A Novel Low-Energy Route for the Extraction of Copper and Cobalt Metals/Alloys from the Zambian Sulphide Concentrates

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Abstract

Conventional smelting of copper – cobalt – iron sulphide concentrates result in the oxidation of cobalt and iron, which are subsequently lost into the slag. The emission of SO_2 bearing gas from smelting causes serious health and environmental problems. In this research, three different types of copper–cobalt–iron sulphide concentrates, derived from froth flotation, were investigated. In this investigation, the concentrates, each containing more than 40 wt % percent gangue material, were directly reduced in the presence of lime and carbon in the temperature range of 1073 K – 1573 K, for the production of an alloy containing copper, cobalt and iron. We demonstrate the basic principles of process physical chemistry for the recovery of alloy by carrying out a detailed process analysis utilising the predictions from thermodynamic equilibrium and the results from the kinetics of reduction reaction. The effect of temperature on the reduction kinetics and alloy formation were determined and analyzed in detail.

Key words: CoFe alloy, reduction, SO_2, process chemistry

Introduction

Nearly 80 % of the copper produced in the world originates from the sulphide mineral concentrates [1], roasting and smelting are the common methods employed during metal recovery from such concentrates. In Zambia, copper sulphides minerals are predominately associated with cobalt and iron sulphide minerals. Most pyrite minerals contain significant amount of cobalt as the ionic radius of Fe^{2+} (0.076 nm) and Co^{2+} (0.074 nm) are very close to each other [2], which may permit solid solubility in sulphide mineral matrix.
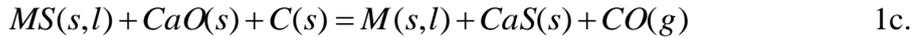
Smelting of copper - cobalt - iron sulphide concentrates result in sulphur dioxide emission and loss of cobalt and iron into the slag via oxidation. Most of the smelting slag in Zambia contains up to 1.5 % weight and 25 % weight cobalt and iron, respectively. Cobalt is a valuable metal which is used in high temperature applications, lithium batteries, and high-temperature magnets. According to London Metal Exchange, the spot price of cobalt was $30,000 per tonne, compared with the $7130 per tonne price for copper and $555/tonne for steel. Most copper-cobalt smelter slag is processed in Zambia for metal recovery at great cost by remelting the quenched smelter slag and reprocessing.

In Zambia, the Cu /Co ~10, since cobalt is nearly 5 times dearer than copper, losing significant quantities of cobalt into slag is equivalent to the loss of 50 % weight of copper in the slag. Froth flotation concentrates containing up to 2 % weight cobalt are treated by roasting, leaching, and electro-winning of copper and cobalt. The major disadvantage of roasting of sulphide concentrates with high gangue concentration is that the SO_2 bearing gas produced is too dilute for economic acid or elemental sulphur production. Release of such dilute gases is unacceptable for environment and detrimental for animal and plant life. SO_2 is also a green house gas with 3-4 times more radiation absorption properties than CO_2.

Mineral sulphides can be directly reduced in the presence of a basic oxide and reducing agent [3-9]. The presence of a basic oxide; e.g. lime is essential as it acts as an exchange medium for S^{2-} ions in the mineral concentrates, shown by MS, in equation 1a. Once the exchange reaction 1a, transforms a sulphide into an oxide, the reduction reaction 1b may then yield metal and CO gas, depending on the magnitude of kinetic barriers.

$$MS(s,l) + CaO(s) = MO(s,l) + CaS(s) \qquad\qquad 1a$$

$$MO(s,l) + C(s) = M(s,l) + CO(g) \qquad\qquad 1b$$
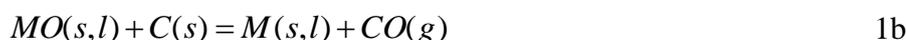
The overall reaction 1c is the sum of reactions 1a and 1b:

$$MS(s,l) + CaO(s) + C(s) = M(s,l) + CaS(s) + CO(g) \qquad \text{1c.}$$

Experimental Procedure

Nchanga, Nkana and Baluba froth flotation concentrates from Zambia were used in this investigation and mineralogical composition is shown in table 1. The reduction experiments were carried out isothermally in order to analyse the overall kinetics of reduction reaction 1c as a function of temperature. The generic experimental set up is discussed in detail elsewhere [3], which was adopted in this study, except in this investigation the thermogravimetric balance was a commercial saritorius microbalance with sensitivity in the sub milligram range. The reaction tube was purged with argon gas at 0.5 litres (minute)$^{-1}$ through out the experiment for maintaining an inert atmosphere and sweeping off the product gas mixture, so that the equilibrium in eq.1c can be shifted in the forward direction.

