STUDY OF KINETICS INVOLVED IN OXIDATION OF NONFERROUS METAL SULPHIDES

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

Bachelor of Technology

In

Metallurgical and Materials Engineering

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Under the Guidance of

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CERTIFICATE

This is to certify that the thesis entitled "*STUDY OF KINETICS INVOLVED IN OXIDATION OF NONFERROUS METAL SULPHIDES*" submitted by Sri Vishal Netaji Waddar, Roll No. 10604029 & Sri Jitendra Kumar Behera, Roll No. 10604031 in partial fulfillment of the requirements for the award of Bachelor of Technology degree in Metallurgical and materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any Degree or Diploma

Date **(Dr. GAURI SHANKAR AGARWAL)**

ACKNOWLEDGEMENT

Our heart pulsates with the thrill for tendering gratitude to those persons who helped us in completion of the project.

The most pleasant point of presenting a thesis is the opportunity to thank those who have contributed to it. Unfortunately, the list of expressions of thank no matter how extensive is always incomplete and inadequate. Indeed this page of acknowledgment shall never be able to touch the horizon of generosity of those who tendered their help to us.

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Chapter 1

ABSTRACT

In the present investigation, an attempt has been done to study the simultaneous effects of the major processing variables on the extent of oxidation of commercially pure sphalerite ore pellets. These process variables taken into consideration were time and temperature. The oxidation was carried inside a muffle furnace where there was mild oxidation in the presence of atmospheric air. The pellets were charged for roasting inside the furnace in a graphite crucible. This process of roasting was carried out at four temperatures 750^0 C, 800^0 C , 850^0 C and 900^0 C .The project goal is to compare the oxidation or roasting at different temperature and time. At all instance of comparison one of the parameter was kept constant. The percentage (degree) of oxidation of sphalerite pellets was calculated at 15, 30, 45 and60 minutes, after the furnace reached the predetermined oxidation temperature. The experiments were statistically designed such that the effect of each variable can be quantitatively assessed and compared. The results showed that, temperatures above 850^0C, time remaining constant, with the increase in temperature there is increase in the rate of oxidation (roasting) of sphalerite ore pellets. Further more for a constant temperature with the increase in time of exposure, rate of oxidation of Sphalerite (ZnS) pellets increases. This is valid for temperature range above 850^0C. Another observation was made that temperature remaining constant, the rate of oxidation of Sphalerite (ZnS) ore pellets increases with time of exposure to attain a maximum limit than suddenly decreases followed by increment in the rate again. This observation was made in the temperature range of less than 800^0C.

CHAPTER-2

INTRODUCTION

Introduction

2.1 ZINC

Zinc makes up about 75 ppm (0.0075%) of the Earth's crust , making it the 24th most abundant element there. Soil contains 5–770 ppm of zinc with an average of 64 ppm. Seawater has only 30 ppm zinc and the atmosphere contains 0.1–4 $\mu g/m^3$. The element is normally found in association with other base metals such as copper and lead in ores. Zinc is a chalcophile ("sulfur loving"), meaning the element has a low affinity for oxygen and prefers to bond with sulfur in highly insoluble sulfides. Chalcophiles formed as the crust solidified under the reducing conditions of the early Earth's atmosphere. Sphalerite, which is a form of zinc sulfide, is the most heavily mined zinc-containing ore because its concentrate contains 60–62% zinc. [1]

World zinc resources total about 1.8 gigatonnes . The first production of zinc in quantity seems to have been in india and china. In India, zinc was produced at Zawar from the 12th to the 18th centuries. The sphalerite ore found here was presumably converted to zinc oxide via roasting. [1]

There are two methods of smelting zinc: the pyrometallurgical process and the electrolysis process. Both methods are still used. Both of these processes share the same first step: roasting. [2]

Some of the important naturally ocurring minerals of zinc are

- Sphalerite (ZnS)
- Zincite (ZnO)
- Franklinite($ZnO(Fe,Mn)_2O_3$)
- Smithstone ($ZnCO_3$)

The zinc ores are usually associated with several impurities or compounds , mainly sulphides of Pb,Cu,Cd . Of these minerals sphalerite is most common zinc ore . sphalerite is a yellow to white crystalline fluorescent compound that occurs naturally . [2]

Zinc is extracted from its ore, and is almost never found in the free elemental state. In order to obtain elemental zinc, the impurities must be removed by reduction processes . [2]

2.2 ROASTING

The roasting of an ore or a concentrate is a metallurgical process, involving gas-solids reactions at elevated temperatures, which precedes smelting in pyrometallurgy and leaching in hydrometallurgy.

In general, very few ores and concentrates in their native form are suitable for direct conversion to metal. An oxide is more easily reduced to the metal than a sulphide, and leaching becomes easier if the metal were present as a sulphate, chloride, or oxide. Therefore, the mineral constituent of an ore must be converted into another chemical form. Such a conversion can be brought about by roasting. Roasting, by employing oxygen or some other element, aims at the chemical conversion of an ore.

Traditionally, roasting was chiefly used to remove sulphur or other elements such as arsenic and tellurium in the form of a volatile oxide from an ore. Nowadays it encompasses a wide variety of operations including reduction, sulphation and chloridization where the ore is heated to a temperature below the fusion point of its constituents. The product, thus, obtained becomes amenable to subsequent treatment for the extraction of the metal. [2]

The most common example of roasting is the oxidation of metal sulfide ores. The metal sulfide is heated in the presence of air to a temperature that allows the oxygen in the air to react with the sulfide to form sulfur dioxide gas and solid metal oxide. The solid product from roasting is often called "calcine." In sulfide roasting, if the temperature and gas conditions are such that the sulfide feed is completely oxidized, the process is known as "dead roasting." Sometimes, as in the case of pre-treating reverberatory or electric smelting furnace feed, the roasting process is performed with less than the required amount of oxygen to fully oxidize the feed. In this case, the process is called "partial roasting," because the sulfur is only partially removed. Finally, if the temperature and gas conditions are controlled such that the sulfides in the feed react to form metal sulfates instead of metal oxides, the process is known as "sulfation roasting." Sometimes, temperature and gas conditions can be maintained such that a mixed sulfide feed (for instance a feed containing both copper sulfide and iron sulfide) reacts such that one metal forms a sulfate and the other forms an oxide, the process is known as "selective roasting" or "selective sulfation. [1]

2.2.1 Roasting of zinc sulphides

Zinc sulphides can be roasted in pots, muffles, travelling grate roasters or multiple hearth roasters in the presence of air. In recent years, however, flash roasters and fluidised bed roasters, which employ oxygen-enriched air, have been developed in order to accelerate roasting operations and to better utilize the exothermic heat of reaction.

The oxide obtained as a result of roasting is reduced by carbon to yield the metal. It can be noted that about 40 percent of the world's zinc is obtained by this method.

For roasting of zinc sulphides, the reactions may be written as

$$2ZnS + 3\ O_2 \rightarrow 2ZnO + 2SO_2$$ [2]

2.3 Concept of Ellingham diagram

In Ellingham diagram, highly stable sulphides are found at the bottom and the less stable sulphides occupy higher positions. [2]

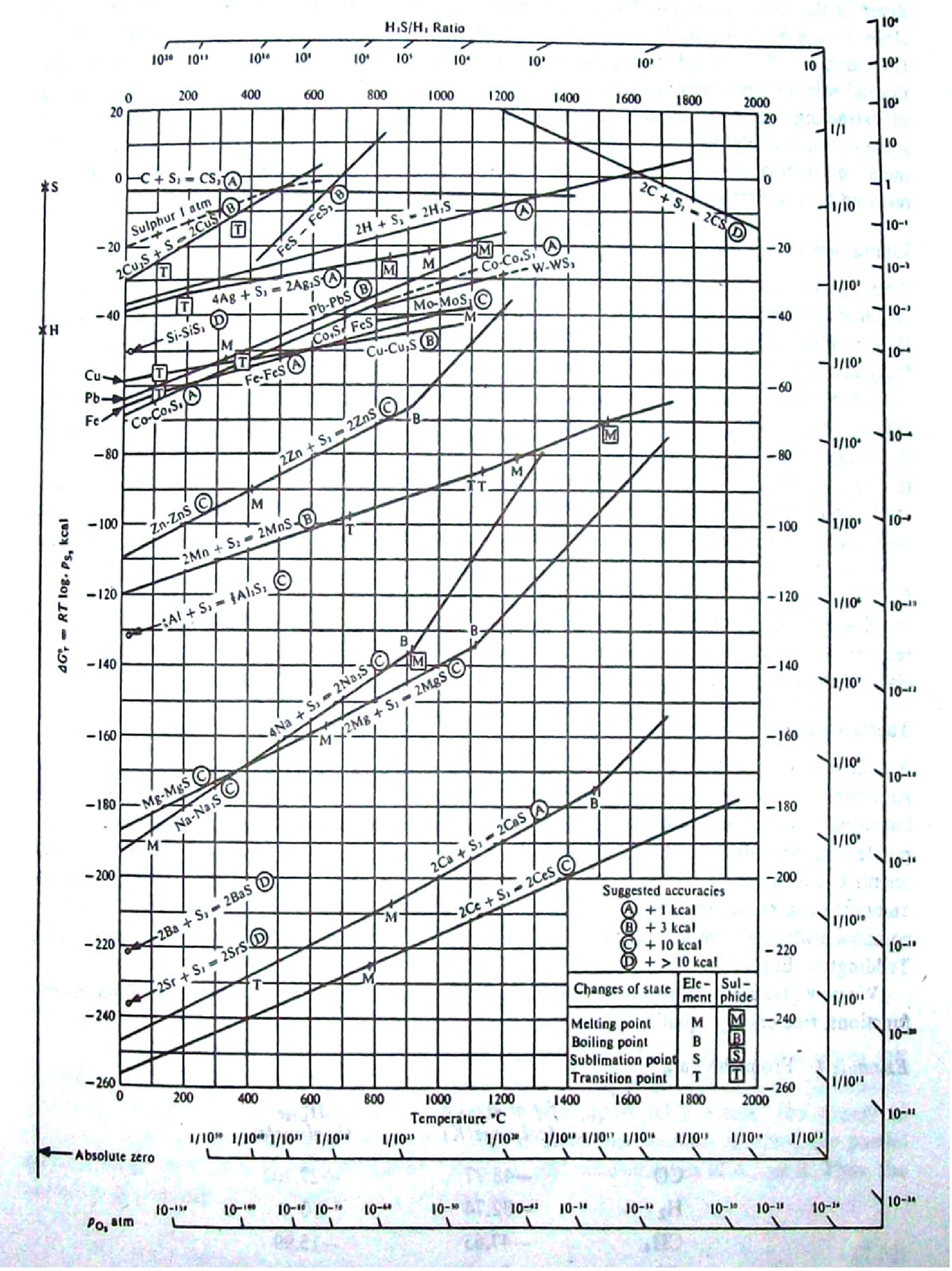
An element occupying a lower position in the diagram can always reduce the sulphides of other metal lying above it, when all the reactants and products are in their standard states. [2]

