

## Effect of annealing treatment on the crystallisation and leaching of dumped base metal smelter slags

Kasonde Maweja<sup>a,\*</sup>, Tshikele Mukongo<sup>b</sup>, Richard K. Mbaya<sup>c</sup>, Emela A. Mochubele<sup>d</sup>

<sup>a</sup> Element Six Production (Pty) Ltd, DRL, PO Box 561, Springs 1560, South Africa

<sup>b</sup> Columbus Stainless, Middelburg, Mpumalanga, South Africa

<sup>c</sup> Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa

<sup>d</sup> Innovation Fund<sup>1</sup>, PO Box 2600, Pretoria 0001, South Africa

### ARTICLE INFO

#### Article history:

Received 28 September 2009

Received in revised form 7 June 2010

Accepted 7 July 2010

Available online 15 July 2010

#### Keywords:

Smelter slag

Annealing

Crystallisation

Metals distribution

Leaching

### ABSTRACT

Leaching tests of base metals contained in two smelter slags were undertaken in ammonia and nitric acid solutions aiming to recover Co, Cu and Zn. Leaching tests were conducted at 25 and 60 °C at pH = 0 and 3 in HNO<sub>3</sub> and pH = 12 in NH<sub>4</sub>OH media. XRD analysis revealed that the dumped slags were amorphous. Annealing these slags at 1180 °C produced crystalline phases comprising diopside, magnetite and fayalite. SEM and EDS analysis revealed that Cu and Pb compounds have concentrated in the magnetite phase, whereas another phase rich in Zn and Cu was located in the diopside matrix. ICP-OES analysis of the pregnant leaching solutions (PLS) showed that 30–60% of Co, Cu and Zn were released from the amorphous slags treated in HNO<sub>3</sub> at pH = 0, and lesser in ammonia. However, the contamination by Fe and Pb was higher at pH = 0. The contamination of the PLS obtained by leaching of the crystallised slags remained low. The low Fe and Pb contamination was attributed in this case to the chemical stability of the crystalline phases formed upon annealing treatment. The higher solubilisation of metals contained in amorphous slags was attributed to the collapse of silicate structures during nitric acid leaching at pH ~ 0.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Blister copper was produced in the Southern province of the Democratic Republic of the Congo from chalcocite and bornite concentrates through a matte smelting and oxygen converting process. This process had generated ~1,200,000 t of slag (S1). These slags were dumped in sites neighbouring densely populated areas. A carbothermal reduction treatment of this slag was developed for the recovery of copper and cobalt in a white alloy [1]. The slag generated in this cleaning process is named (S2) in the present work. This pyrometallurgical cleaning process of the slag S1 presents two major disadvantages. It is energy consuming (~150 kWh/t) and it generates CO<sub>2</sub>, CO and SO<sub>2</sub> containing fumes which are rejected into the ambient air. The slag (S2) formed during the carbothermal reduction of the slag S1 is dumped in a separate site located not far from the populated area. Slag S1 contains heavy metals such as Cu, Co, Pb and Zn at industrially exploitable levels. Thus these slags are not appropriate for dumping and necessitate further cleaning by recovery of the heavy metals. A hydrometallurgical treatment of

these slags S1 is believed to be energy efficient than the pyrometallurgical process and it will produce less pollution of the ambient air. The conditions which favour the leaching of the base metals which are beneficially recoverable from these slags S1 and the chemical stabilisation of the slag S2 were investigated in the present work. Leaching of the base metals contained in S1 will generate residues which can be stabilised and disposed in engineered landfills without major risks of pollution.

Slags are commonly calculated to optimise the collection of the gangue constituents as well as the oxide phases formed upon smelting of metallic ores. The composition of a slag therefore depends on the raw materials and the smelting technology used. Amounts of metals or matte phases are mechanically drawn in the slag during tapping. Hence, the slags contain and may become potential sources of base metals and constitute hazardous risks to both the human health and the environment [2]. Contamination of the environment may occur by various mechanisms, i.e.; the dissolution of the heavy metals such as copper, cobalt, lead and zinc from the dumped slags in acidic rain water, and the mechanical erosion and transportation of the dust particles by the air. The recovery of the base metals from the smelter slags or alternatively their chemical stabilisation into phases that are less soluble in acidic and basic media are means of reducing the risks of pollution of the environment.

Ettler et al. [3] have shown that the distribution of zinc between the crystalline and glass phases in Pb-smelter slags depended on the

\* Corresponding author. Tel.: +27 833650952.

E-mail address: [mawejak@yahoo.fr](mailto:mawejak@yahoo.fr) (K. Maweja).

<sup>1</sup> Innovation Fund is an initiative of the Department of Science and Technology, South Africa.

**Table 1**

Chemical compositions [wt%] of the copper matte smelter slag S1 and the carbothermally reduced slag S2.

	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	FeO	FeS	CoO	Cu <sub>2</sub> S	CuO	ZnO	PbO	MnO	TiO <sub>2</sub>	Total
S1	5.6	6.0	32	8.6	27	2.4	2.2	2.0	0.7	6.2	0.9	0.8	4.8	99.2
S2	7.2	7.6	40	11	23		0.5		0.3	3.1	0.2	1.6	5.3	99.8

blast furnace charge and temperature, as well as the cooling conditions of the slag. Saffarzadeh et al. [4] work on melting treatment of municipal solid waste (MSW) slags at about 1300 °C in semi-oxidizing to oxidizing atmosphere followed by air cooling or water quenching have shown that a notable amount of heavy metals (Cu, Fe, Pb, Sb, Ni) were significantly enriched in metal-rich inclusions and preserved in the silicate glass matrix of the slag produced.

Various techniques including oxidative or reductive leaching, carbothermal reduction with or without slag modifiers were investigated by several metal producing units worldwide for metals beneficiation or for the chemical stabilisation of toxic heavy metals such as Cr, Pb, etc. contained in the smelter wastes [1,5–13]. Leaching test of steel slags showed that the solubility of elements such as Cr, Mo and V from slag modified by means of re-melting and water-granulation, as well as by re-melting and semi-rapid cooling in crucibles was very low [14–16]. Kuo et al. [17] suggested that water quenching and high SiO<sub>2</sub> content, both enhanced the glassy amorphous phase to distribute more uniformly in slag.