Table 1 – Mineralogical composition of froth flotation concentrates in % weight

	Cu_2S	$CuFeS_2$	Cu_5FeS_4	$CuCo_2S_4$	FeS_2	SiO_2	Other
Nchanga	28.29	5.80	11.08	0.2	4.93	34.53	17.84
Nkana	0.7	8.60	5.00	2.20	10.10	19.00	54.4
Baluba	0.5	54.80	0.6	1.94	15.49	9.13	17.54

The froth flotation concentrates were mixed in stoichiometric ratios with lime and carbon by following equation 1(c). Since the Zambian concentrates contain up to 2 % weight cobalt, in order to fully understand the behaviour of cobalt during carbothermic reduction, we also designed experiments in which we mixed an additional 10 weight % CoO in the concentrate/lime/carbon mixture for tracking the elemental distribution between the slag forming gangue and the alloy phase during the course of reaction. This is an important approach for the overall analysis of loss of cobalt into the gangue minerals, under reducing condition.

All reacted samples were analysed by optical microscopy, and x-ray powder diffraction and scanning electron microscopy techniques. A portion of the reacted material was ground in a mortal and pestle for x-ray powder diffraction which was carried out using the Philips X'pert machine with Cu Kα (0.15417 nm) radiation, at an acceleration voltage of 40 KV. For microscopic analysis, a portion of the pellet was mounted in resin and left for 12 hours to cure, followed by grinding and polishing to 1 μm, for cross-sectional examination of phases present using optical and scanning electron microscopic (SEM) analysis. For SEM, the polished surface was coated with 5 nm of platinum for minimizing the charging of the prepared surface during analysis; without a platinum coating the surface may charge and adversely affect the image quality. The energy dispersive X-ray (EDX) was carried out on several areas for obtaining a semi-quantitative chemical analysis of phases, which can be then utilized to supplement the phase analysis data from X-ray powder diffraction. The EDX data can also be transformed into an elemental map of compositions, showing the dissemination of each element over the cross-section under examination.

Results and Discussion

The percent reduction (%R) was calculated by taking the ratio of the apparent or observed reduction in weight at time "t" due to to the loss of CO gas, with stoichiometric weight loss via reaction 1c and the resulting equation is given in equation 29a)

$$\% \, Re\,ductionat\,any\,time = \frac{Weight\,loss\,at\,any\,time}{Theoretical\;weightloss} \times 100 \qquad \text{....................2(a); and}$$

$$Theoretical\;weightloss = \frac{\%\,S}{100\%} \times \frac{28\,(RMM\;of\;CO)}{32\,(RMM\;S)} \times Weight\,of\,Concentrate \qquad \text{............2(b)}$$