Carbon and hydrogen lie in upper position in the diagram, hence they are less stable. Hydrogen cannot be a very efficient reducing agent in the direct reduction of a zinc sulphide to zinc, as indicated by the position and slope of H_2S line in below Ellingham diagram. Since carbon has no sulphide analogous to CO to bring about the reduction of zinc sulphide at higher temperatures, it is also an inefficient reducing agent. [2]

The mutual solubility between zinc and their sulphides, in the molten state adds to the difficulties of extracting the metal by the direct reduction of sulphide. Thus it makes us necessary to convert sulphides in to oxides and then go for reduction in normal way. [2]

This is the reason why we go for roasting of zinc sulphides. Zinc sulphides cannot be reduced by carbon and hydrogen as mentioned above, thus it is roasted to form zinc oxides and subsequently zinc oxides are reduced by direct reduction process. [2]

Figure I



Free Energy Diagram for metal sulphides

2.4 AIM

1. To find out the activation energy for roasting of sphalerite ore pellets.
2. To judge the impact of process variables i.e. time and temperature on the roasting process of sphalerite ore pellets.
3. To study different reaction mechanism involved in the roasting of sphalerite ore pellets, the variables being time and temperature.

2.5 Layout

Chapter 3 deals in the process metallurgy involved in extraction of zinc, roasting being a part of it. Chapter 4 is the basic literature review section which has been found helpful in this entire project. Chapter 5 is a discussion about sphalerite pellets. Chapter 6 is about details involving mechanism and kinetics of roasting of sphalerite ore pellets. Chapter 7 consists the point wise description of the experimental steps. Chapter 8 is all about calculation and tabulations involved to obtain the various relationship and to calculate the activation energy. Chapter 9 concludes the study of oxidation of sphalerite ore pellets.

CHAPTER-3

PROCESS METALLUGY

3.1 PROCESS METALLURGY

Zinc is extracted from either zinc blende/sphalerite ore (zinc sulphide).

(1) The zinc sulphide ore is roasted in air to give impure zinc oxide.

$$2ZnS_{(s)} + 3O_{2(g)} ==> 2ZnO_{(s)} + 2SO_{2(g)}$$

(2) The impure zinc oxide can be treated in two ways to extract the zinc:

(a) It is roasted in a smelting furnace with carbon (coke, reducing agent) and limestone (to remove the acidic impurities).The chemistry is similar to the iron in blast furnace.

- $C_{(s)} + O_{2(g)} ==> CO_{2(g)}$ (very exothermic oxidation, raises temperature considerably)
- $C_{(s)} + CO_{2(g)} ==> 2CO_{(g)}$ (C oxidised, CO_2 reduced)
- $ZnO_{(s)} + CO_{(g)} ==> Zn_{(l)} + CO_{2(g)}$ (zinc oxide reduced by CO, Zn undergoes O loss)
- or direct reduction by carbon: $ZnO_{(s)} + C_{(s)} ==> Zn_{(l)} + CO_{(g)}$ (ZnO reduced, C oxidised)
- The carbon monoxide acts as the reducing agent i.e. it removes the oxygen from the oxide.
- The impure zinc is then fractionally distilled from the mixture of slag and other metals like lead and cadmium out of the top of the furnace in an atmosphere rich in carbon monoxide which stops any zinc from being oxidised back to zinc oxide.
- The slag and lead (with other metals like cadmium) form two layers which can be tapped off at the base of the furnace.
- The zinc can be further purified by a 2nd fractional distillation or more likely by dissolving it in dilute sulphuric acid and purified electrolytically as described below.

(b)Two stages

- It is dissolved and neutralised with dilute sulphuric acid to form impure zinc sulphate solution.
- $ZnO_{(s)} + H_2SO_{4(aq)} ==> ZnSO_{4(aq)} + H_2O_{(l)}$
- (ii) Quite pure zinc is produced from the solution by electrolysis. It can be deposited on a pure zinc negative electrode (cathode) in the same way copper can be purified. The other electrode, must be inert e.g. for

laboratory experiments, carbon (graphite) can be used and oxygen is formed.

- $Zn^{2+}_{(aq)} + 2e^{-} \Longrightarrow Zn_{(s)}$
- A reduction process, electron gain, as zinc metal is deposited on the (-) electrode
- You can't use solid zinc oxide directly because its insoluble and the ions must free to carry the current and migrate to the electrodes in some sort of solution. [3]

In the extraction of zinc , there are two techniques currently being employed they are

- Pyrometallurgical Extraction
- Hydrometallurgical Extraction

3.1.1 Pyrometallurgical Extraction

The technique used for roasting of CuS is not the same as ZnS because the latter does not melt even at a temperature as high as 1500^0C . Consequently, different methods have to be adopted . In one particular method, the zinc sulphide concentrate, which contains about 55 percent zinc , is roasted at a temperature of about 800^0C . The resultant roasted oxide is first ground and agglomerated and then sintered at 1200^0C so ass to provide a feed in the form of lumps for retort reduction. In the retort, the ZnO is reduced by carbon at about 1200^0C. The zinc which distils off is collected in condensers. The reactions are:

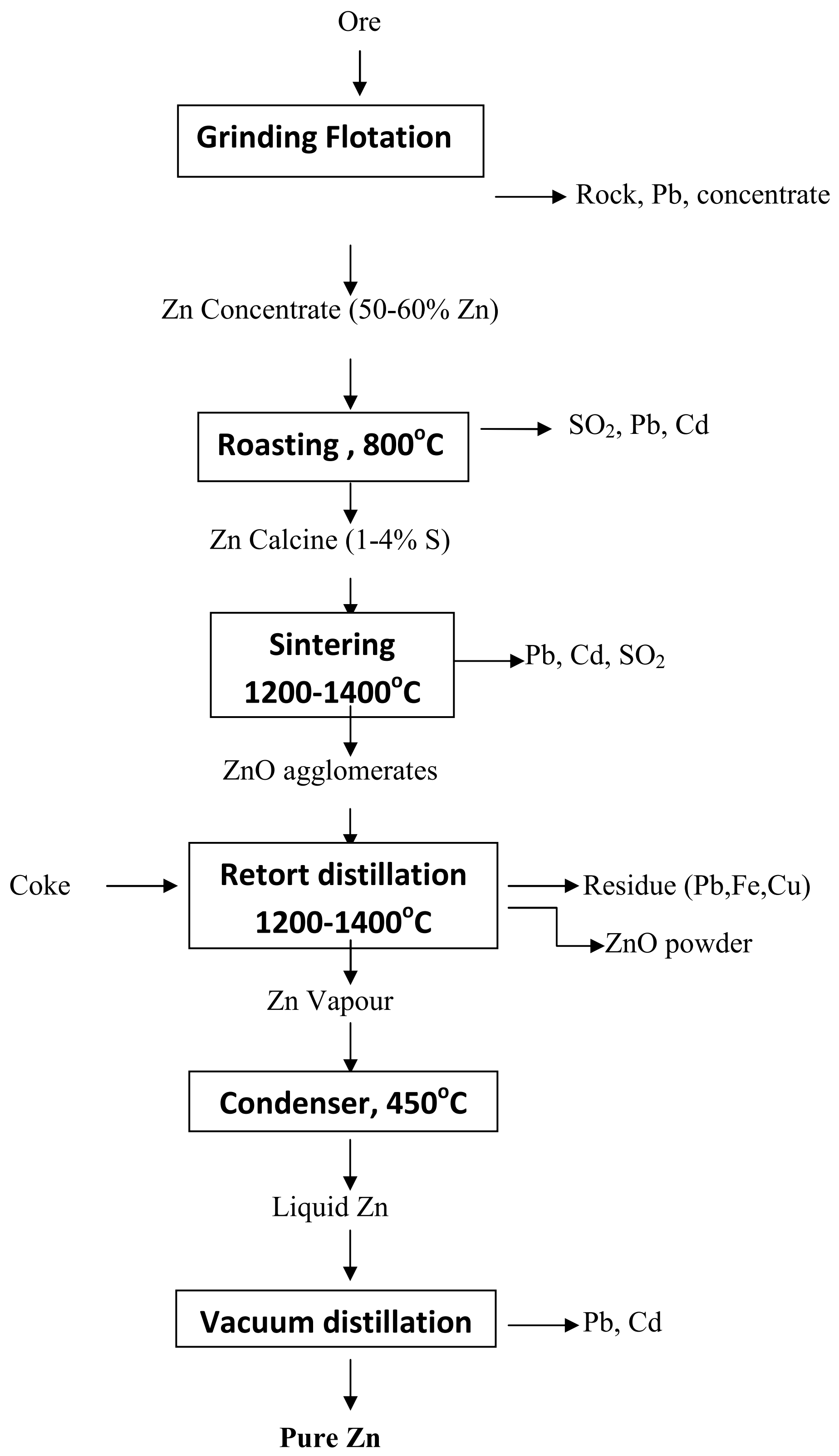
$ZnS + 1.5\ O_2 \rightarrow ZnO + SO_2$ (roasting)

