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Cleaning of a copper matte smelting slag from a water-jacket furnace by direct reduction of heavy metals

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ABSTRACT

Cleaning experiments of a copper matte smelting slag from the water-jacket furnace was undertaken by direct reduction in a laboratory-scale electric furnace. The effects of coal-to-slag ratio, *w*, and the reduction time, *t*, were considered for two different coal/slag mixing procedures. In the first procedure, metallurgical coal was added to the molten slag, whereas in the second procedure, coal was premixed with the solid slag before charging into the furnace. The recovery of heavy metals (Cu, Co), and the fuming of Pb and Zn were investigated. Contamination of the metal phase by iron and the acidity index of the final slag were analysed as these may impede the economical viability of the process.

The lower *w* value of 2.56% yielded a recovery rate of less than 60% for copper and less than 50% for cobalt, and around 70% for zinc. However, increasing *w* to 5% allowed the recovery of 70–90% for Cu, Co and Zn simultaneously after 30–60 min reduction of the molten slag. After reduction, the cleaned slags contained only small amounts of copper and cobalt (<0.4 wt%).

Fuming of lead and zinc was efficient as the %Pb of the residual slag dropped to levels lower than 0.04% after 30 min of reduction. Ninety percent of the lead was removed from the initial slag and collected in the dusts. The zinc content of the cleaned slags quickly dropped to between 1 and 3 wt% from the initial 8.2% after 30 min reduction for *w* value of 5 and after 60 min reduction for *w* value of 2.56. The dusts contained about 60% Zn and 10% Pb. Recovery of lead from fuming of the slag was higher than 90% in all the experimental conditions considered in this study.

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1. Introduction

Dumped slags from copper matte smelting in a water-jacket furnace are a valuable source of base metals but if left untreated, may constitute an ecological threat to the surrounding life. Hence, the cleaning of such slags is important from both economical and environmental perspectives. Pyrometallurgical treatment of slags obtained during matte smelting of the copper sulphide ores would have the great advantage of energy saving as the slag can be treated at its melting temperature when it is tapped from the furnace before it cools down and looses its thermal energy to the ambient air.

The slag considered in this study was formed as a by-product of the matte smelting of a copper sulphide concentrate in a waterjacket furnace. The separation between matte and slag takes place in the crucible by density difference at 1250 °C, with the heavier matte sinking to the bottom of the crucible. This separation mode leads to some physical drawing of matte drops when tapping for slag. The slag, essentially a mixed oxide phase, contains therefore some copper and iron sulphides drawn mechanically but not dissolved.

The removal of heavy metals from slags can be conducted using either a pyrometallurgical or a hydrometallurgical route. Pyrometallurgical route uses mainly reduction of metal oxides contained in the slag and many authors have investigated this process.

Banda et al. [1] utilised CaO, CaF_2 and TiO_2 as slag modifiers during carbothermic reduction of waste smelter slag to reduce the activity of FeO under vacuum and under argon. It appears from their work that TiO_2 effectively reduces the activity coefficient of the FeO in the slag due the strong affinity between the two oxides.

Many researchers [2-5] have proposed empirical equations for estimating the solubility of non-ferrous metals in slags as functions of their chemistry especially of the SiO₂, FeO and CaO contents, as the concentrations of these oxides are believed to have a prominent effect on the recovery of the valuable metals in the slag.

Mackey and Nagamori [6] studied the recovery of zinc from reverbatory furnace slag by fuming with CO gas at 1250 °C. Their

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model explains well the experimental observation that the volatilisation of zinc is suppressed until most of magnetite in the slag is first reduced to FeO in a batch reactor. The solubility limit of copper in slags having various chemical compositions, which affects the limits of copper extractability from smelting slags, was analysed by Bailey and Garner [7]. Sannikov et al. [8] observed a change in the mechanism of zinc distillation and suggested that the zinc distillation rate at 1300 °C passes a maximum corresponding to the specific melt composition of the slag.

Some researchers have proposed the possibility of slag cleaning via the hydrometallurgical routes by roasting with sulphuric acid [9,10] or by roasting with ferric sulphate [11]. The reported recovery of copper, cobalt and zinc achieved using such methods are higher than 80%. However, contamination by Fe appeared to be a major handicap as more than 80% of Fe was simultaneously extracted from the slag [10,11].