Low temperature reduction

Thermal gravimetric analysis (TGA) was carried out between 1073 K and 1323 K in order to study the kinetics of carbothermic reduction. The weight loses were recorded every 10 seconds at the reduction temperature. The x-ray diffraction analysis reveals that metallization was achieved by determining and comparing the relative intensities of diffraction peaks for copper, cobalt and iron metallic phases. No peaks for starting mineral sulphide concentrates were identified in the fully reacted samples, which was characterized by defining the cessation of weight loss due to reaction 1c. The completion of reaction 1c is characterized by examining the x-ray diffraction peaks for three different types of mineral concentrates reduced at 1273 K. In the powder diffraction patterns in Figures 3a to 3c, intense peaks for CaS, pure SiO_2 and metallic phases, and unreacted lime were observed.
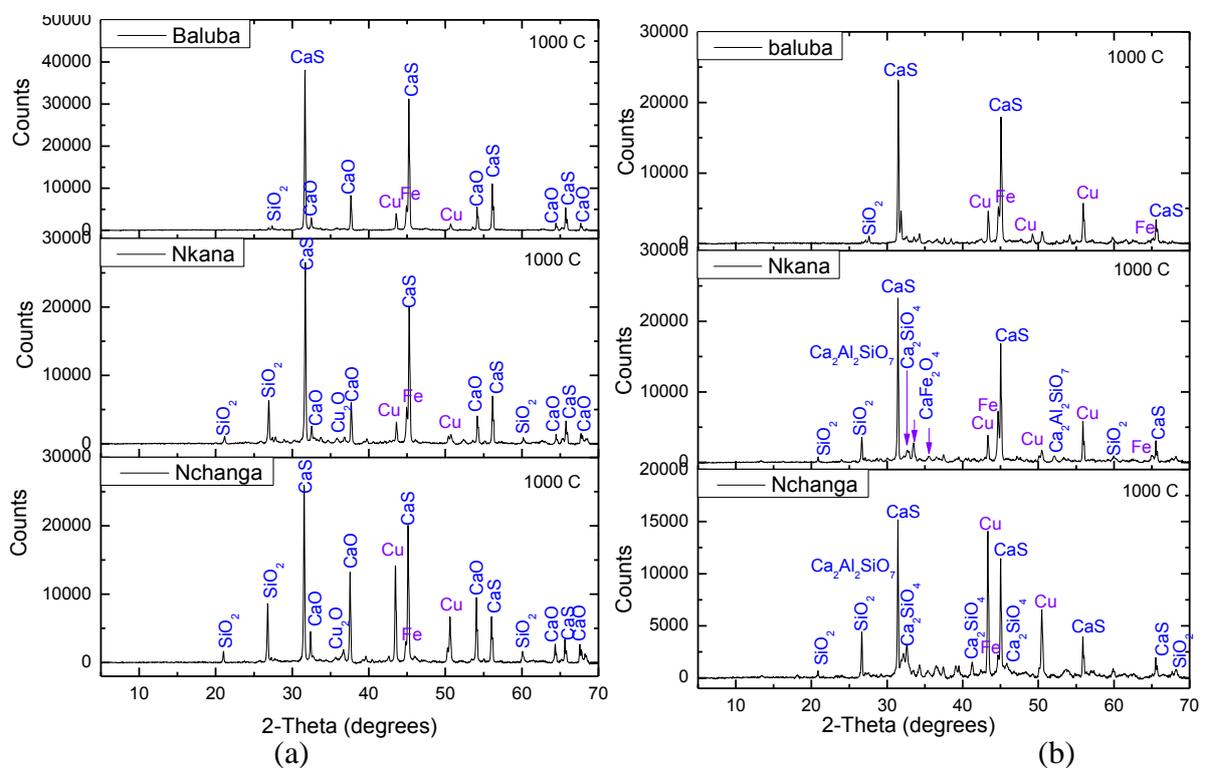

Figure 1 – The XRD powder pattern for the Nchanga, Nkana and Baluba concentrates reduced in the presence of lime and carbon at 1273 K (a) S:CaO:C = 1:2:2 (b) S:CaO:C = 1:2:1

Effect of temperature, lime (CaO) and carbon concentrations

Carbothermic reduction of mineral concentrates in the presence of lime, are endothermic processes and are therefore affected by temperature. For a fixed S/CaO/C ratio, reduction experiments were completed within 30 minutes at 1323 K but were incomplete even after 3 hours at 1073 K. The total percentage reduction (%R) was higher at 1273 K than at 1173 K or 1073 K as shown in figure 2(a). As temperature increases, the rate of carbon monoxide evolution increases due to the reaction between metal oxide and carbon according to equation 1(c). Mineral sulphides were not identified during XRD analysis for the mineral concentrates reacted at and above 1223 K. However, unreacted mineral sulphides (Cu_2S, Cu_5FeS_4) were identified for the experiments carried out for 3 hours at 1073 K.

In order to understand the effect of lime during carbothermic reduction of mineral concentrates, carbon concentration was kept constant. The weight losses at any time were

higher with increase in lime concentration as shown in figure 2(b). Since the exchange reaction depends on the contact surface area of lime with the sulphide mineral, by increasing the ratio of CaO/S the apparent exchange reaction rate might increase, allowing a larger proportion of oxides of Cu, Fe, and Co to form. The Cu, Fe and Co oxides react with carbon and produces carbon monoxide according to equation 1b. When mineral sulphides were mixed with lime and carbon at S:CaO:C=1:1.5:4, 1:2:4 and 1:3:4, there was no mineral sulphides present after 2 hours at 1273 K. However, when the experiment as carried out for 2.5 hours at 1173 K, Cu_2S and Cu_5FeS_4 were present at S:CaO:C=1:1.5:4 but not present for S:CaO:C=1:3:4. Reaction processes are chemically controlled at low temperature and diffusion controlled at high temperature [10]. Mineral concentrates contain gangue materials, as shown in table 1, which reduces the contact area between lime and mineral sulphides. It is therefore important to add lime at least 50 % in excess of the stoichiometric requirement for achieving near completion reaction 1c.

