COBALT RECOVERY FROM OLD NKANA COPPER SLAG VIA SOLID STATE CARBOTHERMIC REDUCTION AND SULPHATION

BY

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A thesis submitted to the University of Zambia in fulfillment of the requirement For the degree of Master of Mineral Sciences in Metallurgy and Mineral Processing

THE UNIVERSITY OF ZAMBIA

LUSAKA

2000
DECLARATION

I declare that this thesis was written in accordance with the rules and regulations governing the award of Master of Mineral Sciences Degree of the University of Zambia. I further declare that the thesis has neither in part nor in whole been presented as substance for award of any degree, either to this or any other University.

Where other peoples' work has been drawn upon, acknowledgement has been made.

Signature of author

Date: 8-03-2000
APPROVAL

This dissertation of Alex Mututubanya is approved as fulfilling the requirements for the award of the degree of Master of Mineral Sciences in Metallurgy and Mineral Processing by the University of Zambia.

Signatures of Examiners:                        Date:

1, .......................................................... 6/3/2000

2, .......................................................... 06/03/2000

3, .......................................................... 10/03/2000
DEDICATION

Dedicated to my wife and children, for having to bear with my absence from home.
ABSTRACT

Large quantities of old copper smelting slag containing cobalt exist at Nkana Division of Zambia Consolidated Copper Mines. Recovery of cobalt from the slag would contribute significantly to the economy of Zambia. A literature review, however, indicated that although processes have been developed for the recovery of cobalt from primary ores and converter slags, none have been for dump slags. The potential economic benefits of cobalt recovery and non-existence of a process for recovery of the metal from dump slags stimulated interest in undertaking the study reported in this thesis.

Thermodynamic considerations indicated that cobalt could be recovered from old Nkana copper slag via solid state carbothermic reduction and sulphation. Consequently, sulphation and carbothermic reduction experiments were carried out in the temperature range 600 to 1000°C for times ranging from 1 to 6 hours. The experiments were aimed at determining whether the two processes could be suitable as pretreatment steps in the recovery of cobalt from old Nkana copper slag. In addition to reaction temperature and duration, other experimental parameters investigated were; particle size of the slag, relative amounts of the reactants and for sulphation only, the effect of air flowrate.

The extent of carbothermic reduction and sulphation were determined by evaluating the percentage of cobalt solubilized from reacted slag samples leached in sulphuric acid to a terminal pH of 1.4-2.0.
Solid state carbothermic reduction was carried out in an inert nitrogen atmosphere with charcoal as a reducing agent. The results obtained indicate that solid state carbothermic reduction produces a partially reduced product which can be selectively leached for cobalt. A fair amount of cobalt was leached (52%) from the -0.60 + 0.150mm fraction of slag reduced with 20 % charcoal at 950 °C for two hours. Difficulties of obtaining higher percentages of cobalt leached were due possibly to the formation, during reduction, of non-leachable cobalt ferrites and carbides.

Solid state sulphation of old Nkana copper slag was carried out using pyrite and cobalt sulphide concentrates as sulphating agents. The highest amount of cobalt leached at 72% was obtained from the -0.045mm fraction of slag sulphated with pyrite. A 1:1 slag to pyrite ratio was found to be suitable for the solid state sulphation of old Nkana copper slag.

The work reported in this thesis consists of four chapters, which are preceded by an introductory section. Chapter one gives the literature review. Chapters two and three are preceded by theoretical considerations, and discuss the results of solid state carbothermic reduction and sulphation, respectively. Each chapter ends with its own references. Chapter four gives the general conclusions.
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INTRODUCTION

At Nkana mine of the Zambia Consolidated Copper Mines (ZCCM), old copper smelting slag dumps exist which contain a significant amount of cobalt. The old slag dumps are estimated to have 15 million tonnes of copper smelting slag with approximately 3 - 4% cobalt [1]. This approximates at least 450,000 - 600,000 tonnes of cobalt, contained in the slag dumps. This is quite a large amount and if exploited could contribute significantly to the economic development of Zambia.

The slag with a high cobalt content was produced and dumped from the inception of the mine in 1932 up to the year 1952. During this period, the copper-cobalt bearing ore was inadequately processed by mineral separation techniques. Consequently, the copper sulphide concentrate produced that went for copper smelting contained about 15% of the cobalt originally present in the ore [2].

During copper smelting of the copper concentrate, virtually all the cobalt that was present in the concentrate ended up in the slag that went for disposal to the dumps. With respect to copper, the old operations were quite satisfactory and the copper content of the slag averaged the same as in present day smelter slag at less than 1% copper. By 1952, tremendous advances had been made in the differential flotation of copper-cobalt sulphide ores. Thus the amount of cobalt in copper concentrates smelted, fell remarkably after 1952 and consequently the level of cobalt in copper smelter slag decreased from 3-4% to about 0.65% [1].
The high amount of cobalt in old Nkana copper smelter slag and the non-existence of a process for cobalt recovery from the slag, stimulated interest in this material as a potential source of cobalt and gave rise to the research reported in this thesis. Interest in the old Nkana copper slag as a source of cobalt appears justified due to the demand for cobalt on the world market and its high price. According to Cobalt News [3], current world production of cobalt stands at 25000 tonnes of which ZCCM contributes just over 2000 tonnes. The market price of cobalt is determined by the suppliers at about US $51000 - $53000 per tonne as at 1997 prices [4]. The demand for cobalt by the year 2000 is forecast at 29,000-30,000 tonnes [3]. The old copper slag at Nkana mine, furthermore, appears to be an attractive material for cobalt extraction due to declining ore grades of copper from which cobalt has always been recovered as a by-product. Due to the limited availability of cobalt raw materials, it would be advantageous if the old copper slag is exploited for cobalt recovery. At present, the copper sulphide ores from which cobalt is recovered as a by-product contain about 0.08 to 0.18% cobalt. The research reported in this thesis on cobalt recovery from old Nkana copper slag was preceded by a literature review which follows in the next section. The review first examines the structure of conventional copper concentrate smelting slag and conventional converter slag. Converter slags are considered in the review in order to identify similarities and differences with matte smelting slags, as processes have been developed for cobalt recovery from the former but not the latter. The review then considers processes currently being used and those that have been proposed for cobalt recovery from converter slags and cobalt bearing copper and nickel ores. This is
aimed at assisting in the assessment of possible pyrometallurgical pretreatment options that could be used for cobalt recovery from old Nkana copper slag. In this study experiments were conducted, involving solid state carbothermic reduction and sulphation, between 600 - 1000°C to determine a suitable pretreatment technique for slag, which could be used to obtain a reduced or sulphated product, from which cobalt can be extracted by hydrometallurgical processes.
CHAPTER ONE

LITERATURE REVIEW
1.1 COMPOSITION AND STRUCTURE OF CONVENTIONAL COPPER SMELTING SLAGS

Conventional copper matte smelting is the oldest process employed in the production of copper from sulphide concentrates. The process may employ a reverberatory furnace, electric, or a blast furnace to smelt a blended charge of sulphide concentrates and fluxes. Conventional copper matte smelting has been described by many workers [5-9]. It is a partial oxidation process carried out at a high temperature (1200-1300°C). The decomposition and oxidation reactions, of the sulphide minerals lead to the production from the charge, of three separate phases, namely, matte, slag, and an off-gas containing sulphur dioxide (SO₂) [10]. The matte is a molten mixture of metal sulphides that containing almost all the cobalt and copper present in the feed. Matte is described by the formula Cu₂S·FeS, the composition and properties of matte are considered by reference to the Cu₂S - FeS binary system, the Cu₂S - FeS - FeO and Cu₂S - FeO - Fe₂O₃ ternary systems [11,12]. The matte (relative density of about 5.5) which is denser than the slag (relative density of about 3) settles to the bottom of the furnace and after tapping goes for copper converting. The slag which settles at the top of matte is tapped separately and disposed to the dumps. The slag is formed from gangue minerals in the charge, fluxes that are added, and from the portion of iron sulphide minerals in the charge, that is oxidized during smelting. In conventional copper matte smelting, slags are formed at about 1300°C. The slags produced slags have a matrix of ferrous silicates and thus contain iron and silica as principal components.
Magnetite, alumina, lime, magnesia and alkali oxides are present in smaller amounts. Cobalt and copper oxides are present in variable amounts in the slag, their presence in the slag constitutes loss of valuable metal. Their recovery, especially that of cobalt, from smelting slag is the subject of the research reported in this thesis.

In matte smelting, it is desirable that a fluid slag be formed at the lowest temperature possible, the slag composition controlled, so that it can be readily separated from the matte with minimum loss of valuable metal entrained. The composition of the slag is determined by the constituents of the original copper sulphide concentrates and fluxes that are smelted. Generally, the slag contains about 35-40% SiO₂, 20-30% FeO. The percentage of magnetite and other oxides (CaO, MgO, MnO, Al₂O₃) vary but do not exceed 20%.

The composition of copper smelting slags and the phases that are present in the slag during smelting are considered by referring to the CaO-FeO-SiO₂ system. Figure 1-1 shows the partial liquidus surface for the CaO-FeO-SiO₂ system. The diagram shows areas and composition of slags that can be formed below 1300°C. A low melting compound, fayalite is formed below 1200°C. Fayalite which has the formula 2FeO.SiO₂ is a major component of copper smelting slags. All other oxides exist in solution in fayalite and by replacing iron to form different types of compounds (ferrites and silicates).
Figure 1.1 Partial liquidus surface diagram for the CaO -FeO -SiO₂ system showing composition of slags, formed below 1300 °C in matte smelting [15], where C = CaO and S = SiO₂
Lime (CaO) can replace iron to form compounds of the type 2CaO·SiO₂, 3CaO·SiO₂ and 4CaO·3SiO₂. Depending upon the lime content in the slag, the presence of such compounds influence the fluidity (viscosity) of the slag. The effect on slag viscosity of other oxides such as Al₂O₃, MgO, MnO, has been reported [13, 14]. Only small amounts of these oxides, less than 10 % can be tolerated to obtain a fluid enough slag. The influence of the various oxides on properties such as viscosity and observed behaviour of copper smelting slag are explained by the ionic theories on slag structure.

The ionic theories originally put forward by Temkin and Flood have been described by many authors [15-18]. According to these theories the oxides in molten slag are dissociated to different extent and are present in the slag as cations and anions. Basic oxides like CaO are completely dissociated into calcium and oxygen ions. The later are taken up by acidic oxides in slag, SiO₂ and Al₂O₃ to form complex ions such as SiO₄⁻⁴ and Al₂O₃⁻³. The presence of complex ions in slag increases viscosity, which inhibit matte separation from slag and contributes to an increase in metal entrapped in slag. Although the slag produced is relatively fluid, with viscosity in the range 500-2000 cP, some matte particles (which contain Cu₂S and CoS among other sulphides) remain entrapped and are lost with the slag. The extent of cobalt and copper loss by such mechanical entrapment also depends on the grade of matte and weight of slag, produced in the furnace.
The distribution of cobalt in copper smelting slag, has been reported by some workers [19, 20]. It is estimated that up to about 30-40% of the cobalt entering a reverberatory furnace is lost to the slag. Of this cobalt, 45% is lost by way of matte entrapment. The remainder of the cobalt is lost into slag (i.e. about 55%) as chemically dissolved in oxidic slag components. Such entrapped cobalt would be recoverable from the solidified slag by way of sulphide froth flotation if the slag is slowly cooled, crushed and ground. Without slow cooling of the slag, matte which is immiscible with the slag has insufficient time to coalesce and remains suspended in the slag matrix as extremely fine particles hardly recoverable by flotation.

The chemically dissolved cobalt has been found to be concentrated in fayalite and magnetite in which it replaces some iron to form cobalt silicates and ferrites [20]. In terms of processing slags to recover contained cobalt, concentration of the cobalt in these phases by mineral processing techniques can therefore be virtually ruled out. In flotation tests conducted on Nkana smelter reverberatory furnace slag [20], the flotation tailings contained about 59% cobalt.

Furthermore, direct leaching of the slag would also not be expected to be selective for cobalt, irrespective of the lixiviant used. This is because the ferrite and silicate structures would need destroying before cobalt reports into solution.
As indicated earlier, at the time the old Nkana smelter slag was being produced, the copper and cobalt contents were at about 1% and 3-4%, respectively. Although the cobalt content of the old Nkana slag is very high by current standards, it is clear from the overall composition of the material and its melting point that cobalt recovery from the slag by any purely pyrometallurgical method may possibly not be economic on account of high energy cost.

1.2 CONVERTING OF COPPER MATTE

Iron-copper mattes produced by Conventional Copper matte smelting are a mixture of metal sulphides. Even though they are represented by a simple chemical formula \( \text{Cu}_2\text{S}.\text{FeS} \), they are complex and contain sulphides of other metals such as cobalt sulphide and oxygen dissolved in solution. Precious metals such as gold, silver, selenium, tellurium etc. also concentrate in the matte phase. Converting of matte produced by conventional copper matte smelting is carried out in Peirce-Smith converters at temperatures of about 1100 to 1200°C, by introducing air or oxygen enriched air into molten matte in the converter to oxidize the iron and copper sulphides. Matte at about 55% Cu is converted to blister copper of about 98% Cu. A slag is produced during converting, containing; up to 4-10% Cu, 2% Co, 20-25% \( \text{SiO}_2 \), 40-45% Fe and 30-35% \( \text{Fe}_3\text{O}_4 \)[20]. Large amounts of \( \text{SO}_2 \) are given off during converting, which may be routed to acid making plants. Converting of matte is a two stage process, involving oxidation of iron and copper sulphides as follows [6,7,10]:
(a) First stage of converting (slag blow); In the first stage of converting iron sulphide (FeS) is oxidized to wustite (FeO) and slagged off by adding a silica flux. The oxidation of FeS is an exothermic reaction, temperatures may rise up to 1300°C. The atmosphere in the converter is highly oxidizing. Part of the FeO is oxidized, to magnetite-Fe₃O₄. Some copper and cobalt sulphides are oxidized during this stage. The oxides are sulphidised back to matte by the FeS. The reactions that occur during the first stage of copper matte converting can be expressed as follows:

\[ FeS + \frac{3}{2}O_2 = (FeO) + SO_2 \]  \hspace{1cm} 1.1

This reaction is highly exothermic, and causes the converter temperature to rise rapidly during oxidation of FeS. The siliceous flux added reacts with the FeO according to the reaction:

\[ (2FeO) + (SiO_2) = (2FeO.SiO_2) \text{ (fayalite slag)} \]  \hspace{1cm} 1.2

Depending upon the partial pressure of oxygen in the furnace some of the FeO reacts with oxygen, to form magnetite:

\[ (6FeO) + O_2 = (2Fe_3O_4) \]  \hspace{1cm} 1.3
At the same time the cobalt sulphide in the matte is oxidized to cobaltous oxide-CoO and cobaltosic oxide- Co$_3$O$_4$. The cobalt oxides dissolve in the converter slag, depending upon the extent of the following reaction:

$$[\text{FeS}] + (\text{CoO}) = [\text{CoS}] + \text{FeO} \quad 1.4$$

The above reaction is important in determining the cobalt content of slag and matte. At the beginning of the first stage, any cobalt oxide formed is sulphidised by the FeS still present and cobalt is concentrated in the matte. Towards the end of the first stage, the matte contains less FeS to react with the cobalt oxides. Any cobalt oxides formed dissolve in the converter slag.

