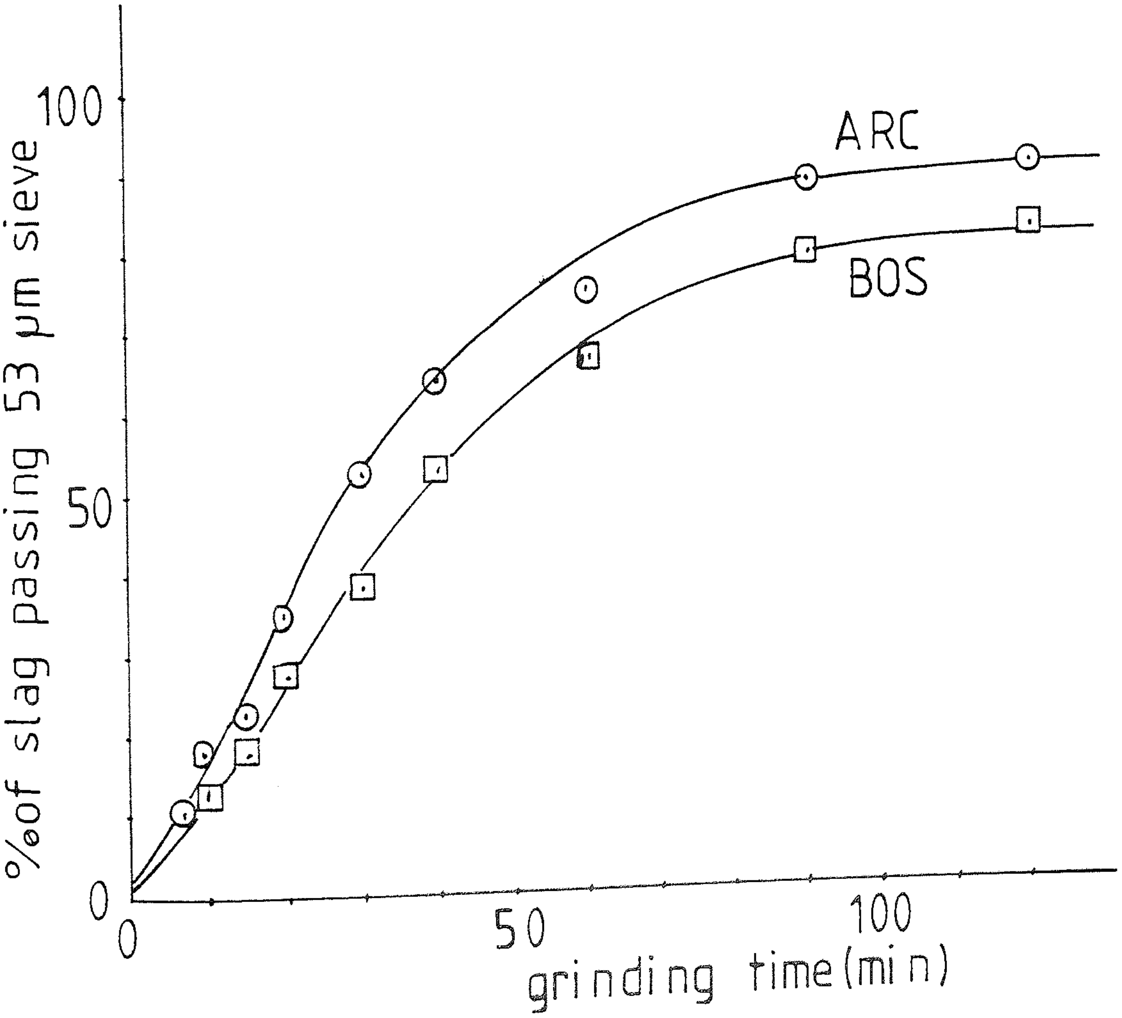
Grinding Time	Feed			7 minutes			10 minutes			15 minutes			20 minutes		
Fraction µm size	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer
+3350	167	66.3	33.7	60	23.9	76.1	29	11.6	88.4	25	10.2	89.8	16	6.5	93.5
-3350+2800	14	5.5	28.2	8	3.2	72.9	3	1.2	87.2	1	0.4	89.4	-	-	93.5
-2800+1003	40	15.9	12.3	42	16.9	56.0	15	6.0	81.2	2	0.8	88.6	0.5	0.2	93.3
-1003+600	11	4.3	8.0	30	11.9	44.1	22	8.8	72.4	11	4.5	84.1	0.5	0.2	93.1
-600 +295	8	3.2	4.8	34	13.5	30.6	43	17.2	55.2	43	17.5	66.6	5	2.0	91.1
-295 +180	3	1.2	3.6	16	6.3	24.3	34	13.6	41.6	31	12.6	54.0	26	10.6	80.5
-180 +125	2	0.8	2.8	14	5.6	18.7	22	8.8	32.8	31	12.6	41.4	36	14.6	65.9
-125 +53	4	1.6	1.2	22	8.7	10.0	40	16.0	16.8	46	18.8	22.6	76	30.9	35.0
-53	3	1.2	-	25	10.0	-	42	16.8	-	55	22.6	-	86	35.0	-
TOTAL	252	100.0		251	100.0		250	100.0		245	100.0		246	100.0	

TABLE 4.6

GRINDING TESTS FOR ARC SLAG

Grinding Time	30 minutes			40 minutes			60 minutes			90 minutes			120 minutes		
Fraction µm size	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer	wt.g	wt.%	Cum.wt. % Finer
+3350	9	3.6	96.4	5	2.0	98.0	6	2.4	97.6	3	1.2	98.8	1.5	0.6	99.4
-3350+2800	-	-	96.4	-	-	98.0	-	-	97.6	-	-	98.8	-	-	99.4
-2800+1003	1	0.4	96.0	2	0.8	97.2	0.5	0.2	97.4	1	0.4	98.4	0.5	0.2	99.2
-1003+600	0.5	0.2	95.8	1	0.4	96.8	1	0.4	97.2	0.5	0.2	98.2	0.5	0.2	9.0
-600 +295	1	0.4	95.4	0.5	0.2	96.6	1	0.4	96.8	0.5	0.2	98.0	0.5	0.2	98.8
-295 +180	1.5	1.2	94.2	0.5	0.2	96.4	0.5	0.2	96.4	0.5	0.2	97.8	0.5	0.2	98.6
-180 +125	18	7.3	86.9	1	0.4	96.0	1	0.4	96.0	0.5	0.2	97.6	0.5	0.2	98.4
-125 +53	85	34.5	52.4	78	31.5	64.5	50	20.0	76.0	19	7.6	90.0	16	6.4	92.0
-53	130	52.4		160	64.5		190	76.0		225	90.0		230	92.0	
TOTAL	246			248	100.0		250	100.0		250	100.0		250	100.0	

FIG 4,3 GRINDABILITY OF STEEL MAKING SLAGS



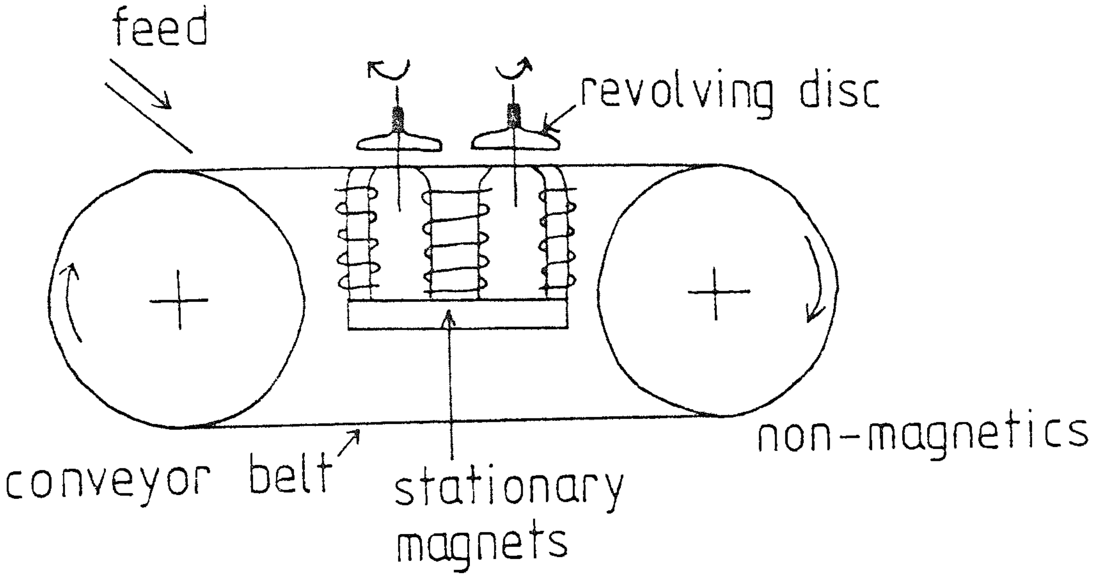


FIGURE 4.4 Schematic representation of Magnetic Separator

The current density and gap on this separator can be easily arranged to give the correct conditions for materials not having uniform magnetic susceptibilities.

4.2.2.2 Magnetic separation tests

Samples of 20 g prepared from individual fractions (see 4.2.1) were passed through the separator to calibrate the gap and the magnetic field strength against the recovery and iron grade of the magnetic products.

The magnetic field strength was maintained at the current density of 0.2 and 0.5 amp as the distance of the gap ranged from 0.4 to 1.0 cm. The magnetic concentrates from these runs were analysed by the author by means of wet chemical methods and the results are shown in tables 4.7 - 4.14.

TABLE 4.7

MAGNETIC SEPARATION TESTS OF BOS SLAG

Gap 0.4 cm   Current 0.2 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt. of conc g	Fe % of con	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	22.0	4.41	14.7	15.8	2.33	5.3	39.2	2.08	52.8
-2800+1003	20	20.1	4.02	10.6	18.3	1.93	9.4	22.2	2.09	48.0
-1003+600	20	19.9	3.98	8.6	23.2	2.00	11.4	17.4	1.98	50.2
-600 +295	20	19.5	3.89	7.0	15.6	1.79	13.0	16.1	2.10	46.0
-295 +180	20	19.2	3.85	6.4	24.1	1.54	13.6	17.0	2.31	40.0
-180 +125	20	18.2	3.65	5.6	23.8	1.33	14.4	16.1	2.32	36.4
-125 +53	20	18.1	3.61	4.7	26.2	1.23	15.3	15.5	2.38	34.1
-53	20	18.1	3.63	9.5	19.2	1.82	10.5	17.2	1.81	50.1

* Calculated

TABLE 4.8

MAGNETIC SEPARATION TESTS OF BOS SLAG

Gap 0.4 cm   Current 0.5 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt. of conc g	Fe % of conc	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	22.0	4.41	19.5	19.6	3.81	0.5	12.0	0.60	86.4
-2800+1003	20	20.1	4.02	18.5	20.4	3.77	1.5	16.6	0.25	93.8
-1003+600	20	19.9	3.98	17.2	21.3	3.67	2.8	11.1	0.31	92.2
-600 +295	20	19.5	3.89	16.1	20.8	3.34	3.9	14.1	0.55	85.8
-295 +180	20	19.2	3.85	14.4	21.2	3.05	5.6	14.3	0.80	79.2
-180 +125	20	18.2	3.65	12.9	21.1	2.72	7.1	13.1	0.93	74.5
-125 +53	20	18.1	3.61	10.2	22.7	2.31	9.8	13.3	1.30	64.0
-53	20	18.1	3.63	17.1	19.3	3.30	2.9	11.4	0.33	90.9

* Calculated

TABLE 4.9

MAGNETIC SEPARATION TESTS OF BOS SLAG

Gap 1.0 cm   Current 0.2 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt. of conc g	Fe % of conc	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	22.0	4.41	0.51	39.7	0.20	19.49	21.6	4.21	4.5
-2800+1003	20	20.1	4.02	0.59	52.9	0.31	19.41	19.1	3.71	7.7
-1003+600	20	19.9	3.98	0.59	50.2	0.30	19.41	18.9	3.68	7.5
-600 +295	20	19.5	3.89	0.36	49.6	0.18	19.64	18.9	3.71	4.6
-295 +180	20	19.2	3.85	0.19	56.7	0.11	19.81	18.9	3.74	2.8
-180 +125	20	18.2	3.65	0.20	45.5	0.09	19.80	18.0	3.56	2.4
-125 +53	20	18.1	3.61	0.48	40.8	0.19	19.52	17.5	3.42	5.3
-53	20	18.1	3.63	No separation						

* Calculated

TABLE 4.10

MAGNETIC SEPARATION TESTS OF BOS SLAG

Gap 1.0 cm   Current 0.5 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt. of conc g	Fe % of con	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	22.1	4.41	8.8	19.9	1.75	11.2	23.7	2.66	39.7
-2800+1003	20	20.1	4.02	8.8	21.2	1.86	11.2	19.3	2.16	46.3
-1003+600	20	19.9	3.98	7.1	23.3	1.66	12.9	18.0	2.32	41.7
-600 +295	20	19.4	3.89	6.4	24.3	1.56	13.6	17.1	2.33	40.1
-295 +180	20	19.2	3.85	7.4	22.9	1.70	12.6	17.1	2.15	44.1
-180 +125	20	18.2	3.65	7.7	22.7	1.75	12.3	15.4	1.90	47.9
-125 +53	20	18.1	3.61	5.8	23.2	1.35	14.2	15.9	2.26	37.4
-53	20	18.1	3.63	3.1	21.1	0.65	16.9	17.6	2.98	17.9

* Calculated

TABLE 4.11

MAGNETIC SEPARATION TESTS OF ARC SLAG

Gap 0.4 cm Current 0.2 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt.of conc. g	Fe % of con.	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	14.8	2.97	9.7	21.6	2.09	10.3	8.5	0.88	70.4
-2800+1003	20	17.3	3.46	7.2	21.4	1.54	12.8	15.0	1.92	44.5
-1003+600	20	15.1	3.01	6.2	24.9	1.54	13.8	10.6	1.47	51.2
-600 +295	20	14.7	2.95	5.5	21.9	1.20	14.5	12.1	1.75	40.7
-295 +180	20	14.8	2.96	6.0	20.5	1.23	14.0	12.3	1.73	41.5
-180 +125	20	15.6	3.13	5.9	20.2	1.19	14.1	13.7	1.94	38.0
-125 +53	20	18.3	3.66	6.0	23.7	1.42	14.0	8.8	1.74	38.8
-53	20	13.2	2.64	6.6	16.4	1.08	13.6	11.5	1.56	40.9

* Calculated

TABLE 4.12

MAGNETIC SEPARATION TESTS OF ARC SLAG

Gap 0.4 cm   Current 0.5 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt. of conc. g	Fe % of con.	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	14.9	2.97	17.0	16.5	2.80	3.0	5.7	0.17	94.3
-2800+1003	20	17.3	3.46	15.0	20.2	3.03	5.0	8.6	0.43	87.7
-1003+600	20	15.1	3.01	13.5	19.3	2.60	6.5	6.3	0.41	86.4
-600 +295	20	14.7	2.95	12.0	18.4	2.20	8.0	9.4	0.75	74.4
-295 +180	20	14.8	2.96	10.9	18.2	1.98	9.1	10.8	0.98	66.9
-180 +125	20	15.6	3.13	10.6	18.3	1.93	9.4	13.0	1.20	61.7
-125 +53	20	18.3	3.66	12.5	20.3	2.54	7.5	14.9	1.12	69.4
-53	20	13.2	2.64	19.5	13.4	2.61	0.5	6.0	0.03	98.9

* Calculated

TABLE 4.13

MAGNETIC SEPARATION TESTS OF ARC SLAG

Gap 1.0 cm   Current 0.2 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt.of conc.	Fe% of con.	Amount of Fe in conc g	Wt. of tailing	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	14.9	2.97	1.9	50.4	0.95	18.1	11.2	2.02	32.0
-2800+1003	20	17.3	3.46	1.05	58.0	0.60	18.95	15.1	2.86	17.3
-1003+600	20	15.1	3.01	0.78	52.3	0.41	19.22	13.5	2.60	13.6
-600 +295	20	14.7	2.95	0.41	47.1	0.19	19.59	14.0	2.76	6.4
-295 +180	20	14.8	2.96	0.75	34.3	0.25	19.25	14.1	2.71	8.4
-180 +125	20	15.6	3.13	0.77	50.1	0.38	19.23	14.3	2.75	12.1
-125+53	20	18.3	3.66	1.2	51.1	0.61	18.8	16.2	3.05	16.7
-53	20	13.2	2.64	No separation						

* Calculated

TABLE 4.14

MAGNETIC SEPARATION TESTS OF ARC SLAG

Gap 1.0 cm   Current 0.5 Amp

Fraction size	Wt.of feed g	Fe % in feed	Amount of Fe in feed g	Wt. of conc. g	Fe % of con.	Amount of Fe in conc g	Wt. of tailing g	* Fe% of tailing	Amount of Fe in tailing g	Fe Recovery %
-3350+2800	20	14.9	2.97	5.23	43.4	2.27	14.77	4.7	0.70	76.4
-2800+1003	20	17.3	3.46	2.86	35.4	1.01	17.14	14.3	2.45	29.2
-1003+600	20	15.1	3.01	3.80	29.1	1.11	16.20	11.7	1.90	36.9
-600 +295	20	14.7	2.95	4.00	22.7	0.90	16.00	12.8	2.05	30.5
-295 +180	20	14.8	2.96	4.76	20.8	0.99	15.24	12.9	1.97	33.4
-180 +125	20	15.6	3.13	5.71	18.9	1.07	14.29	14.4	2.06	34.2
-125 +53	20	18.3	3.66	6.00	21.8	1.30	14.00	16.8	2.36	35.5
-53	20	13.2	2.64	1.50	19.2	0.29	18.50	12.7	2.35	11.0

* Calculated

4.2.2.3 Metallic iron recovery tests

A small hand magnet was employed for the metallic iron prill recovery of the magnetic untreated slags. The plus 53 μm fraction of the samples was spread on a surface to give a monolayer of particles. The hand magnet was then swept over particles by maintaining the distance between the magnet and particles as even as possible. The magnetic particles were attracted to the magnet and were mainly metallic iron particles or particles with small amount of impurity.

The iron grades and recoveries of the concentrates are shown in table 4.15 and figures 4.5 and 4.6.

4.3 Discussion

As can be seen from figures 4.1, 4.2 and 4.3 the grindability of ARC slag is greater than BOS slag for the same grinding period.

The particle size of BOC and ARC slags can be decreased almost linearly up to 60 min grinding period. A transition zone can be detected between 60 min and 90 min grinding. From 90 mins upwards a very small increase was achieved in the grinding rate of the slags.

The magnetic field strength was directly proportional to the iron grade and iron recovery. As the distance between the belt and the pole was increased, lower values of the recovery were obtained, but simultaneously higher iron grades were achieved.