$ZnO + CO \rightarrow Zn\ (g) + CO_2$ (reduction)

$C + CO_2 \rightarrow 2CO$

It should be noted that the partial pressure of CO in the retort gases has to be maintained at a high level in order to prevent the oxidation of Zn to ZnO by the CO_2 present in these gases. The zinc sulphide always contains some lead sulphide. In order to eliminate this lead sulphide to a large extent during the initial stages of roasting, i.e. by vitalisation, a hearth roaster is employed. The remaining lead sulphide is removed during sintering which is carried out at rather high temperatures. In order to prevent the distillation of any lead present in the zinc concentrate along with the zinc and to obtain a high-grade zinc, it becomes essential to ensure that feed for retort distillation has a low lead content. In most cases, roasting is carried out in a fluid bed roaster rather than in a conventional hearth roaster is autogenous. Further, a fluid bed roaster provides a good control over the temperature, ensures a rapid roasting rate and a high throughput of zinc calcine, and generates SO_2 which is suitable for acid production. The calcine obtained as a result of roasting is subsequently sintered in a Dwight-Llyod sintering machine to provide lump feed for retort reduction and to eliminate residual sulphur, cadmium and lead. [2]

Figure II



Flowchart for Pyromettalurgical Extraction of Zinc by reduction of ZnO by carbon

3.1.2 HYDROMETALLURGICAL EXTRACTION

Hydrometallurgical processes have been used for the extraction of zinc from wide variety of ores , including extremely low-grade ores. These processes not only yield zinc with a high degree of purity but they also lead to a higher rate of recovery of valuable by products than pyrometallurgical processes.

In a hydrometallurgical process , the zinc concentrate is first roasted in same manner as in the retort process .In this case , however ,a greater control is exercised over the roasting operation in order to minimize the formation of the ferrite $ZnO.Fe_2O_3$. As already mentioned , although this ferrite could be easily reduced , it is found to be virtually unleachable in the earlier hydrometallurgical processes, rendering it highly undesirable. This drawback has been overcome in the recently developed Jarosite and Goethite processes. The roasted zinc concentrate is dissolved in an acid and the valuable by-products are precipitated out .The leach solution is finally electrolyzed for the recovery of zinc.

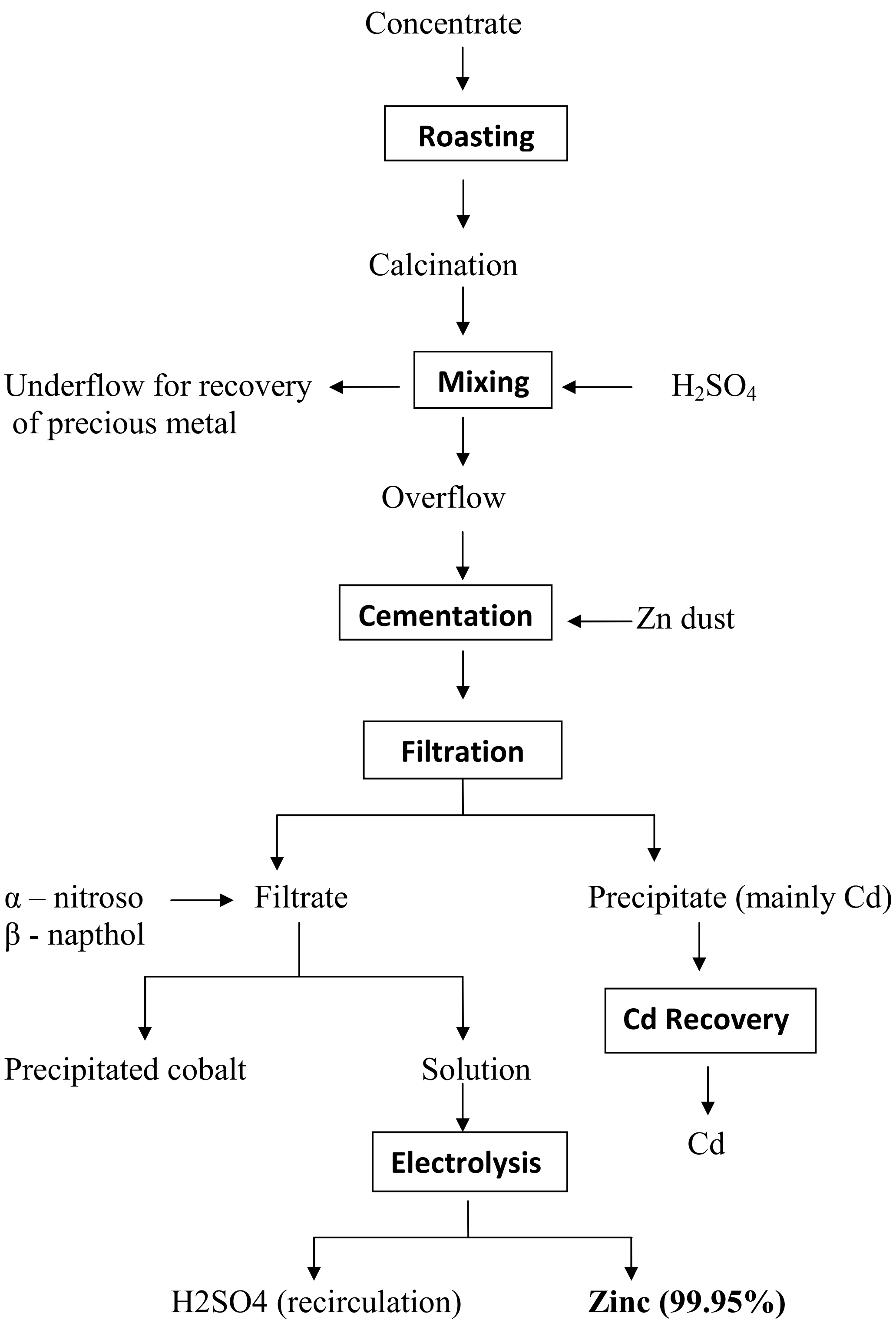
Since the position of zinc is rather high in the electrochemical series, it should be ensured that the foregoing solution is free of other elements such as Cd, Pb, Cu, Fe, As, and Ge. If not, the zinc deposited on the cathode of the electrolytic cell would be highly contaminated. Consequently, the removal of the aforementioned elements becomes an absolute necessity. Further, the presence of Cu and Fe is known to reduce the current efficiency during electrolysis. Even minute traces of As and Zn (few parts per million parts of copper) could prove almost disastrous because not only do these elements drastically reduce the current efficiency but they also render the deposit black and unsatisfactory.

The flow sheet for the hydrometallugical extraction process for zinc is based on the following scheme:

1) Dissolution of the zinc calcine in sulphuric acid
2) Precipitation of cadmium by adding zinc dust to the leach solution. i.e., cementation.
3) Precipitation of cobalt from leach solution by adding α-nitroso-β-napthanol.
4) Adjustment of the pH of the leach solution to about 5.3 to hydrolyze aluminium and iron and addition of MnO2 to oxidize iron to the trivalent state and to produce a precipitate that is flocculent and can absorb the entire quantity of As, Sb, and Ge.
5) Electrolysis of the purified leach solution using a cell with a Pb-Ag anode and an aluminium cathode.

The fig. shows a simplified flow sheet for the hydrometallugical zinc extraction process. As is evident from the flow sheet, the most important by-product is most importantly perhaps cadmium. It should, however, be noted that the cadmium obtained by cementation normally contains some lead, copper, and residual zinc. To eliminate these constituents, the cadmium is first dissolved in sulphuric acid, when only zinc and cadmium go into solution. When this solution is subjected afresh to cementation by zinc dust, a purer variety of cadmium in the form of a sponge is precipitated. This sponge is redissolved in sulphuric acid, and the solution is electrolyzed in order to obtain pure cadmium. [2]

Figure III



Flowchart for Hydrometallurgical Extraction of Zinc

Chapter 4

Literature Review

From ancient times the occurrence of zinc in man made artifact is can only be judged by its presence in Brass. Ever since the discovery of copper, zinc has been used as an alloying agent for its hardening. It has been a fact that retorts were used for roasting of zinc ores which resulted in a light in weight, smoky zinc oxide which the Greeks termed "Pompholyx" or "Philosopher's wool". The ore must be oxidized to its respective oxide i.e. here it is ZnO, this is because the reduction of ZnS to Zn is very difficult. For the next step of reduction of ZnO to Zn it is important to have temperature around 1000^0C because zinc is not formed at temperature below 950^0C, since the boiling point is 913^0C. [4]

Present case scenario suggests 80% of the total production of zinc is from zinc sulphide concentrate. The processes involved are roasting-leaching-electrowinning.[5] In maximum of the cases the feed to the roaster furnace is mainly a mixture of zinc concentrates and sometimes some amount of secondary materials like oxides are also fed along with the zinc concentrate to blend with the concentrate. Zinc ash formed as a casting product is fed to the furnace. The variables involved in the roasting process is mainly the concentrate mixture. So it is important for us to know the composition of the concentrates. For knowing the composition of the concentrate the basic factor to we should get hold of is the mineralogy of the concentrates. Most Zn concentrates are sulphides but there are also oxides. [6]

The most common Zn minerals are the following:

- Sphalerite, zinc sulfide, ZnS, (Zn,Fe)S, cubic, trimorphous with martraite and wurtzite.
- Wurtzite, zinc sulfide, ZnS, (Zn,Fe)S, hexagonal and trigonal polytypes, trimorphous with martraite sphalerite.
- Marmatite, (Zn,Fe)S ferroan sphalerite.
- Martraite, ZnS, trigonal, trimorphous with sphalerite and wurtzite.[6]

Other important factors are the chemical analysis and grain size distribution of the concentrate.

These factors influence in the roasting behaviour as well as that of the roasting bed.