(b) The second stage of converting (also referred to as the copper blow or blister forming stage) consists of oxidizing the "white metal"-Cu$_2$S, to blister copper. A number of reactions occur during oxidation of Cu$_2$S involving formation of copper oxide and blister copper. At the beginning of the blow the copper oxide can be reduced to copper by Cu$_2$S. As the sulphur content decreases more copper oxide is formed and a slag rich in Cu$_2$O is produced. The overall reaction occurring during this stage can be represented as follows:

$$[\text{Cu}_2\text{S}] + \text{O}_2 = (2\text{Cu}) + \text{SO}_2 \quad 1.5$$
Selective oxidation of iron, cobalt and copper sulphides during converting is possible because of differences in the affinity for sulphur, and relative stabilities of iron, cobalt and copper oxides. FeO is stabilised by reacting with silica to form fayalite, cobalt and copper oxides readily dissolve in the converter slag.

1.2.1 The nature and structure of copper converting slag

Converter slags produced by converting iron - copper matte are described as ferrous silicates. They are saturated with respect to silica and magnetite. The presence of silica and magnetite makes the slag highly viscous. The composition of the slag is determined by the matte grade, fluxes added and the highly oxidising atmosphere in the converter. The major components of converter slag are iron, silica, cobalt and copper. The iron exists as magnetite and combined with silica in fayalite. Cobalt and copper are present as sulphides and oxides, mechanically entrapped and chemically dissolved in fayalite and magnetite. About 60 % of the cobalt present in the original charge to the reverberatory furnace is lost into converter slag, of this 70 % is chemically dissolved, and mechanically entrapped cobalt accounts for about 30 % [20]. The low amount of entrapped cobalt in a highly viscous converter slag confirms that the cobalt present in slag is chemically dissolved in ferrites and silicates. The slag contains many other impurities which dissolve in matte during smelting and are oxidized during converting of the matte. Typical composition of Nkana converter slags containing cobalt is given in Table 1-1.
Table 1-1 Typical Composition of Nkana Converter Slag:

<table>
<thead>
<tr>
<th>%Cu</th>
<th>% Co</th>
<th>%SiO₂</th>
<th>% Fe</th>
<th>%Fe₃O₄</th>
<th>%Al₂O₃</th>
<th>% CaO</th>
<th>% MgO</th>
<th>% S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.75</td>
<td>2.57</td>
<td>21.98</td>
<td>44.95</td>
<td>33.68</td>
<td>2.95</td>
<td>1.02</td>
<td>0.70</td>
<td>2.36</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% Bi</th>
<th>% Pb</th>
</tr>
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<tr>
<td>0.009</td>
<td>0.0042</td>
</tr>
</tbody>
</table>

In general, the composition of converter slag is considered with reference to the FeO-Fe₂O₃-SiO₂ ternary system which is presented in Figure 1-2 [6]. The diagram represents a partial liquidus surface of the system, showing regions of composition in which fayalite slags are formed at temperatures below 1300°C. The regions are marked fayalite, wustite, magnetite and tridymite. They are bounded by the lines ABCD. Slags whose composition lie in the magnetite or tridymite regions are saturated with respect to magnetite or silica. Increasing oxygen partial pressure (from 10⁻¹⁰ to 10⁻⁹), increases the chances of the slag being saturated with magnetite. The presence of magnetite and silica in converter slag makes the slag viscous. High viscosity makes separation of the slag from the white metal - Cu₂S difficult resulting into high cobalt and copper losses into the slag.
Figure 1.2 Partial liquidus surface diagram for the FeO - Fe₂O₃ - SiO₂ system showing areas in which fayalite slag forms below 1300°C, bounded by the lines ABCD [6]
Converter slags are treated to recover cobalt and copper, using similar techniques as described for smelting slags. That is cobalt which is mechanically entrapped about 30% can be recovered from converter slags by flotation. The chemically dissolved cobalt 70% can not be recovered by this process unless the slag is slowly cooled. At smelters, where conventional matte smelting is practiced, the converter slag is recycled to the reverberatory furnace to recover both entrapped and chemically dissolved cobalt as matte. This practice however does not permit separate recovery of cobalt. The cobalt which dissolves in matte, continues to circulate between reverberatory furnace matte and the converter slag. Further, the presence of magnetite in recycled slag increases viscosity of matte smelting slag, making complete recovery of cobalt from slag to matte difficult in the smelting unit. This results in increased cobalt loss into slag discarded to the dump. To avoid the problems associated with slow cooling and recycling of converter slag, cobalt is recovered by separate treatment of the converter slag.

1.3 RECOVERY OF COBALT FROM CONVERTER SLAGS

Treatment of converter slags from converting of matte in conventional matte smelting is carried out in molten state to recover cobalt because of its value, and to reduce metal loss into slag, in order to improve the efficiency of the smelting process. The mechanically entrapped cobalt can be recovered by concentration.
into a low grade matte, by allowing the cobalt to settle from the slag as matte or by flotation [20]. The chemically dissolved cobalt can be recovered by treating the slag under conditions which promote exsolution of the metal from ferrites and silicates.

A number of pyrometallurgical processes have been developed, for separate treatment of converter slag to recover cobalt and copper. These processes are based on settling with addition of reductants and sulphidising agents to molten liquid slag to obtain an alloy or matte containing cobalt. Further treatment of the alloy and matte by hydrometallurgical processing to recover cobalt separated from copper and iron is required. The various processes and technologies currently employed in pyrometallurgical treatment of converter slags and plants employing these processes have been reviewed [19 21] The major features of processes that have been developed, are summarized below: [19 - 28]:

Reverberatory Furnace

Main Features - Treatment of converter slag using the reverberatory furnace has been practiced for long time in conventional matte smelting. Molten converter slag is recycled to the smelting furnace, where reduction of the oxides by FeS and settling of matte occur. The reverberatory furnace can also be operated as a separate unit from the smelting furnace, for treating slags. The still bath allows for good settling of entrained matte. Coal or coke can be added to reduce metal oxides, making it
possible for the recovery of chemically dissolved cobalt and copper \([19,22,23]\).

**Advantages** - No moving parts which makes it easy to operate the unit. The still bath is good for settling of matte. Sulphides and reducing agents can be easily introduced by charging through the roof.

**Disadvantages** - Low heat transfer makes it difficult to attain high temperature, resulting in formation of viscous slag and accumulation of magnetite from converter slag. The process is unsuitable for treating solidified slag, were high temperatures are necessary for melting the slag.

1.3.2. Electric Furnace

**Main Features** - The electric furnace is widely used in the treatment of either molten or solid converter slag. It is employed for simple settling, sulphidation and carbothermic reduction to recover metals such as cobalt in matte or alloy form \([19,24,25]\).

**Advantages**: Efficient heat generation, good temperature control, attainment of high temperature, agitation can be applied.

**Disadvantages**: Energy consumption required for smelting solid slag vary about 100 to 130 kWh/tonne \([24]\). Cost of electricity, is a major limitation to the application of the process. Its use is limited to areas where electricity is readily available and cheap. Convective slag flow around the electrodes inhibits matte - slag separation. The process does not allow for separate recovery of cobalt.
1.3.3 Kennecott slag Cleaning Process

Main Features: This was developed and commercialised in the 70's by Kennecott Copper Corporation (U.S.A). It utilises an electric furnace in a two stage process to recover copper and other non-ferrous metals from converter slags. The first stage involves reduction, in which coke and lime are added to molten slag to reduce magnetite and other metal oxides. In the second stage a sulphur bearing material is added to sulphidise the metals [25]. Copper in slag can be reduced to less than 0.5%. Power consumption is reported at 300 kWh/tonne.

Advantages - Both solid and liquid slags can be treated, possibility of adaptation to alloy or matte production.

Disadvantages- High energy requirements, problems associated with magnetite, such as increasing slag viscosity, and accumulation onto the furnace bottom. The process is patented, there are no other reports of plants constructed based on this technology. The process does not allow separate recovery of cobalt. Further treatment of the matte is necessary, to separate copper and cobalt.

1.3.4 Siromelt

Main Features - The process was developed at CSIRO (Australia) in the 1970's for the recovery of metals from slag. Heat is supplied by combustion of fossil fuel. The process uses top injection of solid reductants using a submerged top entry lance. Both molten and solid materials are treated. The later require melting before
reduction can occur. Reaction and smelting rates are reported to be high. The bath is well stirred, and the atmosphere and temperature are readily controlled. Entrained and chemically dissolved cobalt are all recovered[19,26].

Disadvantages - Settling time is required, the highly turbulent bath result in poor separation of slag from matte or alloy and may lead to metal loss into slag. Excessive refractory wear. Additional fuel may be required for melting solid slag.

1.3.5 Ausmelt Technology

Main Features: The process was established in 1981, at CSIRO(Australia). It is similar to the Siromelt. It uses a top entry submerged lance to inject solid reductants into the molten bath. The Ausmelt technology has found application in the recovery of metals from slag and primary extraction from concentrates. Ten plants, with two in the Southern African Development Community (SADC) region, in Zimbabwe and Botswana, were commissioned between 1990 and 1998 with more being built in other parts of the world. High reaction rates, good temperature control in a highly stirred bath are reported. The technology is being viewed as a possible alternative to reverberatory furnace smelting and Peirce-Smith Converter, because of its compactness, high reaction rates and through puts[19,26]

Disadvantages - This seemingly successful process, may lie in the difficult of obtaining good matte slag separation without prolonged settling times, during which
additional fuel may be required and without the possible requirement of a settler in
which to hold and separate molten material. The process seems suitable for
treatment of molten slag. Additional fuel for melting, is required in the treatment of
solid slag. It does not allow for separate recovery of cobalt.

1.3.6 Top Blown Rotary converter (TBRC)

Developed at Boliden (Sweden) for treatment of converter slag to recover copper
and nickel. The process can be considered for the recovery of cobalt in form of
matte. Pyrite and sulphide concentrates are used to sulphidise the metal oxides.
Matte is blown to blister in another TBRC. The copper content of the slag can be
reduced to less than 1%. The process is commercialised. Both converter slag and
sulphide concentrates are treated [27].

Advantages: - The furnace rotates, giving the desired stirring of the molten bath.
The stirring promotes contact between slag and added sulphides. Reaction rates
are high, Heating is by a flame which strikes the surface of the bath.

Disadvantages: - Requires settling time for slag and matte to separate, high
refractory wear induced by the rotation of the vessel. Requires complex equipment
for the rotary movement.
1.3.7 The Rotary process

The process is used to treat solidified and molten slag to produce matte. Heat is supplied by combustion of fuel above the molten bath. Combustion can be controlled to provide a reducing or an oxidizing atmosphere in the furnace. The rotary movement helps to agitate the bath and results in faster reaction rates than the reverberatory furnace [19]. The disadvantages of the process lie in the refractory erosion, which is enhanced by the movement of the molten material. The rotary process has a possibility for the pretreatment of slag based on solid state reduction.

1.3.8 Top injection (Top Jetting)

A number of processes have been proposed which consist of injecting mixtures of air, reducing gases and particles of coal into molten slag using a lance[19,28]. The lance is kept well above the molten bath of slag. The heat is provided by the combustion of fuel and reductant. A flowsheet has been proposed for reduction of flash furnace slags, by top injection of solid reductants from experimental data[28]. The proposed flow sheet is shown in Figure 1-3 for the recovery of cobalt from slags. The advantages reported are high rates of reaction and there is no need to recycle slag from the reduction furnace. The process is experimental and not yet proven.
Figure 1.3 Proposed flowsheet for the recovery of cobalt from copper smelting slags [28]
The number of processes given in the foregoing section were originally meant for the recovery of copper from molten converter slag. Most of these, were developed at plants were cobalt did not occur in converter slag. The wide range of the processes suggests specific application, being tailored to the treatment of slags of a particular composition. The processes are based on carbothermic reduction and sulphidation in molten state to produce an alloy or matte. The processes can equally be applied to the recovery of cobalt from molten converter slag, since cobalt forms an alloy with copper and iron, and readily dissolves in a low grade iron - copper matte. The processes are suitable for the treatment of molten slag. Application to the recovery of cobalt from solid slag, such as the old copper slag at Nkana, could be limited by energy required to melt the slag and to obtain high enough temperature to keep the slag molten and fluid, which is essential for separation of alloy and matte from slag.

1.4 RECOVERY OF COBALT FROM COBALT-BEARING COPPER ORES

Cobalt occurs in many different mineral forms, scattered all around the world including the deep sea nodules. Cobalt rarely occurs on its own, it is often found associated with copper in sulphide and oxide minerals. In Zambia the major cobalt bearing copper mineral is carrolite, a mixed copper - cobalt sulphide (CuCo₂S₄). Small amounts of oxide and carbonate minerals also occur. The variety of cobalt minerals that exist account for a wide range of extraction techniques that are employed to recover cobalt metal. The processes used are tailored to suit particular
type of minerals being processed. The processes currently being used in the recovery of cobalt from cobalt-bearing copper ores have been reviewed and described in [29]. The processes include pyrometallurgical and hydrometallurgical treatment, or a combination of both. Cobalt recovery from cobalt-bearing copper sulphide ores, consists of: separation of cobalt and copper by differential flotation, to obtain cobalt and copper sulphide concentrates. The copper concentrates are sent for smelting, for the recovery of copper. The cobalt concentrates are treated by a combination of pyrometallurgical and hydrometallurgical processing, involving sulphation roast, leaching, and electrowinning, to recover cobalt metal.

### 1.4.1 The Roast-Leach-Electrowinning (RLE) Process

The (RLE) process combines thermal pretreatment and hydrometallurgical processing of the cobalt sulphide concentrates to recover cobalt metal. The basic steps involved in the recovery of cobalt by the RLE process shown in Figure 1.4: The RLE process consists of roasting of the sulphide concentrates at temperatures of 685 to 700°C to convert sulphide minerals to water soluble sulphates, leaching of the roasted concentrates (calcine) in dilute sulphuric acid to obtain a solution containing cobalt, copper, iron and other metal impurities such as zinc and nickel. Copper is recovered first by electrowinning from a purified leach solution. Cobalt hydroxide is precipitated from solution of purified copper tankhouse spent electrolyte at pH 6.5 - 7. The cobalt hydroxide, is redissolved in cobalt tankhouse electrolyte, to obtain a leach solution containing about; 35 - 40 gpl cobalt, less than
0.5ppm copper and 20 -30gpl acid, from which cobalt is recovered by electrowinning, as electrowon cathodes. The RLE process is well established in Zambia, with plants operating at Nkana and Chambishi mines. The major advantage of the process is that it employs a fluid bed roaster for thermal pretreatment of concentrates, which is associated with high reaction and conversion rates for sulphides. Fuel requirements are low since conversion of sulphides is an exothermic reaction. The process is able to sustain operating temperatures without addition of fuel. The disadvantages of the process are high consumption of lime, metal loss during precipitation, large amounts of gypsum are produced which at the moment are unutilised. Possibilities exist for treating old Nkana copper slag by the RLE process by adding the slag to the roaster feed and using higher roasting temperatures. The limitation is that the RLE process is autogeneous, treatment of the slag, may require, adaptation of coal or fuel oil firing to maintain desired temperatures, adding further costs to the process.
Figure 1.4 Basic steps in the recovery of cobalt by the RLE process [29]

Legend:  
Cu S.E = Copper spent electrolyte.  
Co S.E = Cobalt spent electrolyte.
1.5  RECOVERY OF COBALT FROM COBALT - BEARING NICKEL ORES

Cobalt is recovered from cobalt - bearing nickel sulphide and oxide ores using well established, pyrometallurgical and hydrometallurgical processes. These are well described elsewhere [30] and have been reviewed recently [29, 31, 32, 33].