Investigation was conducted on two smelter slags, in this work, to assess the optimum leaching conditions for Cu, Co and Zn contained in the dumped amorphous slags as well as in the crystallised slags annealed at about 1100 °C. The effect of the annealing treatment on the distribution of base metals between crystallised phases; and on the leaching of base metals in nitric acid and in ammonia media was studied at 25 and at 60 °C. Hence this work contributes to establish a novel approach to the recovery of the base metals contained in the amorphous slags dumped in sites surrounding several metals producing units. The leaching residues would be less toxic to the environment than the current slags. An alternative is suggested for the chemical stabilisation of Cu, Fe, Pb, Co and Zn against acidic or basic leaching from the dumping tails.

## 2. Materials and methods

Samples of 400 kg of slags were collected from the dumping sites of a copper matte smelter (S1) dumped during the period 1965–1994 and from the current retreatment plant of the first slag by carbothermal reduction (S2). Copper, cobalt, lead and zinc contained in the copper matte smelter slag (S1) were partially recovered and concentrated in white alloy by retreatment in an electric arc furnace. In industrial practice, the two slags are rapidly quenched and granulated in high pressure high flow rate water jets during tapping from the respective smelters. The particle sizes of the water granulated slags vary between 0.5 and 5 mm. The chemistries of the as-received slags were determined by means of inductive coupled plasma optical emission spectroscopy (ICP-OES).

Samples of the slags were dry milled to <220 μm. 100 g of the milled slags were placed inside silica crucibles and covered with silica lids. The crucibles were then introduced in an electric muffle furnace equipped with a feedback control system of temperatures and heated up in air at an ambient pressure. The annealing treatment consisted of a heating up at the step of 20 °C/min and dwelling at temperature ranging between 1100 and 1180 °C for 2 h. The slags were then cooled down in three different conditions, i.e.; water quenched, air cooled and furnace cooled. The corresponding cooling rates were estimated to be >1000, 150 and 3 °C/min respectively. The annealing temperature range was selected to be below the smelting temperatures of the as-received slags, which are 1250 °C and 1400 °C for slag S1 and S2 respectively, but still higher than

the melting temperatures of Cu, Pb and Zn which are estimated at 1083, 327 and 420 °C respectively. The cooling rates were selected to be close to those used in industrial practice.

20 g of the milled slag powders were poured in 250 ml Erlenmeyer glass vessels containing the leaching solution at the reaction temperature (25 or 60 °C). A solid to liquid mass ratio equal to 1 g:10 ml was considered for the tests. The leaching was conducted in HNO<sub>3</sub> solution at pH ~ 0 and pH ~ 3, and in NH<sub>4</sub>OH solution at pH ~ 12, at 25 and at 60 °C for 2 h in magnetically agitated solutions. The leaching sensitivity of the slags was estimated by the difference in mass between the initial slag and the leaching residues washed in water and dried at 100 °C for 24 h. The release of Cu, Co, Pb, Zn in the pregnant leach solutions and the contamination by Fe were evaluated by monitoring their concentrations in the pregnant leaching solutions by means of ICP-OES.

The Cu, Co and Zn contents are still high in these slags, especially in slag S1. Hence it is an object of these leaching tests to determine the conditions which enhance the recovery of these metals from the slags.

The phase compositions of the initial amorphous slags S1 and S2, as well as those of the annealed materials were determined by means of X-ray diffraction (XRD) in a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and fixed-receiving slits with Fe filtered Co Kα radiation. The XRD samples were prepared by milling the slag samples using McCrone micronising. 20 wt% of silicone standard (Aldrich 99.9%) was added to the milled samples prior to analysis for the quantitative determination of the amorphous materials in the slags. The phases were identified qualitatively using X'Pert Highscore plus software and quantitatively using the Rietveld method (Autoquan Program).

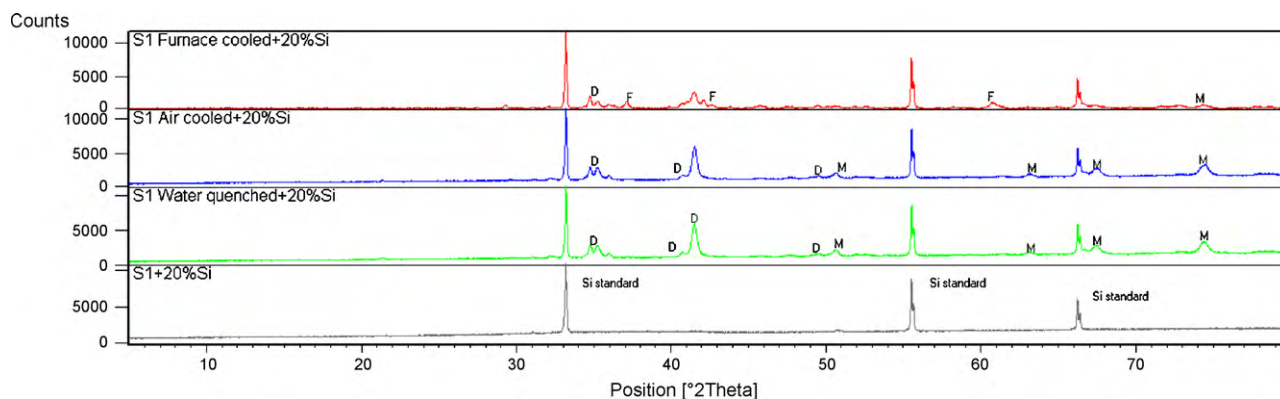
Microanalysis of the polished samples of various as received and annealed slag materials was done using scanning electron microscopy (SEM). Phase distributions were analysed in backscattered electron mode and elemental analysis was done by energy dispersive X-ray spectroscopy (EDS) in the SEM Philips equipment.

## 3. Results and discussion

### 3.1. Crystallisation upon annealing treatment

The chemistries of slags S1 and S2 are given in Table 1. The basicity of the two slags, ((CaO+MgO)/SiO<sub>2</sub>), remained close to 0.45, whereas the silica content of S2 was higher than the saturation value of 38 wt% for the formation of tri-dimensional silicate structures [18]. The high silica content and lower basicity render these slags prompt to amorphisation and glassification during the fast cooling down in high pressure high flow rate water jets [17].