Direct reduction of a copper matte smelting slag from a waterjacket furnace was undertaken in this study by utilising the latent heat energy of the molten slag, thus resulting in a 'cleaned' slag by removal of the lead, copper, cobalt and zinc from the dumped slags.

2. Thermodynamic considerations

2.1. The slag

The chemical composition of the slag used in this study is presented in Table 1. The CaO, FeO and SiO₂ contents were optimised in order to achieve the following:

- A melting temperature of between 1200 and 1250 °C,
- An acidity index of 1.2–1.5,
- A good viscosity of less than 5 poises, and
- A density of 3.5 ± 0.3 g/cm³, thus allowing an easy mechanical separation from the matte having a density 5 g/cm³.

The acidity index, *i*, of the slag is defined using the wt% of oxides in the slag as follows:

$$i = \frac{\text{SiO}_2}{\text{CaO} + \text{MgO}} \tag{1}$$

The acidity index of the slag is an indicator of the chemical potential reactivity between the slag and the MgO-based refractory used in both the slag cleaning and the water-jacket furnaces.

The plant produced 18,000–22,000 tons of slag monthly which contain the amount of metals presented in Table 2.

The copper, cobalt and zinc contents of this slag are high and may justify an economic treatment for their extraction. Moreover the leaching of these metals by rainwater, may lead to the contamination of underground as well as surface water, and poses a health hazard for the surrounding populations, vegetations and animals.

Table 1

 $Chemical \ composition \ in \ wt\% \ of the \ slag \ ex-water-jacket \ furnace \ in \ the \ Lubumbashi \ plant \ in \ the \ Democratic \ Republic \ of \ the \ Congo$

Cu	1.4
Со	2
ZnO	10
PbO	0.5
SiO ₂	31
FeO	29
CaO	10
Al ₂ O ₃	7
MgO	5
S	0.6
Precious metals	10 g/ton

Table 2

Amounts in tons of heavy non-ferrous metals thrown away monthly in the slag

Cu	288-352
Со	360-440
Zn	1440-1760
Pb	83-100
Precious metals	180–220 kg

The present work is aimed at extracting these four metals simultaneously. Lead and zinc can be further extracted in the form of dust since they are volatile. In addition the residual contents in the final slag can be substantially reduced to respective contents of less than 0.5 wt% for Cu and Co, to around 2% for Zn; and to less than 0.05 wt% in the case of Pb.

Analysis revealed that 80% of the copper in the matte smelting slag were present as Cu_2S , which indicates that physical trapping and mechanical drawing of Cu in the slag had occurred during matte making in the crucible of the water-jacket furnace. The remaining 20% were in oxidised state.

2.2. Fusibility of the slag and substitution of metal oxides

The thermodynamic calculations were done considering a molten slag, a reactant (e.g. C, CaS, FeS) and a gas phase at temperatures in the range of between 1250 and 1300 °C. Particular precautions were considered to maintain the slag in the liquid state.

Indeed, the ternary phase diagram of the slag system FeO-CaO-SiO₂ predicts fusibility of the slag for the highest limits in CaO at 28% and SiO₂ at 38%. At this high level of SiO₂, however, polymerisation reactions occur readily between the silicate anions, thus producing three-dimensional structures with high viscosity that may lead to reduced fluidity and slow separation of the matte from the slag. In addition, high corrosion of the MgO-based refractory may also result from the increased acidity of the slag. For these reasons, one should counter any tendency of increasing the SiO₂ level during the reduction process. FeO can be added for that purpose as it helps to lower the surface tension and the viscosity of the slag by breaking the polymerised chains. The ternary diagram, however, suggests an upper limit of the FeO content at 29% for the slags fusible at 1250 °C. The FeO content in the starting slag, being already at that limit, cannot be increased further during the cleaning process.

Another option is to introduce lime into the slag. Lime is a strong base that can reduce the solubility of weak bases in the slag, increasing therefore their activities by substitution, as illustrated in the following equation:

$$(CuO_{0.5} - FeO) + CaO \rightarrow CuO_{0.5} + (CaO - FeO)$$

$$(CuO_{0.5} - SiO_2) + CaO \rightarrow CuO_{0.5} + (CaO - SiO_2)$$
(2)

Similar substitutions from the slag structure also occur for ZnO and CaO making these non-ferrous metal oxides reactive with a reducing agent such as carbon or a sulphide such as CaS. Alumina can also be used for such substitution instead of CaO.