The Zn content for concentrates is in the range of about 45–60%. The S content is about 30%.Along with these factors the impurity level has also an significant effect on the behaviour of roasting.[6]

Elements that must be handled during leaching and purification operations to avoid problems in electrolysis operation are for instance Co, Ni, Cd, Ge, Sb and Tl. [6]

In this roasting process the sulphur from the sphalerite [(Zn,Fe)S] gets converted to sulphur dioxide and subsequently into sulphuric acid. The sphalerite is in turn converted into ZnO and a small fraction of it which contains iron as an impurity gets converted into $ZnFe_2O_4$. The ZnO (calcine) undergoes the leaching operation to produce $ZnSO_4$, this leaching operation is carried out in weak acid or neutral environment. Leaching is done mainly for purification which is than subjected to electrowinning. Roasted ZnO contain small amounts of partially reacted sphalerite. The surfaces of these particles have been converted to uniform, porous, banded masses of (Zn,Fe)O or ZnO + $ZnFe_2O_4$. The particle mostly retains their approximate morphology of the original sphalerite grain. The majority of the original sphalerite has reacted; only a small portion remains un-reacted. The surface portion of the particle has been converted to a fine-grained uniform and porous mass of ZnO + $ZnFe_2O_4$. A relatively dense (Zn,Fe)O phase occurs between the sphalerite core and the ZnO + $ZnFe_2O_4$ layer. The (Zn,Fe)O phase contains a trace amount of sulfur. It appears that the outer uniform and porous ZnO + $ZnFe_2O_4$ layer formed from the inner dense (Zn,Fe)O phase, which in turn, formed from the sphalerite (Zn,Fe)S. The fluidized bed roasting results in the sulphur from the sphalerite to diffuse out of the particles. The zinc and the iron present in it gets converted into (Zn,Fe)O. As iron present in (Zn,Fe)O phase migrates outwards and reaches the periphery of the particle, there is forms $ZnFe_2O_4$. This resultant porous structure of ZnO and $ZnFe_2O_4$ agglomerates to form large, spherical masses. This leads to the formation of a compact shell on the outer surface which continues to grow in inward direction, eventually the particle as a whole becomes compact. There is a subtle chance of defluidization to occur with agglomerates formed from ZnO particles that are cemented by zinc oxysulphate and zinc sulphate. [5]

The procedural variable like the particle size, sample mass, partial pressure of oxygen, heating rate and the composition of the sample pan has a great effect in the oxidation process of sulphides. The change in partial pressure results in change in the phases that ought to be formed, this can be demonstrated by the predominance area diagram at a particular temperature.[7]

When oxidation of sulphides are carried out under mild oxidizing condition i.e. in the presence of air and a moderate hating rate of 10^0C – 20^0C, there will be formation of oxides given by the equation:

$2MS_{(s)} + 3O_{2_{(g)}} ==> 2MO_{(s)} + 2SO_{2_{(g)}}$[7]

The reaction is exothermic, this is due to the formation of SO_2.When oxidation is done, after certain time an oxide coating is formed, this oxide coating can be quite protective. This oxide coating can inhibit the diffusion process of oxygen to the unreacted sulphide. This inhibition which is temporary may lead to other transformations. For example, further dynamic heating of the sample within the protective coating may produce decomposition of the sulphide.

Since many of the sulphides have excess sulphur, there may be decomposition into a sulphides and liberation of sulphur may occur. For example chalcopyrite ($CuFeS_2$) gives bornite (Cu_5FeS_4). [7]

$$5CuFeS_2 ==> Cu_5FeS_4 + 5FeS + S$$

The formation of sulphate can be by two ways:

1. Direct oxidation of sulphides

$$MS_{(s)} + 2O_{2_{(g)}} ==> MSO_{4_s}$$

2. The sulphation of oxides with sulphur trioxide

$$MS_{(s)} + 1.5O_2 ==> MO_{(s)} + SO_{2_{(g)}}$$

$$SO_{2_{(s)}} + .5O_2 ==> SO_{3_{(g)}}$$

$$MO_{(s)} + SO_{3_{(g)}} ==> MSO_{4_s}$$

$$MS_{(s)} + 4SO_{3_{(g)}} ==> MSO_{4_s} + 4SO_{2_{(g)}}$$ [7]

Mr. M.F Chase suggested that a rapid method, suitable for determining the sulphur in roasted blend. He suggested heating the ore sample in a current of air, which resulted in the evolution of sulphur dioxide fumes. These fumes were to be absorbed in an excess of a standard alkali solution and titrating the excess. Based on this suggestion, the method described by him was worked up and has been in regular use since then [8]

Consider a kiln, the constituent of the sphalerite ore are converted into there respective oxides. But some of the part remain in its original sulphide condition and a small part of the zinc may be present as zinc sulphate. Heting this ore in a current of air to its bright red condition results in conversion of all these sulphides into its oxide state. The final product is metallic oxides along with sulphur dioxide and a small amount of sulphur trioxide. The sulphate od zinc formed decomposes to give zinc oxide and sulphur trioxide. The calcium sulphate present does not decompose by heat and remains in an unaltered state until the temperature is raised. The presence of calcium sulphate might seem to be a drawback to this method as even in the best roasting condition the calcium in the ore will always retain its sulphur. So the value obtained by this method is called "false sulphur" value. There happens to be a unforeseen phenomenon where there is formation of fumes of zinc oxide as long as there is some amount of sulphide present which is not oxidized .[8]

This is a very good indication of completion of decomposition of sulphides and sulphates and of the absorption of sulpur oxides. This fume is not appreciably dissolved in alkali solution. Numerous tests of absorption have shown that faint traces of zinc is not enough to determine. To prove that it is zinc oxide, it is collected over distilled water in an inverted bottle which was then covered and allowed to stand until the fume had settled. It was then dissolved in a little dilute hydrochloric acid and potassium ferrocyanide solution added. This gave the white zinc ferrocyanide precipitate. Phenolphthalein is used as the indicator in the titration .[8]

The temperature of the particle undergoing roasting is found to be 10^0C more in case of roasting at 800^0C and 20^0C for 900^0C .[9]

At all temperatures below 880^0C the penetration of oxygen was uniform over the faces, the interface of ZnO and ZnS is defined sharply, the corners of the sulphides remains sharp till this temperature. There is onset of diffusion controlled mechanism from a temperature of 880^0C and the reaction behaviour is completely diffusion controlled at a temperature greater than 900^0C. [9]

After roasting the along with the conversion of zinc concentrate to zinc oxide, the main problem in the conversion is that it is not effective due to the presence of the unaffected zinc sulphide present. The other problem is the presence of zinc ferrite which retains a considerable amount of zinc with it.[10]

Dimitrov et al. (1967) studied the kinetics and mechanisms of oxidation of several crystalline forms of ZnS powders and showed that the ZnO oxidation has not only topochemical aspects, but also autocatalytic characteristics. [10]

At a temperature greater than 900^0C, the temperature which is usually found in conventional fluidized bed roaster, lead oxide is formed due to the oxidation of galena (PbS) and the dissociation of intermediate oxidation product. This can be given by the equation:

$$2PbS + 3O_2 \ ==> 2PbO + 2SO_2$$

$$PbSO_4 ==> PbO + SO_3$$

$$PbSO_4.PbO ==> 2PbO + \ SO_3$$

$$PbSO_4.4PbO ==> 5PbO + \ SO_3$$

The complex thermal behaviour of galena renders the products formed during roasting difficult. [10]

Leaching when done in the presence of nitric acid which is a strong oxidizing acid, the acid tends to oxidize the remaining un reacted sulphide. And the residue of this process is quartz (SiO_2) and hematite (Fe_2O_3).[10]

Chapter 5

Pellets

5.1 **Pellets** are approximately spherical lumps formed by the agglomeration of the commercially pure Sphalerite ore fines in presence of moisture and Bentonite as a binder. These pellets formed are air dried for 24 hours. The "**Green Pellets**" that are formed by air drying are dried again in a furnace at 100^0C.

Binders play an important role in pellet formation. The different types of binders used can be classified into following categories:

Organic binders (Dextrin, Starch, Alginate)

Inorganic binders (Bentonite, Cement, Lime, Calcium hydroxide)

Bonding mechanism involves two stages as:

(a) Nucleation (Seed formation**)**

(b) Growth (occurs in two ways: growth by layering and growth by assimilation**)**

5.2 Advantages of pellets:

1. Good oxide forming tendency
2. Good permeability
3. High bulk density
4. High non-ferrous metal content
5. Uniform chemical composition
6. High strength
7. Less heat consumption
8. Ease in handling

5.3 Disadvantages of pellets:

1. High cost of production due to grinding and firing.
2. Swelling and loss of strength inside furnace.
3. Sticking during firing.
4. Resistance to flow of gas more than that in sinter for the same size range due to lower number of voids.
5. Difficulty of producing fluxed pellets.

Chapter 6

Mechanism and Kinetics

6.1 Oxidation under mild oxidizing conditions

An examination of the studies carded out so far under mild oxidising conditions, which implies the use of air as the oxidant and a moderate heating rate of 10 to 20°C min -1, indicates that the following types of reactions may be involved during the oxidation of sulphides.

1. Direct formation of oxide:

The formation of oxide can be expressed in general as:

$2MS(s) + 302(g) \rightarrow 2MO(s) + 2502(g)$

The formation of SO2 is highly exothermic.

2. Formation of sulphate:

The formation of sulphate can take place by two possible reactions.

- The first is the direct oxidation of the sulphide, as shown during the oxidation of nickel sulphide and iron(II) sulphide :

  $MS(s) + 202(g) \rightarrow MSO4(s)$

- The second possibility is the sulphation of the oxide with sulphur trioxide:

  $MS(s) + 1.502(g) \rightarrow MO(s) + SO_2(g)$

  $SO2(g) + 0\text{-}502(g) \rightarrow SO_3(g)$

  $MO(s) + SO3(g) \rightarrow MSO_4(s)$

  $MS(s) + 4SO3(g) \rightarrow MSO_4(s) + 4S0_2(g)$

3. Decomposition of sulphates:

Decomposition of sulphates takes place in two stages, as expressed by the following reactions:

$2MSOn(s) \rightarrow MO.MSO_4(s) + SO_{3(g)}$ and

$MO.MSO4(s) \rightarrow 2MO(s) + SO3(g)$

These reactions are endothermic and there is a loss in the weight.