The percent reduction (%R) was higher for stoichiometric addition of carbon, S:CaO:C = 1:2:1 than at mixtures of S:CaO:C = 1:2:2 and S:CaO:C = 1:2:4. At lower stoichiometric ratio of C: CaO both the SO_2 and CO_2 gases may contribute to overall weight loss, which may then exaggerate the maximum expected reduction via reaction 1c. XRD analysis in figure 1(b) shows that metallization was not complete due to presence of calcium ferrite in the reacted sample. At lower concentrations of carbon, the propensity for SO_2 formation increases according to equations 5. Calcium sulphate may form but decompose to yield lime and SO_2 through reduction calcination [11].

$$3CuO\,(s) + CaS\,(s) = 3Cu\,(s) + CaO\,(s) + SO_2\,(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots..5$$

The overall % reduction were similar at 1273 K for S:CaO:C = 1:2:2 or = 1:2:4 as shown in figure 3(a). However, the % reduction at S:CaO:C=1:2:4 were higher than at S:CaO:C = 1:2:2 at 1173 K as shown in figure 3(b). This is because most processes are chemically controlled at low temperature and diffusion controlled at high temperature [10]. In order to achieve full metallization at lower reduction, carbon concentration must be increased.
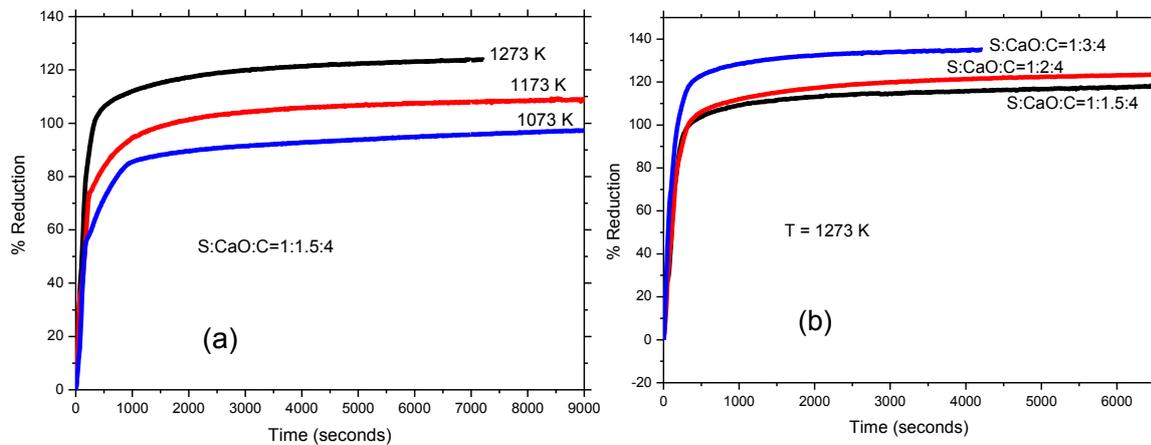