TABLE 4.15
METALLIC IRON RECOVERY RESULTS

Grinding time min	ARC SLAG % material passing 53 micron sieve				BOS SLAG % material passing 53 micron sieve			
	% material passing 53 micron sieve	Weight of mag.conc gram	Wt. % of mag.conc in total	Fe grade % in mag.conc	% material passing 53 micron sieve	Weight of mag.conc gram	Wt. % of mag.conc in total	Fe grade % in mag.conc
7	10.0	37.5	14.9	24.0	10.0	21.0	8.4	24.4
10	16.8	34.0	13.6	29.1	12.3	22.0	8.7	41.7
15	22.6	27.5	11.2	39.7	17.8	18.5	7.5	39.7
20	35.0	21.0	8.5	38.5	27.0	18.5	7.3	53.1
30	52.4	23.0	9.3	49.7	38.0	15.0	6.1	51.7
40	64.5	19.5	7.8	45.8	53.8	11.0	4.4	73.3
60	76.0	18.0	7.2	57.7	66.9	12.5	5.1	69.6
90	90.0	13.0	5.2	68.1	80.8	9.0	3.6	71.0
120	92.0	9.5	3.8	72.0	84.0	9.0	3.6	80.9

FIG 4,5 METALLIC IRON RECOVERY OF BOS STEEL MAKING SLAG

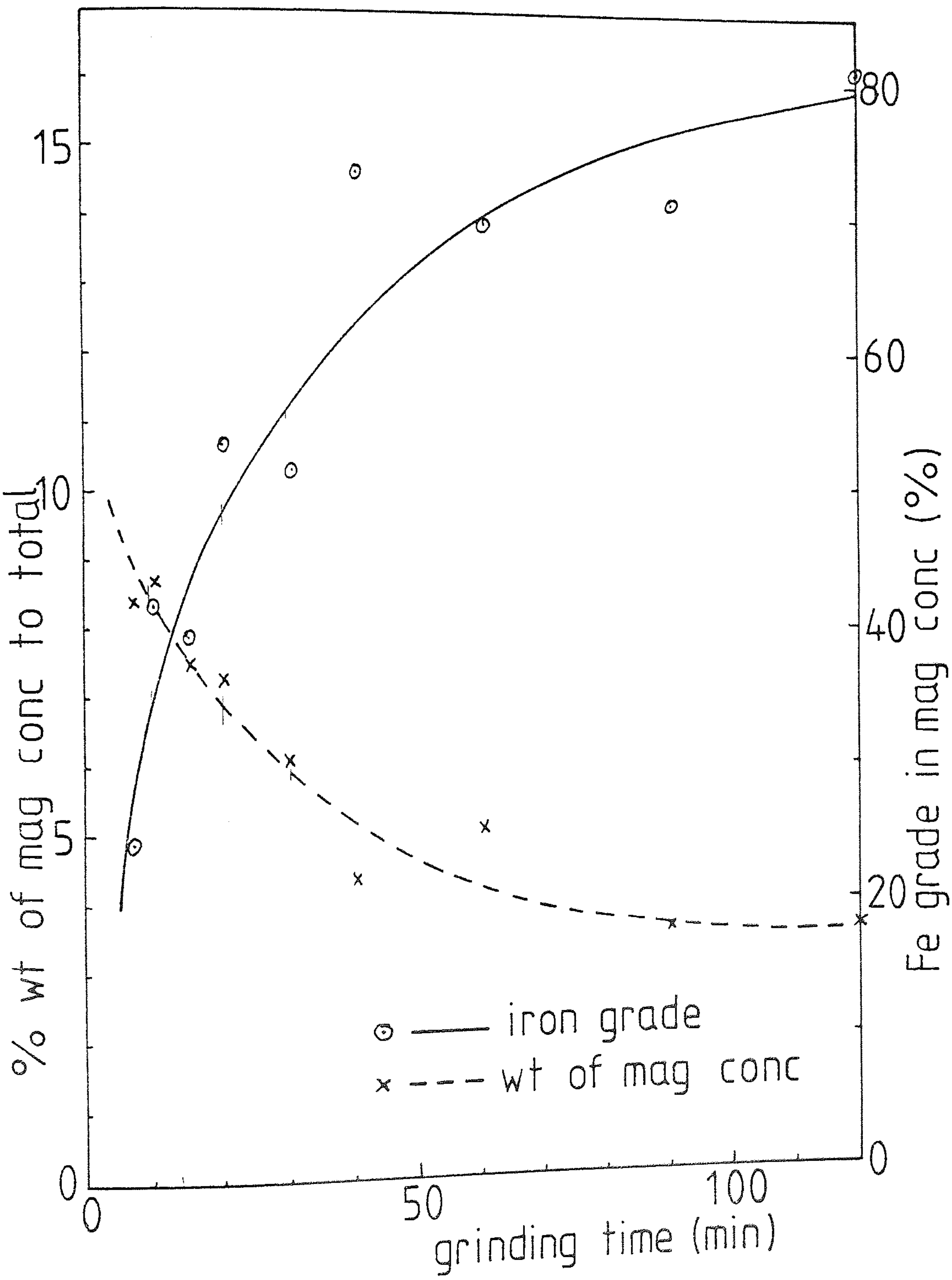
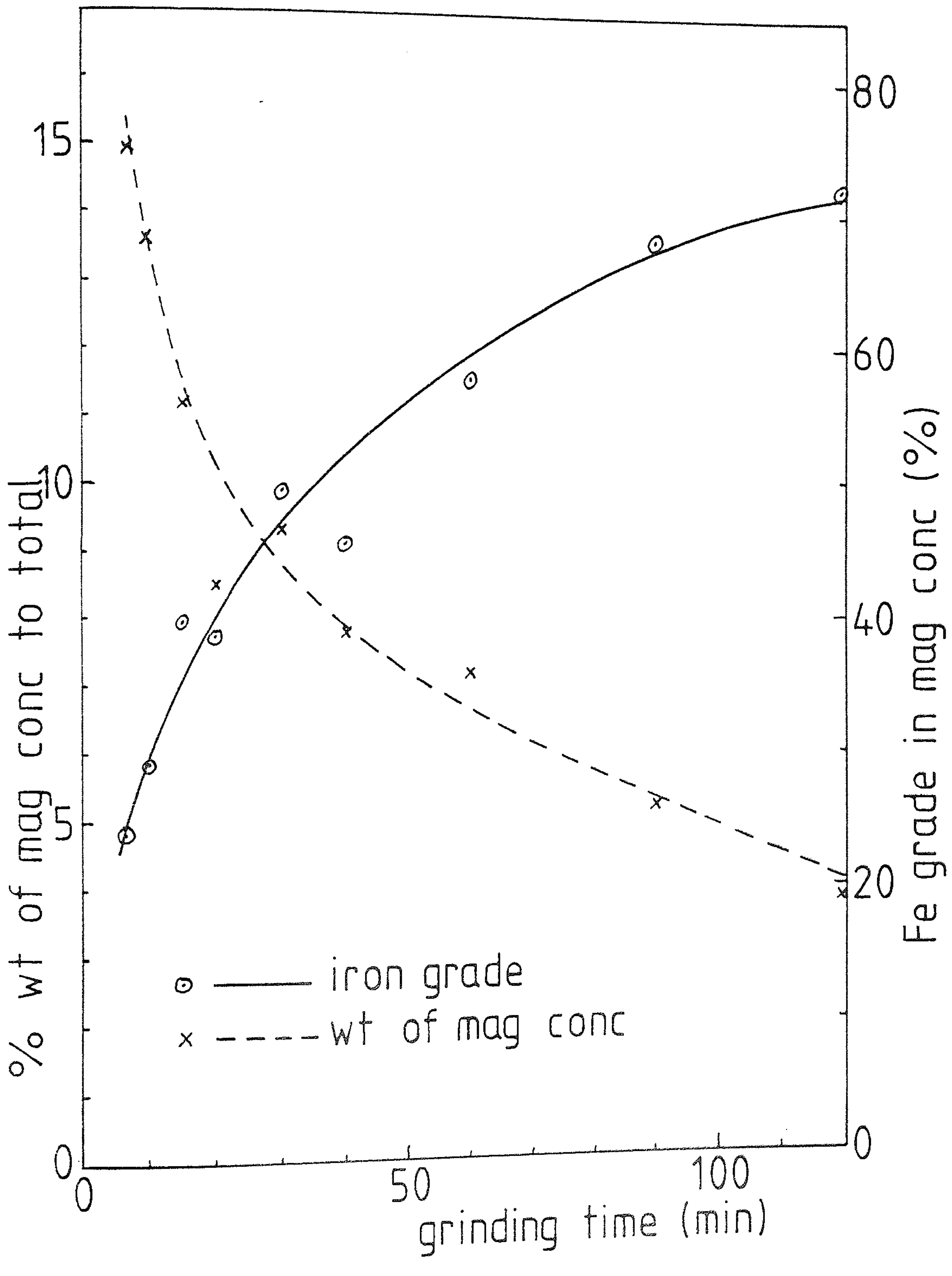


FIG 4,6 METALLIC IRON RECOVERY OF ARC STEEL MAKING SLAG



No separations could be achieved for the fractions finer than 53 µm with the lowest current density and the highest gap distance due to the design limitation of the magnetic separator. Even if these design limitations were overcome it is unlikely the new apparatus would be useful on the industrial scale due to the cost of producing a suitable feed material.

Owing to the high grinding resistance of metallic iron particles of BOS and ARC slags, an enrichment can be spontaneously accomplished by applying a short grinding operation.

Figures 4.5 and 4.6 show that the optimum conditions for metallic prill iron recovery of BOS and ARC slags are given at the intersection point of the curves of iron grades and weight percentage of material in the concentrates. The grinding period for these conditions can be determined along the abscissa.

These conditions for ARC slags gave up to 45% Fe product with 9% of the total sample weight after approximately 30 minutes grinding. BOS slag gave lower values, about 40% Fe grade with 8% material of the total weight after only 15 minutes grinding.

These results indicate that recyclable products may be obtained after a relatively short grinding period by reducing the size of the slags, even though they have been demetallised previously. The economics of such a process can only be determined by pilot and subsequent plant scale tests.

CHAPTER 5

FLOTATION

5.1 Literature Review

5.1.1 Definition and History of Flotation

Flotation is a process for separating finely divided solids from each other by using their surface properties in water and air with the aid of chemical reagents.

Some of the solids, which are suspended in water, are made to adhere to gas bubbles which are generated or introduced, whilst the other solids remain simultaneously unattracted to the bubbles. The adherent solids are removed as a froth of different composition from the pulp.

The earliest use of this principle was by Mansur (33) in the 15th century. He used oil and water to beneficiate ultramarine and azurite.

The first patents were granted to William Haynes in England and to Everson in the U.S.A. for the bulk-oil process (34).

The skin-flotation process patents were obtained in 1892, 1907, and 1914 by various workers (35) and in these cases water was introduced to the bulk-oil system.

Use of gas as a buoyant medium to lighten particles to the point of making them lighter than water was done as early as 1877 by the Bessel brothers (36).

Production of a gas by electrolysis of water and the vacuum generation of gas bubbles were invented by Francis Edward Elmore (37).

Direct size reduction of gas bubbles by a beater or impeller revolving in a pulp was featured in a U.S. patent in 1900 to Sulman, Picard and Ballot and more especially in a U.S. patent in 1910 to Theodore J. Hoover (37). The Hoover apparatus may be recognised as having the essential features of flotation machines of the agitation type.

In 1925 alkali x anthates were recognised as collectors by Keller for sulphide ores and this ended the concept of oil flotation. In about 1935 cationic collectors were used in flotation systems.

5.1.2 Theoretical Aspects of Flotation

5.1.2.1 Thermodynamics of Flotation

5.1.2.1.1 Thermodynamics of Surfaces

The relation between total surface energy and surface tension is

$$E_s = \gamma - T\frac{d\gamma}{dT}$$

where E_s is the total surface energy
γ is the surface tension
T is the temperature

For most liquids the surface tension decreases linearly with temperature (38). The kind of chemical bonds that hold a crystal together have a marked effect on the magnitude of the surface energy of solids. Mineral/ water interfacial tensions are generally much lower than the surface energies, particularly for oxides.

5.1.2.1.2 Thermodynamics of Adsorption

The Gibbs adsorption equation relates the interfacial tension between two phases to the temperature T of the system, the chemical potentials of various species, μ_1, μ_2 ......μ_i, in the bulk and the surface excess or adsorption density of various species Γ_1, Γ_2,......Γ_i at the interface and has the following form (39):

$$d\gamma = -E_s \, dT - \sum_i \Gamma_i \, d \mu_i$$

This equation is highly relevant to flotation through its application to phenomena involving frother systems, wettability, the development of surface charge at mineral/ water interface, etc., because it quantitatively expresses the change in surface tension due to the adsorption of surface active materials.

5.1.2.1.3 Thermodynamics of Wetting

Bubble-particle contact is one of the key factors controlling the process of froth flotation (40).

The general thermodynamic condition for three phase contact is defined by Young's equation for the system depicted schematically in Figure 5.1.

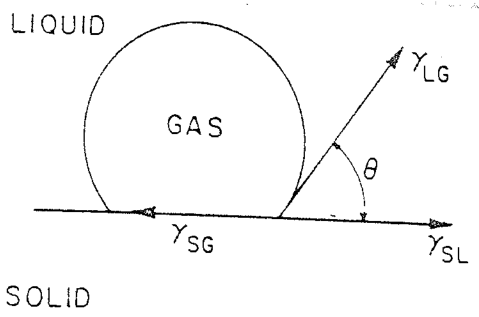


FIGURE 5.1 Schematic representation of the equilibrium contact between an air bubble and a solid immersed in a liquid.

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \text{ Cos } \Theta$$

where γ_{SG}, γ_{SL} and γ_{LG} are the tensions of the solid/gas, solid/liquid and liquid/gas interfaces. The change in the free energy is given by the Dupre's equation:

$$\Delta G = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

Combination of the Dupre's equation with Young's equation gives the following expression for the free energy change:

$$\Delta G = \gamma_{LG} (\text{Cos } \Theta - 1)$$

These two equations are for ideal systems. Several authors (41-44) have done work on the bubble-particle contact by taking into account different factors. They have found that gravitational forces, surface roughness, contamination and temperature, etc., are the main factors which should also be considered at the bubble-particle contact system.

5.1.2.2 Electrical Double Layer at Mineral/Water Interfaces

The adsorption phenomena at mineral/water interfaces is usually controlled by the electrical double layer.

This involves the solid surfaces with a charge and the counter ions make up the surface charge to maintain electroneutrality in an aqueous media (45), Figure 5.2.

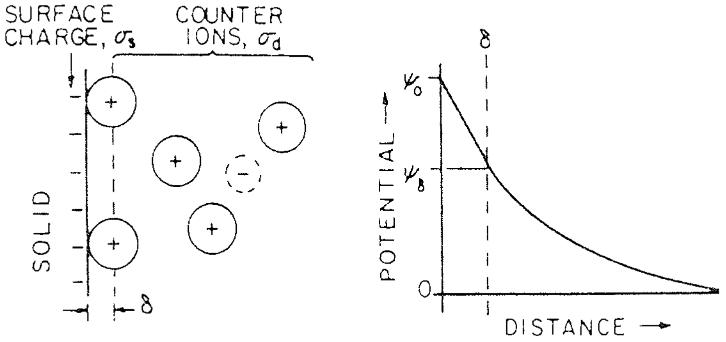


FIGURE 5.2 Schematic representation of the electrical double layer and the potential drop

The closest distance of counter ions to the surface is $(\overset{\delta}{\gamma})$ the stern plane. The surface potential is ψ_0 and at the stern plane $\psi_{\gamma\delta}$. The ions which establish the electrical double layer are called potential-determining ions and they are unique for each class of solid. For oxide minerals, hydrogen and hydroxyl have been considered to be potential-determining ions (46). For example, when Quartz is crushed under water, silicon to oxygen bonds are broken and these broken bonds are very reactive and react with water to give a surface silicic acid. The dissociation of this acid is of course pH dependent (47). This is shown schematically in Figure 5.3

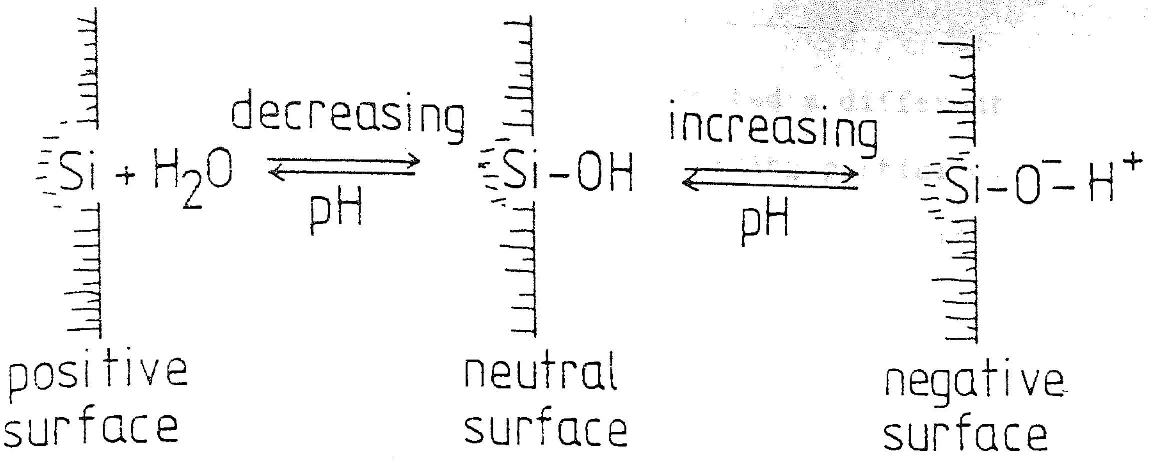


FIGURE 5.3 Schematic representation of the pH dependence of silicic acid

The net charge on the mineral surface will be zero, when the right condition is obtained. The activity of potential-determining ions at which the zero charge occurs is called the point of -zero- charge (pzc).

The importance of the pzc is that the sign of the surface charge has a major effect on the adsorption of all other ions and particularly oppositely charged ones maintaining electroneutrality.

If the counter ions are adsorbed by electrostatic attraction, they are called indifferent electrolytes.

5.1.2.3 The Electrical Double Layer on Oxide Minerals

Since oxide minerals form hydroxylated surfaces when in contact with water; dissociation of H^+ caused by the surface adsorption, hydroxyls can account for the surface charge on the oxide (48,49)

$$MOH_{surf} \rightleftharpoons MO^-_{surf} + H^+_{aq}$$

$$MOH_{surf} + H^+_{aq} \rightleftharpoons MOH_2^+{}_{surf}$$

Parks and Bruyn (50,51) have suggested a different mechanism for oxide surfaces, involving partial dissociation of the oxide and formation of hydroxyl complexes in solution.

$$M_2O_{3\ \mathrm{solid}} + 3H_2O \rightleftharpoons 2M(OH)_{3\ \mathrm{aq}}$$

$$M(OH)_{3\ \mathrm{aq}} \rightleftharpoons M(OH)^{3-m}_{m\ \mathrm{aq}} + (3-m)OH^-_{\mathrm{aq}}$$

$$M(OH)^{3-m}_{m\ \mathrm{aq}} \rightleftharpoons M(OH)^{3-m}_{m\ \mathrm{surf}}$$

The formation of a surface charge by any mechanism would result in an equivalent change in the pH of solution (52).

The effect of temperature on the double layer was studied by various workers (53,54,55) and they found that the pzc of oxides decreases with increasing temperature. In addition to the shifting of the pzc, temperature also affects the charge on the surface of minerals.

5.1.2.4 Effect of Collector Adsorption on Flotation

In order to reduce molecular attraction between the solid and liquid, the collector must be adsorbed at solid/liquid interface.