The XRD patterns in Figs. 1 and 2 show that the water granulated slags S1 and S2 from the smelting plants were amorphous containing 4 and 5 wt% of crystallised phases respectively, whereas the annealed products contained more crystalline materials. The proportions of the crystallised phases in the two slags increased to about 80 wt% after annealing. The crystalline phases formed upon annealing treatment were complex containing diopside-hedenbergite (D), magnetite (M) and fayalite (F) of formula CaMg(SiO<sub>3</sub>)<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>(SiO<sub>4</sub>) respectively in various proportions depending on the composition of the slag and the cooling rate as shown in Tables 2 and 3.



**Fig. 1.** XRD patterns of the amorphous slag S1 from the copper matte smelter and the annealed products cooled down at different rates (D = diopside–hedenbergite, F = fayalite, M = magnetite).

**Table 2**

Phase compositions, in wt%, of slag S1 from the copper matte smelter and after annealing treatment (A = annealed).

	Amorphous	Diopside–hedenbergite	Magnetite	Fayalite
As received	96	3	1	0
A/water quenched	22	38	38	2
A/air cooled	21	40	38	1
A/furnace cooled	20	38	13	29

The proportions of amorphous phases in the annealed slags decreased by a marginal 2–3 wt% when the cooling rate decreased from 1000 °C/min (quenching in water) to 3 °C/min (furnace cooling). The small effect of the cooling rate on the total amounts of crystallised phases in the two slags suggests that the crystallisation of the slags was completed during the heating up of the materials

**Table 3**

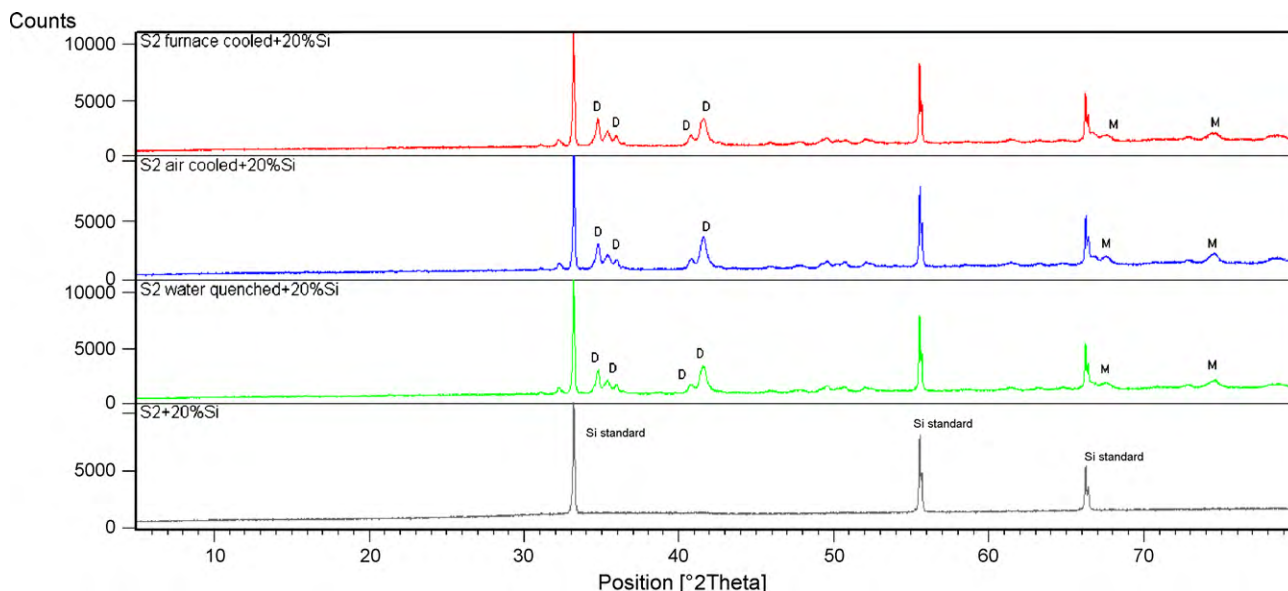
Phase compositions, in wt%, of slag S2 and after annealing treatments (A = annealed).

	Amorphous	Diopside–hedenbergite	Magnetite	Fayalite
As received	95	4	1	0
A/water quenched	24	54	20	2
A/air cooled	22	55	21	2
A/furnace cooled	21	58	18	3

and the dwelling at temperature ranging at about 1100–1180 °C. The proportion of fayalite increased whereas the magnetite content decreased after annealing of S1. Similar trends were observed but to only a less extent in the case of slag S2, which differs from the slag S1 by its cobalt, copper, lead and zinc contents as shown in Table 1. The slag S1 came closer to its smelting temperature than was slag S2 during annealing. In terms of diffusion rate, this means that reactions occurring go faster in S1. Thus the higher diffusion rates of  $O^{2-}$  and  $Fe^{2+}$  in slag S1 led to the formation of more magnetite in this slag in both the water cooled as well as the air cooled conditions than was observed in slag S2. The combination of high diffusion rate of  $Si^{2+}$  ions during annealing of slag S1 and a slow cooling down in the furnace might have enhanced the formation of fayalitic structures simultaneously with magnetite. This process resulted in the observed decrease in magnetite content and the increase in fayalite content after annealing and furnace cooling of the slag S1.