Pyrometallurgical treatment of nickel sulphide concentrates involves similar process steps as in the treatment of copper sulphide concentrates, consisting of smelting of the sulphide concentrates in a reverberatory furnace, electric or flash smelting furnace and converting of matte in Pierce Smith converters [30]. Unlike copper, nickel matte is not converted to produce an impure metal. As this requires operating the converter at very high temperatures above 1500°C. Converting of nickel matte is stopped to obtain a matte product (Bessemer matte) containing small amounts of iron and sulphur which is further processed by hydrometallurgical techniques to separate cobalt from nickel [30].

Pyrometallurgical treatment of oxide ores [31], consists of smelting the nickel oxide ore with the addition of a sulphur bearing material to produce a matte which is treated in a similar manner to matte from smelting of sulphide concentrates to recover cobalt, and pretreatment of nickel oxide ore by carbothermic reduction, to obtain a prereduced oxide material which is processed by hydrometallurgical techniques to recover cobalt [31].
Hydrometallurgical treatment of cobalt bearing nickel sulphides, oxide ores, and matte to recover cobalt is accomplished in a number of stages consisting of:

- Leaching in sulphuric acid, ammonia or chloride solutions to dissolve cobalt and nickel into solution. The lixiviant used depends on the technology employed.
- Hydrogen reduction to precipitate cobalt and nickel as mixed sulphides, hydroxides or carbonates from the leach solution, depending upon the leaching system used to leach the cobalt bearing materials.
- Redissolution of the cobalt and nickel precipitates to obtain a solution from which cobalt and nickel can be separated by solvent extraction techniques.
- And finally recovery of cobalt from the strip solution by electrowinning.

Leaching is carried out at ambient temperature and atmospheric pressure, or at high temperature and pressure. Sulphide concentrates are directly leached in sulphuric acid or ammonia at high temperature and pressure such as the Sherrit Gordon process. Mattes are leached in sulphuric acid by atmospheric pressure and the acid pressure leach processes. Laterites and other oxidised materials are leached by the acid pressure leach and by the Caron process. The later consists of leaching reduction roasted materials in ammonia ammonium carbonate solution [32 - 36]. The leaching of sulphide and oxide minerals, and their behaviour in solution have been studied by many workers [37,38] who have shown that leaching involves both heterogeneous and homogeneous reactions at the sulphide/oxide mineral surface and in the bulk of solution. The reactions result into dissolution of cobalt, nickel and
impurities such as iron, zinc. The conditions necessary for dissolution of a metal oxide or sulphide can be obtained by examining the appropriate potential - pH diagram. The diagrams are constructed for conditions at 25 °C and one atmosphere pressure. These can be extrapolated to obtain conditions at higher temperature. The potential - pH diagram shows, for a particular leaching system the possible equilibria that can be established between soluble and insoluble compounds during leaching and for different values of pH.

Figure 1.5 shows the Co-H₂O system at 25°C, one atmosphere pressure and unity activity of the phases [34]. The diagram shows solid and soluble phases that exist under different conditions of pH. In the Co - H₂O system the solid phases shown are CoO, Co₃O₄ or Co(OH)₃. CoO₂ and metallic cobalt(Co). The soluble phases being Co²⁺ at low pH and HCoO²⁻ above pH 12. Existence of stable phases under different conditions of pH is utilised in the separation of cobalt from nickel by reduction and precipitation. Gaseous reduction of cobalt and nickel from purified leach solution is an electrochemical process. Hydrogen under pressure is passed through the solution resulting into selective precipitation of cobalt and nickel. Reduction and precipitation of cobalt and nickel from solution takes place because they exist as Co²⁺ and Ni²⁺ ions which are reduced according to the following reactions:

\[ \text{Co}^{2+} + 2\text{e}^- = \text{Co} \quad 1.6 \]

The overall reduction reaction can be written as follows for reduction of cobalt:

\[ \text{Co}^{2+} + \text{H}_2 = \text{Co} + 2\text{H}^+ \quad 1.7 \]
\[ \text{Ni}^{2+} + 2\text{e}^- = \text{Ni} \quad 1.8 \]

Which are anodic reactions. The electrons come from hydrogen which is oxidised by a cathodic reaction;

\[ \text{H}_2 = 2\text{H}^+ + 2\text{e}^- \quad 1.9 \]

The pH of the solution is controlled for precipitation to occur, and be able to retain the precipitates in solid form according to the potential - pH diagram. Cobalt and nickel are precipitated as sulphides, hydroxides and carbonates from leach solutions, obtained by leaching cobalt-bearing nickel minerals and matte in ammonia, sulphuric acid and chloride solutions. Final separation of cobalt from nickel consists of hydrometallurgical treatment of the precipitates. The processes that have been developed and used for the recovery of cobalt from mixed precipitates have been described by many workers [29 - 36]. A summary of these processes, based on their findings, is given in the section below:

1.5.1 Falconbridge process

Employs a chloride leach system and solvent extraction (SX) to separate cobalt from nickel using Tri-isoctylamine (TIOA). TIOA stripped with cobalt tankhouse electrolyte. and cobalt electrowon at pH 1.3-1.4. The process is commercially applied. Major advantage is that hydrogen reduction is not required. Cost of SX reagents may be a disadvantage.
1.5.2. SLN Process

Treats sulphide matte using the chloride leach system. Ferric chloride$_3$ and chlorine are used as leachants. Iron is removed by solvent eXtraction (SX) using Tri-Butyl phosphate (TBP). Cobalt is separated with Tri-iso-octylamine (TIOA), without precipitation. Hydrochloric acid (HCl) is used for stripping, to obtain cobalt chloride solution which is sold for cobalt recovery. The process is commercially applied.

1.5.3 Sumitomo Process:

Recovers Co from Ni-Co mixed sulphides, by acid pressure leaching in sulphuric acid at 150-160° C. Fe, Cu, Zn are removed at pH 2. Co and Ni are separated in two stages; (i) Co and Ni extracted from sulphate solution with versatic acid, HCl used to strip Ni and Co into chloride solution. (ii) TIOA is used to extract Co from chloride leach solution. Co electrowon from strip solution, Ni from the raffinate. The process has commercial application.
Figure 1.5 Potential-pH (Pourbaix) diagram for the Co - H₂O system at 25 °C and one atmosphere showing phases that are stable under different conditions of pH [34]
1.5.4 Nippon Process (Hitachi)

First commercial plant was commissioned in 1975. Treats mixed Ni-Co sulphides and scrap using acid pressure leach at 140-170°C. Oxidation of Fe and Cu with ammonia followed by precipitation with sodium hydrogen sulphide. SX to remove Zn using (D2EHPA) at pH2-3. Cobalt is extracted by alkyl phosphoric acid reagent (M2EHPA) and Ni by LIX64N. Co cathode electrowon on bagged stainless steel blanks.

1.5.5 Sherrit Process

Developed in 50s in Canada, the process has been adopted by Outokumpu (Kokkola, Finland). Treats mixed sulphides by acid pressure leach using sulphuric acid at 150°C, 1150 kPa. Fe oxidised with air and ammonia and removed. Cobalt is then oxidised to a stable cobalt (III) which forms soluble pentamine ion Co(NH₃)₆⁺. Co(III) is then reduced to Co(II) which is precipitated with hydrogen at 180°C and 4300kPa in powder form as final product. Ni is recovered as nickel ammonium sulphate.
1.5.6 INCO Process

The refinery was commissioned in 1983 at Port Colborne (United Kingdom). In this process mixed carbonates are leached in sulphuric acid. Cobalt hydrate is precipitated with sodium hypochlorite followed by redissolution of cobalt hydrate in spent electrolyte in the presence of sulphur dioxide. Solution purification is by ion exchange to remove Zn, Cu, and Ni. Cobalt cathode is electrowon using stainless steel blanks. The process seems to offer the least number of process steps.

1.5.7. Rustenburg Refiners Process

Cobalt is produced as cobalt sulphate heptahydrate in a two stage treatment of cobalt-bearing nickel-copper matte consisting of acid pressure leach to obtain a sulphate solution. Cobalt hydroxide precipitation with electrolytic nickel additions followed by scrubbing the hydroxide with spent electrolyte to remove nickel. In the second stage, the cobalt hydroxide with cobalt:nickel ratio of 3:1 is dissolved in sulphuric acid and formaldehyde at pH 4 to give a sulphate solution from which cobalt is extracted using D2HEPA at 50 °C, to yield a strip solution from which cobalt heptahydrate is recovered as product. Limitation non-recovery of metallic cobalt.
1.5.8 Carbonyl Process

Oldest process known for separation of cobalt from nickel. INCO have operated the carbonyl process refinery at Clydach (Wales, U.K) since 1902 and is similar to the Mond process. The process is based on the reaction of nickel with carbon monoxide; \( \text{Ni} + 4\text{CO} = \text{Ni(CO)}_4 \) and combines pyrometallurgy and vapourmetallurgy. INCO refinery at Clydach treats a Ni-Co-Cu-PM alloy to produce granules which are fed to the carbonylation plant.

Ni is removed as \( \text{Ni(CO)}_4 \) vapour which is cooled to recover Ni. Cobalt is recovered from the residue by leaching and precipitation as cobalt hydroxide.

This chapter demonstrates that a wide range of processes are used in the recovery of cobalt from cobalt bearing ores. The number of processes and stages involved illustrates the difficulties experienced in the recovery of cobalt and that not a single process can be universally employed. The review of the processes has shown that both pyrometallurgical and hydrometallurgical treatment of cobalt bearing ores, mattes and slags is necessary to recover cobalt.
1.6 POSSIBILITIES FOR COBALT RECOVERY FROM OLD NKANA COPPER SLAG

Old Nkana copper reverberatory furnace slag which has an approximate composition of 35-40% silica, 20-30% iron, 3-4% Co and 1% Cu has a significant amount of cobalt which would be desirable to recover. As discussed in Section 1.1 it has previously been estimated that up to about 30-40% of the cobalt entering a reverberatory furnace is lost to the slag. Of this Cobalt about 45% is lost in matte particles entrapped in the slag. The remainder of the cobalt lost in reverberatory slag is chemically dissolved in ferrite and iron silicate oxidic slag phases.

If copper reverberatory furnace slag is slowly cooled, crushed, and ground and is then subjected to sulphide froth flotation, the cobalt in entrapped matte particles (but not that in oxidic phases) can be recovered. Without slow cooling of the slag (as happens when reverberatory slag is dumped), matte which as a phase is immiscible with the slag has insufficient time to coalesce and remains suspended in the slag matrix as extremely fine particles. Such fine matte particles are hardly recovered by sulphide flotation. Therefore if old Nkana copper slag could be reclaimed, melted, and cooled slowly, it is likely that up to about half the cobalt in the slag could be recovered by flotation. A major disadvantage of attempting to recover cobalt in old Nkana copper slag by flotation, would be the energy required for slag melting. This has been estimated at about 86.51 KWh per tonne of slag (Appendix 1A). This would translate into an energy cost of $4.6 per tonne of slag assuming melting was
done with electrical power costing $0.054 per Kwh. For such an expenditure in energy for melting, the value of the cobalt that would be in a cobalt concentrate recovered by flotation would be $1163. It is possible that the fuel that would be used to melt old Nkana copper slag could be reduced if a strategy of adding a portion of reclaimed slag to current arisings of molten converter slag could be adopted. The other disadvantage of the flotation method, is the non recovery of the cobalt in oxidic phases of the old Nkana copper slag which would remain unaddressed. An attempt to utilize other mineral processing techniques for concentrating cobalt present in old Nkana copper slag would also have limited success, since the cobalt in ferrites and silicates cannot be isolated by such methods.

Direct leaching of the slag as a means of cobalt extraction would also not be expected to be selective for cobalt, irrespective of the lixiviant used. This is because the ferrite and silicate structures would have to be destroyed before cobalt reports into solution. It appears that one way of recovering cobalt present in oxidic phases of the slag would be via thermal pre-treatment steps which would be aimed at the solid state exsolution of cobalt from ferrites and silicates.
Thermodynamic considerations whose details will follow in Chapters 2 and 3 reveal the feasibility of solid state carbothermic reduction and sulphation of the slag as away of converting the cobalt in oxidic phases into acid soluble form. Consequently, laboratory experiments on the solid state sulphation and solid state carbothermic reduction of old Nkana copper slag followed by leaching in acidified aqueous solution at pH 2 were carried out and are reported in this thesis. As indicated earlier, cobalt recovery from the slag by any purely pyrometallurgical method would possibly not be economic on account of high energy cost. Cobalt matte or ferro-alloy formation, if thermodynamically and kinetically feasible, would in practice require simultaneous treatment of a small amount of old Nkana copper slag with current arisings of molten converter slag.
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CHAPTER TWO

RECOVERY OF COBALT FROM OLD NKANA COPPER SLAG VIA SOLID STATE CARBOTHERMIC REDUCTION
2.1 THEORETICAL CONSIDERATIONS

The literature review carried out in Chapter 1 revealed that of the cobalt lost in copper reverberatory furnace slag, that which is chemically dissolved in ferrite and iron silicate oxidic slag phases is difficult to recover. One way of recovering cobalt present in these phases would be via thermal pre-treatment steps which would be aimed at the solid state exsolution of cobalt from ferrites and silicates.

This study explores the possibility of solid state carbothermic reduction of the slag as a thermal pre-treatment step for converting cobalt in oxidic phases of the slag into acid soluble form.

Carbothermic reduction refers to processes in which metal oxides are reduced to their lower oxide form or metal using carbon or carbon monoxide as reducing agents. Even when solid carbon is used as the reductant, it is known, however, that the reduction of metal oxides is mainly by carbon monoxide which forms from carbon under furnace operating conditions. Depending on the conditions under which carbothermic reduction is conducted, which are governed by the metal oxide that has to be reduced, a metal or lower oxide produced may be a solid, a melt, or in the gaseous state. An appropriate furnace would have to be used in each case. The experiments described in this chapter involve solid state carbothermic reduction of old Nkana copper slag in which cobalt in complex oxidic phases would be reduced to CoO and Co which are leachable in moderate strength sulphuric acid. The important reactions that are expected to take place during reduction of cobalt oxides with carbon can be expressed as follows[1]:

42
Co₃O₄ + C = 3CoO + CO  

ΔG° = 17100 - 56.35T  cal mol⁻¹

CoO + C = Co + CO  

ΔG° = 29700 -37.85T  cal mol⁻¹

From the Gibbs free energy values for the reactions in equations 2.1 and 2.2, the equilibrium temperature at which ΔG° becomes zero is about 300 and 500°C for the reduction of Co₃O₄ and CoO with carbon, respectively. This suggests a thermodynamic possibility of solid state carbothermic reduction of the slag to produce a partially reduced slag in which the cobalt would be present as a mixture of CoO and Co which can then be leached in sulphuric acid.