Bleier et al (56) have reported that there is a good correlation between the flotation recovery of quartz in the presence of amines and the decrease in the surface tension of the water/air interface.

Collector adsorption systems can be divided into three groups

(1) Physisorption
(2) Chemisorption
(3) Chemically reacting collectors,

The latter can be considered under (2).

The first one is characterised by a heat evolution and adsorption decreases with increase in temperature. The ions are adsorbed only through such forces as electrostatic attraction and hydrophobic bonding (in the use of collectors the hydrocarbon chains are attracted by Van der Waal's forces to the surfaces). Ball and Fuerstenau (57) worked on the aqueous dodecylammonium acetate/quartz system, in which there was a decrease in the adsorption density and a shift in the pzc as the temperature went up.

As the temperature increases the recovery in flotation increases with chemisorption. The collector forms covalent bonds with metal ions in the surface of the mineral and this causes a strongly adsorbed film which is difficult to remove, such as hydroxamates strongly chemisorb on chrysocolla and hematite.

5.1.2.5 pH Effect on Flotation

The effect of pH on flotation systems is great, especially with respect to collector ionization, surface charge and mineral solubility. Therefore, any study of flotation has to take into account the temperature dependence of the dissociation constant of water and pH (58). This will be discussed in detail in the next sections.

5.1.3 Collectors

5.1.3.1 Cationic Flotation of Oxides and Silicates

5.1.3.1.1 Types of Cationic Collectors

A number of cationic surfactants have been used as flotation collectors for oxide minerals. The widely used ones are amines, particularly primary amines.

Collecting properties of these surfactants depend on such characteristics as ionization constant, solubility, ionic head size, hydrocarbon chain length, branching of the hydrocarbon chain and critical micelle concentration (CMC) (59), Tables 5.1 and 5.2.

Patches of associated collector ions at the mineral/water interface have been termed hemimicelle by Gaudin and Fuerstenau, and the concentration at which they form the critical hemimicelle concentration C.H.M.C. This is shown diagramatically in Figure 5.4

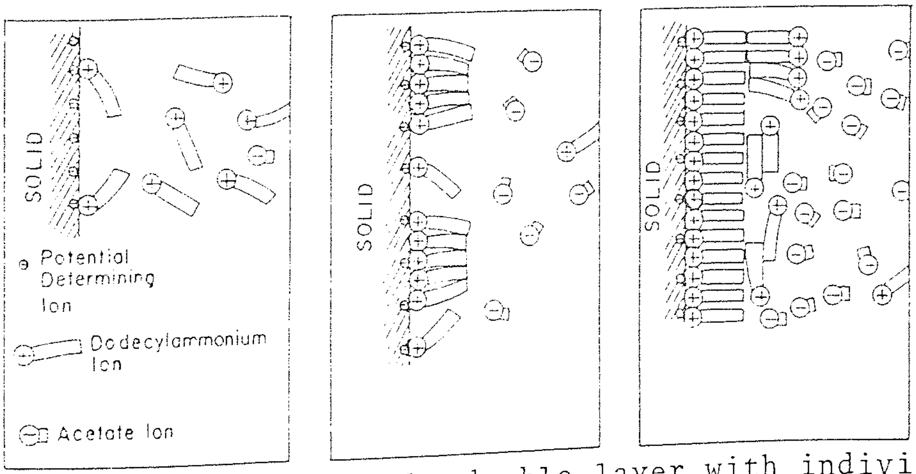


FIGURE 5.4 Structure of the double layer with individual ion adsorption (left), hemi-micelle formation centre, and multi-layer adsorption (right)

TABLE 5.1

CATIONIC COLLECTORS

Collector	Formula*	Ion
Primary Amine salt	$RNH_3C\ell$	RNH_3^+
Secondary Amine salt	$RR^1NH_2C\ell$	$RR^1NH_2^+$
Tertiary Amine salt	$R(R^1)_2NHC\ell$	$R(R^1)_2NH^+$
Quarternary Ammonium Salt	$R(R^1)_3NC\ell$	$R(R^1)_3N^+$
Sulfonium salt **	$RS(R^1)_2C\ell$	$RS(R^1)_2{}^+$
Alkyl Pyridinium salt		

* R represents a hydrocarbon chain usually 10 carbon atoms or greater, R^1 is a short alkyl chain usually a methyl group.

** Phosphonium, iodinium and arsenium compounds are also known.

TABLE 5.2

PHYSICAL CONSTANTS OF SELECTED 12-CARBON PRIMARY. SECONDARY, TERTIARY, AND QUARTERNARY AMINES

Amine	Ionization constant	Solubility of Molecular Species (M)	Diameter of charged head (A^o)	CMC (M)
N - dodecylamine	4.3×10^{-4} 25^oC	2×10^{-5} 25^oC	3.7	0.014 30^oC (Chloride Salt)
N - Methyldodecylamine	10.2×10^{-4}	1.2×10^{-5}	intermediate	
Dimethyldodecylamine	5.5×10^{-5}	7.2×10^{-6}	intermediate	
Trimethyldodecylammonium hydroxide	1 (The hydroxide is very strong base)	Not applicable	5.9	0.016-0.020 30^oC (Chloride Salt)

The solubility of the molecular species and critical micelle concentration depend strongly on hydrocarbon chain length (60,61).

Measurement of the CMC was made at the natural pH of these systems and the values of CMC decreases with increase in pH value of solution. An increase in ionic strength of a solution will also decrease the CMC (62).

5.1.3.1.2 Adsorption of Cationic Collectors at the Solid/Liquid Interface

Several methods of studying adsorption of cationic surfactants at solid/liquid interfaces have been employed. These include adsorption isotherms, electro kinetic data and contact angle measurements (63,64,65-72).

The following general statements can be made for the mechanism of adsorption of cationic surfactants.

1 - According to the hemimicelle concept of adsorption, for significant adsorption to occur, the surface potential of the substrate should be negative, so that the H.C.M.C. is reached before the CMC in solution. However, flotation is possible below the pzc when longer-chained homologues are used.

2 - The effect of hydrocarbon chain length on adsorption is related to the free energy decrease due to the expulsion of each CH_2 group from the aqueous phase by association of hydrocarbon chains. A lower

quantity of collector is required for longer chained collectors.

3 - The hemimicelle concentration depends on the ratio of charged to neutral species in the double layer.

4 - The effect of pH in adsorption
  (a) H^+ and OH^- establish the surface electrical potential, and

  (b) OH^- concentration establishes the extent of hydrolysis of weak base collector.

5 - Neutral molecules lower the CMC and C.H.M.C. and increase the negative electrical potential of the double layer.

6 - Inorganic cations reduce collector adsorption.

7 - Multi-valent anions (such as SO_4^{2-} and SiF_6^{2-}) have potential for adsorbing on positive sites on minerals and promote adsorption of cationic collectors on positively-charged oxides and silicates.

5.1.3.1.3 Effect of Basicity

In the case of amines which have weak bases, the association constant is important because it determines the proportion of ionic species to neutral molecules in the system (59).

The following is the example for dodecylamine:

$$RNH_{2(aq)} + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$K_b = \frac{[RNH_3^+]\,[OH^-]}{[RNH_{2\ aq}]} = 4.3 \times 10^{-4}$$

$$RNH_{2(s)} + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$K_{so} = [RNH_3^+]\,[OH^-] = 8.6 \times 10^{-9}$$

$$RNH_{2(s)} \rightleftharpoons RNH_{2(aq)}$$

$$K_s1 = [RNH_{2(aq)}] = 2 \times 10^{-5}$$

From these equations it can be seen that pH substantially changes the form of dodecylamine.

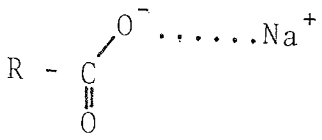
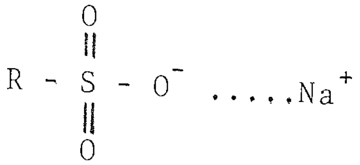
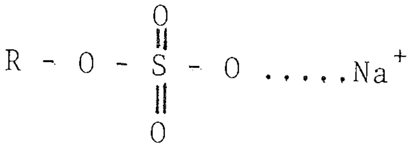
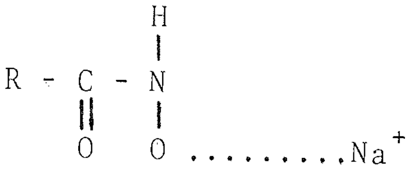
5.1.3.1.4 Effect of Long Chained Neutral Molecules

The presence of neutral long-chained molecules can be attributed to the lowering of the CMC. The principal function of the neutral molecules is to lower the electrostatic energy of repulsion between adjacent charged ionic polar groups of the collector (73).

5.1.3.2 Anionic Flotation of Oxides and Silicates

5.1.3.2.1 Types of Anionic Collectors

Oxides and silicates can be floated with several anionic collectors which generally have more than 10 carbon atoms. The chemical structure of various anionic collectors are presented as follows:

Collector	Structural Formula
Carboxylate	 $R-C(=O)-O^{-}\cdots\cdots Na^{+}$
Sulphonate	 $R-S(=O)_2-O^{-}\cdots\cdots Na^{+}$
Alkyl sulphate	 $R-O-S(=O)_2-O\cdots\cdots Na^{+}$
Hydroxamate	 $R-C(=O)-N(H)-O\cdots\cdots\cdots Na^{+}$

R represents the hydrocarbon chain

The presence of double bonds increases the solubility significantly over that of saturated homologues, (Oleic acid and abietic acid) (38) and the stability of metal-collectors assumes a most significant role in these systems (57).

In addition to these properties, the strength of the acids of the various anionic collector is also important (39,42,56). The carboxylic and hydroxamic acids are weak acids where as sulphonic and alkyl sulphuric acids are strong acids.

5.1.3.2.2 Specific Adsorption

5.1.3.2.2.1 Anion Adsorption

Divalent anions, such as sulphate, have been shown to adsorb specifically on positively-charged surfaces whereas univalent ions, such as chloride, do not. Modi and Fuerstenau (74,75) have shown that corundum changes zeta potential sign at pH 6.5 in the presence of 5.10^{-4} mole, litre^{-1} sodium sulphate but keeps a positive sign with 10^{-1} mole, litre^{-1} NaCl.

5.1.3.2.2.2 Cationic Adsorption

Polyvalent metal ions also adsorb specifically on oxides and silicates, this phenomenon occurs when the cation involved hydrolyses to its first hydroxyl complex.

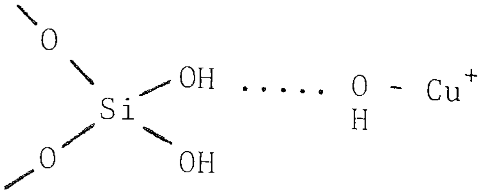
Adsorption experiments by Clark and Cooke (76) show limited adsorption of hydrated calcium ion on quartz from approximately pH 4 to 11. However, in the pH range where $CaOH^+$ is present in significant concentration, namely above about pH 11 extensive adsorption of $CaOH^+$ occurs.

Similar observations have been made in the aluminium/quartz system (77,78), the iron/quartz system (79), the nickel/quartz system (80) and the ferrous iron/chromate system (81).

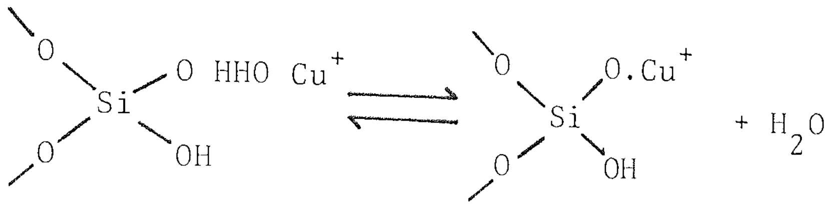
Three mechanisms of adsorption have been suggested (82,83)

1 - Water formation by combination of the hydroxyl ion of the hydroxy complex and adsorbed hydrogen ion. Hydrogen bonding could occur between adsorbed

hydrogen ion and the hydroxy complex as follows (82):



2 - Hydrogen bonding of hydroxy complex with the surface



3 - Formation and adsorption of metal hydroxide on solid surface.

5.1.4 Effect of Mineral Crystal Structure on Flotation

The nature of floatability of a mineral largely depends on its crystal structure. The types of bonds holding atoms together in crystals have a significant effect on determining the surface properties.(84)

It is strongly believed that 2 $CaO.SiO_2$ and $3CaO.SiO_2$ are in the orthosilicate group. With fracture of the Si-O bonds a polar surface results, i.e. a hydrophilic surface.

5.1.5 Activators

These reagents alter the chemical nature of mineral surfaces so that they become hydrophobic due to the action of the collector. Activators are generally soluble salts which ionise in solution, the ions then react with the mineral surface.

Soluble metallic salts activate quartz and silicates for flotation with anionic collectors in certain pH regions. Where the neutral hydroxide or hydroxy complex is adsorbed, the adsorption of hydroxy species causes the quartz zeta potential to change sign and become positive. Anionic collector ions are then adsorbed by Coulombic attraction and as a result flotation is obtained (85).

5.1.6 Depressants

Depression is used to increase the selectivity of flotation by rendering certain minerals hydrophillic, thus preventing their flotation.

In the absence of metal salts, flotation with dodecylamine is obtained over most of the pH range. This, of course, corresponds to the fact that the quartz surface is negative and thus Coulombic adsorption of cationic amine can take place. In the presence of metal salts the quartz will have positive zeta potential in certain pH ranges. Coulombic adsorption of amine will not, therefore, take place under these conditions and metal species (such as $FeCl_2$, $AlCl_3$, $Pb(NO_3)_2$) can be said to act as depressants.

The pH regions in which the depression is obtained with a collector of amines correspond to the pH regions in which the metal species acts as activator for anionic collector flotation (86).

Starches are used as depressants successfully in cationic flotation of quartz from iron oxides. The adsorption of a cationic starch increases with increasing pH indicating a strong electrostatic interaction between the positively charged functional groups of the starch and the negatively charged mineral surface (87). Quartz is more electronegative than hematite in aqueous solution for the pH range 7-11, since their pzc's are at a pH near 2 and 6.7 respectively, and, hence attract a great amount of cationic starch as compared to the attraction by hematite.

Sodium silicate is used as a dispersant for slimes coating mineral surfaces, but it is also used as a depressant in some systems, depressing silicates and calcite in fluorite-calcite and scheelite-calcite separations.

5.1.7 Frothers

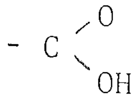
When mineral surfaces have been rendered hydrophobic by the use of a collector stability of bubble attachment, especially at the pulp surface, depends to a considerable extent on the efficiency of the frother.

Frother action is due to the ability of the frother to adsorb on the air-water interface, because of its surface activity and to reduce the surface tension, thus stabilising the air bubble.

Frothers must be to some extent soluble in water in order to be distributed evenly in an aqueous solution. Most effective frothers include in their composition one of the following groups:

Hydroxyl - OH

Carboxyl



$-C\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}$

Carbonyl = C = O

Amino group - NH_2

Sulpho group - OS_2OH - SO_2OH

The acids, amines and alcohols are the most soluble of frothers. Pine oil which contains aromatic alcohols, the most active frothing component being terpineols, $C_{10}H_{17}OH$, has been widely used as a frother. Cresol (cresylic acid) $CH_3C_6H_4OH$, has also had wide use.

5.1.8 Temperature and Conditioning

The temperature of flotation systems, especially for those in which collectors adsorb chemically, is important because temperature controls mineral solubility, collector solubility and mobility of collector ions. For example, Cooke, Iwasaki and Choi (88) obtained 10% recovery of hematite from an iron ore using stearic acid as collector at 25°C and recovery was found to be 96% at 50°C.

In the case of very insoluble oxides, such as hematite and silicates, conditioning assumes a most significant role. A hematitic ore (89), which contained 42% iron was conditioned for three minutes in the presence of a collector, recovery was only 19%. With 5, 7 and 10 minute conditioning periods in the absence of collector, recoveries of 56, 73 and 72 percent were obtained.

However, with minerals that possess greater solubility in water than hematite conditioning in the absence of collector results in decreased flotation response.

5.2 Experimental Work

5.2.1 Grinding of samples

Samples of ARC and BOS slags were ground in 500 g samples in a rod mill after being crushed in a jaw crusher. The grinding period was maintained for 60 minutes before separating the metallic iron prills magnetically from the product. This was achieved on a Rapid magnetic separator, using a gap of 10 mm between the poles and a current density of 2.5 amp. The non-magnetic fractions were then returned to the mill for a further 60 minute grinding. The finished products were stored in polythene bags.

79.1% of BOS slag and 86.4% of ARC slag were finer than 45 μm after this grinding process.

5.2.2 Flotation Test Procedure

All flotation tests were carried out in a 2.5ℓ Fagergren type flotation machine. 500 g batches of samples were prepared from mixed ground products by riffling. Samples were initially conditioned with 1000 cc water and Na_2SiO_4 as dispersant for 5 minutes. The speed of the impeller was maintained at a high r.p.m. value. The pulp was then deslimed to give a cut size less than 10 μm and this repeated again after another 5 minute conditioning. The deslimed pulp was returned to the machine and the make up water was added to give the initial pulp density. The desired pH was obtained by using diluted H_2SO_4 acid. After 2 minutes conditioning the collector was introduced and followed by 5 minutes conditioning. The pulp was then made up to 2500 cc volume by adding water and the speed of the impeller decreased. The frother was added to the pulp dropwise and after 2 minutes conditioning air was introduced to the system. The pulp was floated for 5 minutes. The products were collected in separate dishes and dried for metallurgical assessment. Table 5.3 shows the chemical reagents used in the flotation tests.

5.2.3 Effect of Free Lime

Owing to the high free lime content of the slags which was 8.0% for ARC slag and 5.5% for BOS slag, determined by W.C. Hanna method (90), the pulp had a very high pH value which was about 12.5. The free lime in the pulp was hydrolysed to form calcium hydroxide which gave was hydrolysed to form calcium hydroxide which gave calcium sulphate from the reaction with sulphuric acid, as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O$$

An excessive amount of calcium sulphate was caused by these reactions as well as causing a high consumption of sulphuric acid to obtain the desired pH value. The relationship between the acid consumption and the excess amount of material produced according to the pH values are shown in Figures 5.6 and 5.7, and tables 5.4 and 5.5.