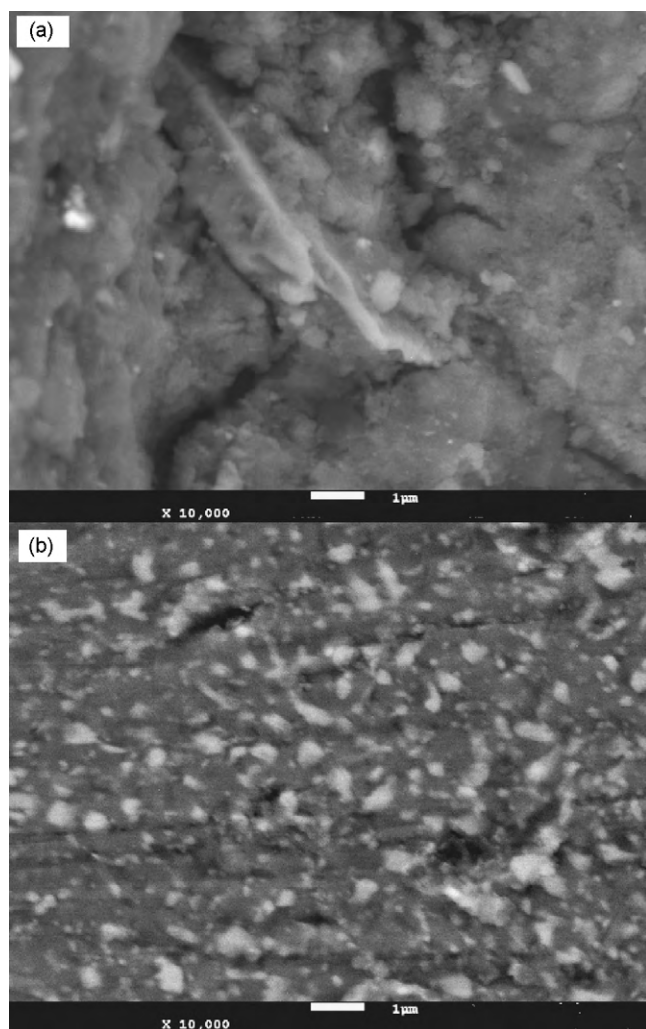
### 3.2. Base metals distribution

An approach to the understanding of the interaction between magnetite, fayalite and the distribution of metals such as Cu, Co, Pb and Zn in the crystallised phases formed during the annealing treatment was undertaken by means of SEM and EDS techniques.



**Fig. 2.** XRD patterns of the amorphous slag S2 and the crystallised products of annealing cooled down at different rates (D = diopside–hedenbergite, M = magnetite).



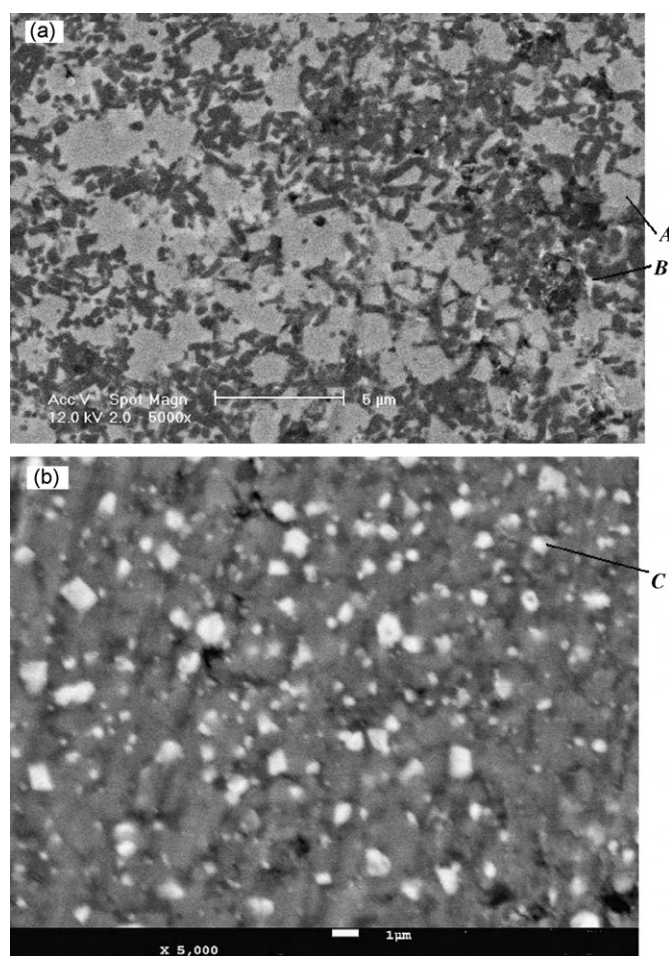


**Fig. 3.** SEM micrographs of (a) amorphous slag S1 and (b) the crystallised slag after annealing at 1100–1180 °C and furnace cooled at 3 °C/min showing magnetite/fayalite (bright areas) and the diopside–hedenbergite matrix (dark areas). Scale bar = 1 µm.

Typical microanalyses of phase distributions in the as-received slag S1 and in the heat treated materials are illustrated in Fig. 3. At least two phases were formed by annealing of the amorphous materials S1 in Fig. 3a. Magnetite phase was uniformly distributed in the diopside matrix formed in annealing of the slag S1, as shown in Fig. 3b. The distribution size of the magnetite mineral phase (bright phase) in the annealed materials, became smaller when the cooling rate decreased from >1000 °C/min (water quenched) to 3 °C/min (furnace cooled). This could be attributed to the competition between the formation of magnetite and fayalite during slow cooling down in the annealed materials. However, the size of the magnetite mineral phase and the fayalite content remained practically unchanged upon cooling down, at different rates, in the annealed slag S2.

It infers from the above observation that the effect of the cooling rate on the amounts of magnetite and fayalite formed in the annealed slags depends on the base metals contents and the diffusion of  $\text{Fe}^{2+}$ ,  $\text{O}^{2-}$ ,  $\text{Si}^{4+}$  at the annealing temperature.

High resolution SEM imagery showed substantial differences between the characteristics of the magnetite phases formed in annealing of S1 and S2 as illustrated in Fig. 4. A glassy phase consisting of magnetite, rich in matte constituents such as Cu and Pb, was formed as interstitial matrix between the large magnetite mineral phases in the annealed slag S1. The magnetite mineral



**Fig. 4.** High resolution SEM image showing: (a) glassy phase (A) rich in magnetite, Cu and Pb, phase (B) rich in Zn, Cu and Fe in slag S1 annealed and furnace cooled and (b) smaller magnetite phase (C) formed in annealed slag S2.

phases formed during the annealing treatment of slag S2 were smaller than those produced in annealing of the slag S1 as shown in Fig. 4b. The EDS area analysis of the magnetite (bright phase) formed in annealing of S1 and furnace cooling suggests that it enclosed two microscopic phases. The phase A in Fig. 4a consisted of magnetite containing at about 2–6 wt% Cu and 4–12 wt% Pb, whereas the phase B in the same figure had a composition close to the diopside–hedenbergite containing at about 7–11 wt% Zn and 12 wt% Cu. Zinc and copper oxides contained in the slag S1 were therefore preferentially dissolved in the diopside–hedenbergite matrix, whereas Pb and the major fraction of Cu were enclosed in the fayalite–magnetite mineral phases.