4. Solid-solid reactions:

Solid-solid reactions can occur between the reaction products formed during the oxidation of sulphides, the most common being the reaction between unreacted sulphide and sulphate. When a particle of sulphide is oxidised, the reaction usually takes place via a shrinking core process. The oxygen attacks the outer surface, and the reaction front moves inwards. Both oxide and sulphate can be formed simultaneously, but it appears that the oxide forms an outer layer, and the sulphate exists between the oxide and the unreacted sulphide core . There is obviously some overlap and the boundaries are not distinct. Sulphur exists in a central core; then there is a decrease in a rim near the surface and, finally, in the outermost rim it is usually difficult to detect the sulphur. Hence, it is possible for the reaction to occur between the inner core sulphide and the sulphate.[7]

5. Ion diffusion processes:

In ternary sulphides, it is possible during the heating stage for one of the cations to preferentially diffuse towards the oxygen/oxide interface.

6.2 Main reactions and thermodynamics

The product of roasting is called calcine and the reaction is exothermic. The reaction occurs in the particles through the diffusion of O_2 on the surface of the concentrate particles. During roasting ferrites are also formed, such as $ZnFe_2O_4$, $CuFe_2O_4$ etc. Some major reactions are presented below:

The main reaction in roasting**:**

$$\mathbf{ZnS + 1.5\ O_2 \Rightarrow ZnO + SO_2}$$

Other reactions of importance:

$$\mathbf{2\ FeS + 3.5\ O_2 \Rightarrow Fe_2O_3 + 2\ SO_2}$$

$$\mathbf{2\ FeS_2 + 5.5\ O_2 \Rightarrow Fe_2O_3 + 4\ SO_2}$$

$$\mathbf{PbS + 2\ O_2 \Rightarrow PbSO_4}$$

$$\mathbf{Cu2S + 2\ O2 \rightarrow 2\ CuO + SO2}$$

$$\mathbf{CaCO3 + SO2 + 0.5\ O2 \rightarrow CaSO4 + CO2}$$

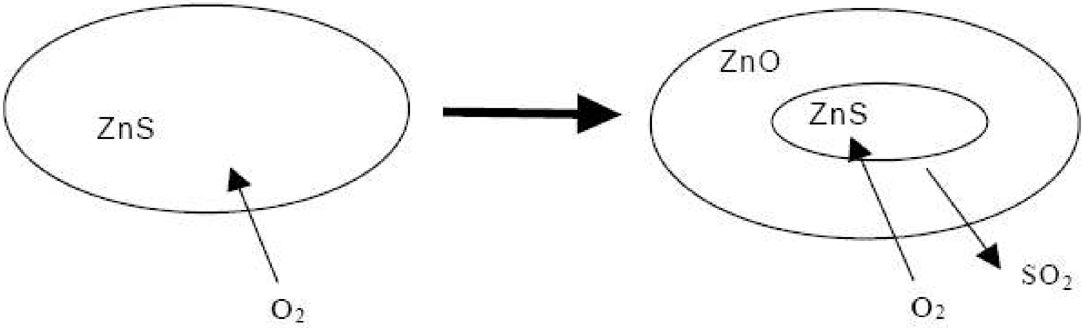
The ferrite formation reaction:

$$\mathbf{ZnO + Fe2O3 \rightarrow ZnO.Fe2O3}$$

$$\mathbf{CuO + Fe2O3 \rightarrow CuO.Fe2O3}$$

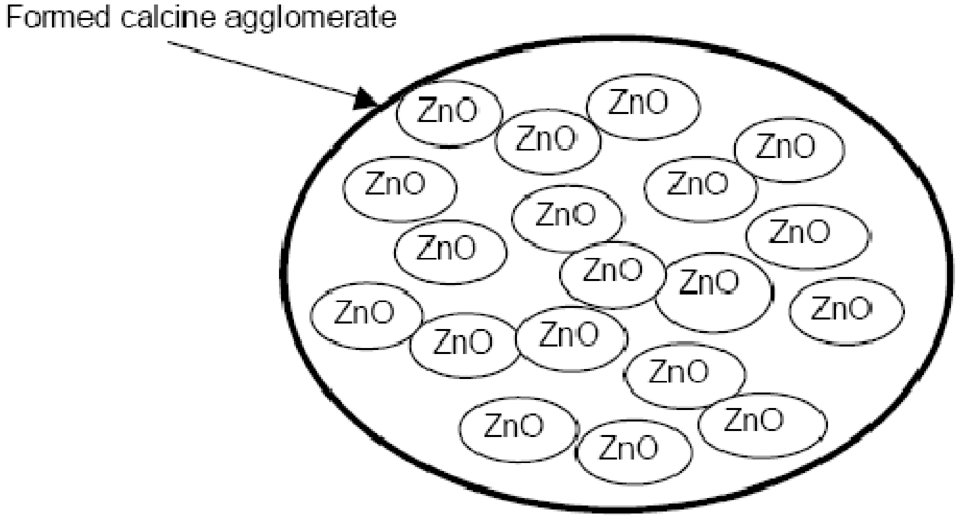
Also, agglomeration between particles takes place in the bed, which leads to larger Particles. The growth mechanism is essential for the behaviour of the bed, but due to its complexity, understanding of the mechanism is limited. Control of the bed particle size distribution is of major importance for stable roasting conditions. [7]

Figure : IV



Schematic drawing of the reaction principle. The sulphide mineral particle reacts with oxygen. The product is calcine (mostly ZnO). During the reaction SO2 gas is formed.[7]

Figure : V



Schematic drawing of a calcine agglomerate formed of many small calcine particles. Bonds are formed between particles due to molten phases.[7]

6.3 KINETICS OF OXIDATION PROCESS

Reaction kinetics of sphalerite ore pellets oxidation deals with the rate at which zinc oxide is converted to metallic zinc by removal of sulphur. The rate at which the ore is oxidized influences the production rate, which ultimately determines the economic feasibility and competitiveness of the process technology involved .Thus the reaction rate in roasting is of prime importance. The oxidation of zinc oxide to metallic zinc proceed though various kinetic steps and one of them is the slowest step, which control the overall reaction rate .The different rate controlling factors which control the overall rate of oxidation are given below:

6.3.1 Boundary Layer Control

In boundary layer control the overall oxidation rate is controlled by the diffusion of gas and heat through the boundary layer of the gas which builds up around each particle. The rate of diffusion of the gas through the boundary layer is proportional to the gas concentration gradient across the layer. Secondly, the rate of heat flow to the particles is proportional to the temperature gradient across the boundary layer. In most direct oxidation process contact between gas and solids is achieved by counter current flow of preheated gas to the movement of the bed of solids.

6.3.2 Phase Boundary Reaction Control

The chemical reaction at the ZnS- ZnO interface is the rate controlling factor. In this case the rate of oxidation per unit area of the remaining zinc sulphide is found to be constant with time. This mechanism is called “Phase Boundary Reaction Control”. When counter diffusion of reducing gas and product gas on the oxidized outer layer is sufficiently fast, the concentration of oxidizing gas at the reacting surface is effectively the same as it’s concentration at the particle surface. In such case the rate of reaction at the zinc sulphide-zinc oxide interface would control the overall oxidation rate. This mechanism is unlikely at the very start of the oxidation, when the zinc oxide layer is very thin, or for very small porous grains of zinc oxide**.**

6.3.3 Gaseous Diffusion Control

The rate of oxidizing gas inward and product gas outward through the oxidized zinc layer can control the rate of oxidation of zinc sulphides. This phenomenon is generally associated with large ore particle and is known as “Gaseous Diffusion Control”. When gaseous diffusion is the rate controlling step, the rate of diffusion of reducing gas inward and product gas outward through the porous layer of metallic zinc surrounding the unoxidized inner core particle, is slower than the rate of reaction. During such occurrence the concentration of the reducing gas will decrease that of product gas will increase at the interface. The change in the gas composition will slow down the oxidation rate until a pseudo steady state is established.

6.3.4 Mixed Control

When both Gaseous Diffusion Control and Phase Boundary Reaction Control combine influence the rate of oxidation, the mechanism is referred to as “Mixed Control”. Mixed control has been proposed by several experiments to reconcile the complexities and conflicting results obtained from direct oxidation of zinc oxides with simpler mechanism. In mixed control, the gas boundary layer, the phase boundary reaction and gaseous diffusion act together under pseudo steady state condition to determine the overall reaction rate. Different mathematical models equations are proposed to represent different rate controlling steps, which are given below

EQUATION	**CONTROLLNG STEP**
$1- (1-f)1/3 = kt$	Chemically Controlled
$- \ln (1-f) = kt$	Chemically Controlled
$[1 – (1-f)1/3]2 = kt$	Diffusion Controlled
$1- 2/3f – (1 - f)2/3 = kt$	Diffusion Controlled
$k' [1-2/3f – (1-f)2/3] +D/r0[1-(1-f)1/3] = kt$	Mixed Controlled

Chapter 7

Experimental

7.1 Collection of raw materials

Commercially pure Sphalerite (ZnS) ore was used for this study. The ore was in its crushed state when obtained, with -8+14 mesh size.

The ore was made into pellets of average diameter of 2 cm for Sphalerite ore. The binders used were water and a very small amount of Bentonite. The method used for making pellets was "Hand Rolling".

The hand rolled pellets were air dried for 24 hrs. After which the green pellets were furnace dried for 1 hour at a temperature of 100^0C to ensure complete removal of moisture in the pellets.

7.2 Procedure for Oxidation

- The pre-dried pellets, dried at 100^0C were taken four at a time.
- The pellets were weighed individually (Initial Weight = W_1) and put in the graphite crucible marked A, B, C, and D.
- These four crucibles were put in a muffle furnace first at 750^0C with D being the first one to be put into it followed by C, B than A.
- Time was noted and the crucibles were taken out in the opposite order at an interval of 15 minutes that is, A after 15 minutes, B after 30 minutes, C after 45 minutes and D after 60 minutes.
- The weight of each sample was calculated (Final weight = W_2) after removing from the furnace.