2.3. Sulphuring treatment and volatilisation

The sulphuring treatment aims at recovering copper sulphide and cobalt sulphide from the slag into the matte, whereas zinc sulphide sublimating at 1182 °C and above under atmospheric pressure would be trapped in bag filters as a dust.

For comparison purpose, the thermodynamic data for a sulphuring treatment of the slag by CaS and FeS to form Cu₂S, CoS and ZnS and SO₂ are presented in Table 3 and Table 4, respectively.

Table 3 Thermodynamic data for the sulphuring treatment by CaS at 1500 K or 1223 $^\circ\text{C}$

Oxide sulphured	$\Delta G_{1500\mathrm{K}}$ (kcal)	Κ	$\Delta H_{1500\mathrm{K}}$ (kcal)	Character
Cu ₂ O	-42.873	17.7×10^{5}	-4.931	Exothermic
CoO	6.291	0.1212	4.204	Endothermic
ZnO	-14.8	143.40	6.679	Exothermic

Table 4

Thermodynamic data for the sulphuring treatment by FeS at 1500 K or 1223 °C

Oxide sulphured	$\Delta G_{1500\mathrm{K}}$ (kcal)	Κ	$\Delta H_{1500\mathrm{K}}\mathrm{(kcal)}$	Character
Cu ₂ O CoO	-31.363 5.279	37150 0.1701	-25.444 -16.309	Exothermic Exothermic
ZnO	-3.23	2.956	-13.834	Exothermic

The basic reaction considered is

$$M_x O + CaS \rightarrow M_x S + CaO \tag{3}$$

It is inferred from Tables 3 and 4 that a sulphuring treatment will not be efficient in the case of CoO and ZnO as the equilibrium constant of the corresponding reactions are low. However thermodynamics predicts good reactivity between Cu₂O and CaS as well as between Cu₂O and FeS. The decantation time necessary to separate the Cu₂S formed from the slag can be approximated using the empirical law [3,5,7]:

$$\frac{dC_{Cu}^{slag}}{dt} = 2.303(K_{1i}K_{2i} - K_{2i}C_{Cu}^{slag})$$
(4)

where K_{1i} and K_{2i} are parameters, respectively, equal to 0.26 wt% and 0.00105 min⁻¹ for a slag composition of 29 wt% FeO, 31 wt% SiO₂, 10 wt% CaO.

Substitution of these values in Eq. (4), considering an initial slag containing 1.4-1.5 wt% Cu and a final slag with 0.5 wt% Cu would yield, after integration, about 16 min as decantation time after sulphuring to separate Cu₂S from the slag.

However, sulphuring the slag will have the shortcoming of losing the unreacted CoO and ZnO to the slag. It also presents a risk of increasing the FeO level of the slag beyond 29 wt% if FeS is used as reactant. This may take the slag out of the fusibility domain of the FeO-CaO-SiO₂ system at 1250 °C.

2.4. Reducing treatment during smelting

Smelting in a reducing environment aims at recovering the nonferrous metals Cu and Co in a liquid phase containing the metals and the corresponding sulphides after decantation. Since zinc boils at 911 °C, it would therefore be collected in bag filters together with the lead. Table 5 shows the thermodynamics data for the reducing reactions.

According to Table 5, the thermodynamics is favourable for the reduction of the four metals of interest (Pb, Co, Cu and Zn), but contamination of the metal phase by iron, and to some extent by lead, is also likely to happen.

Table 5

Thermodynamics data for the reduction of slag oxides by C with formation of CO at 1223 $^\circ\text{C}$

Oxide reduced	$\Delta G_{1500\mathrm{K}}$ (kcal)	K	Character
Cu ₂ O	-43.934	25×10^5	Exothermic
CoO	-27.425	$9.91 imes 10^3$	Exothermic
ZnO	-19.336	657	Exothermic
PbO	-39.75	62×10^3	Exothermic
FeO	-17.23	324	Exothermic

The Ellingham diagram shows that the stability lines of ZnO and FeO are very close to each other, which suggests that reduction by C will occur simultaneously for the two oxides. However, according to thermodynamics data the reaction, as shown in Eq. (5), can take place, thus enhancing the emission of zinc vapour and limiting the contamination of the metal phase by iron:

$$ZnO + Fe \rightarrow Zn + FeO$$
 (5)

$$G = 53.370 + 10.355 \log T - 67.43T \tag{6}$$

$$\log k_p = 17.731 - \frac{11.666}{T} - 2.262 \log T \tag{7}$$

and

$$\log p_{\rm Zn} = \log k_p - 0.301 \tag{8}$$

The corresponding partial pressures of zinc are 0.372 and 0.607 atm at 1250 and 1300 $^{\circ}$ C, respectively. These high values of partial pressure imply that the emission of zinc vapour will be significant and the reduction of ZnO will take place preferably to that of FeO.