The above distribution of metals was particularly observed after the slower cooling rate of the annealed slags in the furnace.

### 3.3. Recovery of metals and leaching sensitivity of the slags

The effect of the pH, temperature and leaching time on the release of the base metals contained in the amorphous and in the crystallised slags was investigated. The curves of recovery rates of base metals and Fe from the amorphous slag S1 at various pH in nitric acid and in ammonia solutions showed that Cu, Co, Fe, Pb and Zn contained in the amorphous slag S1 were more leachable at pH=0 as illustrated in Fig. 5. The recovery rates of copper were the lowest among the base metals leached at pH=0 due to its presence mainly as  $\text{Cu}_2\text{S}$  in the copper matte smelter slag S1; whereas Zn, Co, Pb and Fe were present in oxide forms. Furthermore, an

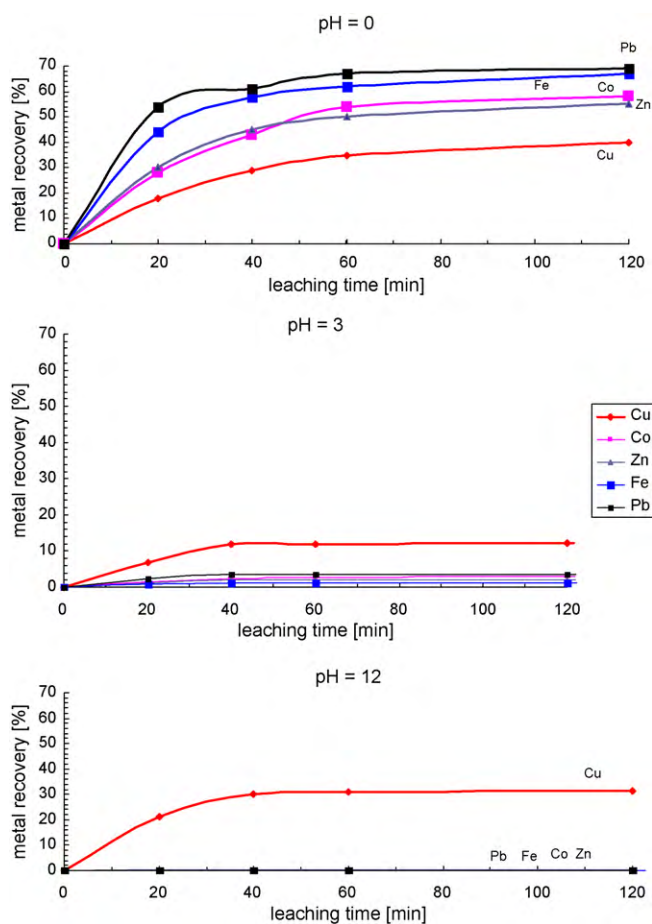
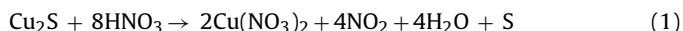


Fig. 5. Recovery of metals from the amorphous slag S1 by leaching in  $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$  at various pH.

oxidative reaction is needed for the dissolution of copper from the  $\text{Cu}_2\text{S}$ , unlike the neutralisation reaction between nitric acid and the oxides  $\text{ZnO}$ ,  $\text{PbO}$ ,  $\text{CoO}$  and  $\text{FeO}$ . The occurring reaction between  $\text{Cu}_2\text{S}$  and  $\text{HNO}_3$  at room temperature and  $\text{pH}=0$  is represented in the chemical Eq. (1):



Fine particles (yellow-brown) were observed in the gel formed in the PLS of leaching for 2 h at  $\text{pH}=0$  of the amorphous copper matte slag S1, and kept for 5 days at  $25^\circ\text{C}$ . Such particles were not observable in the gel formed in leaching of slag S2 which did not contain a matte phase. These particles might be attributed to the presence of sulphur in the slag S1.

The recovery rates of all metals from the amorphous slag S1 decreased at  $\text{pH}=3$  as shown in Fig. 5. It was noticed that unlike at the  $\text{pH}=0$ , the dissolution rate at  $\text{pH}=3$  of copper from the amorphous slag S1 was higher than those of Co, Zn, Fe and Pb. However, the recovery rate of copper remained lower than 20%, suggesting that only the copper present in  $\text{Cu}_2\text{O}$  form was dissolved at  $\text{pH}=3$ . The leaching of base metals from the amorphous slag S1 in am-

monia solution at  $\text{pH}=12$  was more selective for copper. Between 20 and 30% of copper contained in the amorphous slag S1 was dissolved in ammonia, whereas Fe, Pb and Co contents of the pregnant leaching solutions remained lower than the sensitivity limits of the ICP-OES equipment used. The undetectable levels of Fe, Co and Pb in the solutions obtained by ammonia leaching were confirmed by means of atomic absorption spectrometry analysis. The dissolution of more than 20% of copper from the slag S1 indicates that  $\text{Cu}_2\text{S}$  was soluble in ammonia as the copper present in oxide form in the slag S1 represented only 20% of the copper total in the slag S1.