The above reactions with solid carbon proceed negligibly as they are limited by the sparse contact between solid carbon and cobalt oxides. The reactions with carbon monoxide which are the main ones responsible for carbothermic reduction may be written as follows [1]:

Co₃O₄ + CO = 3CoO + CO₂  

ΔGₜ = -23700 - 14.65T  cal mol⁻¹

CoO + CO = Co + CO₂  

ΔGₜ = -11 600 - 3.9T  cal mol⁻¹

Carbon dioxide reacts with carbon to produce carbon monoxide according to the
Boudouard reaction:

\[ \text{C + CO}_2 = 2\text{CO} \quad 2.5 \]

\[ \Delta G_T = -40800 + 41.7T \text{ cal mol}^{-1} \]

From a thermodynamic stand-point, assuming solids have non-variable activities, the extent to which reactions in equations 2.3 and 2.4 occur, depends on the furnace temperature and the prevailing partial pressure. That is the ratio of CO\(_2\) gas to CO gas. Thus a predominance area diagram with the axes Log\(P_{\text{CO}}/P_{\text{CO}_2}\) versus the reciprocal of temperature (in Kelvin) is useful for diagrammatically representing the thermodynamic conditions required for the reduction of cobalt and other oxides. Such a diagram is presented in Figure 2.1 for the reduction of selected oxides present in old Nkana copper slag. Data given in Table 2.1 was used to calculate \(P_{\text{CO}_2}/P_{\text{CO}}\) ratios as a function of temperature which were used in the construction of Figure 2.1. Details of the calculations made to generate Figure 2.1 are given in Appendix 2A. The diagram is constructed for the range of temperatures over which solid state carbothermic reduction is the subject of interest in this study. At temperatures being considered of below 1000°C, the components of the slag and any reduced species would be in the solid state. Figure 2.1 shows that:

- a range of log \(P_{\text{CO}_2}/P_{\text{CO}}\) values exist over which the stability of an oxide can be considered. The line for each oxide represents equilibrium conditions under which the oxide and the metallic phases can exist together with CO and CO\(_2\) gas mixture.
- increasing the log $P_{CO2}/P_{CO}$ ratio increases the stability of an oxide.

- for any given line of an oxide such as CoO, the ratio $P_{CO2}/P_{CO}$ has a definite value at a given temperature. This suggests that reduction of an oxide can take place under varying conditions of $P_{CO2}/P_{CO}$ ratios and temperatures.

- at any given temperature the oxides above in the diagram can be reduced at high $P_{CO2}/P_{CO}$ ratios or small amounts of CO being present in the gas mixture. Those below

**Table 2.1: Gibbs free energy data obtained from the Gibbs energy of formation of oxides [1]:**

<table>
<thead>
<tr>
<th>CHEMICAL REACTION</th>
<th>$\Delta G_T$ Cal mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2CO = CO_2 + C$</td>
<td>$-40800 + 41.7T$</td>
</tr>
<tr>
<td>$Co_3O_4 + CO = 3CoO + CO_2$</td>
<td>$-23700 - 14.65T$</td>
</tr>
<tr>
<td>$CoO + CO = Co + CO_2$</td>
<td>$-11600 - 3.9T$</td>
</tr>
<tr>
<td>$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$</td>
<td>$-7880 - 12.87T$</td>
</tr>
<tr>
<td>$Fe_3O_4 + CO = 3FeO + CO_2$</td>
<td>$-7120 - 9.15T$</td>
</tr>
<tr>
<td>$FeO + CO = Fe + CO_2$</td>
<td>$-4140 + 5.13T$</td>
</tr>
<tr>
<td>$Cu_2O + CO = 2Cu + CO_2$</td>
<td>$-27000 - 3.92TlogT -8.55$</td>
</tr>
</tbody>
</table>

45
like the oxides of iron require larger amounts of CO or low $P_{CO_2}/P_{CO}$ ratios. This suggests a possibility of selective reduction of the oxides in the old Nkana copper slag by controlling the composition of the reduction gas mixture.

- the curve for the Boudouard reaction in equation 2.5 intersects the curves for the reduction of Fe$_3$O$_4$ and FeO slightly above 600°C. The equilibrium established by this reaction controls the amount of CO generated during reduction of the oxides.

The formation of CO involves two steps [3,4,5,6,]:

- Chemsorption of O$_2$ or CO$_2$ onto the active sites on the surface of carbon, where chemical reactions take place to form CO.

- Desorption and liberation of CO from the carbon surface.

Oxygen comes from the dissociation of the metal oxides. The CO$_2$ from reactions in equations 2.3 and 2.4. In reactions that occur on the solid surface the Shrinking Core model is also used to describe the kinetics and thermodynamics of the process. It is apparent from the thermodynamics of carbothermic reduction above that, furnace temperature and CO$_2$/CO ratio are important parameters that determine the nature of the species formed after reduction. The effect of these parameters on the solid state carbothermic reduction of old Nkana copper slag were investigated in experiments described in the next section. The effect of CO$_2$/CO ratio on reduction was studied indirectly due to a lack of appropriate facilities. This was by changing the relative amount of charcoal in reaction mixtures.
Figure 2.1  \( \log \frac{P_{CO_2}}{P_{CO}} \) Versus \( 1/T \) K  Calculated diagram for reduction of selected oxides
Other carbothermic reduction parameters investigated were reaction time and particle size of the reactants, which are at the core of reaction kinetics. Solid state carbothermic reduction is regarded as a gas-solid reaction since most of the reduction is done by CO gas derived from solid carbon. The rate controlling steps in gas-solid reactions, have been discussed [7]. These include:

- Transport of CO to the oxide surface.
- Diffusion of CO to the reaction interface, which depends on the boundary film thickness, concentration gradients, porosity, and degree of agitation.
- Chemical reaction between CO and the metal oxide. This step depends on reaction temperature and concentration of reactants.
- Diffusion and transport of CO$_2$ from the reaction site to the active site on the surface of carbon.

All these steps are likely to occur in the reduction of cobalt oxides in slag and could influence the kinetics of solid state carbothermic reduction. Kinetic consideration of solid state carbothermic reduction was confined to the study of the effect of temperature and particle size on the reaction rate. The study was carried out in a tube furnace with the reaction mixture packed as a bed in a sample boat. Sample agitation was thus not possible but transport and diffusion processes were to some extent facilitated by nitrogen gas which was flushed through the tube furnace, the particle size of reactants, and porosity in the charge bed. Nitrogen gas also prevented the re-oxidation of species in reduced slag samples while still hot.
2.2 Experimental

Solid state carbothermic reduction of the old Nkana copper slag was investigated in the temperature range of 600 to 1000 °C, using charcoal as a reducing agent. The parameters investigated were; effect of reaction temperature, slag particle size and the amount of reductant in the reaction mixtures.

2.2.1 Materials used in solid state carbothermic reduction

*Old Nkana copper slag:*

The slag used in this study was obtained from Nkana Division of ZCCM, from the old slag dumps. Hence the designation, Old Nkana Copper Slag. The slag sample consisted of different size fractions ranging from fine particles to very coarse lumps. The slag required further preparation to homogenize the sample. 30 kg of the coarse slag sample was reduced to -3mm by crushing in a laboratory jaw crusher and Beater mill. Samples from the crushed slag were taken for chemical analysis to determine chemical composition. The results are given in Table 2.2. Samples of slag from the crushed material were screened by shaking on the laboratory shaker for 15 minutes. The slag retained on each screen was analysed, to determine the cobalt, copper and iron distribution in different size fractions. The results of this analysis are given in Table 2.3. The results show a fairly uniform distribution of cobalt, in the following size ranges: -3.35+0.60, -0.60+0.150, -0.150+0.045 and-0.045mm which were selected, to be used in the experimental work.
The results support, the findings already described in chapter one, that cobalt is chemically dissolved in slag.

**Charcoal**

The charcoal obtained from a local market was crushed and screened to obtain a -0.60 + 0.150 mm fraction, which was mixed with a similar fraction of slag during experiments. The charcoal analysed at 95.5% carbon, 4.0% ash, 0.96% moisture.

The method of proximate analysis was used to determine the carbon content. The amount of carbon required to reduce cobalt, copper, and iron oxides in the slag was stoichiometrically calculated at 0.0528 g carbon per gram of slag.

**Leachant**

The aqueous solution in which reduced samples were leached was prepared by addition of 98% concentrated sulphuric acid to distilled water to give a terminal pH of 1.4 to 2.0 after leaching. The pH range was chosen in line with that used in industrial leaching of roasted copper sulphides (calcine).
**TABLE 2.2: Chemical Analysis Of Old Nkana Copper Slag**

<table>
<thead>
<tr>
<th>CHEMICAL COMPOSITION WT %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
</tr>
<tr>
<td>----</td>
</tr>
<tr>
<td>2.71</td>
</tr>
</tbody>
</table>

Na | K | CaO | MgO | Al₂O₃
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.26</td>
<td>2.84</td>
<td>9.80</td>
<td>2.80</td>
<td>5.80</td>
</tr>
</tbody>
</table>

*Fe₃O₄ was calculated from the analysis of total Fe, FeO and SiO₂

### 2.2.2 Chemical analysis of materials

Chemical analysis of the slag was carried out using standard methods of analysis used by the geochemical laboratory in the School of Mines. A bout 0.2g sample was digested in nitric acid, perchloric acid mixture, evaporated to dryness and leached in 6M hydrochloric acid. After filtration the solution was made up to 100mls in a volumetric flask. A small sample 2-5 mls was taken from the volumetric flask, and was used to analyze for Co, Cu, and Fe content in the sample by atomic absorption spectrometer (AAS).
### Table 2.3: Cobalt, Copper, and Iron Distribution in Different Size Fractions Of Old Nkana Copper Slag.

<table>
<thead>
<tr>
<th>SIZE RANGE (mm)</th>
<th>DISTRIBUTION WT %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>-3.35 + 0.60</td>
<td>2.69</td>
</tr>
<tr>
<td>-0.60 + 0.150</td>
<td>2.71</td>
</tr>
<tr>
<td>-0.150 + 0.045</td>
<td>2.52</td>
</tr>
<tr>
<td>-0.045</td>
<td>2.56</td>
</tr>
</tbody>
</table>

### 2.2.3 Apparatus

Experiments were conducted in a Russian made T-40/600 tube furnace measuring, approximately 60cm long and 3.5 cm inside diameter. A sample boat 9cm long, 1cm wide, and 0.5cm deep was placed inside the tube to hold the sample mixture. The tube furnace was electrically heated and rated at 1200 °C. The diagram of the tube furnace is shown in Figure 2.2. The furnace temperature was measured by a thermocouple placed on one end of the furnace, which also acted as exit for the reaction gases. The thermocouple was connected to a Strohlein instrument controller which was used to set and control temperature by adjusting the current input to about 5 amperes. A portable thermocouple
was used to monitor temperature during the experiments, to determine any variation from the set point. With the furnace temperature set at 1000°C, temperatures were measured along the tube from left to right in the diagram, to determine the hottest zone. The temperature profile measured is shown in Figure 2.3. The difference between set and measured temperatures were within ± 20°C. The other end of the furnace was connected to a nitrogen cylinder via a Platon laboratory flowmeter, which indicated the nitrogen flowrate, in cm³ per minute.
Figure 2.2 Diagram of tube furnace used in experiments

1. Mains supply  
2. Control unit  
3. Silica tube  
4. Flap door  
5. Sample reactor boat  
6. Electrical heating elements  
7. Tube furnace  
8. Control thermocouple  
9. Flow meter  
10. Nitrogen cylinder
Figure 2.3 Temperature profile of the tube furnace used in solid state carbothermic reduction with the temperature set at 1000°C
2.2.4 Procedure

Experiments to investigate the effect of temperature on solid state carbothermic reduction of old Nkana copper slag were conducted at three temperatures; 600 °C, 750 °C and 950 °C. Slag consisting of -0.60+0.150 mm size fraction was mixed with 20 % (of slag weight) of -0.60 mm charcoal as the reducing agent. From the mixture, 3g samples were weighed into a sample boat and reduced at each temperature in a nitrogen atmosphere, for varying length of time of 1 to 4 hours. The sample weight was limited to 3 g due to the limitation of the sample boats. Optimisation of the sample weight was not carried out. Nitrogen flowrate was set and maintained constant at 300 cm$^3$ per minute, in all experiments. The reduced slag was leached in acidified solution at terminal pH 1.4 to 2. The solution was analyzed to determine cobalt, copper and iron content.

From the investigations, on the effect of temperature, a high amount of cobalt leached was attained at 950°C and 2 hours reduction time. Consequently, investigations to study the effects of varying the amount of the reductant, and that of particle size of the slag, were carried out at a constant temperature of 950°C and reaction time of 2 hours. The effect of varying the amount of charcoal on solid state carbothermic reduction of old Nkana copper slag was investigated at constant temperature of 950°C. Slag samples consisting of the -0.60+0.150 mm size fraction were mixed with 20, 30, and 40 % charcoal. From each mixture 3g samples were reduced at 950°C for 2 hours in a nitrogen atmosphere. Reduced slag samples were leached in acidified solution at terminal pH 1.4 to 2. The resulting solution was analyzed for cobalt, copper and iron.
The effect of particle size on solid state carbothermic reduction of old Nkana copper slag was investigated using four different size fractions - 3.35 + 0.60mm, -0.60 + 0.150mm, -0.150 + 0.045mm and -0.045mm. For each size fraction a slag sample was mixed with 20 percent charcoal. From the mixture 3g samples were reduced at a constant temperature 950°C for 2 hours in a nitrogen atmosphere. Reduced samples were leached in acidified solution at terminal pH 1.4 to 2.0. The solution was analysed for cobalt, copper and iron content. All experiments on solid state carbothermic reduction were conducted in duplicate in a nitrogen atmosphere. The results of solid state carbothermic reduction are presented and discussed in the next section.

2.2.5 Analysis of reduced slag samples

The amount of cobalt, copper and iron converted to acid soluble form was determined by leaching approximately 0.5g of the reduced material, in 50 mls acidified aqueous solution to a terminal pH 1.4 to 2.0. The duration of leaching was 2 hours while the leaching temperature of 75°C to 85°C was maintained. This is the temperature range used in the industrial leaching of copper calcines. During leaching, the samples were magnetically stirred at constant rate. The resulting solution was analyzed by atomic absorption spectrometer(AAS) for cobalt, copper and iron. The percent cobalt, copper and iron...
leached were calculated relative to the respective total metal present in the initial slag sample. The percentage of the element leached was taken as being equivalent to the amount of metal reduced in slag.

2.3 RESULTS AND DISCUSSION

The leachability of cobalt in pH 1.4 to 2.0 aqueous media after carbothermic reduction in the solid state of old Nkana copper slag was studied using the product from three reduction temperatures. The choice of reaction temperature was based on kinetic and thermodynamic considerations. A temperature of 500°C is considered as the lowest temperature at which reduction of cobalt oxides is thermodynamically possible. A temperature of 950°C was chosen as the upper limit at which solid state reduction can occur without softening of the slag. The results of this work are tabulated in the appendices and discussed in the following sections.