Figure 2- (a) Effect of temperature at S:CaO:C=1:1.5:4 and (b) Effect of changing CaO concentration at 1273 K and during carbothermic reduction of Nchanga mineral concentrate
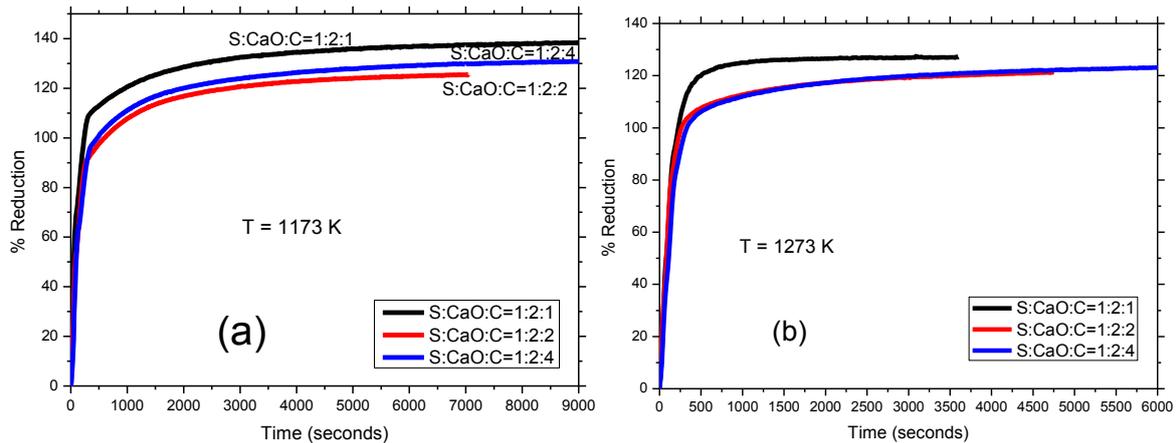
Figure 3 - Effect of changing carbon concentrations during carbothermic reduction of Nchanga mineral concentrates (a) at 1173 K and (b) at 1273 K

High Temperature reduction at 1573 K

Thermal gravimetric analysis was not carried out at high temperatures due to the limitation on equipment. However, mineral concentrates mixed with lime and carbon, were heated at 1573 K in an elevating hearth furnace. The initial and final weights of the samples were taken before and after the experiment, in order to determine the weight losses. Mineral concentrates mixed with lime and carbon were heated from room temperature to 1573 K and held at this temperature for 3 hours, after which the furnace was turned off and the crucible containing the sample was taken out of the furnace and cooled in air. In another experiment, the mineral concentrates were first isothermally reduced at 1273 K for 2 hour, followed by reheating at 1573 K for 3 hours in order to see further phase changes which may occur above the melting point of copper rich alloy.

When Nchanga, Nkana and Baluba mineral concentrates were reduced for 2 hours at 1273 K, a portion of the reacted sample was analysed by x-ray diffraction, cobalt and excess lime were identified from xrd patterns as shown in figure 4a. When the remaining samples which were reduced at 1273 K, were heated and held at 1573 K for 3 hours, cobalt was not identified from xrd patterns in all samples. In addition, excess lime was completely absent from the samples after heating at 1573 K. This was due to formation of calcium silicate compounds as shown in figure 4b. Absence of cobalt peaks from the xrd patterns can be explained as a result of formation of CoFe phase observed in figure 4b. Formation of CoFe phase is possible because solubilities of metals increase with temperature. Iron and cobalt have high melting points, but they exhibit extensive solid solubility in each other [12, 13].

Copper sulphides in figure 4(b) were identified in Nchanga and Nkana samples after reheating the sample at 1573 K. It is very certain that copper sulphides were formed from the reduced copper as there were no copper sulphides after reducing the concentrates at 1273 K, shown in figure 4(a). The gangue content in Nchanga and Nkana concentrates, is about 50 and 73 % weight respectively. The major gangue constitituents were silica and carbonates. Silica reacted with excess lime while carbonates in the gangue might have decomposed to give CO_2 which can lead to oxidation of copper. The oxidised copper can further react with CaS to form copper sulphides and lime and the lime further reacting with silica or any gangue constitituent. Copper sulphides were not identified in the Baluba sample and the silica content in this mineral concentrate was less than 10 % weight. Formation of copper sulphide was not possible for Baluba sample due to presence of excess lime. The formation of copper sulphides at high temperature for Nchanga and Nkana concentrates is still under investigation.
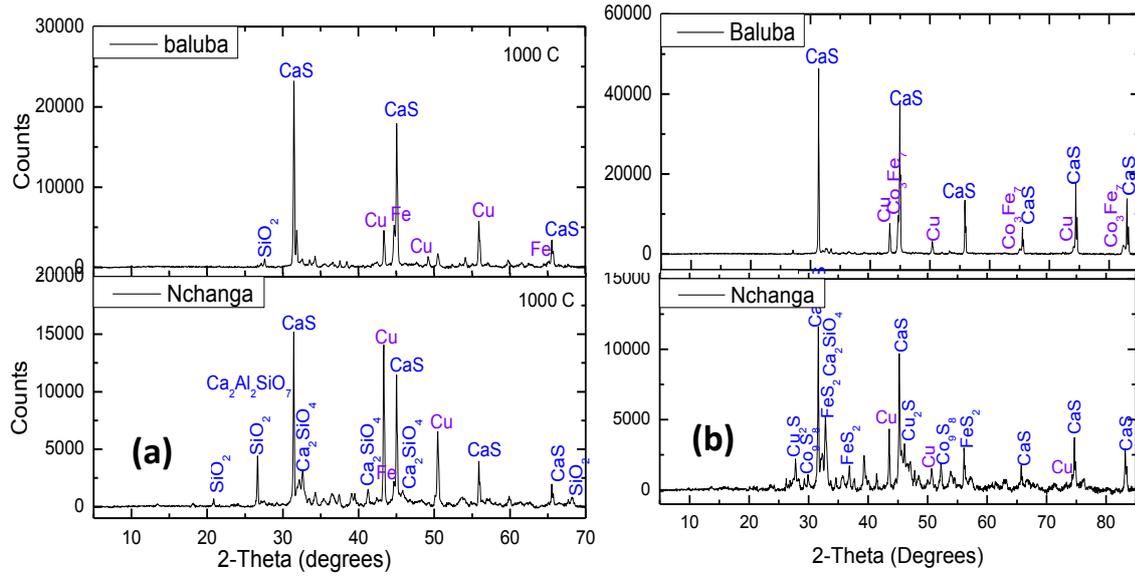
Figure 4 - Carbothermic reduction of mineral concentrates   (a) reduced at 1273 K, (b) reduced samples reheated to 1573 K for 2 hours (S:CaO:C= 1:1.8:2.2)