Typical concentrations of the metals in the pregnant leaching solutions are given in Table 4. Contamination of the leaching solutions by Fe and Pb was high at  $\text{pH}=0$  than at the higher pH, which poses purification challenges in further processing of the solution by a hydrometallurgical route despite the higher recovery rates observed in the first case. It is singularly noticed that the solutions obtained by leaching of the amorphous slag S1 in ammonia were practically exempt of Fe or Pb contamination. However the lower copper and zinc contents in those solutions will render necessary a concentration by solvent extraction or similar techniques before metal extraction by either electrowinning or cementation. A Fe + Pb contamination ratio (CR) defined in Eq. (2) of this work was adopted as comparison factor between pregnant leaching solutions. The CR is indicative of the pollution by Fe and Pb; and the subsequent investment in purification processes needed before extraction of Co, Cu and Zn from the leaching solutions:

$$\text{CR} = \frac{[\text{Fe} + \text{Pb}]}{[\text{Co} + \text{Cu} + \text{Zn}]} \quad (2)$$

Leaching efficiency of the metals from the annealed slag S1 decreased considerably. Fig. 6 illustrates the lower recovery of metals from the annealed slags which were furnace cooled. The recoveries of Co, Fe and Pb from the annealed slag S1 were about 50 times lower than those recorded when leached from the amorphous slag S1. Solubilisation of Co, Fe and Pb from the crystallised slag in nitric acid remained lower than 1%. The recovery of Cu and Zn were about 1.5% in nitric acid at  $\text{pH}=0$ , which is 20 times lower than was the solubilisation from the amorphous slags. It resorts from these results that the crystallisation by annealing and slow cooling down of the slag S1 had increased the chemical stability of the slag. Comparison between curves in Figs. 5 and 6 suggests that the diopside–hedenbergite phase containing cobalt, iron and lead oxides was more refractory to leaching in  $\text{HNO}_3$  and  $\text{NH}_4\text{OH}$  than the copper and zinc compounds at  $25^\circ\text{C}$ .

It was again observed that leaching of the annealed slag by ammonia solution was selective for copper, even though the copper concentration remained low in the PLS. The concentrations of metals in the pregnant leach solutions obtained after leaching for 2 h of the annealed slag S1 slowly cooled down in the furnace are given in Table 5. The leaching of Co, Fe and Pb from the crystallised annealed slag S1 cooled down in air or water quenched yield similar results than those of the annealed furnace cooled slag. Pregnant leach solutions obtained by leaching of the crystallised annealed air cooled slag S1 contained about 5 times more Cu and Zn than those from leaching of the annealed furnace cooled slag. This implies that the crystallisation by annealing stabilised the slag constituents in

Table 4

Metal contents of the pregnant leach solution of the amorphous slag S1 after 120 min treatment at  $25^\circ\text{C}$ .

pH	Metal concentration in the PLS [ppm]						CR	End pH
	Co	Cu	Fe	Pb	Zn			
0	822	666	11,864	517	2295		3.2	2
3	42	198	228	24	87		0.77	3.8
12	1	256	<0.1	<0.1	10		<0.0007	11.3

**Table 5**

Metal contents of the pregnant leach solution of the crystallised annealed slag S1 furnace cooled after 120 min leaching at 25 °C.

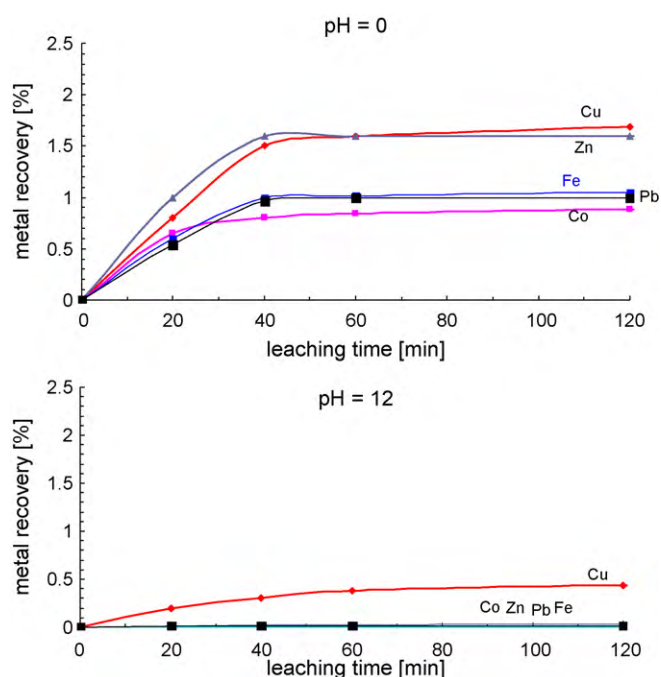
pH	Metal concentration in the PLS [ppm]							End pH
	Co	Cu	Fe	Pb	Zn	CR		
0	13.9	25.6	160	20.7	64.3	1.74	0.7	
3	<0.1	6.0	<0.1	<0.1	2.3	<0.02	3.3	
12	<1	8.6	<0.1	<0.1	1.0	<0.01	11.8	

general; whereas the effect of the cooling rate after annealing on the leachability was slightly significant on the solubilisation of Co, Fe and Pb than on Cu and Zn.

Increasing the temperature of the acid leaching solutions to 60 °C increased the recovery of Co, Cu and Zn from the crystallised annealed slags while keeping the Fe and Pb contamination ratio of the PLS lower. Typical concentrations of the metals in such PLS were 225 ppm Co, 665 ppm Cu, 220 ppm Fe, 221 ppm Pb and 205 ppm Zn. The corresponding Fe and Pb contamination ratio is CR=0.4, which is lower than 3.2 obtained in leaching of amorphous slag S1 at pH=0. The recovery of copper by leaching of the crystallised annealed slag at pH=0, at 60 °C was higher than 50%, similar to those obtained in leaching of the amorphous slag S1. However, solubilisation of Co and Zn dropped to <1/5 of those obtained from the amorphous slags.

The mass fractions of slags dissolved in HNO<sub>3</sub> and in NH<sub>4</sub>OH at various pH are shown in Fig. 7. The results showed that at least 60% of the amorphous materials of slag S1 were leached in HNO<sub>3</sub> at pH ~ 0 at 60 °C after 2 h. However, the crystallised products obtained after annealing of S1 were less leachable in the same conditions. Less than 20% of those materials were leached at pH ~ 0 at 60 °C. The leaching sensitivity of the slag S1 and its annealing products at pH ~ 3 at 60 °C were comparable because it is less acidic, implying that there was less H<sup>+</sup> ions for the reaction. The leaching values ranged between 7 and 9%.