TABLE 5.3

THE CHEMICAL REAGENTS USED IN FLOTATION TESTS

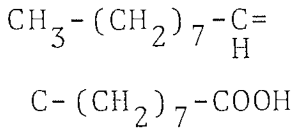
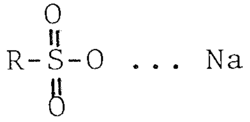
Name	Composition	Application	Consumption g/tonne	Feed concentration
Sodium Silicate	Na_2SiO_4	Dispersant	1000	10% solution
Sulphuric Acid	H_2SO_4	pH modifier	variable	10% solution
Acetic Acid	CH_3COOH	pH modifier	variable	10% solution
Oleic Acid	 $CH_3-(CH_2)_7-\underset{H}{C}= C-(CH_2)_7-COOH$	Collector	230	2.5% solution
Na-Laurylsulphate	 $R-\overset{O}{\underset{O}{S}}-O \ldots Na$	Collector	250	2.5% solution
Lauryl Amine	RNH_3	Collector	250	1% solution
Terpineol	$C_{10}H_{17}OH$	Frother	80	concentrated

TABLE 5.4

H_2SO_4 COMSUMPTION OF BOS SLAG IN FLOTATION

pH value of the pulp	Volume of 20% H_2SO_4 ml	Volume of Con. H_2SO_4 ml	Wt. of H_2SO_4 added kg/tonne
12.4	-	-	-
11.0	60	12	44.2
9.5	120	24	88.4
9.0	180	36	132.6
8.0	240	48	176.8
6.5	300	60	221.0
5.5	360	72	265.2
4.2	410	82	301.7
3.5	460	92	338.5

FIG 5,6 pH VALUES OF FLOTATION PULP (500g solid / 1000cc water) AS A FUNCTION OF H_2SO_4 ADDED

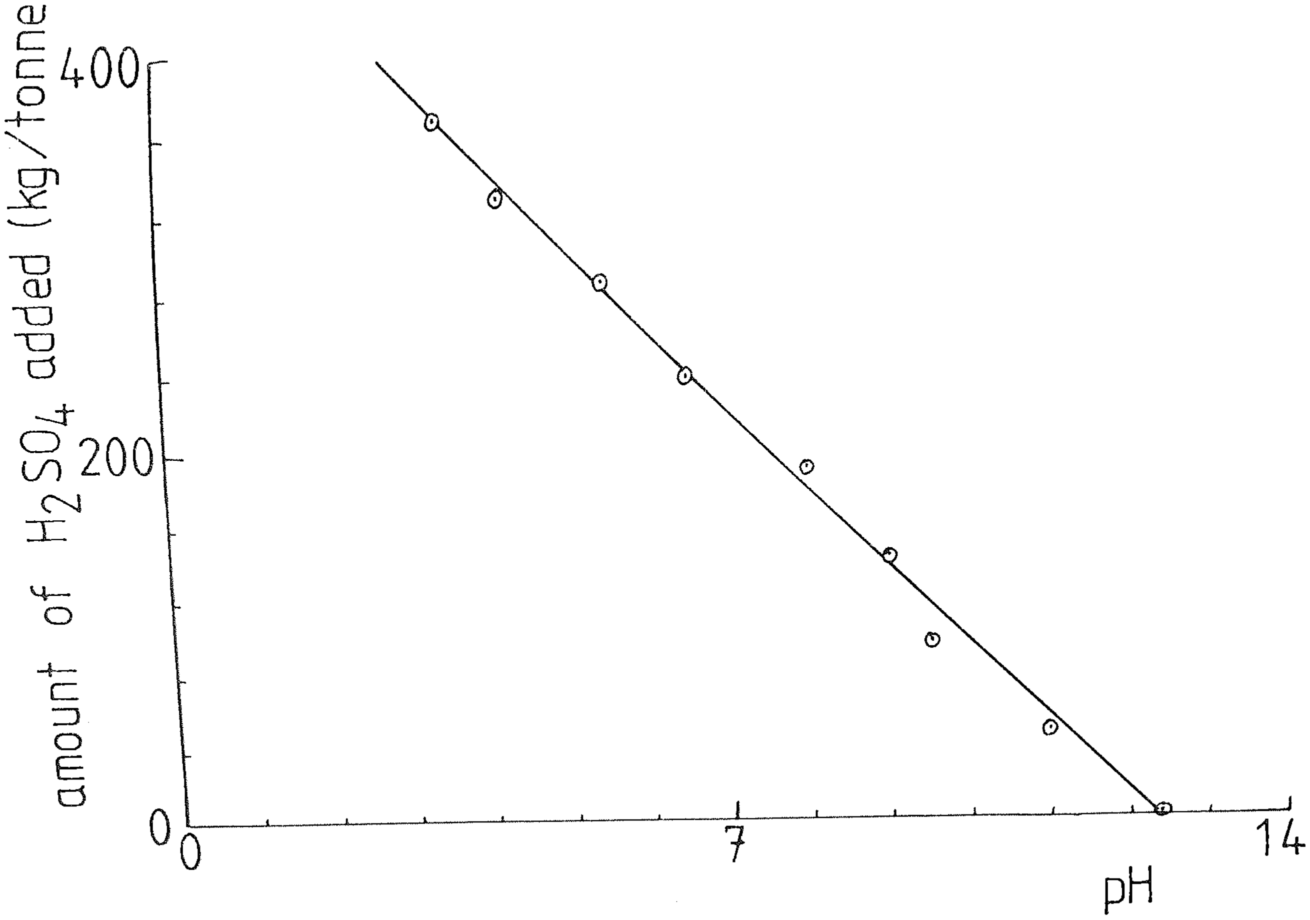
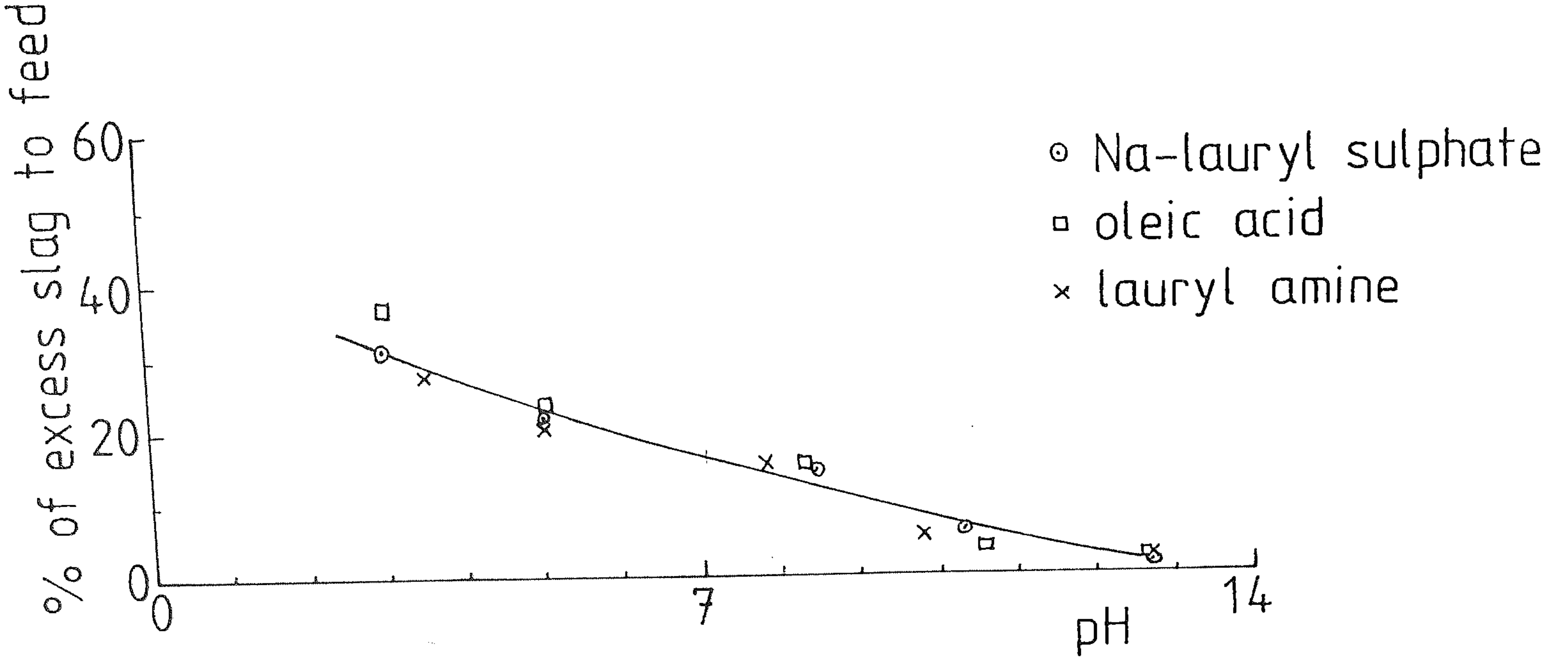


TABLE 5.5

EXCESS AMOUNT OF BOS SLAG PRODUCED WITH H_2SO_4 IN FLOTATION TESTS

With oleic acid			With Na-lauryl sulphate			With lauryl amine		
pH	Excess slag g	% of the feed	pH	Excess slag g	% of the feed	pH	Excess slag g	% of the feed
12.7	10	2.0	12.6	12	2.4	12.6	14	2.8
10.5	24	4.8	10.3	30	6.0	9.8	28	5.6
8.3	79	15.8	8.4	74	14.8	7.8	79	15.8
5.5	114	22.8	5.0	109	21.8	5.5	102	20.4
3.0	188	37.6	3.0	157	31.4	3.5	140	28.0

FIG 5,7 EXCESS AMOUNT OF SLAG PRODUCED WITH COLLECTORS AS A FUNCTION OF pH



It was thought that a weak acid would give better results in respect of acid consumption and particle-acid reaction. Acetic acid was employed for this purpose in dilute solution. Results with this acid are shown in table 5.6 and figure 5.8.

It was assumed that the reaction took place as follows:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$2CH_3COOH + Ca(OH)_2 \rightarrow (CH_3COO)_2Ca + 2H_2O$$

5.2.4 Results

The iron content of the products, float, tailing and deslime, was determined by wet chemical methods on dried samples.

The effect of pH value was found for different types of collectors, such as anionic and cationic collectors. These results are shown in tables 5.7-5.12 and figures 5.9-5.14.

The effect of the collector concentration was also determined by using Na-Lauryl sulphate at the natural pH of the slag and results are shown in table 5.13 and figure 5.15.

5.2.5 Discussion

Although the fineness of ground flotation samples seems not to be satisfactory for the grain liberation (see chapter 3) if the size reduction takes place along the grain boundaries this should give at least particles with

TABLE 5.6

ACETIC ACID CONSUMPTION OF BOS SLAG IN FLOTATION

BOS SLAG

Acetic Acid kg/tonne	pH	Extra amount of slag g	% of total
-	12.7	12	2.4
84	9.5	10	2.0
294	6.5	39	7.8
356	4.0	55	11.0

FIG 5,8 ACETIC ACID CONSUMPTION

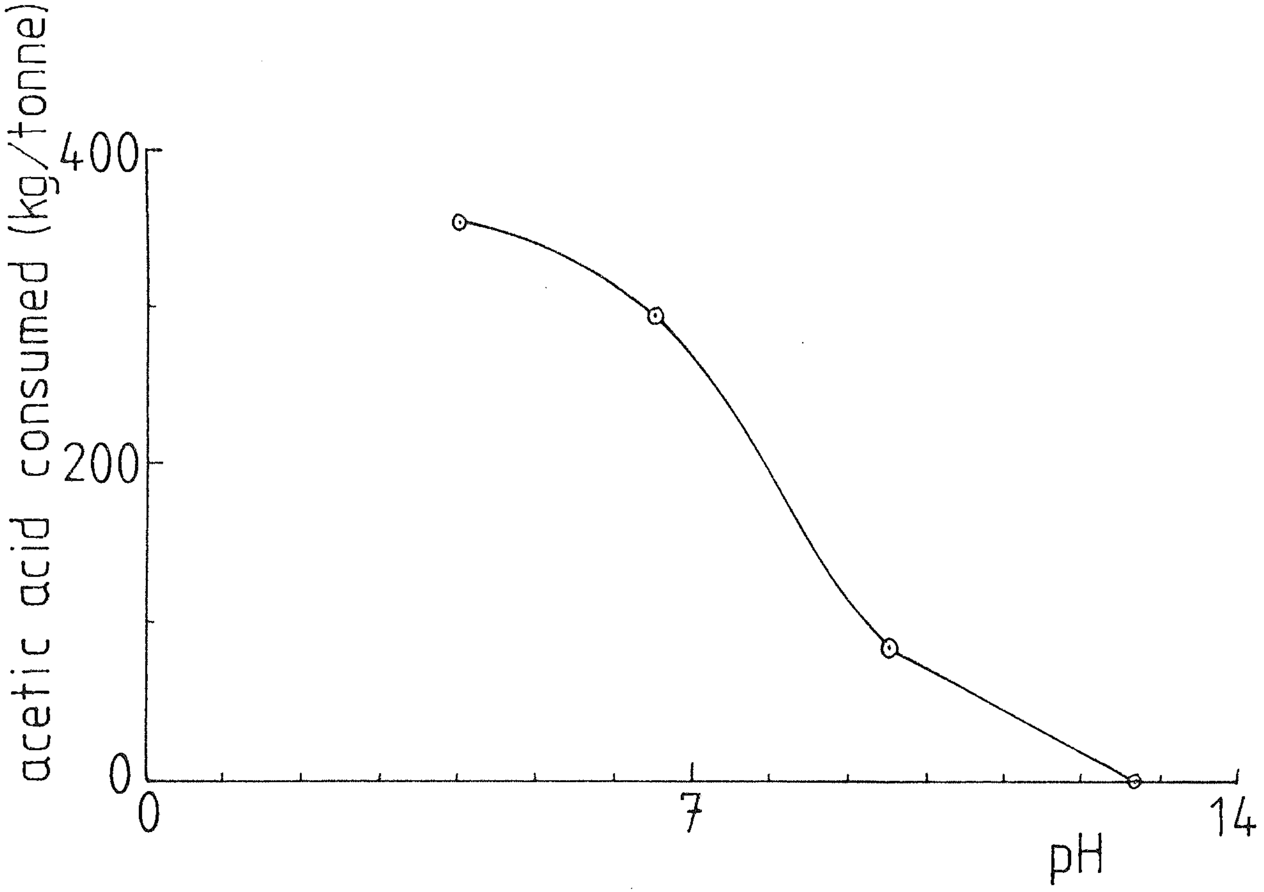


TABLE 5.7

FLOTATION RESULTS OF BOS SLAG WITH Na-LAURYL SULPHATE

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	Test pH	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	19.4	97.0	12.6	232	18.9	43.8	45.1	254	19.1	48.5	50.1	26	18.2	4.7	4.8
500	19.3	96.5	10.3	278	17.4	48.3	50.0	192	18.8	36.0	37.4	60	20.4	12.2	12.6
500	19.7	98.5	8.4	414	16.2	67.0	68.0	140	19.9	27.8	28.3	20	18.3	3.7	3.7
500	19.1	95.5	5.0	488	15.0	73.2	76.7	105	18.6	19.5	20.4	16	17.8	2.8	2.9
500	19.4	97.0	3.0	504	13.8	69.5	71.7	128	17.8	22.8	23.5	25	19.0	4.7	4.8

FIG 5,11 FLOTATION RESULTS OF BOS SLAG WITH Na-LAURYL SULPHATE

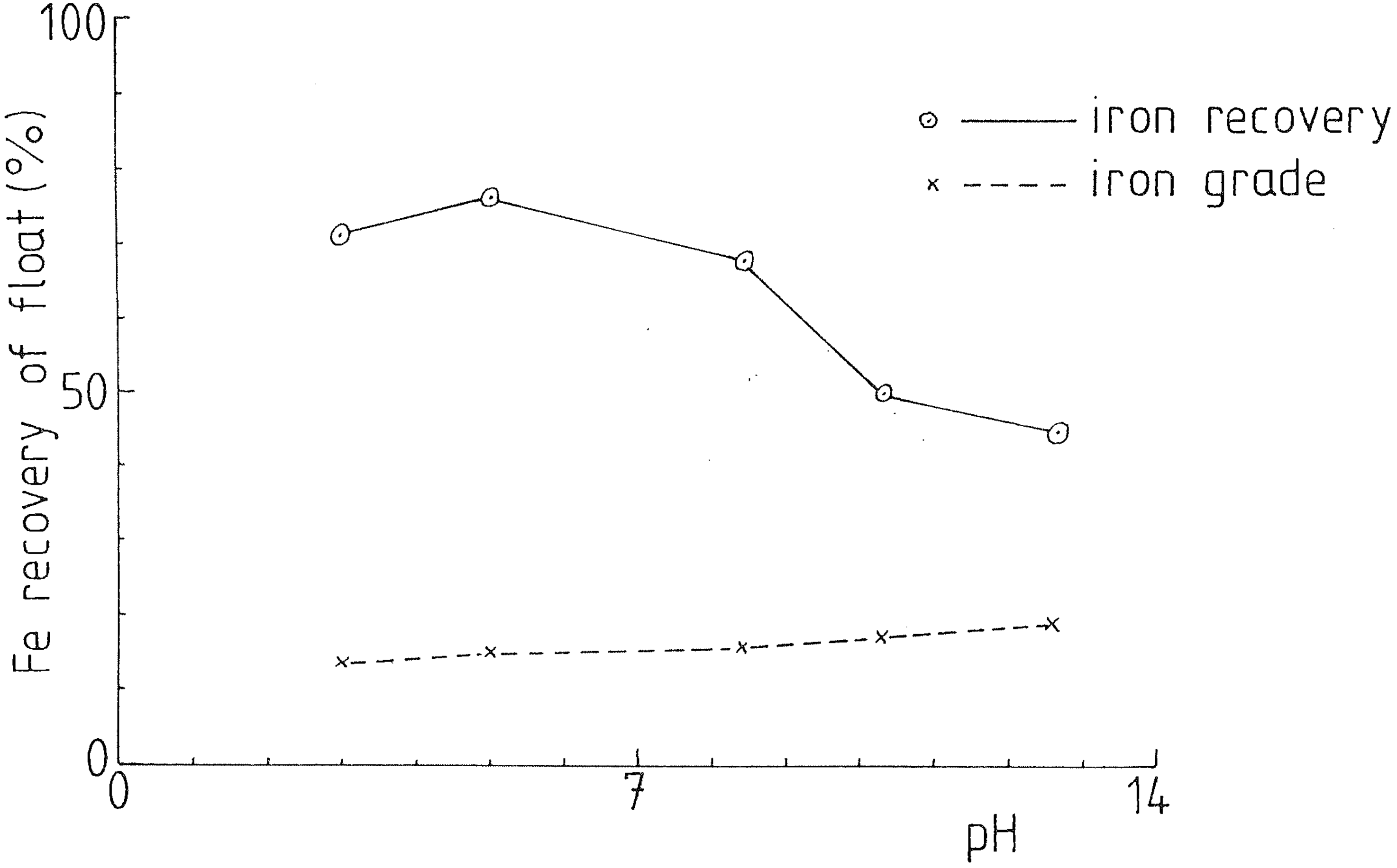


TABLE 5.8

FLOTATION RESULTS OF BOS SLAG AS A FUNCTION OF pH WITH ACETIC ACID AND 500g/tonne Na-LAURYL SULPHATE

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	pH	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	20.3	101.5	12.7	274	20.1	55.0	54.2	228	19.9	45.3	44.6	10	11.6	1.2	1.2
500	20.2	101.0	9.5	318	19.9	63.2	62.6	158	20.2	31.9	31.6	34	17.4	5.9	5.8
500	20.5	102.5	6.5	266	18.4	48.9	47.7	267	19.8	52.8	51.5	6	14.0	0.8	0.8
500	20.0	100.0	4.0	380	18.0	68.4	68.4	150	18.4	27.6	27.6	25	16.1	4.0	4.0