Metal / Alloy formation during carbothermic reduction

The SEM - EDX analysis was carried out in order to confirm the presence of phases obtained during XRD analysis and the results are shown in table 2. Since the unit cell dimensions of γ-iron [nm] is comparable with that of the high-temperature allotrope of cobalt [nm], we expect extensive mutual solubility in liquid and the solid solutions, which is why the alloys of Fe and Co form. The metallic copper similarly shows reasonably high solubility in both in γ-iron and cobalt. The EDX analysis confirms the presence of this alloy as shown in table 2.

Table 2- EDX Semi quantitative results for some selected areas, Nchanga
(S:CaO:C=1:1.8:1.8) reduced at 1273 K

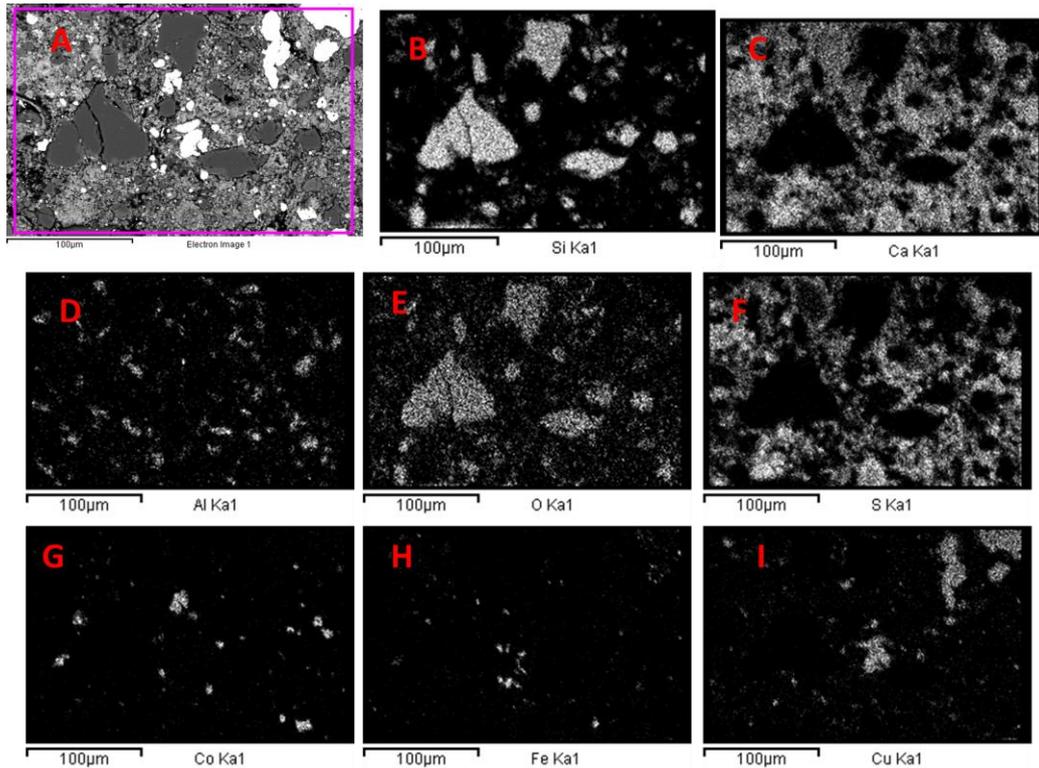| Area	Cu	Co	Fe	Ca	S	O	Si
A	11.49	81.66	2.77	0.9	0.86	1.63	
B	7.01	89.94	-	0.9	0.66	1.63	
C	5.16	57	22.49	4.09	3.49	3.781	
D	5.13	-	93.46	1.38	0.74		
E	0.52	-	0.39	-	-	54.91	44.32
F	93.49	0.32	2.49	-	0.44	3.49	-
G	0.26	-	0.63	-	-	56.63	44.40
H*(Ni = 2.25 %)	91.78	-	1.68	0.16	0.53	1.82	1.18
J	96.36	0.95	1.79	0.26	0.44	-	-
Spectrum 1	13.62	2.41	4.56	20.48	13.62	31.65	10.21