2.3.1 Effect of reaction temperature on solid state carbothermic reduction

The results showing the influence of temperature on solid state carbothermic reduction of old Nkana copper slag are given in Figure 2.4 as percent cobalt leached at different temperatures against reduction time. The results from solid state carbothermic reduction show that, at 950°C the cobalt leached is higher than for 600°C and 750°C reaction temperatures throughout the reaction times investigated. The highest value of cobalt
leached at about 50% Co was attained at 950°C and two hours reduction time. At 950°C and longer reduction time of beyond two hours, the percent cobalt leached decreases. In this range there is a possibility that cobalt which is reduced, forms insoluble carbides and ferrites. Two stable carbides are formed when solid cobalt is carburised, Co₂C and Co₇C [8,9]. The free energy change for formation of Co₂C is given as ΔGT = -3950 + 2.08T [1]. Within this temperature range the free energy for the formation of the carbide is negative and remains almost the same as the temperature increases, from about -2690 kcal at 600 to -1955 kcal at 950°C. The large negative value for the free energy change at 600°C, indicates that carbides can form at much lower temperature. Formation of insoluble carbides can be used to explain the low percent of cobalt leached at 750°C. At this temperature the decrease in the cobalt leached is noticeable after one hour reduction time and continues at longer reaction times. At 750°C it is probable that the observed decrease in the percent cobalt leached is influenced by the thermodynamics of the Boudouard reaction given in equation 2.5. which approaches equilibrium around this temperature. If this occurs the amount of carbon monoxide available for reduction will remain fairly constant. The CO₂/CO ratios depend on temperature and not on the reduction time.

At 600°C the percent cobalt leached continues to increase at longer times of reduction. The observed behaviour can be explained by the low rate of reduction, which continues even at longer times of reduction at this temperature.
Figure 2.4  Effect of Temperature on  % cobalt leached from slag samples reduced at 600, 750 and 950°C for varying times 1-4 hours.

In general, increase in temperature results into high rate of reaction. At high temperature the reaction is expected to reach completion in a short time because the energy available for the reaction is higher. The effect of temperature on a reaction is explained by the Arrhenius equation, which in general terms is expressed as [2,3]:

\[ k = A \exp(-\frac{E_a}{RT}) \]

Where \( k \) is the rate constant the units of \( k \), may be \( \text{mol dm}^{-3} \text{s}^{-1} \), \( k \) varies with temperature
and expresses the rate at which the reactants are consumed in a chemical reaction. The value of $k$ can therefore be used to indicate the rate of a reaction. $A$ is the frequency factor, which is a measure of atomic translations and collisions during a chemical reaction. $E_a$ is the activation energy, that is the minimum energy that must be made available for a reaction to occur. $R$ is the universal gas constant. $T$ is the temperature at which the reaction takes place. In solid state carbothermic reduction of cobalt oxides in old Nkana copper slag in an inert atmosphere, both direct and indirect reduction with carbon and carbon monoxide are possible. The reactions involve mass transfer and diffusion, which are influenced by temperature. Increase in temperature lowers the resistance to diffusion and mass transfer of carbon monoxide, carbon dioxide and oxygen, resulting into high rates of reaction at 950°C, which lead to high percent of cobalt leached within two hours reduction time. Since the highest percentage of cobalt leached was attained at 950°C and two hours reduction time, subsequent experiments to investigate the effect of varying the amount of the reductant and particle size were conducted at constant temperature of 950°C and 2 hours time.

2.3.2 Effect of varying the amount of charcoal on solid state carbothermic reduction

The effect of varying the reductant in slag samples was studied at 950°C and 2 hours reduction time. Samples of the -0.60+0.150mm size fraction of old Nkana copper slag were mixed with 20, 30, and 40 weight percent charcoal. Samples from the mixtures were
reduced for 2 hours each in a nitrogen atmosphere. The results of the investigation presented in Figure 2.5, show the effect of varying the amount of charcoal on cobalt leached from samples reduced by solid state carbothermic reduction of slag at 950°C. The results are plotted as percent cobalt leached against wt % charcoal added. The cobalt leached is higher in slag samples reduced with 20 wt % charcoal (at about 50 % Co leached), and lower (at less than 30% cobalt leached), in slag samples mixed with 30 and 40 percent charcoal. In the presence of excess carbon it is possible that the reduced cobalt oxide particles are carburised, and readily form insoluble carbides (Co₃C and Co₂C) as already discussed, resulting in low percent of cobalt leached from slag samples reduced with 30 and 40 wt % charcoal. Increasing the amount of charcoal in the mixture does not necessarily lead to the formation of more carbon monoxide. In the presence of carbon the CO₂/CO ratios are controlled by the Boudouard reaction. Since the highest amount of cobalt leached was attained with 20 wt % charcoal addition, this amount was therefore used in experiments to study the effect of slag particle size on solid state carbothermic reduction. No investigations below 20% wt. charcoal were conducted.
Figure 2.5 Effect of varying the amount of charcoal on % cobalt leached from slag samples reduced for 2 hours at 950°C.
2.3.3 Effect of particle size of slag on solid state carbothermic reduction

The effect of particle size on solid state carbothermic reduction was studied at constant temperature of 950°C and reduction time of 2 hours. The different particle size ranges used in the investigation were; -3.35+0.60, -0.60+0.150, -0.150+0.045 and -0.045mm of the old Nkana copper slag. A sample of each fraction was mixed with 20% wt charcoal and reduced in a nitrogen atmosphere.

![Graph showing the effect of different particle sizes on % cobalt leached from slag samples reduced at 950°C for 2 hours.](image)

Figure 2.6 Effect of different particle sizes on % cobalt leached from slag samples reduced at 950°C for 2 hours.
The results of the investigation are given in Figure 2.6 as percent cobalt leached from different size fractions against particle size. Figure 2.6 shows a high percent of cobalt leached (at about 50%) in the coarse fractions: -3.35 + 0.60mm, and -0.60 + 0.150mm and low in the fine fractions. The fine particles because of their large surface area are expected to be readily reduced, and the % Co leached should have been higher. The difference in the cobalt leached indicates differences in the mechanisms by which the reduction of cobalt oxides in different particle sizes takes place.

In solid state carbothermic reduction, both direct and indirect reduction of the oxides in slag by carbon and carbon monoxide is possible as described by the reactions in equations 2-1 to 2-4. Reduction of cobalt oxides with carbon monoxide is a gas-solid reaction, in which diffusion of the gas to the surface of cobalt oxides, is necessary for the reduction reaction to occur, to form CO₂ and the metal. It is probable that resistance to interparticle diffusion in the coarse fractions was less than in fine size fractions during carbothermic reduction of the slag, resulting in the high percent cobalt leached in the former.

Direct reduction requires that the reactants are in contact, it is thus promoted by having the reactants in a fine form and well mixed. Direct reduction of fine size fractions slag readily occur, it is possible that the fine cobalt oxide particles which are reduced are carburized, resulting into formation of insoluble carbides and subsequent low percent of cobalt leached.
The results of solid state carbothermic reduction of old Nkana copper slag indicate that solid state carbothermic reduction of the slag is possible to produce a leachable product, under the conditions utilized in this study. To minimise formation of insoluble carbides, the addition of the reducing agent requires control.

REFERENCES


CHAPTER THREE

COBALT RECOVERY FROM OLD NKANA COPPER SLAG VIA SOLID STATE SULPHATION
3.1 THEORETICAL CONSIDERATIONS

Sulphation is a roasting process widely employed to convert sulphide and oxide materials into sulphates which are soluble in dilute acid solution. Roasting of sulphide minerals has been described by several workers [1-6]. In the primary extraction of cobalt from copper and nickel sulphide ores, roasting of the sulphide concentrates is usually a preliminary step. The calcine produced is then leached and the metals in solution are separated and recovered by hydrometallurgical processing.

Sulphation of sulphides involves oxidation of sulphide minerals to form oxides and the subsequent reaction of the oxide formed with sulphur trioxide, to form a sulphate.

Sulphation of cobalt in oxide ores and oxidized secondary materials requires the addition of sulphur or sulphur bearing materials to provide the sulphating gases. This would be the case if old Nkana copper slag was to be subjected to a sulphating roast. This chapter considers the sulphating roast of old copper slag at Nkana, using pyrite and cobalt sulphide concentrates as sources of sulphur.
3.1.1 Thermodynamics of Sulphating Cobalt Oxide:

The sulphation of cobaltous oxide (CoO) present in old Nkana copper slag would be expected to occur according to the following chemical reactions [7].

\[
\begin{align*}
\text{CoO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 &= \text{CoSO}_4 & \text{(3.1)} \\
\Delta G_T &= -69230 - 27.03T \log T + 137.18T \text{ cal.mol}^{-1} \\
\text{CoO} + \text{SO}_3 &= \text{CoSO}_4 & \text{(3.2)} \\
\Delta G &= -46630 - 27.03T \log T + 192.36T \text{ cal.mol}^{-1} \\
\text{SO}_2 + \frac{1}{2}\text{O}_2 &= \text{SO}_3 & \text{(3.3)} \\
\Delta G &= -22600 - 55.98T \text{ cal.mol}^{-1}
\end{align*}
\]

These reactions are simplified. Some of the cobalt is chemically combined in silicates and magnetite, rather complex equations are required to represent actual reactions. However, they can be used to predict the thermodynamic behaviour, and to speculate on the kinetics of solid state sulphation of cobalt oxide. Expressions for the equilibrium constants for the above reactions indicate that the reactions have a strong dependence on gas pressures and would be expected to be temperature dependent, since equilibrium constants are affected by temperature.
For example the equilibrium constant for equation 3.1, $K_{3.1}$, can be written as:

$$K_{3.1} = \frac{1}{P_{SO_2}} \cdot \frac{1}{(P_{O_2})^{1/2}}$$

$$\ln K_{3.1} = - \left( \ln P_{SO_2} + \frac{1}{2} \ln P_{O_2} \right)$$

The equilibrium constant is related to the Gibbs free energy

$$\Delta G_T = -RT \ln K_{3.1} \quad 3.4$$

That is, $\Delta G_T = RT \left( \ln P_{SO_2} + \frac{1}{2} \ln P_{O_2} \right) \quad 3.5$

Similar expressions can be written for the reactions in equations 3.2 and 3.3.

As can be noted from the expression of free energy in equations 3.1 and 3.4, the Gibbs free energy and the equilibrium constant for the reaction in 3.1, decrease as the temperature is increased. Therefore at a very high temperature the reverse of equation 3.1 (i.e. cobalt sulphate decomposition) which is undesirable becomes feasible. Sulphation with sulphur trioxide (equation 3.2) is also favoured by low temperature. At the same time, formation of SO$_3$ from SO$_2$ (Equation. 3.3) is also thermodynamically more likely to occur at low temperatures[2,4,6,8]. Therefore all the three equations; 3.1-3.3, indicate that relatively low temperatures should favour the sulphation of CoO. Conditions of temperature and gas partial pressures (compositions) under which sulphation of CoO can be carried out can be predicted by examining the predominance area diagrams for the cobalt-sulphur-oxygen system shown in Figures 3.1 (a), and 3.1 (b), at 873 K, and 973 K respectively. The diagrams were constructed from values of log $P_{SO_2}$ and log $P_{O_2}$ calculated using data shown in Table 3-1. Details of the calculation can be
found in the Appendices.

Table 3.1  Data used for constructing Co-S-O predominance area diagrams [7]

<table>
<thead>
<tr>
<th>REACTION</th>
<th>ΔGT Calories mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>2CoO = 2Co + O₂</td>
<td>111800 - 33.7T</td>
</tr>
<tr>
<td>Co₃O₄ = 3CoO + ½O²</td>
<td>43800 - 35.4T</td>
</tr>
<tr>
<td>CoSO₄ = CoO + SO₂ + ½O₂</td>
<td>69230 + 27.03TlogT -137.18T</td>
</tr>
<tr>
<td>3CoSO₄ = Co₃O₄ + 3SO₂ + O₂</td>
<td>77250 + 32.24TlogT -160.02T</td>
</tr>
<tr>
<td>CoS₂ + 5O₂ = CoO + 2SO₂</td>
<td>165727 -9.46T</td>
</tr>
<tr>
<td>CoS₂ + 3O₂ = CoSO₄ + SO₂</td>
<td>234974 + 27.0TlogT - 146.54T</td>
</tr>
</tbody>
</table>

Figures. 3.1 (a), and 3.1 (b) are rather simplified as they only show one sulphur compound of cobalt (CoS₂). Other forms of cobalt sulphides, like cobalt pentlandite (Co₉S₈) and linnaeite (Co₃S₄) have been found to exist and incorporated in diagrams reported elsewhere [8]. In the old Nkana copper slag cobalt is present in form of oxides such as CoO and combined as ferrites and silicates[9,10].
Figure 3.1 Predominance area diagram for the Co-S-O system calculated at 873 K and (b) 973 K showing the effect of temperature on the stability of phases
Figure 3.2 Superimposed predominance area diagrams (a) Cu-S-O [----] and Co-S-O [-----], (b) Co-S-O [-----] and Fe-S-O [-----]
In support of what is already discussed, in the set of diagrams (Fig. 3.1) it can be seen that the predominance area for CoSO$_4$ decreases as temperature increases from 873 to 973K, showing that CoSO$_4$ is unstable at high temperature and is likely to decompose and form cobalt oxides [2,8,11]. The size of the predominance area indicates the range of gas compositions over which a particular compound is stable and over which sulphation can occur. Theoretically at 973K, for example, CoO can be sulphated between oxygen partial pressure (P$_{O_2}$) of between $10^{-4}$ and $10^{-11}$ and P$_{SO_2}$ of between 10$^5$ and 10$^4$. Industrial gas composition under which sulphation of copper and cobalt sulphides contains about 8% SO$_2$ and 4% O$_2$ and this is represented by point A and hatched circle on the superimposed Cu-S-O:Co-S-O and the Fe-S-O:Co-S-O systems shown in Figure. 3.2(a) and 3.2(b) [2,11]. In this same gas composition range, the diagrams reveal that, copper would, under equilibrium conditions, exist as CuO.CuSO$_4$ while iron would occur as Fe$_2$O$_3$. Figures 3.1 and 3.2 suggest that selective sulphation of old Nkana copper slag could be achieved at some temperature and gas composition such that cobalt and copper (in ferrites and silicates) form acid soluble sulphates and oxysulphates, respectively, while iron forms hematite, an oxide that is insoluble in moderate strength mineral acids. The sulphating gases SO$_2$ and SO$_3$ are provided by the oxidation of the sulphides with oxygen in the air. The composition of the gases is indicated by the partial pressure of sulphur dioxide (P$_{SO_2}$), sulphur trioxide (P$_{SO_3}$) and oxygen (P$_{O_2}$) according to the
reaction in equation 3.3. The partial pressures are determined by the air supplied to oxidize the sulphides. \( P_{SO_3} \) is high for large values of \( P_{SO_2} \) and \( P_{O_2} \).

Predominance area diagrams (e.g. Figs. 3.1 and 3.2) are based on a number of simplifying assumptions, such as activities of one for each solid phase, which would rarely hold for heterogeneous materials like slags. Another limitation of predominance area diagrams is that the kinetics of reactions cannot be inferred from them. These limitations gave rise to the need to perform sulphation experiments to determine the actual conditions that would be required for the selective sulphation of cobalt, copper, and iron present in old Nkana copper slag.