2.5. Main consideration

From thermodynamic considerations, sulphuring will not be efficient for the recovery of cobalt and zinc and will also lead to significant modification of the slag composition. However, the direct reduction of the molten slag by carbon may be efficient for the simultaneous recovery of lead, cobalt, copper and zinc from this slag. Hence this is the method considered in the current experimental work. Carbon used for the reduction process will be added in the form of a metallurgical coal.

3. Experimental procedure

Direct reduction of the copper smelting slag by carbon was conducted in an electric furnace with horizontal electrodes, model Barnes Birlec, 550 kVA, 550 V.

The temperature was fixed at between 1200 and $1250 \circ C$ in all the experiments.

The weight of metallurgical coal was calculated considering the average composition of the slag given in Table 1, and 80% weight of carbon in the coal. This consideration yields a ratio w = weigh of coal/weight of slag = 2.56%. Note that the reduction of FeO was not considered.

Three values of the ratio w = 2.56%, 5% and 10% were considered in this study to elucidate the effect of higher w values on metal recovery and iron contamination. However, experiments conducted using the high w value of 10% did not yield satisfactory results and the results were thus only briefly mentioned. Two loading conditions were considered. In the first case, coal was added to the molten slag, while in the second case, coal was premixed with the solid slag before loading into the furnace. The reduction time of the molten slag was varied from 30 to 120 min. Twenty kilograms of slag and the corresponding weight of coal were loaded into the furnace for each experiment. The separation of the metal phase from the slag was done by decantation and by a two step tapping: first the slag and then the metal phase. The gas and the dusts formed during reduction were drawn in by a centrifugal exhauster and sent back to the bag filters through a channelling system of stainless steel. The metal phase, the dusts and the slag were analysed using atomic absorption spectroscopy.

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4. Results and discussion

4.1. Coal added to the molten slag at $1250 \degree C$

The first series of experiments consisted of a direct reduction by loading the coal in the furnace once the slag was completely molten. The amount of copper, cobalt, lead and zinc recovered in the metal phase and in the dust is presented in Figs. 1 and 2 for the ratio w = 2.56% and 5%, respectively.

The corresponding chemical compositions of the metal phases and the residual slags after reduction are shown in Fig. 3a and b, respectively, for the ratio w = 2.56%; and in Fig. 4a and b for w = 5%.

Close to 60% of the copper contained in the slag are recovered in the metal phase after 30 min of reduction when w = 2.56% (Fig. 1). The slag contains less than 0.5 wt% Cu and the metal phase contains between 23 and 29 wt% Cu, in the reduction times considered (Fig. 3a and b). The recovery of copper increased from 60% for the *w* value of 2.56–80% when *w* is increased to 5% as shown in Figs. 1 and 2. The cleaned slag thus also contained less copper, 0.4 wt%. However, the Cu content in the metal phase dropped to between 11 and 14 wt% due to an increased Fe contamination, especially at long reduction times of over 100 min.

By increasing the coal-to-slag ratio to 10%, the degree of metal recovery was not improved. Instead the contamination by iron became unacceptably high in this case with metal phases containing up to 60 wt% Fe. This amount of Fe contamination is also observed for w = 5%, but the amount of metal recovery was better than for the case of w = 2.56%.

The recovery of cobalt from the initial slag was found to be 2 times higher when the coal-to-slag ratio *w* increased from 2.56% to 5%. The recovery of cobalt increased from 70% after 30 min reduction to 90% after 120 min reduction, for w = 5%. The slag contained less than 0.5 wt% Co. The metal phases were richer in cobalt



Fig. 1. Recovery of copper, cobalt, lead and zinc for coal-to-slag ratio w = 2.56%, coal added to molten slag.



Fig. 2. Recovery of copper, cobalt, lead and zinc for coal-to-slag ratio w = 5%, coal added to molten slag.



Fig. 3. (a) Metal phase composition after reduction for w = 2.5%, coal added to molten slag. (b) Slag composition after reduction for w = 2.56%, coal added to molten slag.