The amorphous slag S2 was more refractory to leaching than the matte smelter slag S1 in both acidic and basic media. The leaching sensitivity in acid solution dropped after annealing of S2 to values less than 20 wt%. Leaching values of S2 in ammonia solution

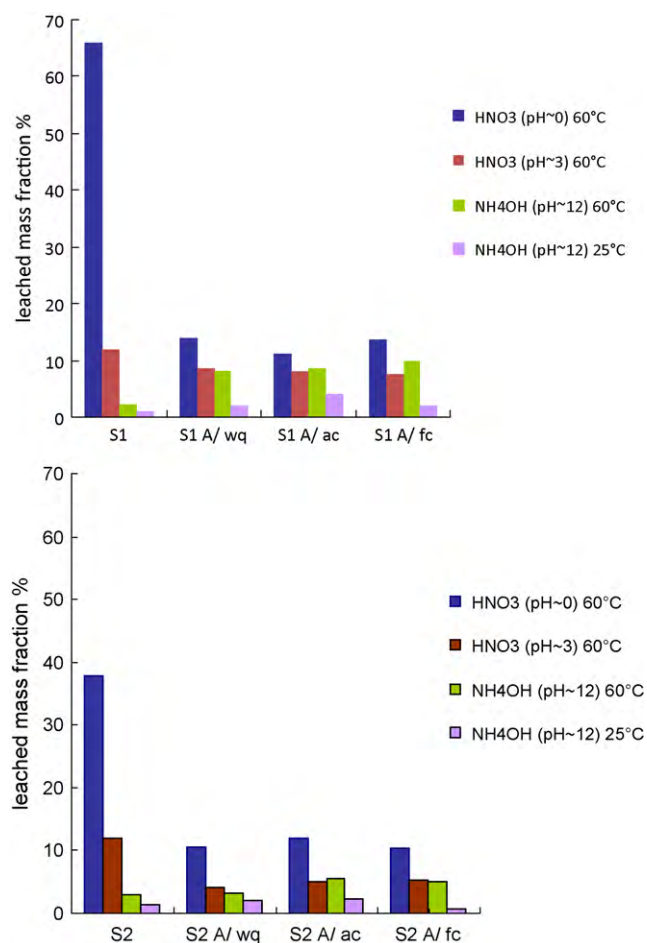
**Fig. 6.** Recovery of metals from the crystallised annealed furnace cooled slag S1 by leaching in HNO<sub>3</sub> and NH<sub>4</sub>OH at various pH.

were lower than those observed in the case of the matte smelter slag S1.

A singular gel formation was observed in the entire volume of pregnant leach solutions obtained at pH=0 when the slags S1 and S2 were amorphous. Such gel formation was not observed neither in leaching solutions obtained at pH=3 and 12, nor was it after leaching of the crystallised annealed slags, even at pH=0. Hence, the large mass losses in leaching of the amorphous slags S1 and S2 at pH=0 was attributed to the collapse of the amorphous silicate structures in these materials.

It infers from the leaching test results that the annealing treatment improved the chemical stability of both the copper matte smelter slag S1 and the retreatment slag S2. Chemical stabilisation by crystallising annealing treatment may therefore be seen as a general behaviour for metals smelter slags.

The XRD analysis indicated that typical acid leaching residues of the annealed smelter slag S1 consisted of diopside CaMg(SiO<sub>3</sub>)<sub>2</sub>, hedenbergite Ca(Fe,Mg)(SiO<sub>3</sub>)<sub>2</sub> and contain a copper–zinc–

**Fig. 7.** Mass loss [%] after leaching in HNO<sub>3</sub> and NH<sub>4</sub>OH at 60 °C and at 25 °C for 2 h of the smelter slag S1 and the retreatment slag S2 in the as-received states, and in annealed and water quenched (A/wq), annealed and air cooled (A/ac), annealed and furnace cooled (A/fc) conditions.



chromium–iron oxide complex  $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_{1.1}\text{Fe}_{0.9}\text{O}_4$ . On the other hand, typical residues from the ammonia leaching consisted of diopside and hedenbergite. It appears from these XRD results that  $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_{1.1}\text{Fe}_{0.9}\text{O}_4$  complexes contained in the crystallised annealed slag S1 were leachable in ammonia at  $\text{pH} = 12$ , at  $25^\circ\text{C}$ .

#### 4. Conclusion

Leaching tests of Co, Cu and Zn contained in a copper matte smelting slag (S1) and in the retreatment slag of the first one in an electric furnace (S2) were conducted in ammonia and in nitric acid solutions. The work aimed at determining the efficiency of release of these metals from the slags and the subsequent contamination by Fe and Pb which shall be considered in further purification of the PLS and recovery of the metals.

XRD analysis has shown that both the copper matte smelter slag S1 and the retreatment slag S2 were amorphous, and contained less than 6% of crystalline materials.

The two slags, S1 and S2, have crystallised during an annealing treatment at temperature comprised between  $1100$  and  $1180^\circ\text{C}$ . The crystallised slags contained a diopside–hedenbergite matrix, magnetite and fayalite mineral phases. The crystalline materials represented  $\sim 80$  wt% of the two slags in the annealed conditions.

The cooling rate after annealing (between 3 and  $1000^\circ\text{C}/\text{min}$ ) had a marginal effect on the total amount of residual amorphous material. This indicated that crystallisation of the slags took place during the heating up and on dwelling at high temperature. However, it appeared that the slow cooling rates favoured the formation of fayalite on the magnetite phase. This was particularly observed in the furnace cooled slag S1. The amount of magnetite phase in annealed S2 was less affected by the cooling rate.

Slag compositions and cooling rate after annealing had various effects on the phase compositions and on the distribution of metals in the crystalline phases formed thereof. A “glassy” phase rich in Cu and Pb was formed in and around the magnetite phase, whereas copper and zinc oxides were found in the diopside–hedenbergite matrix. Lead contents in the glassy and magnetite areas increased as the cooling rate decreased.

Larger magnetite mineral phases were formed in the annealed slag S1 than was observed in the retreatment slag S2. This was attributed to molten lead or copper sulphide particles that acted as nucleation sites for the magnetite formation upon heating up of the matte smelter slag S1.