FIG 5,10 FLOTATION RESULTS OF BOS SLAG WITH ACETIC ACID AND Na-LAURYL SULPHATE

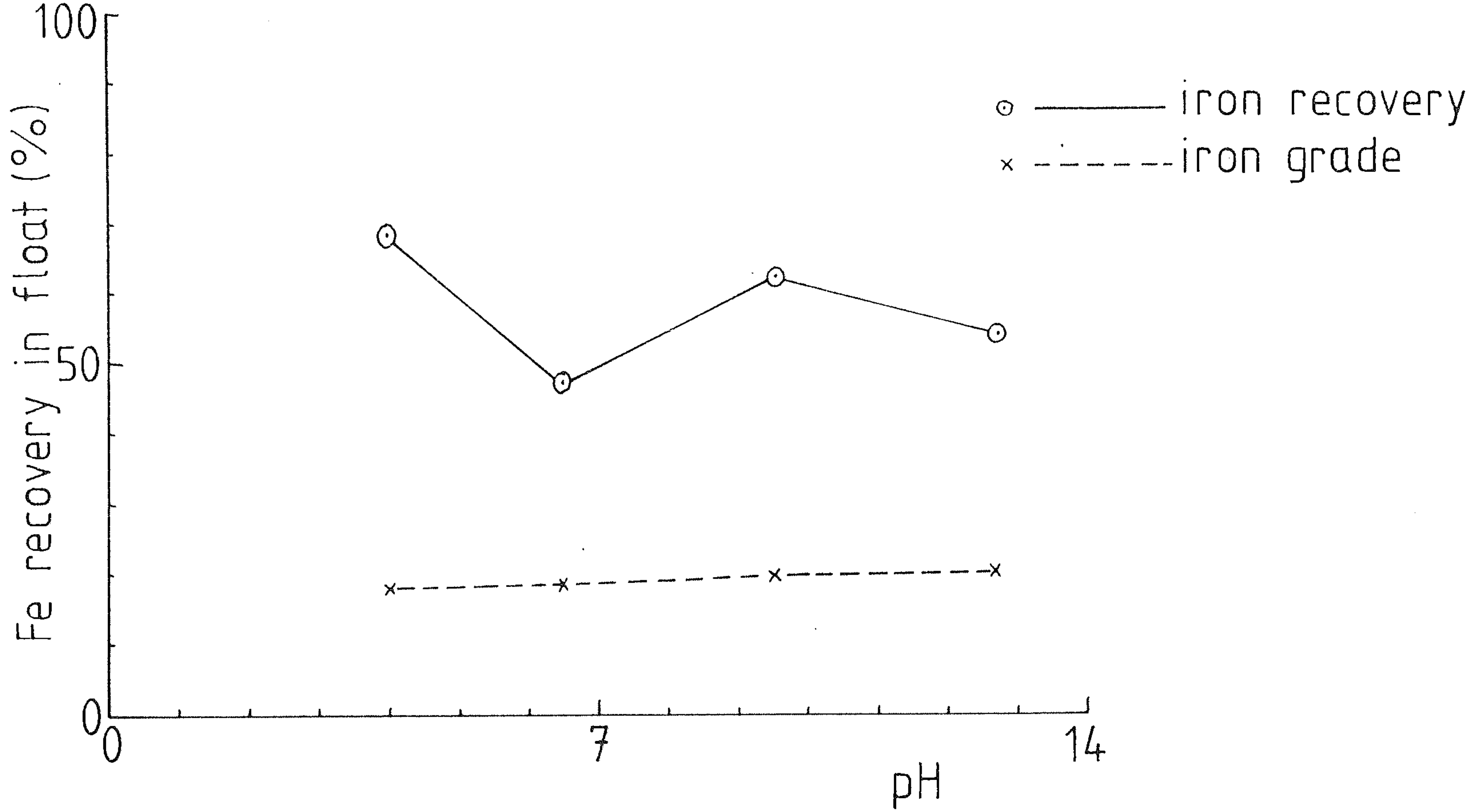


TABLE 5.9

FLOTATION RESULTS OF BOS SLAG WITH LAURYLAMINE

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	Test pH	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	19.6	98.0	12.6	173	17.8	30.8	31.5	326	19.8	64.5	65.8	15	18.2	2.7	2.7
500	20.2	102.0	9.8	204	18.5	37.7	36.9	310	19.5	61.1	60.9	14	15.6	2.2	2.2
500	19.7	99.5	7.8	342	16.5	56.4	56.7	224	18.2	40.7	40.9	13	18.8	2.4	2.4
500	19.1	95.5	5.5	338	14.9	50.4	52.8	248	17.1	42.4	44.4	16	17.2	2.7	2.8
500	19.4	97.0	3.5	480	14.2	68.2	70.3	140	18.0	25.2	26.0	20	18.0	3.6	3.6

FIG 5,9 FLOTATION RESULTS OF BOS SLAG WITH LAURYL AMINE

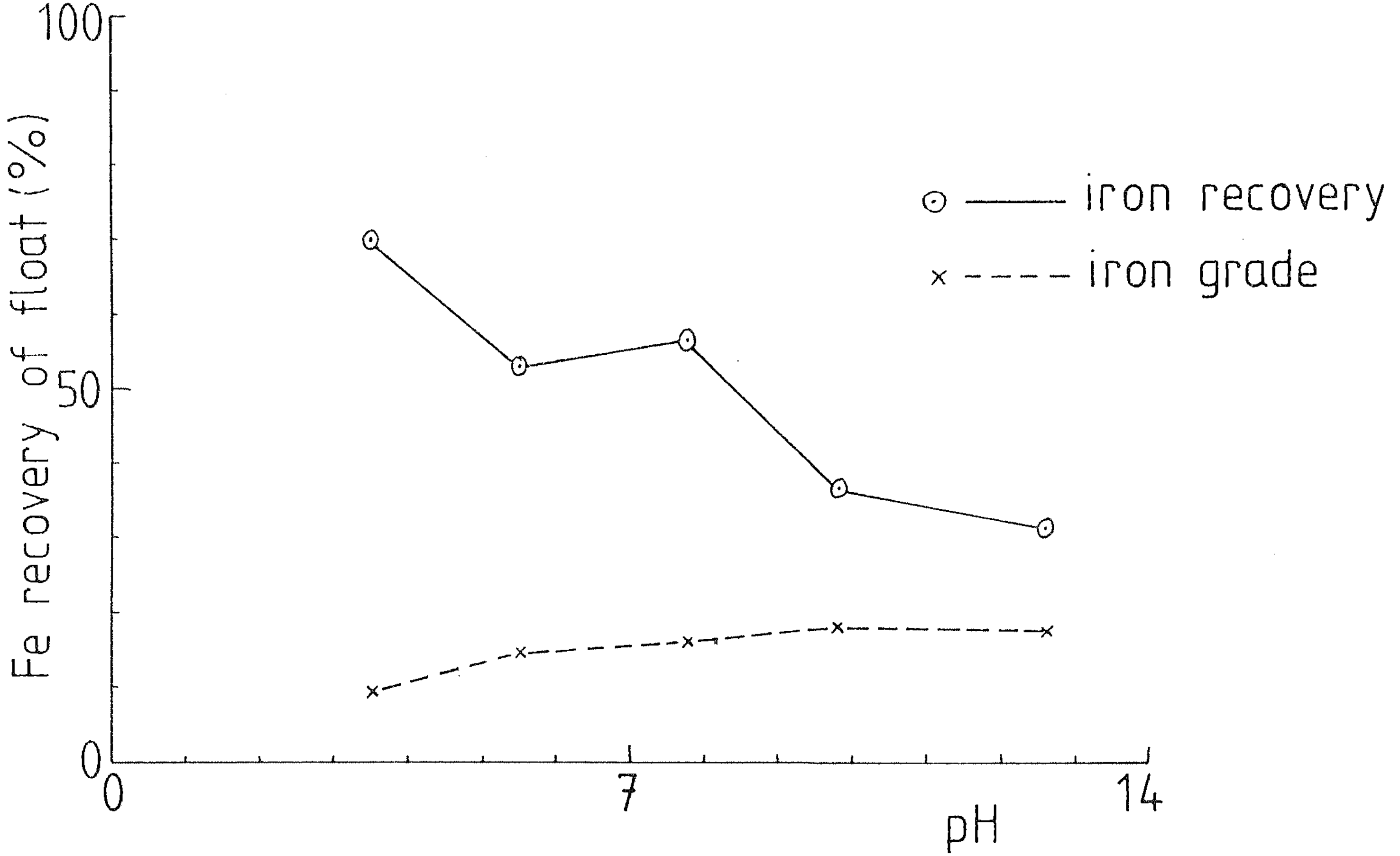


TABLE 5.10

FLOATION RESULTS OF ARC SLAG WITH OLEIC ACID

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	pH	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	16.9	84.5	12.3	162	16.0	25.9	30.7	330	16.1	53.1	62.8	26	21.0	5.5	6.5
500	16.3	81.5	9.0	194	13.3	25.8	31.7	294	16.7	49.1	60.2	42	15.7	6.6	8.1
500	16.5	82.5	6.5	348	14.1	49.1	59.5	164	16.0	26.2	31.8	47	15.3	7.2	8.7
500	16.9	84.5	4.0	335	12.9	43.2	51.1	237	14.9	35.3	41.8	38	15.8	6.0	7.1

FIG 5,12 FLOTATION RESULTS OF ARC SLAG WITH OLEIC ACID

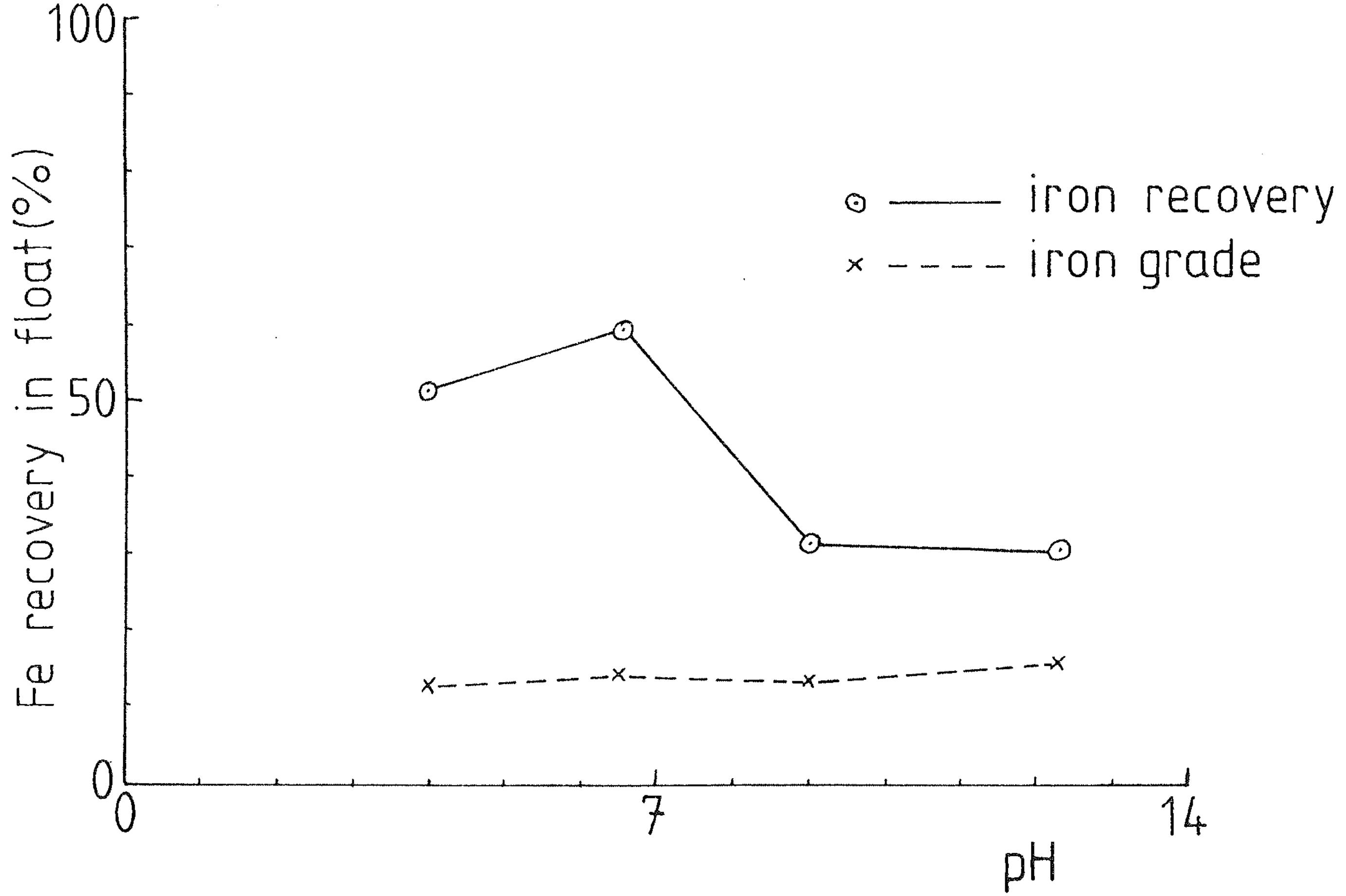


TABLE 5.11

FLOTATION RESULTS OF ARC SLAG WITH LAURYLAMINE

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	pH	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	16.5	82.5	12.4	186	14.6	27.5	33.3	282	17.2	48.5	58.8	42	15.6	6.5	7.9
500	16.4	82.0	9.0	208	12.9	26.8	32.7	274	17.6	48.2	58.8	46	15.3	7.0	8.5
500	16.1	80.5	6.0	346	13.4	47.7	59.3	178	15.2	27.1	33.6	38	14.9	5.7	7.1
500	16.5	82.5	3.5	342	11.9	38.5	46.7	270	13.7	37.0	44.8	46	15.2	7.0	8.5

FIG 5,13 FLOTATION RESULTS OF ARC SLAG WITH LAURYL AMINE

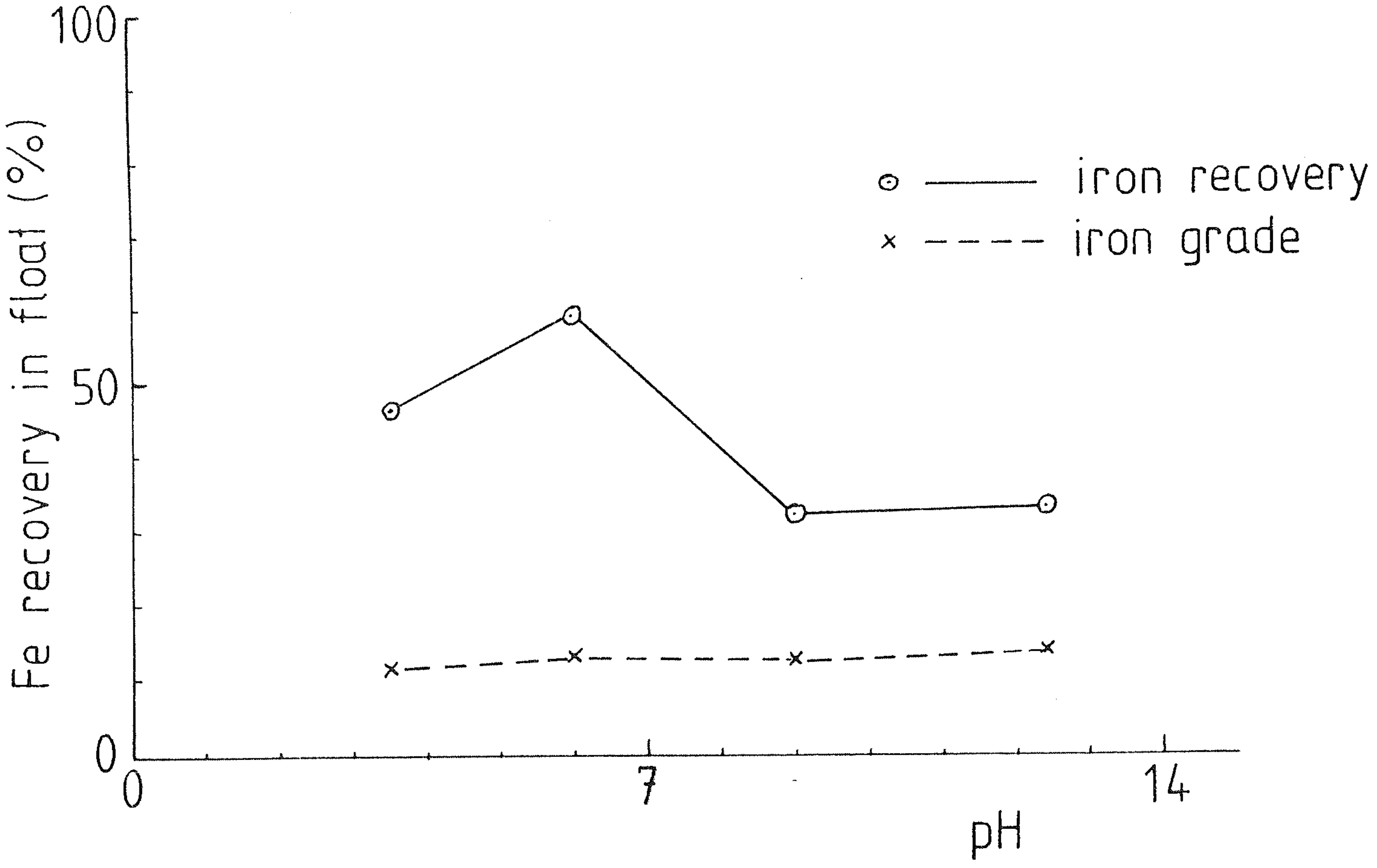


TABLE 5.12

FLOTATION RESULTS OF BOS SLAG WITH OLEIC ACID

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	Test pH	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	18.5	92.5	12.7	208	17.0	35.4	38.3	280	19.0	53.2	57.5	22	17.9	3.9	4.2
500	19.4	97.0	10.5	68	14.4	9.8	10.1	400	19.0	76.0	78.4	56	20.0	11.2	11.5
500	19.4	97.0	8.3	200	13.7	27.4	28.3	376	17.8	66.9	68.9	16	17.0	2.7	2.8
500	19.5	97.5	5.5	390	14.1	55.0	56.5	178	19.1	34.0	34.8	46	18.5	8.5	8.7
500	19.4	97.0	3.0	440	13.6	59.8	61.7	200	14.6	29.2	30.1	44	18.2	8.0	8.2