Figure 5 – Backscattered elections (BSE) image for the Nchanga concentrate which was reduced at 1273 K with 10% CoO added to the mineral concentrates before reduction in the mixture (S:CaO:C=1:1.8:1.8). (A) sample area investigated, (B) Ca distribution, (C) C distribution, (D) Co distribution, (E) Fe distribution, (F) Cu distribution.

Metallic phases appeared bright under backscattered elections (BSE) imaging. Semi quantitative results in all analysed areas of the reacted samples in table 2, well correspond to the predictions from the phase diagram. The maximum solubility of copper in cobalt is about 20 % weight, whereas that of cobalt in copper is nearly 10 % weight. Maximum solubility of iron in copper and copper in iron is 4.1 % and 15 % weight respectively [14] and the results in table 2 shows the maximum solubility of iron in copper and copper and iron are 1.79 % weight and 5.13 % weight respectively. From semi quantitative analysis in table 2, it is possible to produce copper over 96 % weight purity in a single step. Elemental mapping in figure 8 further shows that the reduced metals (copper, cobalt and iorn) have limited solubility in each other at 1273 K. Figure 8 also shows that sulphur was tied up with calcium which was identified as CaS during x-ray diffraction analysis. Mass balance in spectrum 2 of table 2 further shows that there is no sulphur loss during metal / alloy production.