  This same procedure was repeated for temperatures 750^0C, 800^0C, 850^0C and 900^0C.

$$\%\boldsymbol{Oxidation} = \frac{[\boldsymbol{Amount\ of\ weight\ change\ (W_1 -\ W_2)}]}{\boldsymbol{Total\ amount\ of\ removable\ Sulphur}} \times \mathbf{100}$$

Chapter 8

Results and Discussion for Sphalerite ore pellets

8.1 Tabulation

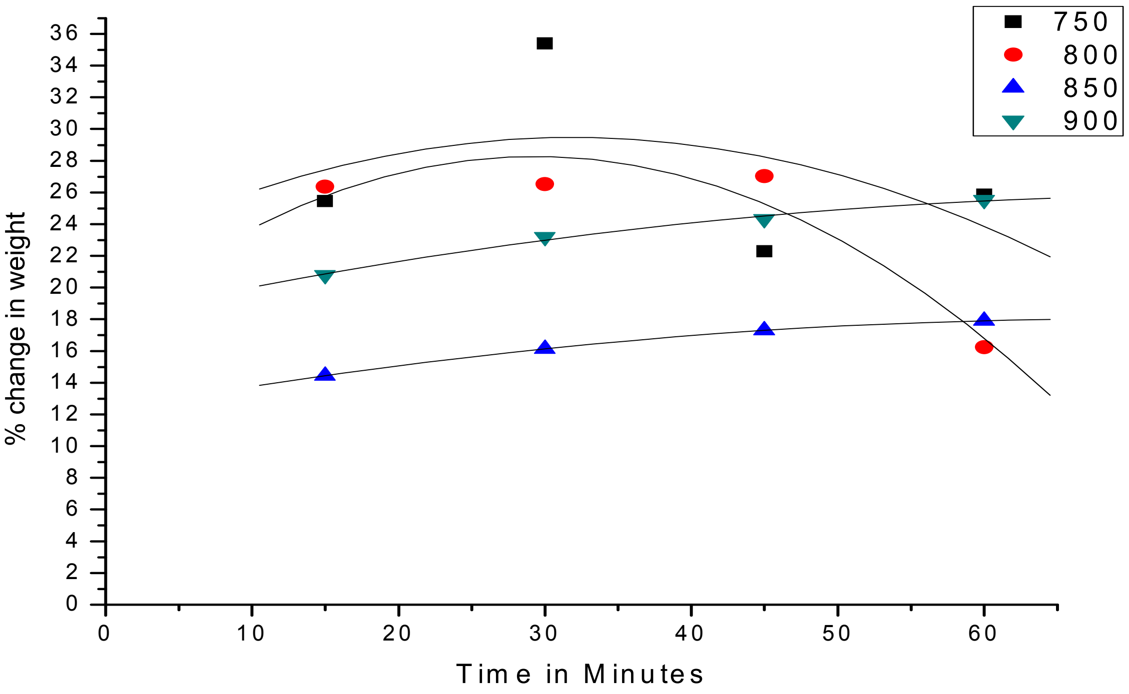
Table-1

Temperatures (in ^{0}C)	A(taken out after 15 minutes)	B (taken out after 30 minutes)	C (taken out after 45 minutes)	D (taken out after 60 minutes)
750	W_1= 18.69 grams	W_1= 15.17 grams	W_1= 16.01 grams	W_1= 17.13 grams
	W_2=13.93 grams	W_2= 9.61 grams	W_2= 12.44 grams	W_2= 12.70 grams
800	W_1= 18.35 grams	W_1= 17.29 grams	W_1= 18.01 grams	W_1= 13.30 grams
	W_2= 13.51 grams	W_2= 12.71 grams	W_2= 13.14 grams	W_2= 11.14 grams
850	W_1= 14.11 grams	W_1= 13.38 grams	W_1= 11.56 grams	W_1= 17.06 grams
	W_2= 12.07 grams	W_2= 11.22 grams	W_2= 9.56 grams	W_2= 14.00 grams
900	W_1= 16.17 grams	W_1= 14.86 grams	W_1= 14.96 grams	W_1= 12.37 grams
	W_2= 12.80 grams	W_2= 11.40 grams	W_2= 11.32 grams	W_2= 9.21 grams

Table-2

Temperature (in ^{0}C)	**Percentage Change in weight(W_1-W_2) in % for A**	**Percentage Change in weight(W_1-W_2) in % for B**	**Percentage Change in weight(W_1-W_2) in % for C**	**Percentage Change in weight(W_1-W_2) in % for D**
750	**25.46**	**35.41**	**22.29**	**25.86**
800	**26.37**	**26.54**	**27.04**	**16.24**
850	**14.45**	**16.14**	**17.30**	**17.9**
900	**20.80**	**23.2**	**24.33**	**25.54**

Figure-VI

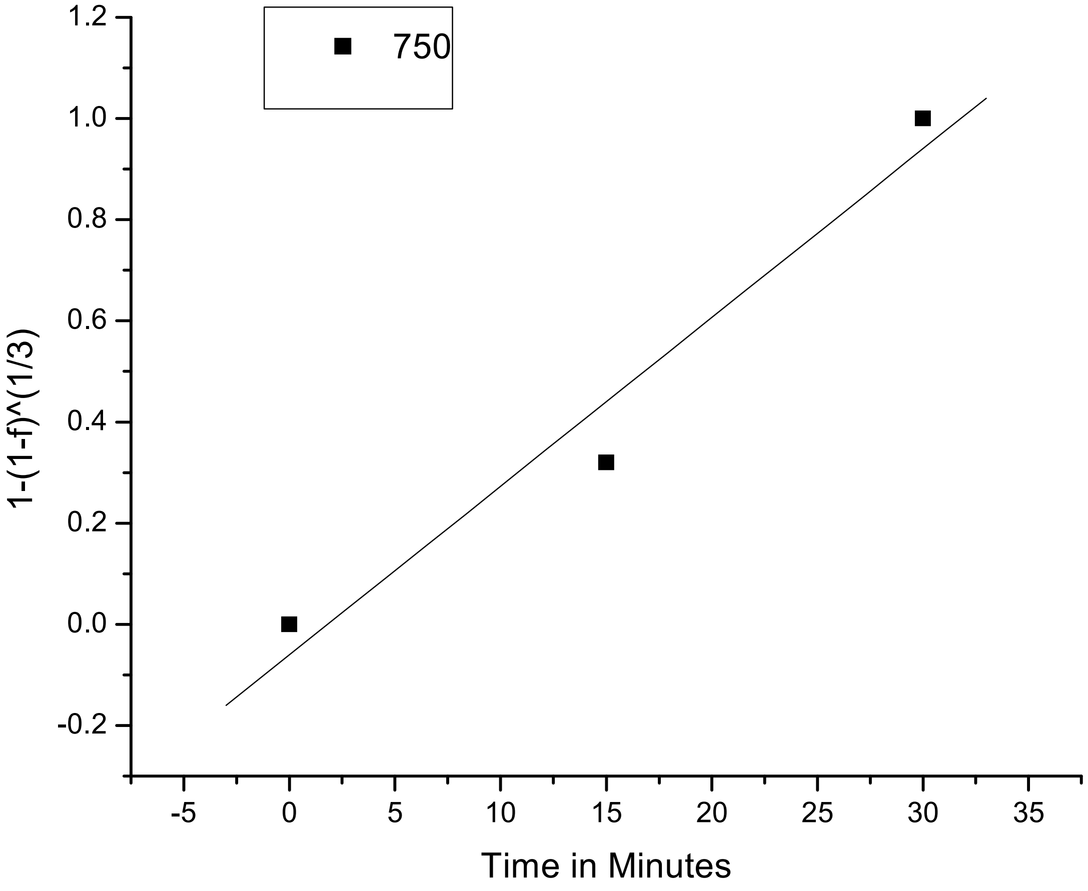


8.2 Modelling

Kinetic Model

The plots of 1-(1-f)$^{1/3}$ vs. time gave straight line which determined the most appropriate kinetic model for the roasting of sphalerite ore pellets at a temperature of 750^{0}C up to 30 minutes time. The kinetic model for this sulphur removed would be $\mathbf{1-(1-\boldsymbol{f})^{\frac{1}{3}}=\boldsymbol{Kt}}$, where t is time, f is the fraction of oxidation and K is the rate constant.