(24–26 wt%), for the lower *w* ratio of 2.56%. The cobalt contents in the metal phase were slightly lower, 20–22 wt%, for the ratio w = 5%. The higher ratio w = 10% yields similar results to those of w = 5%. Again this is a direct result of the higher Fe contamination at the higher *w* ratios.



Fig. 4. (a) Metal phase composition after reduction using a ratio w = 5%, coal added to molten slag. (b) Slag composition after reduction using a ratio w = 5%, coal added to molten slag.

t (min)		Compositio	omposition (wt%)									
		Cu	Со	Zn	Fe	CaO	SiO ₂	Pb	S			
	Final slag	0.56	1.42	5.9	23	11.6	33.75	0.2	0.95			
15	Metal	42	28	1.1	23							
	% recovery	47	27	28	15							
	Final slag	0.47	1.46	5.2	22	11.0	32.5	0.16	0.11			
60	Metal	35	26	1.1	28							
	% recovery	56	25	37	19							

Table 6 Phase compositions for w = 2.56% at different reduction times *t* after complete melting

Coal and solid slag were mixed and homogenised at room temperature prior to charging into the furnace.

For the *w* ratios of 2.56% and 5%, fuming of lead and zinc was efficient as the %Pb of the residual slag dropped to levels lower than 0.04% after 30 min of reduction. Over 90% of the lead was removed from the initial slag and collected in the dust. The zinc content of the slag quickly dropped to between 1 and 3 wt% from the initial 8.2% after 30 min reduction. The recovery of zinc was higher than 70% after 60 min of reduction. The metal phases were poor in zinc; with only 1.5 wt% because zinc volatilised above 911 °C and was predominantly collected in the bag filters.

4.2. Coal mixed with solid slag before loading the reduction furnace

In the second series of experiments, the initial slag and the coal were mixed and homogenised before being charged into the furnace. The heating of the loaded furnace up to $1250 \degree C$ took 120 min. The corresponding results for a ratio w = 2.56% are illustrated in Table 6.

The recovery of copper, cobalt and zinc remained low for w = 2.56%, while the fuming of the lead remained higher than 90%.

The recovery of the metals from the slag is presented in Fig. 5 for a ratio w = 5%, and the corresponding metal phase compositions are shown in Fig. 6.

It is inferred from Figs. 2 and 5 that the recovery of zinc decreases whereas the reduction of FeO is enhanced when the coal is mixed with the solid slag before loading the furnace. FeO reduction occurs faster since Fe% peaks at 60 min in Fig. 5 and at 120 min in Fig. 2. Faster reduction rate could be the result of homogenisation of the charge This implies that in solid state the reduction of FeO takes place preferentially to the reduction of ZnO. This seems not to be the case in liquid state or at higher temperature where the continuous removal of the zinc vapour from the reactor enhances the reduction of ZnO. The slag obtained after reduction under these conditions contained less than 0.5 wt% Cu and less than 0.5 wt% Co, similar to the case where the coal was added after melting of the slag. However, the zinc content of the





Fig. 5. Recovery of copper, cobalt and zinc for coal-to-slag ratio w = 5% coal and solid slag mixed at room temperature and homogenised before loading the furnace.



Fig. 6. Metal phases compositions for w = 5% coal mixed with solid slag at room temperature and homogenised before loading the furnace.

slag remained higher than 3% in this case as shown in Fig. 7, as opposed to \sim 2% in the case when coal is added to the molten charge.

It was observed that the recovery of 80% for both copper and cobalt was achieved with the ratio w = 10% when the reduction time was higher than 180 min. Simultaneously 70% of the zinc and more than 80% of the lead were volatilised, and the metal phases contained more than 40 wt% Fe, similar to the case of w = 5%, at t > 120 min.

4.3. Dusts

Experiments that yielded more than 70% volatilisation of the total zinc from the slags were repeated for a complete analysis of the dust. The dust was captured in four bag filters. Unfortunately, the inlet of the centrifugal exhauster also introduced air into the stainless steel channelling system which probably led to some oxidation of the metals collected.