FIG 5,14 FLOTATION RESULTS OF BOS SLAG WITH OLEIC ACID

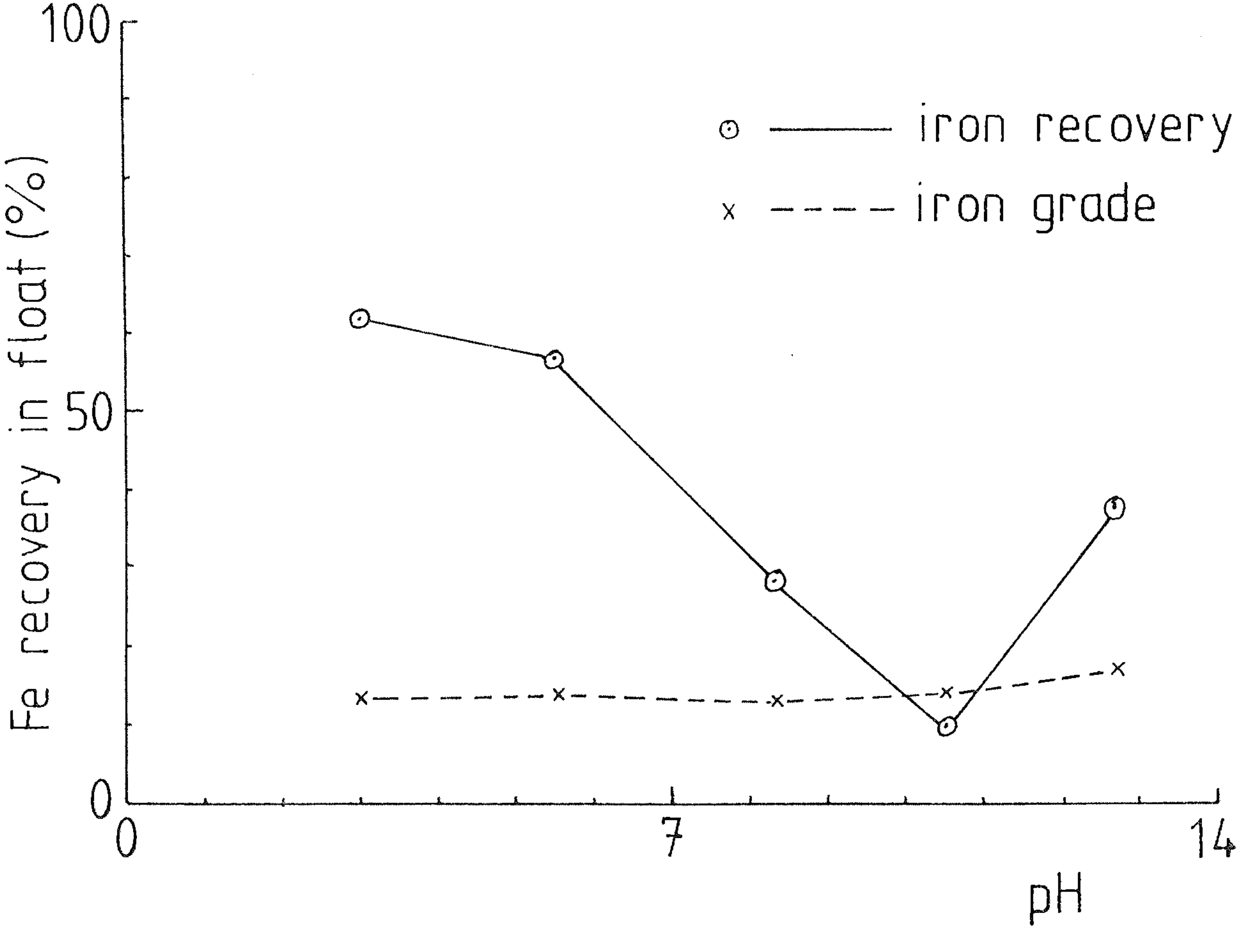


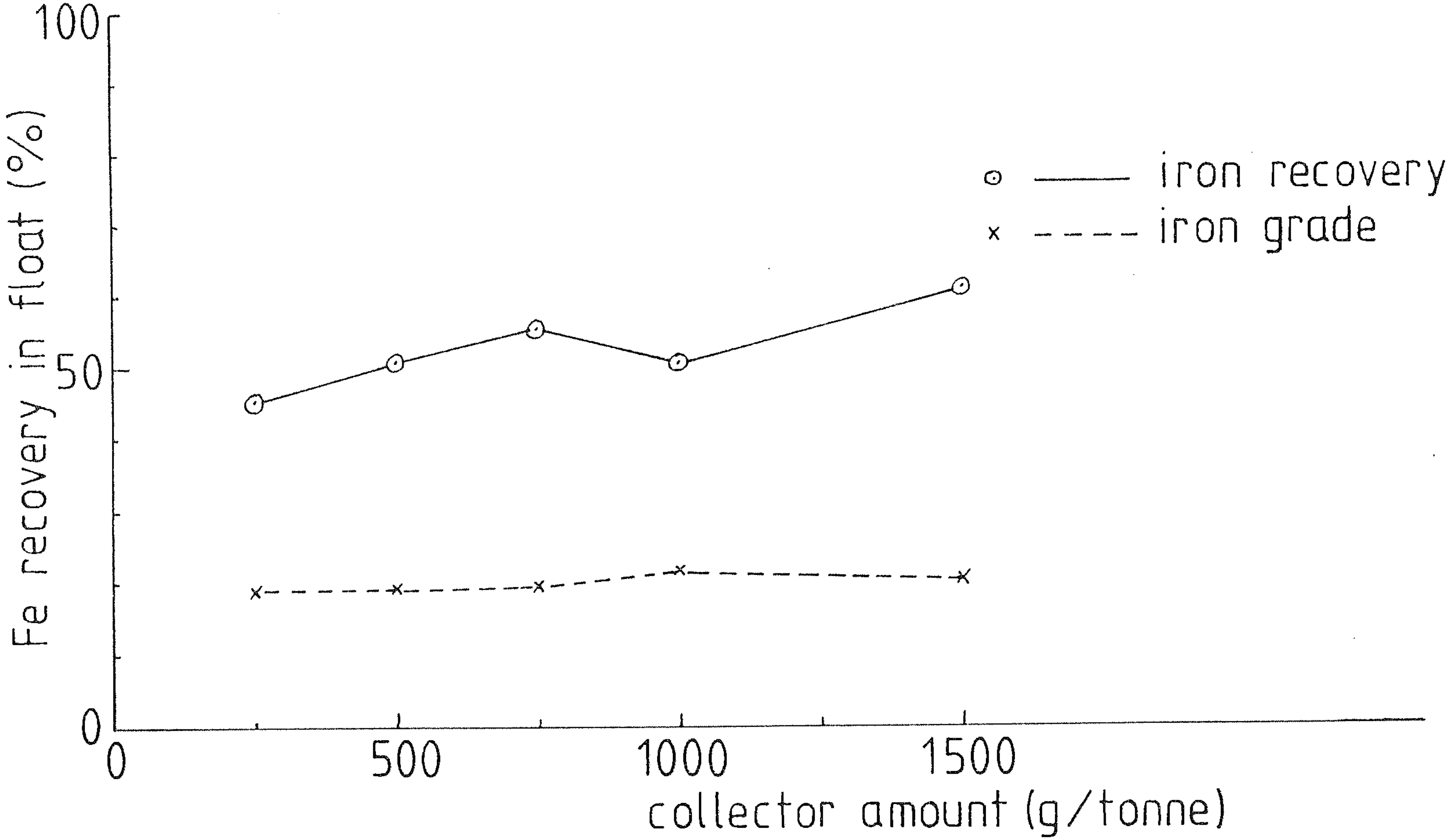
TABLE 5.13

FLOTATION RECOVERY OF BOS SLAG AS A FUNCTION OF Na-LAURYL SULPHATE CONCENTRATION AT pH OF 12.4

FEED				FLOAT				TAILING				DESLIME			
Wt. g	Fe grade %	Amount of Fe g	Amount of coll for g/tonne	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %	Wt. g	Fe grade %	Amount of Fe g	Fe Recovery %
500	19.4	97.0	250*	232	18.9	43.8	45.1	254	19.1	48.5	50.1	26	18.2	4.7	4.8
500	19.6	98.0	500	262	19.1	50.0	51.0	227	19.2	43.5	44.4	24	19.0	4.5	4.6
500	19.5	97.5	750	272	19.7	53.5	54.8	202	18.4	37.0	37.9	36	19.6	7.0	7.3
500	21.8	109.0	1000	254	21.7	55.1	50.5	242	20.4	49.3	45.2	24	19.2	4.6	4.3
500	20.9	104.5	1500	314	20.5	64.3	61.5	172	20.5	35.0	33.5	26	20.2	5.2	5.0

* at pH of 12.6

FIG 5,15 FLOTATION RESULTS AS A FUNCTION OF Na-LAURYL SULPHATE CONCENTRATION AT NATURAL SLAG pH



100% liberated from gangue comprising 30% of the total particles. In addition to this, particles with down to 60% free surface can be said to be suitable for flotation. Further grinding would increase the amount of deslime which would have caused problems.

There is no reference in the literature to the flotation properties of wustite and ferrites, which are the iron containing phases in the slags. It is believed that they should have shown surface properties similar to those of goethite, hematite, and magnetite.

Silicates have been studied extensively by Manser (91). Although alite and dicalcium silicates were not mentioned in this study, silicates were generally floated readily with anionic and cationic collectors.

In the flotation of the slags up to 75% recoveries were obtained but the iron grade was almost unchanged. The flotation recoveries were generally higher, below pH 9. In this region the production of calcium hydroxide was higher and this might well be the reason why high recoveries and an unchanged iron grade were obtained. The decline in the recovery curves at approximately pH 8-10 may be attributed to the pzc of the iron containing phases. A transition zone of particle surface charges in this region may be observed, Figure 5.14.

The interference of calcium hydroxide with the particle surface can take place in two ways.

Firstly, the dissolved calcium hydroxide in aqueous solution reacts with sulphuric acid and forms the basic salt calcium sulphate. This salt then precipitates on the particles indiscriminately to give a uniform surface.

Secondly, free lime is hydrolysed by water on particle surfaces and reacts with acid to form calcium sulphate. Since these reactions inevitably take place in the pulp the selectivity on the particle surfaces for both types of collector cannot be achieved.

The effect of collector concentration did not show any significant change in the iron grade, but a slight increase in the recovery.

The use of acetic acid as a pH modifier gave better results for the region above pH 9 but the all over consumption was higher and there was no increase in the iron grade.

Having high acid consumption and acid-free lime reactions in the flotation of the slags, no improvements can be made in the iron grade. This method is unlikely to be the one used in the beneficiation of the slags.

CHAPTER 6

FLOCCULATION

6.1 Literature Review

6.1.1 Introduction

The processing of fine-grained ores frequently results in the production of ultrafine particles which respond poorly to conventional physical separation techniques.

Fine particles in a fluid suspension tend to follow the motion of the fluid under the influence of any external force applied to achieve separation. The formation of larger units by selective aggregation is thus a promising way to overcome this hydrodynamic limitation.

Aggregates can be formed in the following ways:

Electrolytic coagulation: Electrolyte additions decrease the electrostatic repulsion between particles and promote aggregation in accordance with the D.L.V.O. theory. This phenomenan has been employed for removing coloured impurities from fine kaolin (98 percent minus 2 μm)(92,93) and seems to be suitable for the separation of sub-micron material (94).

Hydrophobic Bonding: Surface-active agents can adsorb at the mineral/water interface and render the solid hydrophobic. Particle/particle adhesion is favoured by the attraction between the hydrophobic coatings on the different particles and the resultant reduction in the area of hydrophobic mineral/water interface.

Gaudin and Malozemoff (95) managed to aggregate galena slimes selectively by using a range of compounds of the xanthate type, and floated the flocs produced. Fine-grained barite has been selectively flocculated and floated by small additions of anionic reagents at an approximate pH value of 9.5, corresponding to only a 20 percent monolayer coverage on the barite (96).

Magnetic Bonding: Aggregates stabilized by magnetic forces without the addition of any reagent. Dispersants are necessary to prevent entrapment of material in the magnetic flocs.

Shimoizaka et al (97) were able to separate magnetite from pyrophillite, using low-intensity fields, but were unable to separate hematite from pyrophillite, even in high-intensity fields.

Polymer Bridging: Particle-particle briding by long chain high molecular weight polyelectrolytes. Most of the recent work on selective aggregation has been concerned with the selective flocculation by high molecular weight polymers. This leads to the formation of larger and stronger flocs than can be achieved by any of the above mechanisms.

This process is generally termed as flocculation and will be the subject of the following practical work and will be discussed in detail in the subsequent sections.

6.1.2 Theoretical Aspects of Flocculation

6.1.2.1 Flocculation Mechanisms

It is believed that the flocculation of suspensions by organic polymers involves two different mechanisms. It may occur by a polymer-bridging mechanism in which polymers are adsorbed with one or more segments bonded to different particles in the suspensions or, it may be facilitated by decreased electrostatic repulsions between particles. These result from partial or complete charge neutralization by polyelectrolytes or colloidal species of opposite charge to the particles in the suspensions.

The involvement of these mechanisms is dependent on the nature of the surfaces, size, type, structure, configuration and molecular weight of the polymer and the ionic environment of the particles.

6.1.2.2 Polymer Bridging

It has been claimed that the major contribution to the total degree of flocculation is due to polymer bridging (98-101), rather than to neutralisation of the charge on the particles by polyelectrolytes of opposite sign, but some workers have shown (99,101,104) that negatively-charged suspensions may be flocculated by polyelectrolytes of similar sign. Some non-ionic polysaccharides are also very powerful flocculants (103).

The amount of flocculant added is considerably less than the total amount which can be adsorbed since bridges will be formed only between particles which have some vacant adsorption sites.

6.1.2.3 Electrostatic Effects

The second contribution to the total degree of flocculation will be due to the influence of charged polyelectrolytes in neutralising the effective charge on particles in the suspension. Inter-particle bridging will be facilitated by reduced electrostatic repulsions between the particles. The behaviour of these will vary according to their size. The smaller particles (e.g. 0.1-10 μm) will show some resemblance to lyophobic colloids.

Flocculation may be induced by highly charged organic polyelectrolytes, which according to the Schyltze-Hardy rules, will be much more effective as flocculants than the simple inorganic ions. Only if the concentration of the finer solids is sufficiently high in the suspension will the larger particles be incorporated in the flocs.

6.1.2.4 Adsorption of Flocculants

The adsorption may involve several types of bonding and these will vary with the chemical nature of the surfaces and the functional groups of the polymer. The bonds may be classified according to their type and energy. Ionic bonds (energy 600-850 kJ/mole), hydrogen bonds (energy 20-40 kJ/mole) and dipolar interactions (energy <20 kJ/mole) are frequently involved. Bonds of lower energy may be formed by induced polarisation (London - Van der Waals' forces) in molecules which are normally uncharged (104,105).

Polyelectrolytes which contain carboxylate, phosphate or sulphonate groups in their structures, e.g. hydrolysed polyacrylamide, may be adsorbed by solids having metal ions in their lattices. This adsorption is due to the influence of ionic bonds. Multivalent cations may also act as bridges between anionic sites in the polymer chain and particles may be linked together by this mechanism (106).

Neutral polymer molecules are adsorbed through the influence of low energy bonds. Hydrogen bonds formed between OH or NH groups and the surface atoms (usually oxygen) of the solid particles, are probably the principal mode of attachment of neutral polymers.

The efficiency of a flocculant is largely determined by its adsorption characteristics. A polymer can adsorb much more than a monolayer (all segments adsorbed) yet the shape of the isotherm precludes multilayer adsorption (107).

6.1.3 Factors Affecting Flocculation

6.1.3.1 Effect of Concentration of Polymer

As more and more is adsorbed the number of extended loops increases but at the same time the number of surface sites available for bridge formation is reduced and at high surface coverage this leads to a reduction in flocculation. La Mer and Smellie (108) calculated that for optimum flocculation the surface coverage should be about 50%. Other adsorption studies showed that this value is between 10 and 33% (109-111).

6.1.3.2 Effect of Molecular Weight of Flocculant

Most workers have reported a continued improvement in flocculation with increasing molecular weight of the flocculant (109,112-114), apart from Healy and La Mer who found an optimum value (101). Sakuguchi and Nagase(113) showed that there is a relationship between the size of a macromolecule (characterised by its intrinsic viscosity) and its efficiency as a flocculant.

It has been shown that for polymers of similar chemical nature a linear molecule chain is more effective than a cross-linked (115) or highly branched one (116) of similar molecular weight.

6.1.3.3 Strength of the Floc

The coagulated sediment of a coarse suspension is readily redispersed by vigorous agitation (117) while similar flocculated material is far more resistant to shear.

Although Read and Kitchener (118) have directly confirmed the mutual "adhesiveness" of flocculated particles by measuring the effect of flocculants on the adhesion of individual quartz particles to a polished silica plate, no absolute measurements of adhesiveness are known.

Weitser and Paskutskia (119) attempted to measure the mechanical strength of flocs in a clay-polyacrylamide system. Their method consisted of allowing the flocs to form and settle and then subjecting them to intensive agitation until the former dispersed state was regained. The results indicate that the resistance of the floc to shear increased rapidly at low concentrate of polyacrylamide to an optimum value. Higher dosages of flocculant did not reduce the strength of the floc.

6.1.3.4 Effect of Polymer Addition

For the most efficient use of the flocculant it should be uniformly distributed throughout the suspension. Linke and Booth (99) showed that the "haze" of suspended particles left in the supernatant liquid after flocculations had occurred, even at low concentrations, was due to particles which had adsorbed a disproportionately large amount of flocculant and become stabilised.

McCarty and Olsen (120) presented data showing the improvement in flocculation occurring when multistage addition of dilute flocculant solution is employed. Kuzkin and Nebera (106) suggest that vigorous agitation during polymer addition should improve distribution. This may cause the degradation of polymer at super coated flocs at high shear rates.

6.1.3.5 Effect of Agitation

6.1.3.5.1 During Floc Formation

In a slowly coagulating colloidal suspension, collision frequently between the particles is determined by Brownian motion (prekinetic flocculation).

It is necessary to apply gentle agitation to the suspension to attain a convenient rate of flocculation (orthokinetic flocculation).

The kinetics of flocculant adsorption are diffusion controlled (121) and agitation would promote more rapid adsorption which could be beneficial.

6.1.3.5.2 The Flocculated Suspension

The effect of agitation on a flocculated suspension is complex. It is generally agreed that, although flocs are resistant to immediate redispersion, prolonged or intense agitation can cause considerable deflocculation (110,99,120,121).

Some workers found an optimum time of agitation to produce max flocculation (123-125) but Kane et al (126) reported that the polyacrylamide-silica system was independent of duration of agitation.

6.1.3.5.3 Exposure of Fresh Surface

The occlusion of untreated particles into a floc network and multistage addition of flocculant would also provide an uneven distribution of polymer within a floc. If such a structure were to be mechanically degraded the adsorbed macromolecule by virtue of its large number of degrees of freedom could penetrate into regions of low polymer concentration, e.g. adsorption occurring on the interlamellar surface of clays (127).

6.1.3.6 Solid Content of Suspensions

The importance of orthokinetic flocculation on the flocculation of low solids content suspension has been mentioned above.

At higher solids content the increased frequency of particle collisions should provide a more efficient usage of the polymer, but this would be very dependent on the uniformity of mixing. In fact, at very low solids content (less than 0.1% by weight solids) a linear relationship between solids content and optimum polymer concentration has been found (109,111). A similar relationship has been established for solids content up to 50%, for the polyacrylamide-silica system (99,128).

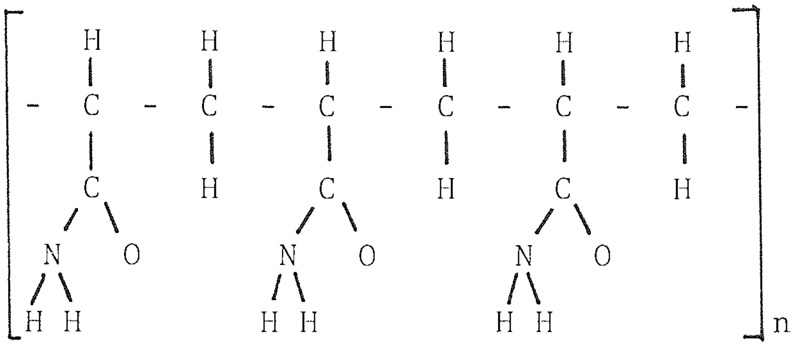
6.1.3.7 Particle Size

Linke and Booth (99) found that the optimum polymer concentration to solid ratio was directly proportional to the specific surface area, La Mer et al (123) found that the ratio proportional to the square of the specific surface area. However, it should be said that the mechanism of polymer adsorption and the floc formation are independent of particle size.