The parameters investigated in this research on solid state sulphation of old Nkana copper slag, are the effects of sulphur-sources, temperature, air flowrate, particle size of the slag, as well as the relative amount of reactants. The sulphur-sources used were pyrite and cobalt sulphide concentrates.

### 3.1.2 Kinetic Considerations of Solid State Sulphation

Reaction kinetics are concerned with the evaluation of reaction rates, rate controlling factors and mechanism of the reactions, by considering the nature of the reactants and type of chemical reactions. The characteristics of heterogeneous reactions are well described
elsewhere [12,13]. Solid state sulphation of old Nkana copper slag qualifies to be considered as a heterogeneous reaction since the gas phase components $O_2$, $SO_2$, and $SO_3$ would participate in the reaction as noted in equations 3.1-3.3. Thus, solid state sulphation of old Nkana copper slag can be classified as a gas-solid reaction.

In gas-solid reaction systems, the overall reaction can be split into a number of intermediate steps as listed below [2]:

- Mass transfer of gaseous reactants and gaseous products between, the bulk phase and the surface of the reacting solid particle.
- Diffusion of gaseous reactants or products through the pores of a solid reaction product or through the pores of partially reacted solid.
- Adsorption of the gaseous reactants onto and desorption of gaseous products from the solid surfaces.
- The actual chemical reaction between the adsorbed gas and the solid.

Considering the sub-steps listed above, the kinetics of solid state sulphation would be expected to be influenced by a number of factors. These factors would include: concentration of reactants and products, temperature, diffusion coefficients, type and form of the reactants, and the sulphation equipment used. Currently the fluid bed roaster and the multiple hearth furnace are popular in the sulphation of cobalt bearing, copper sulphide mineral concentrates[1,5,11].

Of the parameters listed above with a possible influence on sulphation, those
related to diffusion cannot be independently studied, as they depend on several factors such as; the nature of the reactants and products, the prevailing hydrodynamic conditions, and temperature.

Sulphation experiments to investigate the parameters stated above were carried out in a tube furnace. Although industrial roasting operations could hardly be expected to be done in a tube furnace, roasting results obtained with a tube furnace are nevertheless important as they reveal trends that would be similar with results that would be obtainable in an industrial roaster.
3.2 EXPERIMENTAL

Solid state sulphation experiments to convert cobalt oxides in old Nkana copper slag into cobalt sulphates, \((\text{CoSO}_4)\), soluble in dilute acid solution, were carried out using cobalt sulphide obtained from Nkana concentrator, and pyrite concentrates from Nampundwe mine. Preparation of slag and concentrate samples was carried out to ensure complete mixing and homogeneity of materials used in experiments and to determine cobalt, copper iron and sulphur content in slag and concentrates. The characteristics of the slag and sulphur bearing materials used in the experiments follow in the sections below.

Table 3.2: Chemical Analyses of Old Nkana Copper Slag and Concentrates.

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>CHEMICAL ANALYSIS % Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>NKANA SMELTER DUM SLAG</td>
<td>2.71</td>
</tr>
<tr>
<td>SULPHIDE CONCENTRATE</td>
<td>1.66</td>
</tr>
<tr>
<td>PYRITE CONCENTRATE</td>
<td>0.77</td>
</tr>
</tbody>
</table>

*\(\text{Fe}_3\text{O}_4\) content in slag calculated from total iron and FeO analysis.
Table 3.3 Distribution of Co, Cu, and Fe in Different size fractions of Screened slag samples used in experiments:

<table>
<thead>
<tr>
<th>SIZE RANGE - mm</th>
<th>CHEMICAL ANALYSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>-3.35 + 0.60</td>
<td>2.69</td>
</tr>
<tr>
<td>-0.60 + 0150</td>
<td>2.71</td>
</tr>
<tr>
<td>-0.150 + 0.045</td>
<td>2.52</td>
</tr>
<tr>
<td>-0.045</td>
<td>2.56</td>
</tr>
</tbody>
</table>

3.2.1 Materials used in solid state sulphation experiments:

The Old Nkana copper slag:

The old copper slag used in this study was obtained from Nkana smelter. Preparation of the old Nkana copper slag was carried out to make it suitable for use in the experiments. The slag was crushed down to 3.35mm in a laboratory Beater Mill and screened to obtain four different size fractions (-3.35+0.60, -
0.60+0.150, -0.150+0.045, -0.045 mm). The size ranges were arbitrarily chosen to ensure that the slag could be thoroughly mixed with the sulphating agents during experiments. The average cobalt, copper, and iron content in the old Nkana copper slag, pyrite and cobalt concentrates is given in Table 3.2. and that of the different size ranges in Table 3.3. A detailed composition of the slag can be found in Table 2.2 of chapter two.

Sulphating Agents:

Pyrite and cobalt sulphide concentrates obtained from Napundwe Mine and Nkana Division of ZCCM respectively, were used as sulphating agents. The concentrates were obtained in their fine form of flotation product. Screen analysis of the sulphide concentrate showed that 60% of the particles were less than 0.075 mm or minus 200 mesh. The pyrite contained a lot more coarse particles and less than 60% passed through the 0.075 mm mesh size. The minus 0.075mm fraction was used in sulphation experiments. The cobalt, copper, iron and sulphur content of the concentrates were determined and are given in Table 3.2.

The weight of the sulphide and pyrite concentrates required for sulphation of 1 g slag sample were calculated stoichiometrically at 0.44g pyrite and 0.81g sulphide concentrate respectively, from the sulphur content of the concentrates and the cobalt, copper and iron contents of the slag. The actual amounts used in the experiments were above stoichiometric requirements.
The slag and concentrate were dried before mixing. Mixtures were kept covered during the course of the experiments. Standard analytical methods, already reported in chapter two, were used to determine cobalt, copper, iron, and sulphur in slag and concentrates. Sulphur was determined gravimetrically by precipitation as barium sulphate. A 0.5 g sample was digested in concentrated nitric acid with the addition of potassium chlorate - bromine mixture and evaporated to dryness. The residue was dissolved in hydrochloric acid (HCl) and the solution filtered. The filtrate was made up to 300 mls. The solution was then boiled with the addition of 10% Barium chloride solution, and left overnight to precipitate sulphur as barium sulphate from the solution. After filtration, the precipitate together with the filter paper was placed in a platinum crucible and ignited in a muffle furnace set at 900°C. The weight of the residue was obtained and used to calculate the percent sulphur in the pyrite and sulphide concentrates. These are presented in Table 3.2.

3.2.2 Apparatus used in solid state sulphation experiments:

The apparatus used in solid state sulphation experiments is shown schematically in Figure 3.3. It consisted of a Russian made tube furnace approximately 60 cm long and 2 cm inside diameter electrically heated and rated at 1200°C. A silica boat about 9 cm in length 1 cm wide and 1.5 cm deep
containing a sample was placed inside the tube and heated at a preset temperature for the desired time. The furnace temperature was set by controlling the current input at 5 amperes by a STROHLEIN INSTRUMENT controller. The actual temperature was measured by a thermocouple placed on one end of the furnace. A portable chrome alumel thermocouple was used to monitor temperature during the course of the experiments. The temperatures were found to vary within ±20°C from the set temperature.

3.2.3 Experimental Procedure

Experiments on solid state sulphation of the old Nkana copper slag using pyrite and sulphide concentrates were carried out, to investigate the effect of the following parameters: temperature, variation of pyrite and cobalt sulphide concentrate in the mixture, particle size of slag, and air flowrate, on the conversion of cobalt oxides in slag to sulphates, which are soluble in dilute acid solution. Experiments were conducted using the tube furnace shown in Figure 3.3, at 600, 750, 850, and 950°C, under atmospheric conditions with constant air supply, except for experiments on effect of air flowrates. Air was allowed to enter through an opening at one end of the furnace and out through the other end, where the control thermocouple was positioned. A restricted flow of air was necessary to allow time for the diffusion of oxygen through the packed bed of the sample mixture in a boat and to minimise carry over of the sulphating gases SO₂ and SO₃. Experiments were carried out in duplicate.
Figure 3.3: Diagram of furnace used in Sulphation experiments

1. Mains supply
2. Control unit
3. Silica tube
4. Flap door
5. Sample reactor boat
6. Electrical heating elements
7. Tube furnace
8. Control thermocouple
9. Gas outlet
3.2.3.1 Sulphation of old Nkana copper slag with pyrite

To investigate effect of time and temperature on sulphation of the old Nkana copper slag, the -0.60+0.150 mm size fraction of slag, arbitrarily chosen, was mixed with pyrite concentrate in a 1:1 slag: pyrite ratio. From the mixture 5 g samples were taken and roasted at 600, 750, 850, and 950°C, for varying lengths of time 1-6 hours at each temperature, in the tube furnace, with one end kept open to allow air to enter the furnace.

To study the effect of varying the amount of a sulphating agent, samples of the -0.60+0.150 mm fraction of slag, were mixed with 50, 75, 100, and 150 g of pyrite, representing slag to pyrite ratios of 1:1, 1:1.5, 1:2, and 1:3. From each mixture, 5 g samples were roasted using the optimised time of 4 hours at constant temperature of 600°C. The temperature and time were optimized from the results of the effect of temperature on sulphation. The highest amount of percent cobalt leached was attained at 600°C and 4 hours roasting time.

The effect of particle size was investigated by mixing four different size fractions of slag, shown in Table 3.3 with equal amounts of pyrite in a 1:1, slag to pyrite ratio. From each mixture 5 g samples were roasted in the tube furnace for 4 hours, at constant temperature of 600°C.
Dependence of sulphation on air flowrate was studied by mixing -0.60+0.150 mm size fraction of slag with equal amounts of pyrite in a 1:1 slag to pyrite ratio. From the mixture 5g samples were roasted for 4 hours each at different air flowrates of 300, 700, 1100, and 1600 cm$^3$ per minute. The temperature was maintained constant at 600°C. Air was supplied by a laboratory compressor pump via a Platon flowmeter, which was used to set and regulate the air flowrate.

3.2.3.2 Sulphation of old Nkana copper slag with cobalt sulphide concentrate

Experiments to investigate the influence of time and temperature on sulphation of old Nkana copper slag were repeated, using cobalt sulphide concentrate as the sulphating agent. The -0.60+0.150 mm size fraction of slag was mixed with sulphide concentrate in the ratio of 1:1. From the mixture 5g samples were sulphated (under similar conditions to sulphation with pyrite), using the same apparatus described above for 1-6 hours at 600, 700, 850 and 950°C. Analysis of the sulphated mixtures was carried out to determine cobalt, copper and iron by atomic absorption spectrometer.
3.2.4. Analysis of Sulphated Slag Samples

Chemical analysis of sulphated slag samples was carried out, by weighing 0.5 g samples from the sulphated mixture. Each sample was then leached in 50 mls of acidified aqueous solution at pH2, with magnetic stirring for two hours. The temperature of the solution was monitored during dissolution and controlled at 75-85°C. The pulp was filtered, and the volume of the solution combined with washings was measured. The volume was used in calculating the percentage of the element leached. Cobalt, copper, and iron were determined from the solution by atomic absorption spectrometer. In the absence of analytical techniques to determine the nature and amount of soluble phases formed during roasting, whatever amount of cobalt, copper, and iron was analyzed from the solution was taken as being equivalent to the soluble sulphates formed. The calculated percent leached of an element was taken as a measure of the extent of sulphation. The results of the investigations conducted are described and discussed in the next section.
3.3 RESULTS AND DISCUSSION

Cobalt recovery from old Nkana copper slag via sulphation in solid state was investigated to study the effect of temperature, sulphide addition, slag particle size and air flowrates, on the conversion of cobalt oxides in slag to sulphates.

In this study sulphation to convert cobalt oxides to soluble sulphates was considered, to determine whether this was a suitable pretreatment stage in the recovery of cobalt from old Nkana copper slag. The results of solid state sulphation of old Nkana copper slag using pyrite and cobalt sulphide concentrate are tabulated in the appendices.

3.3.1 Sulphation using pyrite

The results of solid state sulphation of old Nkana copper slag with pyrite concentrate are presented and discussed below:

3.3.1.1 Effect of Reaction Temperature on Sulphation

Figure 3.4 shows the percentage of cobalt leached from the - 0.60+0.150 mm fraction of slag sulphated with pyrite in the ratio 1:1, at 600, 750, 850 and 950 °C under atmospheric conditions. The results of this set of experiments indicate that under the conditions utilised the highest amount of cobalt leached from sulphated samples was about 60 % at 600°C, and
Figure 3.4 Influence of reaction temperature on the % cobalt leached from slag sulphated with equal amounts of pyrite and different temperatures under atmospheric conditions
decreased to about 26 % at 950°C. At 600 °C the high percentage of cobalt leached is in general agreement, that formation of sulphates is favoured at low temperatures[1,4,6]. The predominance area diagrams shown in Figure 3.1 and 3.2 show that sulphates are stable at low temperatures. The reaction between sulphur dioxide- SO₂ and oxygen to form sulphur trioxide-SO₃ is exothermic, it requires low temperature to take place. At 600 °C there will be more SO₃ available for sulphation of cobalt oxides than at higher temperatures. This resulted in a more complete sulphation of the oxides at 600°C and consequently a higher percentage of cobalt leached. At this temperature the cobalt sulphate formed is stable and remains undecomposed. The stability of cobalt sulphate decreases with increasing temperature. This is shown in the predominance area diagrams in Figure 3.1 and Figure 3.2 by a reduction in the stability area for cobalt sulphate as the temperature is raised, from 873 to 973 K. Even though pure cobalt sulphate decomposes at about 980 °C [11], in the presence of other oxides in the slag it is possible that this temperature can be lowered resulting into decomposition of the sulphate and formation of insoluble compounds such as cobalt ferrites, and a lower percentage of cobalt leached. Ferrite formation is enhanced by the presence of cobalt chemically dissolved in magnetite and fayalite, because of its close proximity with iron, in solid solution, cobalt can readily replace iron in these compounds [2].
The $\text{SO}_2$ and $\text{SO}_3$ are volatile, at high reaction temperatures the gases readily escape into the furnace atmosphere reducing the possibility of complete sulphation of the oxides, leading to a decrease in percent cobalt leached, which is evident at 750 °C, 850 °C and 950°C.