Figure-VII (For 750^{0}C)



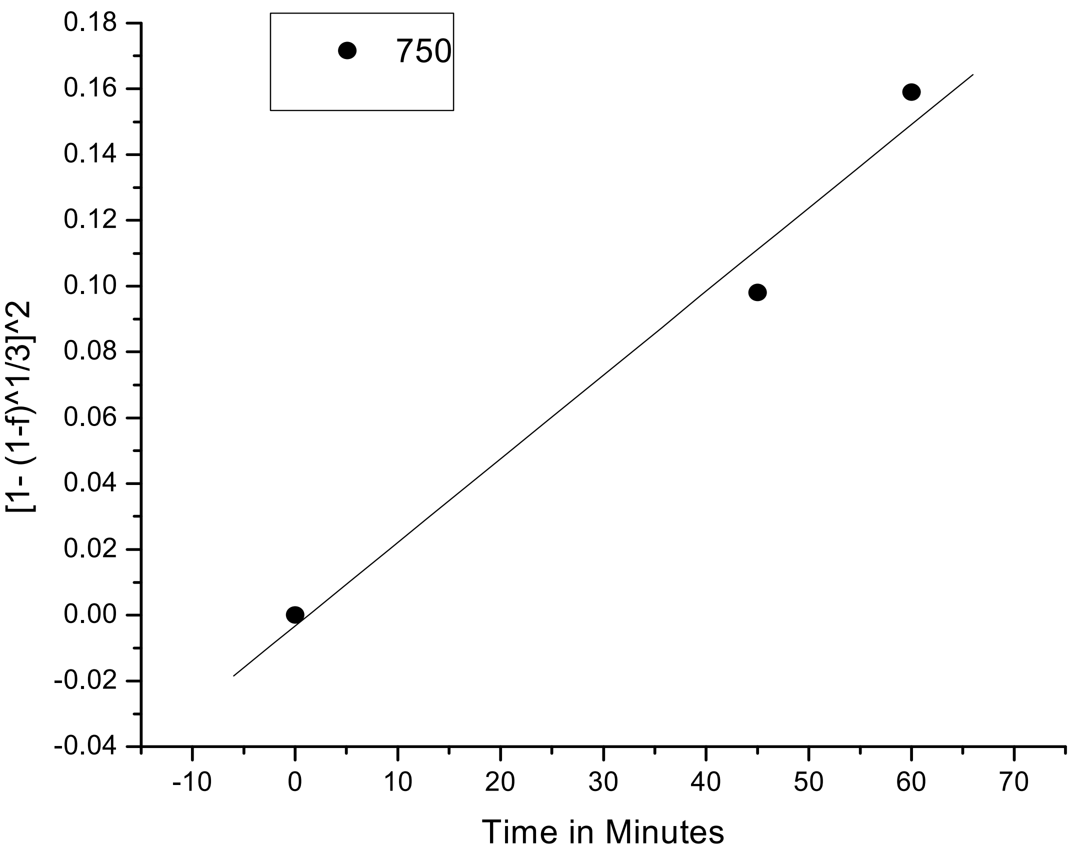
The Slope was found to be 0.03333

***This reaction is chemically controlled upto 30 minutes time.**

Kinetic Model:

The plots of $[1-(1-f)^{1/3}]^2$ vs. time gave straight line which determined the most appropriate kinetic model for the roasting of sphalerite ore pellets at a temperature of 750^0C from 30 minutes time to 45 minutes time. The kinetic model for this oxidation would be $[1-(\mathbf{1}-\boldsymbol{f})^{\frac{1}{3}}]^2 = \boldsymbol{Kt}$, where t is time, f is the fraction of sulphur removed and K is the rate constant.

Figure-VIII **(For 750^0C)**



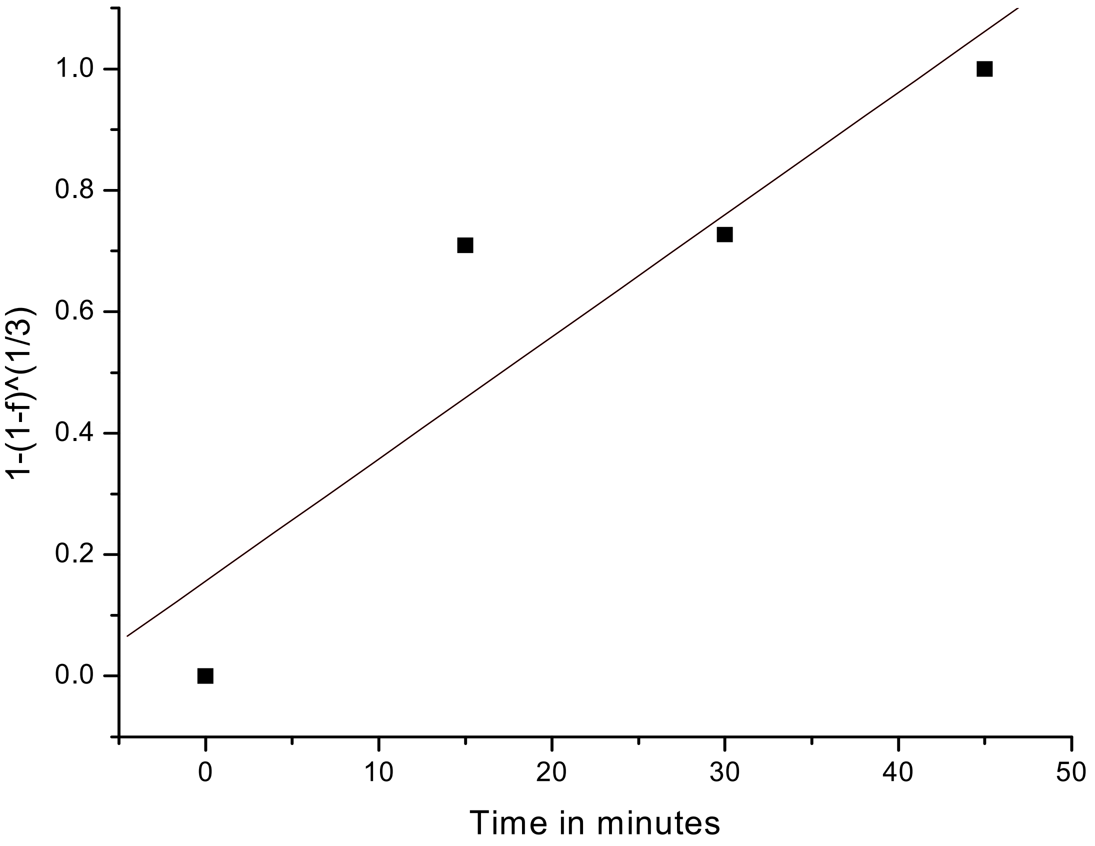
The Slope was found to be 0.00254

***The reaction is diffusion controlled for time greater than a certain time within the range 30-45 minutes.**

Kinetic Model

The plots of 1-(1-f)$^{1/3}$ vs. time gave straight line which determined the most appropriate kinetic model for the roasting of sphalerite ore pellets at a temperature of 800^{0}C in 60 minutes time. The kinetic model for this sulphur removed would be $\mathbf{1-(1-\boldsymbol{f})^{\frac{1}{3}}=\boldsymbol{Kt}}$, where t is time, f is the fraction of oxidation and K is the rate constant.

Figure- IX (For 800^{0}C)



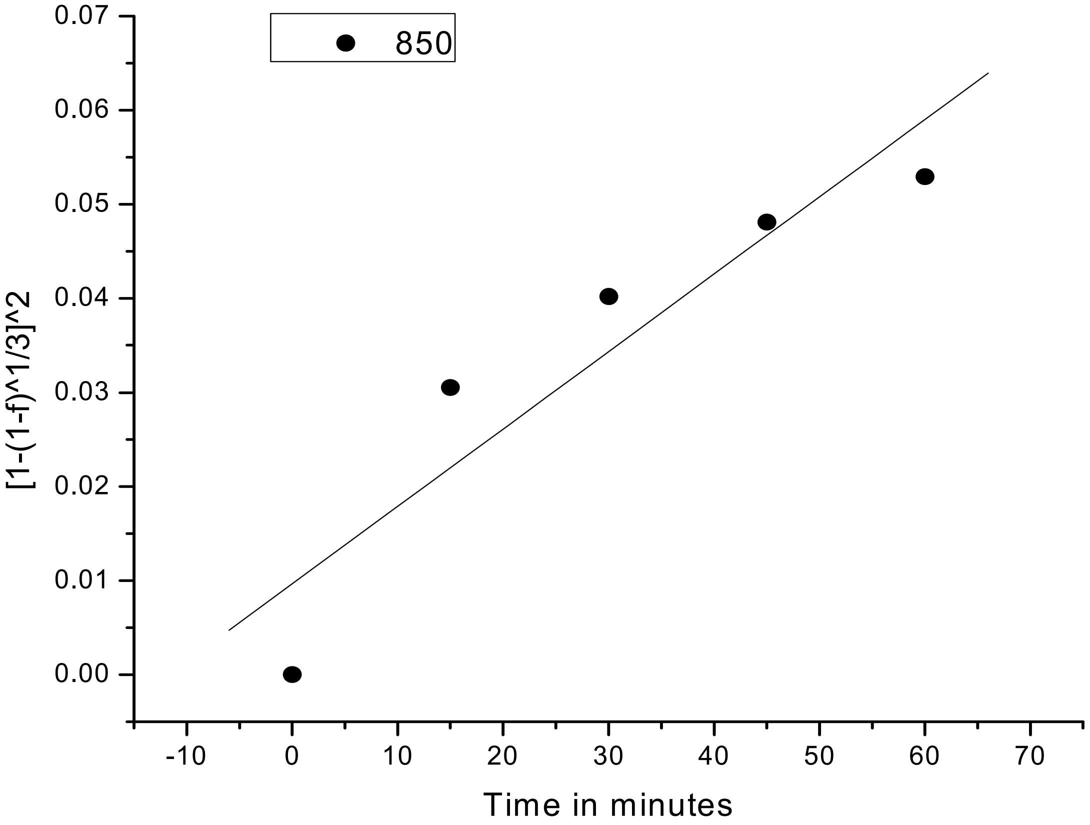
The Slope was found to be 0.02012.

***The reaction here is chemically controlled.**

Kinetic Model

The plots of $[1-(1-f)^{1/3}]^2$ vs. time gave straight line which determined the most appropriate kinetic model for the roasting of sphalerite ore pellets at a temperature of 850^0C for 60 minutes time. The kinetic model for this oxidation would be $[1-(\mathbf{1}-\boldsymbol{f})^{\frac{1}{3}}]^2 = \boldsymbol{Kt}$, where t is time, f is the fraction of sulphur removed and K is the rate constant.