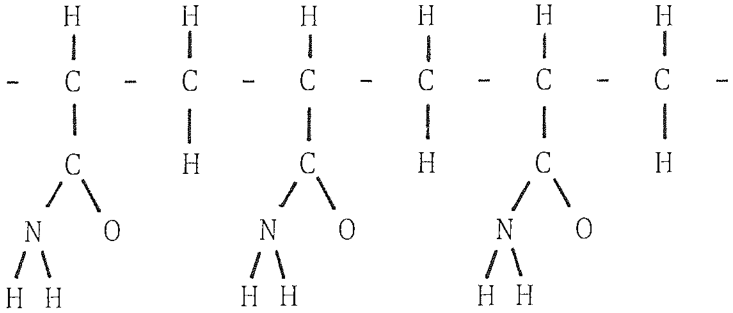
6.1.4 Chemical Aspects of Flocculants

Various types of natural and synthetic high polymers are known which may be used as flocculants under suitable conditions and they may be classified as cationic, anionic and non-ionic. In general, the action of these flocculants is highly specific and no reagent is known which will effectively flocculate a suspension under all conditions (108).

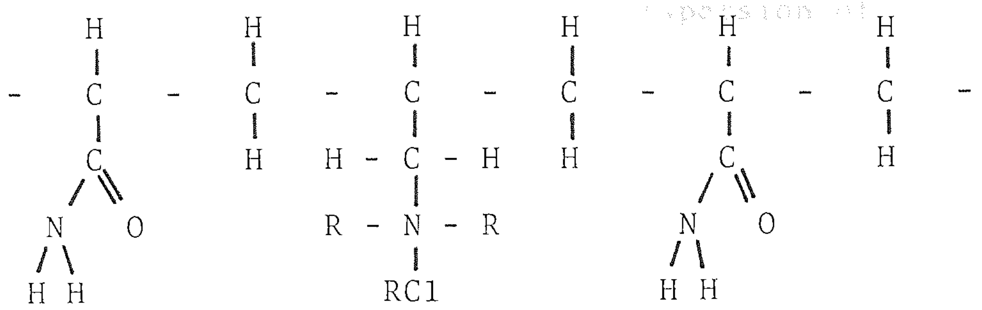
Most extensively employed naturally occurring polymers are based on polyaccharides (gums, starches, etc.) (116) and gelatine (110). These are generally of a complex nature and may be chemically modified to fit into any of the above categories (cationic, anionic, non-ionic) synthetic polymers, many of which are based on polyacrylamide



which itself is non-ionic but can be converted by controlled alkali hydrolysis to a complete or partial anionic character.



Cationic polymers can be prepared by co-polymerising acrylamide with varying amount of Quaternary amines (117).



Less than 1% of polyacrylamide is hydrolysed carboxyl groups when it is manufactured.

Many other synthetic flocculants are based on polyethylene oxide (129).

Co-polymers of maleic analydride (130), polyethyleneimine (132), etc., are also available.

A polyelectrolyte possesses a large number of similarly charged, mutually repelling groups along the polymer chain and this can result in considerable extension of the chain, i.e. an effective increase in the dimensions of the macromolecule.

6.1.5 Selective Flocculation and its Applications

Selective flocculation by use of organic polymers is one of several feasible processes for the separation of mixtures of fine mineral particles, generally in the sub-sieve range (e.g. 0.1 - 50 μm).

The key to the process is that a flocculant selectively adsorbs on only one of the constituents of the mixture, selective flocculation then follows, after which the flocs of one component can be removed from a dispersion of the other.

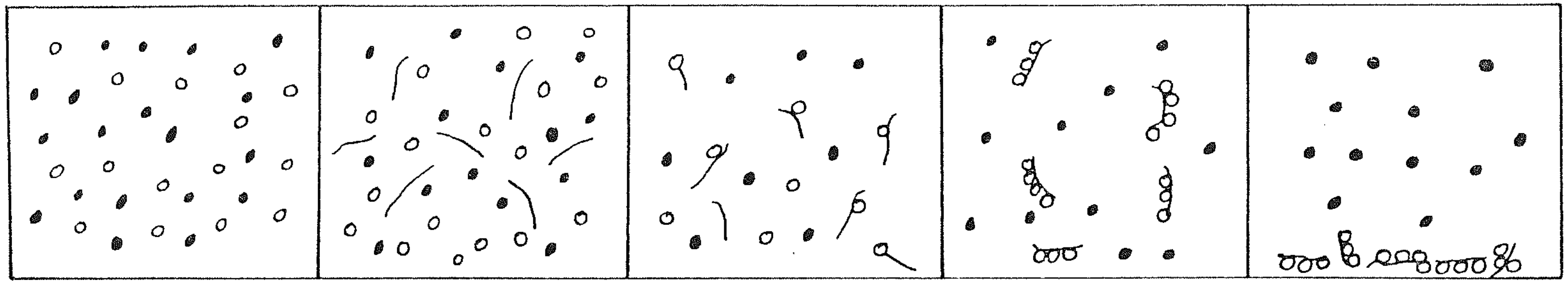
In some instances almost complete separation has been achieved (e.g. galena/quartz (132,133)), but in many others the separations have been only partial. A schematic presentation of selective flocculation is shown in Figure 6.1.

Rubio and Kitchener (134) introduced conventional flotation collectors to provide the necessary basic surface differentiation of the minerals before the flocculant is applied. They used potassium amylxanthate to activate the copper and then followed with polyethylene oxide as the flocculant in chrysocolla/quartz and malachite/quartz-mixtures which were successful on pure substances but not so good with naturally occurring ores.

Selective flocculation is used in the processing of kaolin for the removal of coloured impurities (135-137), fine quartz (138), swelling clays (139), and separation of impurities from boehmite in the treatment of low-grade bauxite (140,141).

The fine-grained non-magnetic oxidised taconites are selectively flocculated by anionic starches after being dispersed by sodium silicate prior to the separation by flotation using cationic collectors (142).

FIG 6,1 A SCHEMATIC DIAGRAM TO ILLUSTRATE THE SUCCESSIVE STAGES IN A SELECTIVE FLOCCULATION PROCESS



1. dispersed solid

2. addition of flocculant

3. selective adsorption of flocculant

4. selective flocculation

5. sedimentation and separation

6.1.6 Application of Selective Flocculation on Steel Making Slags

Although no direct information is available for the flocculation of steel making slags, the grain size and chemical composition of the phases, which constitute the slags, seem to be similar to those which are already successfully flocculated by various flocculants.

The aim of the following work was the determination of a suitable flocculant in respect of the other factors which were encountered during the experiments.

6.2 Experimental Work

6.2.1 Preparation of Samples

Representative samples of crushed BOS and ARC slags were prepared in 250 g lots. They were initially ground dry in a batch rod mill for 60 minutes (speed 60 r.p.m.), having a rod load of 11300 g.

After taking out the ground samples, the metallic iron prills were extracted on a rapid magnetic separator by passing through the samples individually at 3.5 amp current density and 10 mm gap between the poles.

The non-magnetic fractions after separation were returned to the rod mill for further grinding overnight (12-14 hour). The products were finally collected in sealed polythene bags.

6.2.2 Preparation of Flocculants

The flocculants used in the tests were from the Magnafloc range of polyelectrolytes (ex Allied Colloids Company). The properties of the flocculants are listed in table 6.1.

The solutions of the flocculants were freshly prepared before tests by wetting 0.1 g of powder flocculant with 1 ml of methanol in a container on to which water was poured rapidly to obtain the desired concentration. Occasional shaking was applied to help solution.

TABLE 6.1

MAGNAFLOC RANGE OF POLYELECTROLYTES

Name	Molecular Weight	Ionic Characteristic
Magnafloc 139	10 million	Low anionic 10%
Magnafloc E24	13 million	Low anionic 10%
Magnafloc 156	15 million	High anionic 37%
Magnafloc 140	8 million	Medium cationic 10%
Magnafloc 352	12 million	Medium cationic 10%
Magnafloc 455	12 million	Low cationic 5%
Magnafloc 351	13 million	Non-ionic

6.2.3 Procedure for Settling Tests

Objectives:

(1) Dispersion of slag particles

(2) Dispersion of condition agent

(3) Dispersion of flocculant

(4) Attachment of flocculant

(5) Floc formation after stirring (in ∿ 3/4 secs)

(6) Separation (settling of flocs)

20 g samples of the minus 45 μm fraction were used. The tests were carried out in a 1000 ml measuring cylinder (diameter 6.5 cm). Samples were conditioned with 100 ml water in a 200 ml beaker for 10 minutes by a mechanical stirrer at a fixed speed throughout the experiments.

5 drops of 0.1% solution of Na_2SiO_4 were introduced to the pulp as dispersant prior to collector or flocculant addition.

After 2 minutes conditioning, either 1 ml of 1% solution of oleic acid (450 g/tonne) or 5 ml of 0.1% solution of dodecylamine (250 g/tonne) were used as collectors depending upon the experiments.

The flocculants were introduced to the system after 5 minutes conditioning. They were added at a concentration of 0.1% solution by a pipette in 30 seconds to the bottom of the liquid vortex.

The complete conditioning time was 10 minutes and the pulp was transferred to the measuring cylinder. The volume of the pulp was increased to 1000 ml by adding water and mixing the pulp with a plunger activated a few times to avoid any presetting.

A clear interface was not produced. Therefore, it was difficult to determine settling by visual observation of the suspension.

The sediment accumulation was used as a guide for the completion of settling. This was done by recording the time of the sediment peak point just before entering into the compression zone. This period was used as the settling time of the suspended slag particles.

6.2.4 Description of Apparatus used for Separation Tests

In this new series of tests a modified 500 ml separating cylinder funnel (dia. 4.5 cm) was used. An extra tap was fixed at the mid point of the funnel as well as one at the bottom. The unflocculated dispersed part of the pulp was taken out through the tap in the middle, and the flocculated part of the pulp was let out through the base.

A mechanical stirrer was introduced to the system (see Fig. 6.2) and was employed in the conditioning of the pulp before separation.

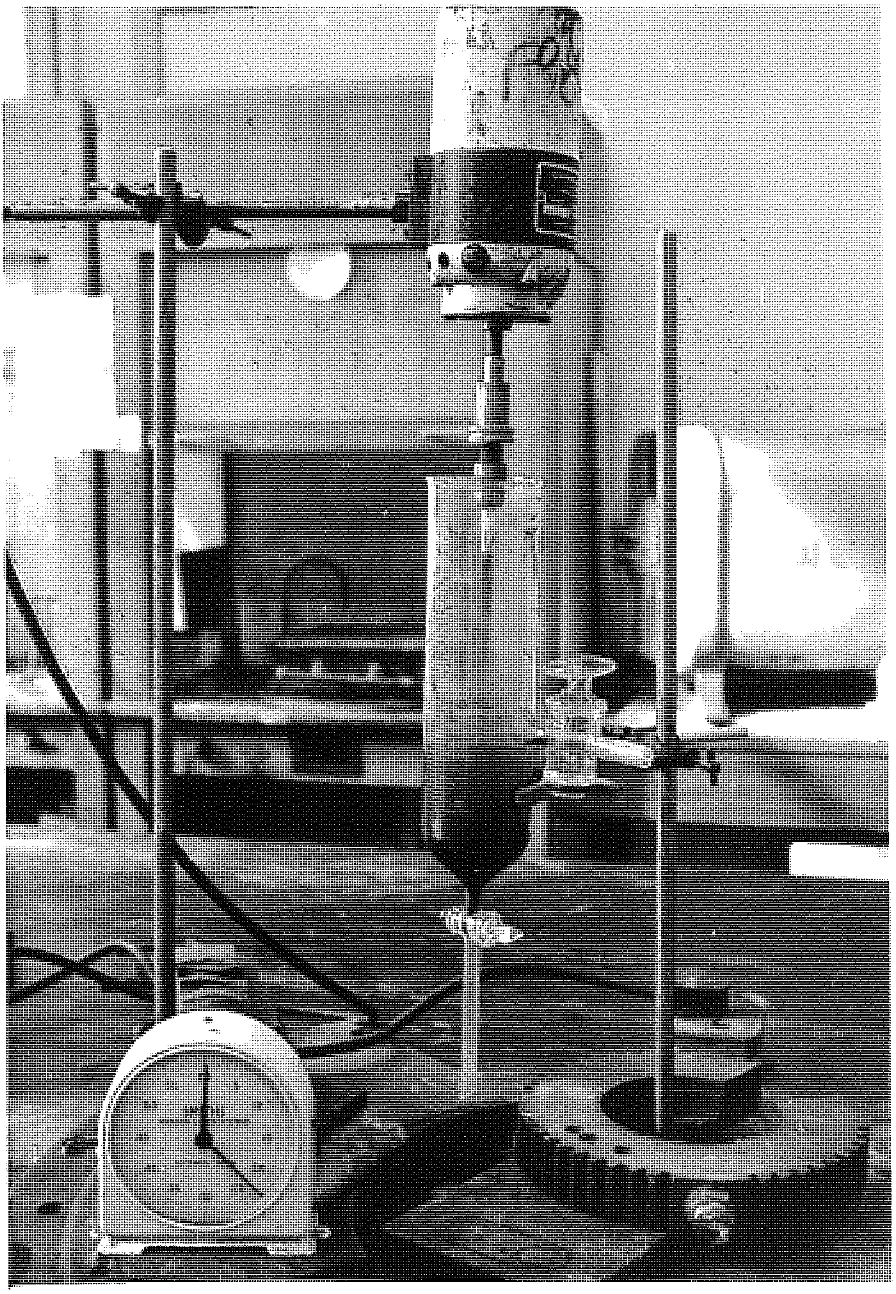


FIGURE 6.2 The Apparatus used in the Experiments

6.2.5 Procedure for Separation Tests

10 g samples were used for these experiments and they were 100% finer than 45 μm. They were initially poured into the separating funnel and water introduced to the system with 5 drops of 0.1% solution of Na_2SiO_4 as dispersant to produce a volume of 200 ml in the separating funnel. The pulp was conditioned for 10 minutes with the mechanical stirrer in all experiments. The speed of the stirrer was kept constant throughout.

Collector addition was made at 5 minutes during conditioning. Two types of collector were employed, anionic (oleic acid (500 g/tonne)) and cationic (dodecylamine 250 g/tonne).

Three types of flocculant were tried - anionic, cationic and non-ionic. The amount of flocculant used was 25 g/tonne for all experiments except for the ones in which the concentration of flocculant was the variable. Flocculants were introduced at 8 minutes during conditioning.

The pulp was made up to 500 ml by adding water after conditioning and immediately the suspended particles were allowed to settle for a fixed period. At the end of this period the middle tap was opened to take out the float part. The settled part was extracted through the bottom tap. The products were collected in separate containers and dried before metallurgical examination.

6.2.6 Results

The settling velocities of the slags are shown in tables 6.2 and 6.3 as a function of the type of flocculant and the type of collector.

The results of pre-separation tests using a fixed separating time of 1 minute are shown in tables 6.4 and 6.5 as a function of collector type as well as pre-selected flocculant type.

The results which were obtained by employing various settling periods, various numbers of cleaning (the repetition of the flocculation process is called cleaning), flocculant concentrations and conditioning times are shown in tables 6.6 - 6.9 for BOS slag and in tables 6.10 - 6.13 for ARC slag.

6.2.7 Discussion

The power of a flocculant is measured by the initial settling velocities of flocs. The flocculants used in this work gave high velocities, up to six times higher than the velocity obtained without any flocculant addition. The results do not (unconditionally) confirm the theory that as molecular weight goes up the effectiveness of flocculant should be increased. It is interesting to note that Magnafloc 352 and 455 were both cationic type collectors, having the same molecular weight, and when no collector was used in the system the settling

TABLE 6.2

SETTLING VELOCITIES OF BOS SLAG cm/sec

Flocculant	Characteristic of flocculant	Mol.weight of flocculant	No-collector	Oleic acid 500g/tonne	Dodecylamine 250g/tonne
Magna 139	Anionic	10 million	0.39	0.19	0.23
Magna E24	Anionic	13 million	0.39	0.29	0.29
Magna 156	Anionic	15 million	0.23	0.23	0.23
Magna 140	Cationic	8 million	0.29	0.29	0.58
Magna 352	Cationic	12 million	0.19	0.46	0.39
Magna 455	Cationic	12 million	0.56	0.70	0.46
Magna 351	Non-ionic	13 million	0.70	0.70	0.47

0.11 cm/sec settling velocity obtained without flocculant addition.

TABLE 6.3

SETTLING VELOCITIES OF ARC SLAG cm/sec

Flocculant	Characteristic of flocculant	Mol.weight of flocculant	No-collector	Oleic acid 500g/tonne	Dodecylamine 250g/tonne
Magna 139	Anionic	10 million	0.16	0.21	0.19
Magna E24	Anionic	13 million	0.19	0.23	0.18
Magna 156	Anionic	15 million	0.17	0.39	0.23
Magna 140	Cationic	8 million	0.19	0.23	0.19
Magna 352	Cationic	12 million	0.39	0.39	0.70
Magna 455	Cationic	12 million	0.33	0.33	0.29
Magna 351	Non-ionic	13 million	0.33	0.39	0.35

0.11 cm/sec settling velocity obtained without flocculant addition.