The collapse of the amorphous silicate structure led to higher dissolution of Cu, Co, Fe, Pb and Zn in nitric acid at  $\text{pH} = 0$ . However a gel formation occurred in solutions kept for longer than 5 days. Dissolution of Co, Fe and Pb decreased at  $\text{pH} = 3$ . Leaching in ammonia was selective for copper contained in the amorphous as well as in the crystallised slags. Concentrations of Co, Fe and Pb in pregnant leach solutions obtained from an ammonia leaching were lower than 0.1 ppm whereas Cu and Zn contents were 256 and 10 ppm respectively. The Fe and Pb contamination of the leach solutions was negligible at  $\text{pH} = 12$ . Typical leaching residues in ammonia consisted of diopside–hedenbergite. Copper–zinc–chromium–iron oxide complexes contained in the slags were leached in ammonia. So was the  $\text{Cu}_2\text{S}$  from the matte which was mechanically drawn in the slag S1.

The annealing treatment, generally improved the leaching refractoriness of the two slags in  $\text{HNO}_3$  and in  $\text{NH}_4\text{OH}$  media. It was observed that increasing the leaching temperature to  $60^\circ\text{C}$  increased the solubilisation of the base metals from the crystallised annealed slag S1, but the pollution of the PLS by Fe and Pb remained low, and there was no gel formation in the PLS obtained at  $\text{pH} = 0$ .

Leaching of the amorphous slags in  $\text{HNO}_3$  at  $60^\circ\text{C}$  is not practically advisable as the collapse of the amorphous silica structure is spontaneous and a viscous gel is formed in the bulk volume of the leaching solution, rendering unpractical any decantation or filtration.

The appropriate treatment for the two slags would therefore consist of:

- For the slag S1: Copper and zinc leaching from the amorphous slag in ammonia at  $25^\circ\text{C}$  for 2 h. Another route would consider the leaching of Co, Cu and Zn from the crystallised slag at  $\text{pH} = 0$ , at  $60^\circ\text{C}$ . This route is a compromise between the good recovery rates of the three metals and the pollution of the pregnant leaching solutions by Fe and Pb. The leaching residues can be chemically stabilised by annealing and used as landfills.
- For the slag S2: A stabilisation by annealing and slow cooling down is recommended.

#### Acknowledgements

The authors are thankful to Dr Sabine Verryn and Fanuel Bambo for the XRD and SEM analysis of the slags and leaching residues respectively.

#### References

- [1] K. Maweja, T. Mukongo, I. Mutombo, Cleaning of copper matte smelting slag from a water jacket furnace by direct reduction of heavy metals, *J. Hazard. Mater.* 164 (2009) 856–862.
- [2] R. Minto, W.G. Davenport, Entrapment and flotation of matte in molten slags, *Can. Min. Metall. Bull.* 65 (720) (1972) 70–76.
- [3] Z. Ettler, J.-C. Johan, E. Touray, Jelinek, Zinc distribution between glass and silicate phases in historical and modern lead-zinc metallurgical slags from the Příbram district, Czech Republic, *Earth Planet. Sci.* 331 (2000) 245–250.
- [4] A. Saffarzadeh, T. Shimaoka, Y. Motomura, K. Watanabe, Characterization study of heavy metal-bearing phases in MSW slag, *J. Hazard. Mater.* 164 (2009) 829–834.
- [5] B. Gorai, R.K. Jana, Premchand, Characteristics and utilisation of copper slag—a review, *Resour. Conserv. Recycl.* 39 (2003) 299–313.
- [6] H. Shen, E. Forsberg, An overview of recovery of metals from slags, *Waste Manage.* 23 (2003) 933–949.
- [7] A.N. Banza, E. Gock, K. Kongolo, Base metals recovery from copper smelter slag by oxidising leaching and solvent extraction, *Hydrometallurgy* 67 (2002) 63–69.
- [8] B. Das, S. Prakash, P.S.R. Reddy, V.N. Misra, An overview of utilization of slag and sludge from steel industries, *Resour. Conserv. Recycl.* 50 (2007) 40–57.
- [9] J.-D. Chou, M.-Y. Wey, S.-H. Chang, Evaluation of the distribution patterns of Pb, Cu and Cd from MSWI fly ash during thermal treatment by sequential extraction procedure, *J. Hazard. Mater.* 162 (2009) 1000–1006.
- [10] C. Arslan, F. Arslan, Recovery of copper, cobalt and zinc from copper smelter and converter slags, *Hydrometallurgy* 67 (2002) 1–7.
- [11] A. Sarrafi, B. Rahmati, H.R. Hassani, H.H.A. Shirazi, Recovery of copper from reverberatory furnace slag by flotation, *Miner. Eng.* 17 (2004) 457–459.
- [12] W.J. Bruckard, M. Somerville, F. Hao, The recovery of copper, by flotation, from calcium–ferrite-based slags made in continuous pilot plant smelting trials, *Miner. Eng.* 17 (2004) 495–504.
- [13] E. Virčíková, L. Molnár, Recovery of copper from dump slag by a segregation process, *Resour. Conserv. Recycl.* 6 (1992) 133–138.
- [14] K.L. Lin, C.T. Chang, Leaching characteristics of slag from the melting treatment of municipal solid waste incinerator ash, *J. Hazard. Mater.* B 135 (2006) 296–302.
- [15] M. Tossavainen, F. Engstrom, Q. Yang, N. Menad, M. Lidstrom Larsson, B. Bjorkman, Characteristics of steel slag under different cooling conditions, *Waste Manage.* 27 (2007) 1335–1344.
- [16] I.-J. Chiou, K.-S. Wang, C.-C. Tsai, Enhancing performance and durability of slag made from incinerator bottom ash and fly ash, *Waste Manage.* 29 (2009) 501–505.
- [17] Y.-M. Kuo, J.-W. Wang, C.-T. Wang, C.-H. Tsai, Effect of water quenching and  $\text{SiO}_2$  addition during vitrification of fly ash—Part 1: on the crystalline characteristics of slags, *J. Hazard. Mater.* 152 (2008) 994–1001.
- [18] Mwema Mutamba Dibwe, Contribution à l'étude des propriétés des scories de la métallurgie du cuivre.—Comportement du cobalt et mesure des viscosités, These de doctorat en sciences appliquées, Université Libre de Bruxelles, 1989.