When the sample which was reduced at 1273 K and then reheated at 1573 K, semi quantitative EDX analysis for some areas showed areas to contain 43.78 % weight Fe, 38.44 Co and 12. 58 % weight Cu. Elemental mapping in figure 9 shows that Co distributed with Fe because of higher solubility between these elements.
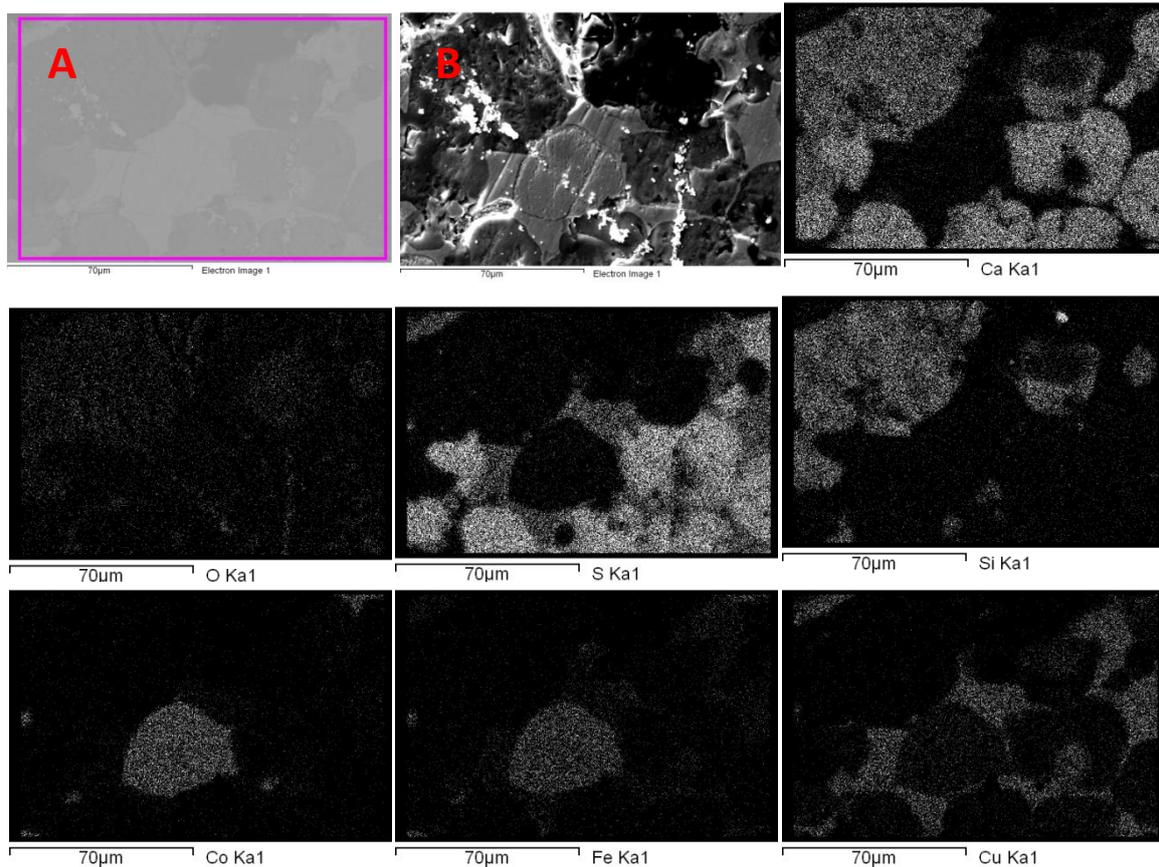
Figure 6 – Elemental mapping showing distribution of elements for Nchanga concentrate (S:CaO:C=1:1.8:1.8), reduced at 1273 K and reheated at 1573 K, with 10% CoO added to the mineral concentrates before reduction in the mixture (A) sample area investigated under (A) BSE imaging, (B) SEM imaging.

Conclusions

- The carbothermic reduction of sulphide mineral concentrates in the presence of lime at different S:CaO:C ratios were investigated in the temperature range 1073 K – 1573 K. The percentage reductions from 1073 K to 1323 K were found to be dependent on temperature. Metallization was incomplete even after 3 hours at 1073 K but completed within 30 minutes at 1323 K.
- The process of metallization depends on S:CaO and S:C ratios, the percentage reduction was higher at S:CaO:C = 1:3:4 than at S:CaO:C=1:1.5:4 as shown in figure 2(b). Metallization was incomplete at stoichiometric addition of carbon (S:CaO:C=1:2:1) due to formation calcium ferrite as shown in figures 1(a) and 1(b).
- Pure silica and excess lime were found in all samples reacted at temperatures below 1323 K but excess lime formed calcium aluminium silicate for the experiments carried out at 1573 K.
- Both xrd and EDX analysis confirmed Cu, Co and Fe phases at temperatures below 1323 K while Cu rich and Co-Fe phases forming at 1573 K as shown from elemental mapping in figures 5 and 6. It looks possible to recover Co from copper sulphides through pyro-metallurgical route by addition of lime and carbon, unlike in conventional smelting where cobalt and iron are oxidised.
- EDX analysis shows that the composition of the alloys formed during carbothermic reduction of mineral concentrates well corresponds to the predictions from the Cu-Fe, Cu-Co and Co-Fe phase diagrams. Some analysed areas during XDX analysis has showed that copper with a purity of over 96 % weight was produced in a single step during carbothermic reduction of mineral concentrates in the presence of lime.

- Copper sulphides were formed in Nchanga and Nkana concentrates but not in Baluba concentrates after reheating the reduced samples at 1573 K. Nchanga and Nkana concentrates contain about 50 and 73 % weight gangue content respectively. The copper sulphides were formed from the reduced copper and calcium sulphide. Detailed analysis on the formation of copper sulphides for Nchanga and Nkana concentrates at 1573 K is still under investigations.

Acknowledgement

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