TABLE 6.4

SEPARATION TESTS OF BOS SLAG

Flocculant	Product	Collector	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %
Magnafloc 156 Anionic	Float	No collector	0.44	18.5	0.08	4.3
	Settled		9.56	18.8	1.79	95.7
	Float	Oleic acid	0.64	20.0	0.13	7.0
	Settled		9.36	18.6	1.74	93.0
	Float	Laury1-amine	0.44	18.5	0.08	4.3
	Settled		9.56	18.8	1.79	95.7
Magnafloc 352 Cationic	Float	No collector	0.40	18.7	0.07	3.8
	Settled		9.60	18.8	1.80	96.2
	Float	Oleic acid	0.75	18.4	0.14	7.5
	Settled		9.25	18.7	1.73	92.5
	Float	Laury1-amine	0.70	19.4	0.13	7.0
	Settled		9.30	18.7	1.74	93.0
Magnafloc 351 Non-ionic	Float	No collector	1.10	18.5	0.20	10.7
	Settled		8.90	18.8	1.67	89.3
	Float	Oleic acid	0.30	21.1	0.06	3.2
	Settled		9.70	18.7	1.81	96.8
	Float	Laury1-amine	0.30	18.9	0.06	3.2
	Settled		9.70	18.7	1.81	96.8

TABLE 6.5

SEPARATION TESTS OF ARC SLAG

Flocculant	Product	Collector	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %
Magnafloc 156 Anionic	Float Settled	No-collector	No Separation			
	Float Settled	Oleic Acid	No Separation			
	Float	Lauryl-amine	0.4	15.9	0.06	3.7
	Settled		9.6	16.3	1.56	96.3
Magnafloc 352 Cationic	Float	No-collector	0.5	16.4	0.08	4.9
	Settled		9.5	16.2	1.54	95.1
	Float	Oleic Acid	0.7	15.9	0.11	6.8
	Settled		9.3	16.2	1.51	93.2
	Float	Lauryl-amine	0.3	16.4	0.05	3.1
	Settled		9.7	16.2	1.57	96.9
Magnafloc 351 Non-ionic	Float	No-collector	0.4	17.6	0.07	4.3
	Settled		9.6	16.1	1.55	95.7
	Float	Oleic Acid	0.3	16.8	0.05	3.1
	Settled		9.7	16.2	1.57	96.9
	Float	Lauryl-amine	0.5	16.4	0.08	4.9
	Settled		9.5	16.2	1.54	95.1

TABLE 6.6

BOS SLAG

THE EFFECT OF SETTLING PERIOD

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Settling Period sec.
Float	0.7	18.9	0.13	6.9	30
Settled	9.3	18.7	1.74	93.1	
Float	1.1	18.5	0.20	10.7	60
Settled	8.9	18.8	1.67	89.3	
Float	0.6	18.9	0.11	5.9	90
Settled	9.4	18.7	1.76	94.1	
Float	0.5	18.9	0.09	4.8	120
Settled	9.5	18.7	1.78	95.2	

TABLE 6.7

THE EFFECT OF CLEANING

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Number of cleaning
Float	1.1	18.5	0.20	10.7	1
Settled	8.1	18.8	1.67	89.3	
Float	1.0	18.0	0.18	9.6	2
Settled	9.0	18.8	1.69	90.4	
Float	1.4	18.1	0.25	13.3	3
Settled	8.6	18.8	1.62	86.7	
Float	1.9	18.5	0.35	18.7	4
Settled	8.1	18.8	1.52	81.3	

* 2 min. conditioning between cleaning stages

** 1 min. settling period

TABLE 6.8

BOS SLAG

THE EFFECT OF FLOCCULANT CONCENTRATION

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Flocculant concentration g/tonne
Float	0.3	17.9	0.05	2.6	12.5
Settled	9.7	18.8	1.82	97.4	
Float	1.1	18.5	0.20	10.7	25
Settled	8.9	18.8	1.67	89.3	
Float	0.6	17.9	0.10	5.3	50
Settled	9.4	18.8	1.77	94.7	
Float	0.7	18.1	0.12	6.4	100
Settled	9.3	18.8	1.75	93.6	

* 1 cleaning and 1 min. settling period

TABLE 6.9

THE EFFECT OF CONDITIONING TIME

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Conditioning Time min.
Float	1.1	18.5	0.20	10.7	10
Settled	8.9	18.8	1.67	89.3	
Float	0.7	18.2	0.13	6.9	20
Settled	9.3	18.8	1.74	93.1	
Float	1.8	17.7	0.32	17.1	30
Settled	8.2	18.9	1.55	82.9	
Float	0.9	14.8	0.13	6.9	40
Settled	9.1	19.2	1.74	93.1	

* 1 cleaning, 1 min. settling period and 25 g/tonne flocculant

The average iron content of the feed is 18.7%.

TABLE 6.10

ARC SLAG

THE EFFECT OF SETTLING PERIOD

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Settling Period sec.
Float	0.4	16.7	0.07	4.3	30
Settled	9.6	16.2	1.55	95.7	
Float	0.7	15.9	0.11	6.8	60
Settled	9.3	16.2	1.51	93.2	
Float	0.3	16.3	0.05	3.1	90
Settled	9.7	16.2	1.57	96.9	
Float	0.8	16.8	0.05	3.1	120
Settled	9.2	16.2	1.57	96.9	

* 500 g/tonne oleic acid

TABLE 6.11

THE EFFECT OF CLEANING

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Number of Cleaning
Float	0.7	15.9	0.11	6.8	1
Settled	9.3	16.2	1.51	93.2	
Float	0.8	16.4	0.13	8.0	2
Settled	9.2	16.2	1.49	92.0	
Float	1.3	16.3	0.21	12.9	3
Settled	8.7	16.2	1.41	87.1	
Float	1.2	14.3	0.17	10.5	4
Settled	8.8	16.5	1.45	89.5	

* 500 g/tonne oleic acid, 2 min. conditioning between cleaning stages and 1 min. settling period.

TABLE 6.12

ARC SLAG

THE EFFECT OF FLOCCULANT CONCENTRATION

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Flocculant concentration g/tonne
Float	0.6	16.5	0.10	6.2	12.5
Settled	9.4	16.2	1.52	94.8	
Float	0.7	15.9	0.11	6.8	25
Settled	9.3	16.2	1.51	93.2	
Float	0.5	16.6	0.08	4.9	50
Settled	9.5	16.2	1.54	95.1	
Float Settled	No separation, settled very rapidly				100

* 500 g/tonne oleic acid, 1 min. settling period and 1 cleaning

TABLE 6.13

THE EFFECT OF CONDITIONING TIME

Product	Weight g	Fe Grade %	Amount of Fe g	Fe Recovery %	Conditioning Time min.
Float	0.7	15.9	0.11	6.8	10
Settled	9.3	16.2	1.51	93.2	
Float	0.5	16.6	0.08	4.9	20
Settled	9.5	16.2	1.54	95.1	
Float	0.8	16.8	0.13	8.0	30
Settled	9.2	16.2	1.49	92.0	
Float	1.4	15.8	0.22	13.6	40
Settled	8.6	16.3	1.40	86.4	

* 500 g/tonne oleic acid, 1 min. settling period and 25 g/tonne flocculant

The average iron content of the feed is 16.2%

velocity with Magnafloc 455 was three times higher than the settling velocity with Magnafloc 352 (Tables 6.2 and 6.3).

Addition of different types of collectors seemed to have very little effect in improving the settling velocities. Better results were obtained with Magnafloc 351 which is a non-ionic flocculant for BOS slag.

The reason for the random results can be related to the pH of the pulp. In these experiments in order to prevent any alterations of particle surfaces by acid additions the pH values were the natural pH values of the slags. These were 12.4 and 12.6 for BOS and ARC slags respectively. The excessive amount of free lime which causes the high pH values, in water, prevents the bridging mechanism to operate successfully. This could explain why the better results with the non-ionic flocculant were obtained. Cationic and anionic flocculants have segments which were altered to cationic or anionic ions in aqueous solution. This meant a reduction in the number of segments along the molecule available for adsorption by almost uniformly charged particle surfaces.

The essence of separation by flocculation is the selective adsorption of flocculants on particles. Specific particles should be amenable to adsorption by the flocculant while the other types are not. This is either determined by the chemical nature of flocculant or by the combination of surface properties of particles and chemical nature of flocculant.

Tables 6.4 and 6.5 show the results obtained by varying flocculant type and by the introduction of different types of surface reagents. Magnafloc 351 without any collector addition gave the best result for BOS slag and Magnafloc 352 with oleic acid showed the best result for ARC slag.

Settling period had a peak of Fe recovery at 60 seconds. Further increase in the settling period did not improve these results.

As more cleaning cycles were applied the recovery went up but did not make any change in the iron grade.

Higher flocculant concentration did not show any significant change in iron grade and iron recovery. This can be related to La Mer and Smellies's theory (108) that there should be an optimum surface coverage of flocculant.

By extending the conditioning time the chance of collision between particles and polymer molecules is increased, but, this also brings about the degradation of the polymer to a limited extent. Small increases were obtained in the recovery of the iron.

The overall improvements in iron grade and iron recovery were very low. This shows that no differentiation can be obtained between particle surfaces (in this case mainly silicates and iron containing phases) by using the chemical reagents mentioned above. As explained previously, this can be accounted for by having high natural pH values (or in other words having free lime).

For the reasons listed above this method seems to be a poor beneficiation process for steel making slags.

CHAPTER 7

GENERAL DISCUSSION

Slag utilisation at present is limited to the recovery of iron prills by partial crushing, screening, magnetisation (3,144). Two scrap metal reclamation plants at Scunthorpe and Aldwarke are shown schematically in Figures 2.1 and 7.1 respectively. The flow sheet of the Scunthorpe plant was produced on the information given by the authorities there and personal observations. The other flow sheet is reproduced from a recent publication (143).

Although some of the metallic iron prills, which are easily separated, had been recovered, the flow sheets of these reclamation plants do not give any indication of the methods towards full possible utilisation of the slags. For example, the following questions were left unanswered for the Aldwarke plant (Fig. 7.1):

1. The Fe prill grade of the original slag was not given.

2. The proportions of the +600 mm fraction, the -600 mm fraction of the weathered material and the Fe prill content of the +600 mm fraction were not given.

3. After drop balling, on what basis was the metal-bearing slag sorted out?

4. Why was the +150 mm fraction after the diverter drum magnetic separation returned to the inspection point even though it was non-magnetic?

5. What were the properties of the 75-600 mm fraction; was it magnetic?

6. How did the inspection pile (or conveyor belt) work, was a large overhead magnet used or something else? How was the slag differentiated between larger, smaller and metal-bearing slag?

7. On what basis was the -6 mm fraction rejected - for being non-magnetic or for having smaller size? If so, why was it recycled to the magnetic separator?

Similar questions can also be asked about the Scunthorpe plant (Figure 2.1).

The discarded fractions of the slags, at all sizes, find no use anywhere at present, apart from as a filler for sites after a considerable period of weathering. A small proportion of slag is also used in road surfacing.

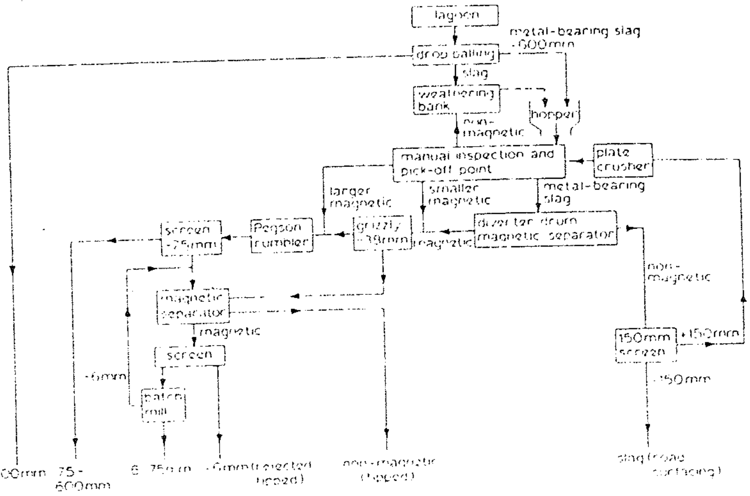


FIGURE 7.1 Schematic representation of scrap reclamation plant at Slag Production Co. Ltd. Aldwarke

There was a need to explore the potential use of the discarded part of the slags by introducing new methods and by improving the performance of the existing utilisation methods.

The possible areas of investigation were:

1. Determination of mineralogical and chemical nature of the slags with respect to the selection of processing methods.

2. Effect of size reduction for larger particles in order to release the entrapped metallic iron prills.

3. The development of a suitable processing method for the enrichments of the other iron containing phases, e.g. as recyclable product.

The phases found in the steel making slags examined were mainly of two types according to their chemical nature;

(1) those containing iron such as wustite ("RO" based), ferrites and metallic iron prills, and

(2) silica containing phases such as dicalcium and tricalcium silicates.

In addition to these phases a considerable amount of free lime existed.

The chemical composition of the slags and the proportions of the compounds constituting the phases varied considerably with the steel making process. Non-stoichiometry of the phases was generally observed, thus a definite chemical description cannot be given for a particular phase. For instance, iron rich areas contained 38.8 - 72.9% FeO for BOS slag and 27.5 - 49.6% FeO for ARC slag (Section 3, Figures 3.2 and 3.3).

The sizes of the phases showed a wide variation. As grain size was controlled by the cooling process and cooling environment an inconsistency in grain size was also found. The silicate phases were usually much larger than those containing iron. 80% of silicate phases were smaller than 60 μm and 80% of the iron containing phase were finer than 40 μm for BOS slag. Similar results were obtained for ARC slag (Section 3, Tables 3.4 - 3.7).

The phases also showed a non-uniformity in shape. The silicates were generally round, prismatic and/or rectangular. The iron containing ones were interdendritic between the silicates and thus had no regular shape.

The differences in the densities of the silicate phases and the iron containing phases seemed to favour gravity separation methods such as shaking table, jig, H.M.S., or Humphrey spiral (Chapter 3, Table 3.8). However the other factor, which is just as important as the density differences in these separations, is the liberation size of particles. These sizes for the slags were well below 40 μm for an acceptable liberation. The operational particle size for the gravity separations is limited to >100 μm for the finest possible size without including other minor factors. Therefore, it was concluded that gravity techniques were not suitable for the successful separation of the slags. The results of some preliminary shaking table runs of the slag mixtures are shown in Tables 7.1 and 7.2.

The application of magnetic separation to the metallic iron prills of the slags after a crushing and grinding operation improved the recovery and grade considerably. The use of a high-intensity magnetic separator, rather than low-intensity enables the separation to operate at smaller feed sizes. The size reduction, was, of course, the other major factor to operate this type of magnetic separator successfully. An extra amount of metallic iron, which was approximately 1-2% of the total slag weight, can be obtained with reasonable iron grades in the products, although the slags used for the separation had already been "demetallised" (Section 4, Figures 4.5 and 4.6).

The magnetic separation of the iron containing phases did not respond as well as the metallic iron prills. The main reason for this was due to the combination of magnetic and non-magnetic parts of the slags. Generally there were non-magnetic compounds in the particles, although most of the grains were magnetic.

The separation of the -50 μm material was not possible with the available type of magnetic separator. This was

TABLE 7.1

SHAKING TABLE RESULTS OF THE SLAGS

Feed size µm	Fe content in feed %	Wt.of Conc. % of total	Fe content in conc. %	Fe Recovery %
-600+295		No Separation		
-295+90	16.9	34.8	22.5	47.7
-90	16.4	29.2	20.8	36.9
* -1003 15 min.	17.9	31.3	20.1	35.3

* The -1003 µm fraction of sample used after 15 minutes grinding.

TABLE 7.2

MAGNETIC SEPARATION RESULTS OF SHAKING TABLE CONCENTRATES

Feed size µm	Fe content in feed %	Wt. of conc % of total	Fe content in conc. %	Fe Recovery %
-90	20.8	5.9	31.7	10.9
-1003	20.1	4.2	37.5	8.0

Current density is 0.2 amp, the gap between poles is 10 mm.

because of design limitations built into the separator. A new design could be tried on the -50 μm fraction of the slags by taking into account design economics (Chapter 4, Table 4.12). However, the costs of grinding and separation are unlikely to make the process economic.

Flotation is a major concentration process today, because it enables the finely crystallised minerals to be upgraded by using their surface properties. The applicable particle size of flotation is 100 - 5 μm depending upon the type of mineral, but generally it is 60 - 10 μm which is not dissimilar to the grain sizes of the phases in the slags studied. Commercial plants are in existence where silica containing and iron containing minerals are floated successfully with anionic or cationic collectors using the correct pulp conditions.

One of the main factors in flotation is the right pH of the pulp. This is obtained by addition of diluted acids or alkalies. In the case of the slags studied in this work the pulp had a very high pH value (12 +) because of the presence of free lime, and, in order to reduce this value, and to determine the right pH conditions, acid additions were made. These resulted in the production of an excessive amount reaction products due to the reactions that had taken place between $Ca(OH)_2$ and acid. The use of a weak acid gave similar results (Section 5, Tables 5.4-5.6).

The consecutive washes of the pulp could not alter the high pH value, because the free lime existed in the slags as unassimilated and alite-derived lime. In other words

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as a solid constituent in the grains. The surface condition would have already been established even after washing because the phases had been in contact with water.

The selection of a collector could not be made effective because of the precipitation of free calcium and hydroxyl ions onto all types of particle surfaces. Reasonable recoveries of float products were obtained in spite of the very poor improvement in iron grade (Section 5, Tables 5.7 - 5.13).

Selective flocculation is applied to pulps containing particles down to the sub-micron range (50 - 0.1 µm). In this process, particles of the same type were coagulated by introducing high molecular polyelectrolytes which are generally based on polyacrylamide. In selective flocculation, the surface of the particles were again the basis of the separation. If one specific group of particles is hydrophobic then other particles in the pulp should be non-hydrophobic in order to obtain effective separation between particles.

To avoid the acid-$Ca(OH)_2$ reaction the pH value of the pulp used was its natural pH value which was approximately 12.5. The use of different characteristic flocculants such as anionic, cationic and non-ionic did not affect the performance of selectivity and settling in any way. This was probably caused by adsorption of Ca and hydroxyl ions on to the particle surfaces before the polymer segments were adsorbed. The use of all types of collectors had no effect on the recovery. On the contrary without any collector the results were slightly improved with a non-ionic flocculant because the flocculation took place in accord with a bridging mechanism without any electrical attractions. (Section 6, Tables 6.1 - 6.5).

Variations of the other factors such as conditioning time, flocculant concentration, cleaning and settling period did not give any significant improvements (Section 6, Tables 6.6 - 6.13). This shows that a uniformity in particle surfaces was created by the presence of high free lime content in the slags.

CHAPTER 8

CONCLUSIONS

1. Steel making slag compositions are dependent upon the process used and in particular, the fluxes added. They are variable in their constitution as is shown clearly in the phase compositions which are usually non-stoichiometric. Generally the silicate phases contain an excess of lime present together with free lime present.

2. The actual grain formation is controlled by the cooling rate and is, consequently, very variable in size and shape. Silicate phases solidify first forming large and multi-shaped crystals. Iron containing phases were precipitated interstitially relatively smaller in size and of irregular shape.

3. Metallic iron prills, usually discarded in the magnetically treated slags, can be successfully recovered by comminution and further magnetic separation. The economic viability of the recovery was unknown.

4. Further concentration of the iron bearing phases by magnetic methods was unsuccessful because of their small sizes. In this work the magnetic separator was unsuitable for a complete appraisal to be made but it is unlikely that magnetic concentration would be an economic method for recovery of iron containing components of the slags.

5. A major interfering constituent in the slags is free lime which makes chemical control of the ore as a pulp very difficult.

6. Flotation was made impossible because of pH control and the contamination of the mineral surfaces by the products from lime and the acid additions. Thus the promoters were unable to function properly.

7. Even if flotation was made to work it would be uneconomic due to the high cost of control acid required.

8. Flocculation would be affected by similar problems since the added flocculants cannot adsorb on real particle surfaces which are likely to be affected by ions produced by the solution of lime in water.

CHAPTER 9

FUTURE WORK

1. As the crystal size of minerals gets bigger the separation processes become less complex and cheaper. Therefore, in order to facilitate the application of mineral processing techniques for steel making slags, the grain growth of the phases should be determined as functions of the cooling rate and conditions of the molten slags.

2. The main economic cost of slag utilisation can be regarded as crushing and grinding. The development of cheaper size reduction processes can be another aspect of investigations.

3. The major problem encountered during the beneficiation of the slags by flotation and flocculation was the presence of free lime. Some preliminary tests were made towards the neutralization of the free lime by heating the slag with an acidic flux (silica sand). The pH values were reduced to approximate pH 9-10 from the original pH 12.5 depending on the free lime to silica sand ratio. A further study is needed to understand the reactions taking place and to evaluate the properties of products for practical purposes such as road stone.

4. The compounds found in the slags are identical to those of cement except the iron containing phases. A study can be conducted to produce a cement from steel making slags by adding necessary fluxes after the removal of iron bearing phases.

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