Figure 3.5 shows the influence of temperature on percent cobalt leached from slag samples sulphated with equal amounts of pyrite for a constant time of 4 hours at 600 °C, 750 °C, 850 °C and 950 °C. The results show a similar effect to that of temperature on percent cobalt leached, which decreases as the temperature is raised. The explanation for this trend has already been discussed above. In general the effect of temperature on a chemical reaction is to increase the rate of the reaction when the temperature is raised. In gas-solid reactions such as those occurring in the sulphation of old Nkana copper slag in solid state, the influence of reaction temperature lies on the effect temperature has on the rate controlling factors such as diffusion and mass transfer [2]. During sulphation of old copper slag in solid state gas-solid reactions take place between the sulphidising agent and oxygen in air, to form sulphur dioxide and sulphur trioxide, and between cobalt oxides in slag with sulphating gases to form soluble sulphates. The reactions involve diffusion and mass transfer and it is possible that either the formation of $\text{SO}_2$ and $\text{SO}_3$ or the sulphation of cobalt oxides can determine the rate and the extent of solid state sulphation of the slag.
Diffusion is an important requirement for a gas-solid such as above to occur. The influence of diffusion on the rate of gas-solid reactions is due to the effect temperature has on the diffusion coefficients of the gases involved in the reaction. The diffusion coefficient is related to temperature exponentially.
by an Arrhenius type equation which is expressed in general terms as [12,13].

\[ D = D_0 \exp(-\frac{E_a}{RT}) \]  \hspace{1cm} 3.6

Where \( D \) is the diffusion coefficient, \( D_0 \) is a constant, \( E_a \) is activation energy, \( R \) and \( T \) are gas constant and absolute temperature respectively. According to the equation above the value of \( D \) will be large at high temperature. Indicating less resistance to diffusion and high reaction rates. However sulphur dioxide and sulphur trioxide are volatile, at high temperatures they readily escape into the furnace atmosphere, reducing the chances for complete sulphation to occur and reduced amount of percent cobalt leached.

Figure 3.6 shows, the percent cobalt, copper and iron leached from the same slag samples sulphated at 600°C. The percent copper and iron leached are low, below 10 and 1%, respectively. The low percentages can be attributed to the formation of insoluble compounds of copper and iron, as can be seen from the predominance area diagrams given in Figure 3.1 and Figure 3.2. The sulphation of Cu₂O proceeds with the formation of insoluble basic salts like CuO.CuSO₄, that of iron oxides proceeds with the formation of Fe₂O₃ which then react with the sulphating gases to form Fe₂(SO₄)₃ [2,14]. The tendency to form insoluble copper and iron compounds is essential to achieve selective sulphation of the oxides in slag. In this investigation, a high percentage of cobalt leached was attained at 600°C and 4 hours sulphation time. Hence
further experiments to study effect of slag particle size, variation of pyrite, and airflow rate were conducted at 600°C and sulphation time of 4 hours.

Figure 3.6 Comparison of %Co, %Cu and %Fe leached from slag sulphated with equal amounts of pyrite at 600°C for varying lengths of time
3.3.1.2 Effect of slag particle size on sulphation

The size fractions used to study the effect of particle sizes on the extent of solid state sulphation of old Nkana copper slag, in increasing fineness were -3.35 + 0.60, - 0.60 + 0.150, - 0.150 + 0.045, and - 0.045 mm. The sulphation temperature and time were maintained constant at 600 °C. and 4 hours. The results of this study are presented in Figure 3.7. The results of Figure 3.7 show a high percentage of cobalt leached in the fine, -0.045 mm size fraction at about 72%. The percent cobalt leached decreases with increasing coarseness of the particles to 52% in the -3.35mm fraction. The rate of reaction is in general increased by reducing the particle size since the surface area over which the reaction takes place increases. The fine particles -0.045mm, because of their large surface area are readily sulphated, resulting in high percentage of cobalt leached. In the slag, cobalt oxide is mechanically entrapped and chemically combined with the silicates.

In the fine size fraction it is possible that both mechanically entrapped and chemically combined oxide particles are liberated and are readily sulphated resulting in high percent of cobalt leached, while for sulphation of coarse particles to occur, diffusion of cobalt and oxygen ions within the particles is necessary. It has been established that formation of cobalt sulphate on cobalt oxide starts on the oxide surface. It involves transfer of cobalt ions from the oxide to the surface of the sulphate, where sulphating reactions occur at
the interface between cobalt sulphate already formed and the sulphating gases [13]. In the coarse size fractions of slag, diffusion of cobalt ions from within the particles is difficult at low temperature and because of the glassy nature of the slag. The result is that, the extent of sulphation and the percent cobalt leached are lowered.

![Graph showing % Cobalt Leached vs Particle Size (mm) increasing coarseness]

Figure 3.7 Percent cobalt leached from slag of different particle sizes sulphated for 4 hours at 600°C under atmospheric conditions.
The results of this study show that solid state sulphation of the old Nkana copper slag is influenced by the particle size of the slag. The -0.045mm size fraction seems to be suitable, in order to attain percent cobalt leached of more than 70%. However, size reductions down to this range are difficult to get practically, but it is safe to say that sizes below 0.150 mm (150 microns) would give high sulphation rates.

3.3.1.3 Effect of varying the amount of pyrite on sulphation

In this study a fixed weight of slag was mixed with pyrite in the following ratios; 1:1, 1:1.5, 1:2 and 1:3, representing 50, 75, 100, and 150 g pyrite addition to the old Nkana copper slag and sulphated at constant temperature of 600°C for 4 hours. Figure 3.8 show results of varying the weight of pyrite added to the mixture on percent cobalt leached from old Nkana copper slag. The results from Figure 3.8, show that as the pyrite content is increased, the percent cobalt leached is lowered from about 50 to less than 10%. The percentage of cobalt leached is lowered even though a large amount of sulphur is available for sulphation. Under the sulphation conditions utilised, it is possible that there is a limitation in the supply of oxygen to react with the pyrite added to produce the sulphating gases. In the presence of excess sulphur, non stoichiometric cobalt sulphides may be formed by reacting with pyrite [8]. Some of these like CoS₂ exist in equilibrium with CoSO₄ as shown in Figure3.1. The Gibbs free energy of reaction for the formation of CoSO₄,
calculated from equation 3.1 is about -32000 cal mol$^{-1}$ and that for the reaction of CoO with pyrite (FeS$_2$) to form CoS$_2$ is about -20000 cal mol$^{-1}$, at 600°C. The closeness of these values suggest that any one of the reactions can take place in preference to the other, depending upon the supply of the sulphating gases. The reactions by which SO$_2$ and SO$_3$ are formed are controlled by the partial pressure (composition) of oxygen in the furnace gases. The reaction of pyrite with oxygen can be expressed by simplified chemical equations as follows:

![Graph showing % Co Leached vs Wt of pyrite added in (g)]

Figure 3.8 Percent cobalt leached from slag samples sulphated with varying amount of pyrite for 4 hours at 600°C
\[ \text{FeS}_2 + \text{O}_2 = \text{FeS} + \text{SO}_2 \]
\[ \text{FeS} + 3/2\text{O}_2 = \text{FeO} + \text{SO}_2 \]
\[ \text{FeS}_2 + 5/2\text{O}_2 = \text{FeO} + 2\text{SO}_2 \]

* as the overall reaction.

These reactions show the dependence of pyrite oxidation on oxygen supply. The SO\textsubscript{2} formed requires further supply of oxygen for conversion to SO\textsubscript{3}.

### 3.3.1.4 Effect of airflow rate on sulphation

The dependence of sulphation on air flow rates were investigated by sulphating the -0.60 +0.150 mm fraction of the old Nkana copper slag with pyrite, in a 1:1 slag to pyrite ratio, for 4 hours at 600°C. The air flow rates was varied from 300 to 1600 cm\textsuperscript{3} per minute. The results of the study are presented in Figure 3.9 as percent cobalt leached against air flow rates. Figure 3.9 shows that the percent cobalt leached decreases as the air flow rate is increased from 0 to 1600 cm\textsuperscript{3} per minute. In figure 3.9, the 0 flowrate represents air flow under atmospheric conditions, in which one end of the tube furnace remained open to allow air to enter by natural draught during the course of the experiments. It was under these conditions in which a high percentage of cobalt leached was obtained at 60%. Increase in air flowrate increases the oxygen available for oxidation of pyrite to form SO\textsubscript{2} and SO\textsubscript{3} and this would have resulted in high percent cobalt leached. As the air flowrate is increased the sulphating gases
are flushed out of the furnace, leading to the reduction in the partial pressure (composition) of SO$_2$ and SO$_3$ in the furnace atmosphere. This could have resulted into low sulphation rates and lower percent of cobalt leached at higher flowrates. Air flowrates should be controlled at least, below 300 cm$^3$ per minute to allow retention of the sulphating gases in the furnace to enable diffusion of the gases to take place.

![Graph showing the effect of Air flowrate on percent cobalt leached from slag samples sulphated with equal amount of pyrite for 4 hours at 600 °C.](image)

Figure 3.9 Effect of Airflowrate on percent cobalt leached from slag samples sulphated with equal amount of pyrite for 4 hours at 600 °C
3.3.2 Sulphation with Cobalt Sulphide Concentrate

Results for the sulphation of the -0.60+0.150 mm fraction of the old Nkana copper slag with cobalt sulphide concentrate in a ratio of 1:1, at 500 °C, 600 °C, 750 °C and 850 °C. are presented in Figure 3.10 as percent cobalt leached against time. Figure 3.10 shows a low percentage of cobalt leached at less than 15% Co at all the temperatures and roasting times. The sulphur content of the cobalt sulphide concentrate at 17.00 % S, which is about half that available in the pyrite could have been insufficient for sulphation of cobalt oxides in slag as well as the cobalt and copper in the concentrate itself. This also suggests that the sulphur in the cobalt sulphide concentrate may exist in solid solution in the complex minerals and is not readily available for sulphation reaction. Because of the low amount of percent cobalt leached in slag sulphated with cobalt sulphide concentrate, further experiments were discontinued.
Figure 3.10 Percent cobalt leached from slag samples sulphated with cobalt sulphide concentrates at different temperatures and time under atmospheric conditions
REFERENCES.


CHAPTER FOUR

CONCLUSIONS
Solid state carbothermic reduction and sulphation were investigated to determine whether these processes could be suitable for the pretreatment of old Nkana copper slag in the recovery of cobalt. The following conclusions can be drawn from the investigations carried out:

- Experiments on solid state carbothermic reduction using charcoal as a reductant showed that pretreatment of the slag within the temperature range 600 to 950°C to produce a partially reduced product which can be leached in sulphuric acid of moderate strength is possible.

- A 52% cobalt leached at terminal pH 2 after leaching was attained from the -0.60 + 0.150 mm slag reduced at 950°C, two hours reduction time, with 20% charcoal addition.

- Increasing the amount of charcoal resulted in decreased percent cobalt leached. The reason given for this is that in the presence of excess carbon, cobalt reduced to Co and CoO is carburised and forms insoluble carbides.

- Reduction temperature and the particle size of the slag have a greater influence on the extent of solid state carbothermic reduction of the old Nkana copper slag. At high temperature exsolution of cobalt from silicates and magnetite is enhanced. Coarse fractions of slag, -3.35 + 0.60 mm and -0.60 + 0.150 mm promote interparticle diffusion since the solids are not tightly packed.
• Solid state sulphation of the old Nkana copper slag can be achieved at a low temperature of 600°C. About 70% cobalt leached was attained at this temperature at four hours sulphation time from the -0.045mm size fraction of slag sulphated with equal amount of pyrite.

• Sulphation of the old Nkana copper slag is influenced by its particle size, lower size fractions below about 0.150mm increase the sulphation rates of the cobalt in slag.

• Increasing the amount of sulphur was found to reduce the sulphation of cobalt in the slag. This is because the oxygen supply was limited which is required to produce sulphaing gases (SO₂ and SO₃).

• Increase in the air flowrate in the reaction chamber decreases the sulphation of cobalt. This is because the sulphaing gases (SO₂ and SO₃) formed are flushed out of the furnace. This reduces the partial pressure of SO₂ and SO₃ in the furnace chamber and subsequently leads to low sulphaion of cobalt.

• Pyrite concentrate was found to be a better sulphaing reagent than cobalt sulphide concentrate. This is due to the higher sulphur content in pyrite (31% S) than cobalt sulphide concentrate (17% S).
APPENDICES
Appendix - 1A

Calculation of energy required to smelt 1 tonne of old copper slag

The energy required is determined by calculating the heat required to melt the slag, which is then converted to electrical energy. The heat required to melt the slag, is calculated by considering the heat required to melt individual oxides in the slag, than compounds. When a substance or compound is heated, it absorbs heat, the heat content $H$ increases. The amount of heat absorbed depends on the heat capacity $C_p$, i.e., the heat required to raise the temperature of one mole of a compound by 1 °C or

$$C_p = (dH/dT)_p$$  \hspace{1cm} (i)$$

at constant pressure. The heat absorbed was used to melt the oxides and not to support chemical reactions. The change in heat content when a compound changes state, i.e., from solid to liquid (molten) state is given by the difference between the heat content of the final and initial states. It is represented by:

$$\Delta H = H_{ms} - H_{ss}$$  \hspace{1cm} (ii)$$

Where $H_{ms}$ is the heat content of the compound at the melting temperature in this case 1573 °K (1300 °C)
$H_{ss}$ is the heat content of the solid compound at 298 °K $\Delta H$ represents the heat absorbed when the compound is heated from solid to molten state. This is taken as the heat required to melt a compound. $\Delta H$ is related to heat capacity.

\[ \Delta H = H_{ms} - H_{ss} = \int C_p \, dT \quad (\text{limits: } T_s \text{ to } T_m) \quad \text{(iii)} \]

\[ C_p = A + BT + CT^2 \]

This is substituted in equation (iii) to enable integration of the equation.

That is; $H_{ms} - H_{ss} = \int TA + BT + CT^2 \, dT \quad (\text{lim. } T_m \text{ and } T_s)$

\[ \int [\int \text{Integrating: } H_{ms} - H_{ss} = \left[ AT + 1/2BT^2 - CT^{-1} \right] T_m - T_s \]

That is: $H_{ms} - H_{ss} = A(1573) + 1/2 B(1573)^2 - C(1573)^{-1} - A(298) + 1/2 B(298)^2 - C(298)^{-1} = A(1573-298) + 1/2B(1573^2-298^2)- C(1573^{-1}-298^{-1})$

This expression was used to calculate $\int H$ values for oxides in slag using $C_p$ data obtained from Metallurgical Thermochemistry by Kubaschewski and Alcock.
<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>$C_p = A + BT + CT^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>13.38 + 3.68T - 3.45T$^2$</td>
</tr>
<tr>
<td>CaO</td>
<td>11.86 + 1.08T - 1.66T$^2$</td>
</tr>
<tr>
<td>FeO</td>
<td>12.38 + 1.62T - 0.38T$^2$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>21.88 + 48.2T</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>25.48 + 4.25T - 6.82T$^2$</td>
</tr>
<tr>
<td>MgO</td>
<td>11.71 + 0.75T - 2.80T$^2$</td>
</tr>
</tbody>
</table>

**CALCULATION**

SiO$_2$: $\int H = 13.38(1573 - 298) + \frac{1}{2} \times 3.68(1573^2 - 298^2) - 3.45(1573^2 - 298^2)$

\[ = 4406.43 \text{ kcal mol}^{-1} \]

at 40% SiO$_2$ or 400 kg SiO$_2$ per tonne of slag. Heat required to melt SiO$_2$ in the slag = 400/60.1 x 4406.43 \[ = 29327.32 \text{ kcal} \]

Since the value of the third term is very small than the first and second terms it is left out from the rest of the calculations.

CaO: $\int H = 11.86(1573 - 298) + \frac{1}{2} \times 1.08(1573^2 - 298^2) = 1303.45 \text{ kcal mol}^{-1}$

at 5% CaO in slag, 1 tonne contains 50 kg CaO.