Figure-X (For 850^0C)



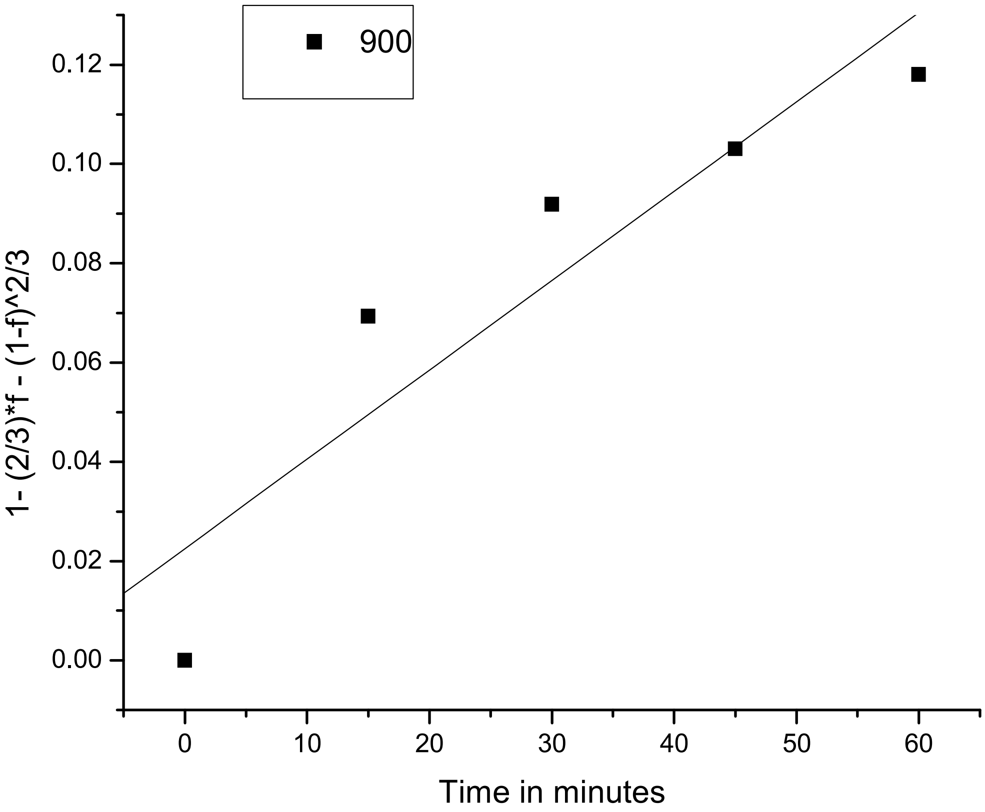
The slope was found to be 8.22667×10^{-4}

*** The reaction here is diffusion controlled.**

Kinetic Model

The plots of [1- (2/3)*f -(1-f)$^{2/3}$] vs. time gave straight line which determined the most appropriate kinetic model for the roasting of sphalerite ore pellets at a temperature of 900^{0}C from 30 minutes time to 45 minutes time. The kinetic model for this oxidation would be $1-\left(\frac{2}{3}\right)\times \boldsymbol{f}-(\mathbf{1}-\boldsymbol{f})^{\frac{2}{3}}=\boldsymbol{Kt}$, where t is time, f is the fraction of sulphur removed and K is the rate constant.

Figure-XI (For 900^{0}C)



The slope of the curve is 0.0018

*** The reaction is diffusion controlled.**

Table-3

Temperature	Value of "k"
750	0.03333(Chemically Controlled)
750	0.00254(Diffusion Controlled)
800	0.02012(Chemically Controlled)
850	8.22667×10^{-4}(Diffusion Controlled)
900	0.0018(Diffusion Controlled)

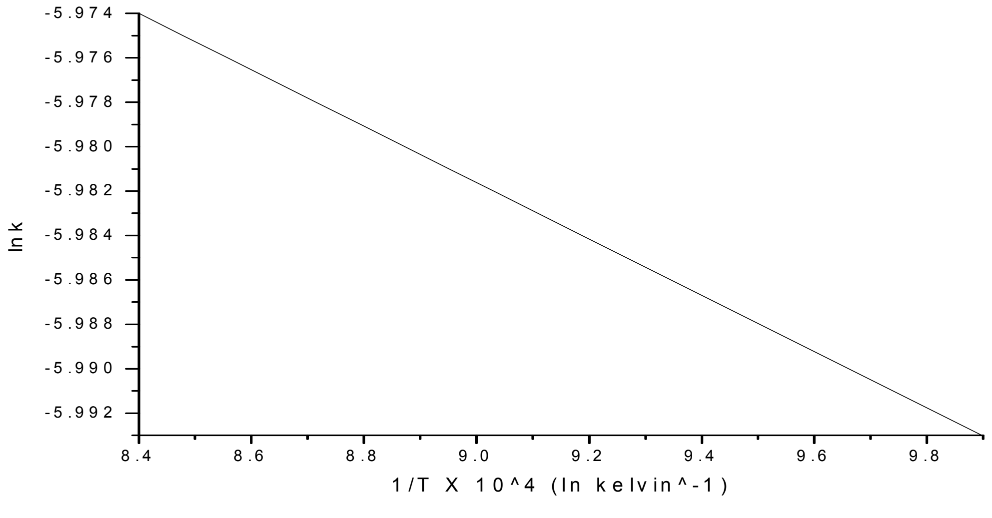
8.3 Activation Energy

$$K = A \times e^{-E/RT} \text{ (Arrhenius Equation)}$$

Where **E** is the activation energy, **A** is the Arrhenius constant or the frequency factor, **T** is the absolute temperature, **K** is the rate constant and **R** is the universal gas constant(**R**=8.314472 $J \cdot K^{-1} \cdot mol^{-1}$).

Slope of **K vs. 1/T** curve gives (-**E/R**).

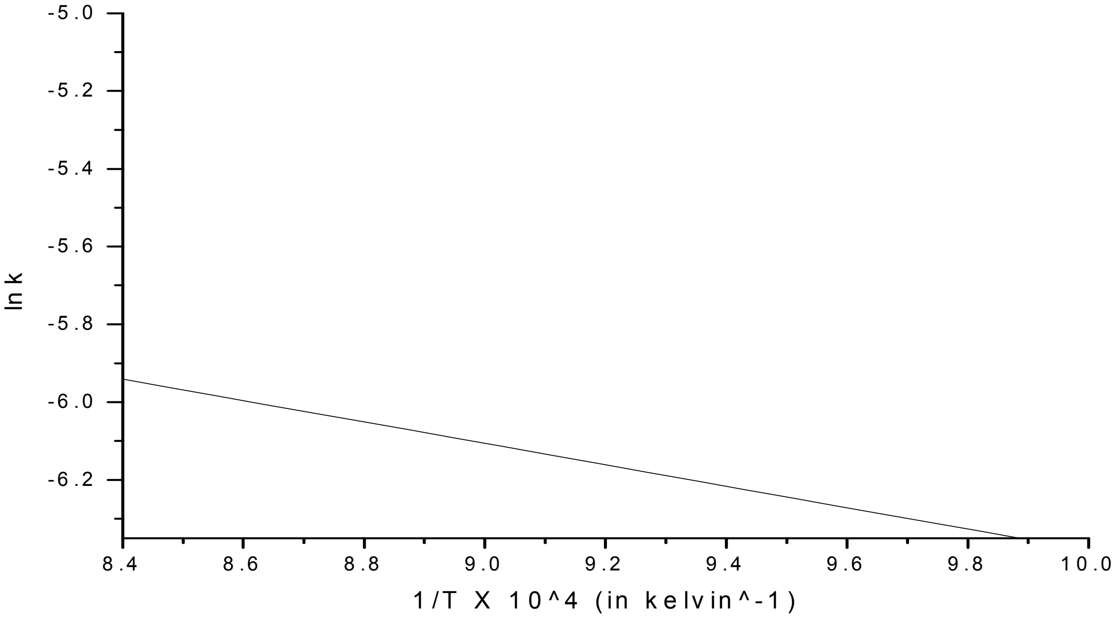
Figure-XII (Diffusion Controlled)



Slope= -0.60343

Activation Energy = $0.60343 \times 8.3144472\, Joule\ mole^{-1}$ **= 5.01722 joule** $mole^{-1}$**.**

<u>Figure-XIII</u> (Chemically controlled)



Slope = -0.6022

Activation Energy = $(\mathbf{0.6022\ \times 8.3144472})\ \boldsymbol{joule\ mole^{-1}}$ **= 5.0069** ***joule mole***$^{-1}$**.**

8.4 Discussion

The oxidation reaction for sphalerite is given by:

$$\boldsymbol{Zns} + \left(\frac{\mathbf{3}}{\mathbf{2}}\right)\boldsymbol{O_2} \ ==> \ Zno + S\boldsymbol{O_2}$$

For this reaction the rate constant (**K**) of the reaction is given by:

$$\boldsymbol{K} = \frac{\boldsymbol{P_{SO_2}}}{\boldsymbol{P_{O_2}}}$$

This rate constant is different for different temperature as the nature of reaction that is whether it is chemically or diffusion controlled, so there will be change in the reaction constant. Along with temperature this also changes with time, temperature remaining constant.

As indicated in the equation the rate constant also depends on the partial pressure of SO_2 and that of O_2. With the increase in the partial pressure of SO_2 there is possibility of backward reaction and with the increase in partial pressure of O_2 there will forward reaction and the attainment of equilibrium is faster.

Temperature remaining constant there is a very good chance of change in the reaction controlling mechanism at lower temperature of roasting that is, as from the above experiments this anomaly is found out at temperatures 750^0C and 800^0C.

Mainly the reaction involves, considering all the range of temperature used it is either chemically controlled or diffusion controlled.

Chapter 9

Conclusion

Conclusion

1. For temperatures above 850^0C i.e. in this study considering the temperature range of $850^0 C \leq T \leq 900^0 C$, time remaining constant, with the increase in temperature there is increase in the rate of oxidation (Roasting) of Sphalerite ore pellets.
2. For a constant temperature with the increase in time of exposure, rate of oxidation of Sphalerite (ZnS) pellets increases. This is valid for temperature range above 850^0C i.e. here $850^0 C \leq T \leq 900^0 C$.
3. Temperature remaining constant, the rate of oxidation of Sphalerite (ZnS) pellets increases with time of exposure to attain a maximum limit than suddenly decreases followed by increment in the rate again. This observation was made in the temperature range of $750^0 C \leq T \leq 800^0 C$.
4. The activation energy (**E**) for chemically controlled mechanism is less than that of diffusion controlled mechanism for oxidation of Sphalerite (ZnS) pellets.

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