Heat required for melting = 50/56.1 x 1303.45 \[ = 1161.7 \text{ kcal} \].
**FeO:** \( \Delta H = 12.38(1573 - 298) + \frac{1}{2} \times 1.62(1573^2 - 298^2) = 1877.97 \text{ kcal mol}^{-1} \)

at 20% FeO, or 200kg FeO per tonne. Heat required = 5223.84 kcal

**Fe\(_3\)O\(_4\):** \( \Delta H = 21.88(1573 - 298) + \frac{1}{2} \times 48.2(1573^2 - 298^2) = 57519.05 \text{ kcal mol}^{-1} \)

at 5%Fe\(_3\)O\(_4\) i.e. 50kg per tonne of slag, Heat required = 12417.76 kcal

**Al\(_2\)O\(_3\):** \( \Delta H = 25.48(1573 - 298) + 2.18(1573^2 - 298^2) = 52329.32 \text{ kcal mol}^{-1} \)

at 5% Al\(_2\)O\(_3\), or 50kg per tonne, heat required = 25651.63 kcal.

**MgO:** \( \Delta H = 11.71(1573 - 298) + 0.38(1573^2 - 298^2) = 921.43 \text{ kcal mol}^{-1} \)

at 3% MgO or 30 kg per tonne, heat required; = 685.93 kcal.

Total heat required is obtained by combining the heat calculated for the oxides = 74467.9 kcal. Conversion of heat to electrical energy:

1kcal = 4.186 kJ

74467.9 kcal = 311722.6 kJ = 311.722 MJ

1kWh = 3.6 MJ

311.722 MJ = 86.51 kWh per tonne of slag.

Cost of electrical energy, at K65 per kWh = K 5628.3 = $4.6 per tonne of slag.

Value of contained cobalt at about 80% recovery, slag to concentrate:

0.80 x30 kg cobalt in one tonne of slag 24 kg cobalt per tonne. Price of cobalt about $ 22 per lb. value of 24kg cobalt = $1163.
APPENDIX 2A:

CALCULATION OF Log $P_{\text{CO}_2}/P_{\text{CO}}$

Data used in the calculation is given in Table 2.1, the relationship between the Gibbs free energy $\Delta G_T$ and the equilibrium constant $K_p$ is utilised.

$$\Delta G_T = -RT \ln K_p$$  \hspace{1cm}  (i)

Where $R$, is universal gas constant, $R = 1.9866$. $T$, reaction temperature. For a generalised reduction of a metal oxide $\text{MO}$, with $\text{CO}$:

$$\text{MO} + \text{CO} = \text{M} + \text{CO}_2$$  \hspace{1cm}  (ii)

The equilibrium constant is given by:

$$K_p = \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$$  \hspace{1cm}  (iii)

The activities of $\text{MO}$ and $\text{M}$ are taken as being equal to unity.

$$\Delta G_T = -RT \ln \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$$

Example: Reduction of cobaltous oxide - $\text{CoO}$

The reduction reaction: $\text{CoO} + \text{CO} = \text{Co} + \text{CO}_2$

The free energy of reaction is obtained from the free energy of formation of $\text{CoO}$ and the oxidation of $\text{CO}$ to $\text{CO}_2$

$$\text{CoO} = \text{Co} + 1/2\text{O}_2$$  \hspace{1cm}  (iv)  \hspace{1cm}  $\Delta G_T = 55900 - 16.7T$

$$\text{CO} + 1/2\text{O}_2 = \text{CO}_2$$  \hspace{1cm}  (v)  \hspace{1cm}  $\Delta G_T = -67500 + 20.75T$
Combining above equations gives the overall reaction;

\[
\text{CoO} + \text{CO} = \text{Co} + \text{CO}_2 \quad \text{(vi)} \quad \Delta G_T = -11600 + 3.9T
\]

\[
\Delta G_T = -RT\ln K_p
\]

\[K_p = P_{\text{CO}_2} \text{ for the reaction in equation (vi).}\]

\[
\Delta G_T = -RT\ln\frac{P_{\text{CO}_2}}{P_{\text{CO}}} = -2.303\log\frac{P_{\text{CO}_2}}{P_{\text{CO}}}
\]

\[
\Delta G_T/-2.303RT = \frac{11600}{4.575T} - 3.9T/4.575T
\]

\[
i.e \quad \log \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{(2535.519 - 0.852)/T}{\text{(vii)}}
\]

Equation (vii) was used to calculate \(\log \frac{P_{\text{CO}_2}}{P_{\text{CO}}}\) for the reduction of CoO at different values of \(T^\circ\text{K}\). Similar expressions, were determined for other oxides in the old copper slag and used to calculate \(P_{\text{CO}_2}/P_{\text{CO}}\) ratios at 873, 1073, 1273, and 1673 K.
APPENDIX 2B

AVERAGE EXPERIMENTAL DATA, USED TO PLOT THE GRAPHTHS IN CHAPTER TWO

Table 1: Average data used to plot Figure 2.5 and 2.6, to show the effect of temperature on solid state carbothermic reduction

<table>
<thead>
<tr>
<th>REDUCTION TIME HOURS</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>COBALT LEACHED %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>12.22</td>
<td>17.29</td>
<td>24.55</td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>27.78</td>
<td>15.66</td>
<td>13.08</td>
<td>7.07</td>
</tr>
<tr>
<td>950</td>
<td>34.43</td>
<td>52.12</td>
<td>23.99</td>
<td>23.39</td>
</tr>
</tbody>
</table>
TABLE 2: Average data used to plot Figure 2.7 to show effect of varying amount reductant (charcoal), on solid state carbothermic reduction

<table>
<thead>
<tr>
<th>WEIGHT % CHARCOAL ADDED</th>
<th>% COBALT LEACHED</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>52.12</td>
</tr>
<tr>
<td>30</td>
<td>29.55</td>
</tr>
<tr>
<td>40</td>
<td>5.03</td>
</tr>
</tbody>
</table>

TABLE 3: Data used to plot Figure 2.8 to show effect of particle size of slag on solid state carbothermic reduction

<table>
<thead>
<tr>
<th>PARTICLE SIZE RANGE (mm)</th>
<th>%COBALT LEACHED</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.35 + 0.60</td>
<td>47.98</td>
</tr>
<tr>
<td>-0.60 + 0.150</td>
<td>52.12</td>
</tr>
<tr>
<td>-0.150 + 0.045</td>
<td>10.63</td>
</tr>
<tr>
<td>-0.045</td>
<td>8.63</td>
</tr>
</tbody>
</table>
APPENDIX 3A

CALCULATION OF Log $P_{S\text{O}_2}$ AND Log $P_{O_2}$ USED IN THE CONSTRUCTION OF THE PREDOMINANCE AREA DIAGRAMS FOR THE Co-S-O SYSTEM AT 873, 973, K SHOWN IN FIGURE 3.1

The predominance area diagram, at a given temperature indicates the phases that are stable under different conditions of gas composition or phases that exist in equilibrium with each other. In a three component system Co-S-O three condensed phases can coexist at a fixed tempetature, and fixed total pressure of the gaseous phase. The phases are separated by boundary lines. Slanting lines show that the stability of the phases depends on both $P_{S\text{O}_2}$ and, vertical lines on $P_{O_2}$. The relationship between Gibbs free energy change for the reaction and equilibrium constant was used to calculate $\log P_{S\text{O}_2}$ and $\log P_{O_2}$. At total pressure $P_{S\text{O}_2} + P_{O_2} = 1$ atmosphere. (e) Data given in Table 3.1 was used in the calculations. The activity of the phases present is taken to be unity. Two reactions from Table 3.1 are used to illustrate the method of calculation:

**Example 1:** Calculation of the boundary line between Co and CoO, for the equilibrium: $2\text{CoO} = 2\text{Co} + O_2$. The equilibrium between Co and CoO depends on $P_{O_2},$ the boundary line is vertical. The equilibrium constant, $K_e = (P_{O_2})^{1/2}$

$$\Delta G_T = -RT\ln K_e$$

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\[ \Delta G_T = -2.303RT \log K_v \]

From Table 4.1, \[ \Delta G_T = 111800 - 33.7T \]

\[ \log K_v = (-111800 + 33.7T) / 2.303RT \]

That is \[ \log P_{O_2} = 2(-111800 + 33.7T) / 2.303RT \]

\[ R = 1.9866 \text{ cal deg}^{-1} \text{ K} \]

\[ \log P_{O_2} = -223600 + \frac{67.4}{2.303 \times 1.9866 \times T} \]

\[ \log P_{O_2} = -223600 + \frac{67.4}{4.575T} \]

\[ \log P_{O_2} = -48874.317 + \frac{14.732}{T} \]

This expression was used to determine values of \[ \log P_{O_2} \] at 873 and 973.

**Example 2:** Calculation of the boundary line between CoO and CoSO₄, for the equilibrium:

\[ \text{CoSO}_4 = \text{CoO} + \frac{1}{2}\text{O}_2 + \text{SO}_2 \]

\[ K_v = (P_{O_2})^{1/2} \times P_{SO_2} \]

\[ \ln K_v = \frac{1}{2} \ln P_{O_2} + \ln P_{SO_2} \]

\[ \Delta G_T = -RT \ln K_v = -2.303RT \log K_v \]

From Table 3.1 \[ \Delta G_T = 69230 + 27.03T \log T - 137.18T \]

\[ \log K_v = -69230 - 27.03T \log T + 137.18T \]

\[ \frac{1}{2.303 \times 1.9866 \times T} \]
That is \( \frac{1}{2}\log P_{O_2} + \log P_{SO_2} = -69230 - 27.03T \log T + 137.18T \)

\[
\begin{array}{cccc}
\text{4.575T} & \text{4.575T} & \text{4.575T} \\
\end{array}
\]

\[=-15132.24 - 5.908\log T + 29.985 \]

\[
\begin{array}{c}
T \\
\end{array}
\]

But \( P_{O_2} + P_{SO_2} = 1 \) atmosphere, giving, \( P_{SO_2} = 1 - P_{O_2} \)

\[\frac{1}{2}\log P_{O_2} + \log(1-P_{O_2}) = -15132.24 - 5.908\log T + 29.985 \]

\[
\begin{array}{c}
T \\
\end{array}
\]

\[\frac{1}{2}\log P_{O_2} + \log 1 - \log P_{O_2} = -15132.24 - 5.908\log T + 29.985 \]

\[
\begin{array}{c}
T \\
\end{array}
\]

\[-\frac{1}{2}\log P_{O_2} = -15132.24 - 5.908\log T + 29.985 \]

\[
\begin{array}{c}
T \\
\end{array}
\]

\[\frac{1}{2}\log P_{O_2} = 15132.24 + 5.908\log T - 29.985 \]

\[
\begin{array}{c}
T \\
\end{array}
\]

\[\log P_{O_2} = 2\times(15132.24 + 5.908 - 29.985) \]

\[
\begin{array}{c}
T \\
\end{array}
\]

\[\log P_{SO_2} = \log K_e - \log P_{O_2} \]

Expressions for the other reactions in Table 3.1 were determined in similar manner.
APPENDIX 3B: AVERARAGE EXPERIMENTAL DATA USED IN THE PLOTTING OF GRAPHS IN CHAPTER THREE.

Table 1: Data used to plot Figure 3.4, and Figure 3.5 to show the influence of temperature on solid state sulphation.

<table>
<thead>
<tr>
<th>ROASTING TIME HOURS</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROASTING TEMPERATURE °C</td>
<td>PERCENT COBALT LEACHED</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>25.56</td>
<td>44.89</td>
<td>52.46</td>
<td>61.51</td>
<td>60.32</td>
</tr>
<tr>
<td>750</td>
<td>34.17</td>
<td>35.77</td>
<td>48.84</td>
<td>50.30</td>
<td>45.39</td>
</tr>
<tr>
<td>850</td>
<td>37.12</td>
<td>38.49</td>
<td>40.84</td>
<td>45.76</td>
<td>50.41</td>
</tr>
<tr>
<td>950</td>
<td>13.31</td>
<td>19.90</td>
<td>20.84</td>
<td>26.46</td>
<td>12.46</td>
</tr>
</tbody>
</table>

TABLE 2: Data used to plot Figure 3.6, % Co, Cu, Fe, in slag sulphated with pyrite at 600 °C

<table>
<thead>
<tr>
<th>ROASTING TIME - HOURS</th>
<th>PERCENT LEACHED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>1</td>
<td>25.56</td>
</tr>
<tr>
<td>2</td>
<td>44.89</td>
</tr>
<tr>
<td>3</td>
<td>52.46</td>
</tr>
<tr>
<td>4</td>
<td>61.51</td>
</tr>
</tbody>
</table>
TABLE 3: Data used to plot Figure 3.7, showing extent of solid state sulphation with slag of different particle sizes, at 600 °C, 4 hours roasting time.

<table>
<thead>
<tr>
<th>PARTICLE SIZE - mm</th>
<th>% Co LEACHED</th>
</tr>
</thead>
<tbody>
<tr>
<td>-3.35 + 0.60</td>
<td>51.53</td>
</tr>
<tr>
<td>-0.60 + 0.150</td>
<td>61.51</td>
</tr>
<tr>
<td>-0.150 + 0.045</td>
<td>68.75</td>
</tr>
<tr>
<td>-0.045</td>
<td>72.76</td>
</tr>
</tbody>
</table>

TABLE 4: Data used to plot Figure 3.8 to show the effect of varying the relative amount of pyrite in reaction mixture, for slag samples roasted for 4 hours at 600 °C

<table>
<thead>
<tr>
<th>WEIGHT OF PYRITE ADDED</th>
<th>% Co LEACHED</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 g</td>
<td>61.51</td>
</tr>
<tr>
<td>75 g</td>
<td>37.02</td>
</tr>
<tr>
<td>100 g</td>
<td>12.40</td>
</tr>
<tr>
<td>150 g</td>
<td>7.92</td>
</tr>
</tbody>
</table>

TABLE 5: Dependence of solid state sulphation on air flowrate. Data used to plot Figure 3.9

<table>
<thead>
<tr>
<th>AIR FLOWRATE cm³ min⁻¹</th>
<th>% Co LEACHED</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61.51</td>
</tr>
<tr>
<td>300</td>
<td>24.20</td>
</tr>
<tr>
<td>700</td>
<td>21.68</td>
</tr>
<tr>
<td>1100</td>
<td>3.19</td>
</tr>
<tr>
<td>1600</td>
<td>0.73</td>
</tr>
</tbody>
</table>
TABLE 6: Sulphation with cobalt sulphide concentrate Data used to plot Figure 3.10

<table>
<thead>
<tr>
<th>ROASTING TIME - HOURS</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMPERATURE °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3.40</td>
<td>6.44</td>
<td>5.70</td>
<td>4.11</td>
<td>4.12</td>
</tr>
<tr>
<td>600</td>
<td>8.17</td>
<td>9.21</td>
<td>4.21</td>
<td>12.60</td>
<td>9.03</td>
</tr>
<tr>
<td>750</td>
<td>8.41</td>
<td>6.31</td>
<td>3.93</td>
<td>3.44</td>
<td>4.37</td>
</tr>
<tr>
<td>850</td>
<td>2.37</td>
<td>1.83</td>
<td>2.48</td>
<td>2.48</td>
<td>2.14</td>
</tr>
</tbody>
</table>