The chemistry of the dusts obtained after reduction of 20 kg of slag at $1250 \degree$ C is presented in Table 7. The *w* ratio of 2.56% and 5% only were considered for the repeated experiments as it was noted



Fig. 7. Slag compositions after reduction for w = 5%; coal mixed with solid slag at room temperature and homogenised before loading the furnace.

wt%	Туре	Composition (wt%)								Weight of dusts (g)	
		Zn	Cu	Со	Pb	FeO	CaO	SiO ₂	Al_2O_3	Cd	
5	А	56	1.70	0.18	10.8	3.87	0.67	2.50	0.40	0.12	426
5	В	60	1.50	0.18	9.6	2.58	0.75	5.50	0.40	0.15	436
2.5 2.5	A B	60 60	1.20 1.50	0.12 0.12	10.0 10.0	2.06 3.20	0.60 0.58	3.20 3.10	0.30 0.20	0.13 0.13	544 427

Table	27						
Com	position	of the dusts	obtained	after reductive	melting of	of 20 kg	of slag

- - - -

Type A: coal mixed with solid slag at room temperature. Type B: coal added to molten slag at 1250 °C.

that the higher ratio, w = 10%, led to higher contamination of the metal phase by iron.

It is inferred from Table 7, that the coal-to-slag ratio, *w*, does not have a significant effect on the composition of the dusts. The zinc content in the dusts is high enough to justify the extraction of this metal via either a hydrometallurgical or a pyrometallurgical route. Volatilisation of zinc at 911 °C and a subsequent condensation step may also be considered as an alternative process. The constraint in choosing the processing route for the extraction of zinc from the fuming dusts is their relatively high lead content which may constitute some health hazards.

The residues after recovery of zinc (60% of the total mass of the dusts) from these dusts will contain at about 8% Cu and 7% Co, making them suitable for further hydrometallurgical extraction of Cu and Co.

4.4. Acidity index of the slag after reduction

It is inferred from Figs. 3b, 4b and 7 that the silica content of the residual slag increases after reductive melting when the ratio of coal to slag increased to w = 5%. It also appears that the silica content of the residual slag is more dependent on the ratio w than on the duration of reduction. The effect of the ratio w is more pronounced when the coal is mixed with the solid slag at room temperature before loading the furnace. Mixing coal with solid slag before loading the furnace led to oversaturated residual slag containing more than 38% SiO₂ and to acidity indexes higher than 1.8 from an initial value of 1.5. The residual slags become therefore more corrosive and viscous. This oversaturation in SiO_2 in the slag is mainly due to the reduction of FeO during the treatment. Consequently, adding CaO to the slag during reduction may be seen as a remedy in order to maintain good metallurgical properties for separation between the phases, as well as for retaining high fluidity of the slag and reducing the consumption of the furnace refractory.

5. Conclusion

In this study it can be concluded that the recovery of heavy metals Co, Cu, Pb and Zn from the copper matte smelting slag from the water-jacket furnace is feasible. The recoveries of these heavy metals were increased substantially when the coal-to-slag ratio, w, was increased from 2.56% to 5%. The lower w ratio of 2.56% yielded a recovery rate of less than 50% for copper and less than 60% for cobalt. However, increasing w to 5% allowed the recovery of 65–90% of Cu, Co and Zn simultaneously after 30–60 min reduction of the molten slag, in the case when coal was added to the molten slag. The recovery attained was slightly less (60–80%) when coal was premixed with the slag.

Lead fuming from the slag is higher than 90% in all the experimental conditions considered in this study.

The lower *w* leads to higher copper (23-35%) and cobalt (24-26%) contents in the metal phases whereas the contamination by iron is kept lower. These contents drop to about 12% and

20%, respectively, when the ratio w = 5% is applied, due mainly to a higher contamination by iron.

Treatment of 20 kg of slag produces at about 0.8 kg of the metal phase.

Further separation of copper, cobalt and zinc is thermodynamically feasible in the temperature range used experimentally, considering that

- The solubility of copper in iron is less than 10%,
- The solubility of copper in cobalt is less than 12%,
- Cobalt has complete miscibility with iron.

The metal phase obtained after cleaning the water-jacket furnace slag would therefore consist of two different and distinctly separate phases, one phase rich in copper and the second phase which rich in cobalt and iron while containing less copper. The two metal phases (the first red and the second grey) were clearly visible after decantation and solidification.

The zinc content of the dust is about 60%. However, separation from lead should be carefully considered as this heavy metal is harmful to the human health. Treatment of 20 kg of slag produces about 0.5 kg of the zinciferrous dusts.

Reduction of the FeO occurs faster when the coal and the solid slag are premixed at room temperature. This subsequently results in even higher iron contamination of the metal phase and an increase of the silica content of the residual slag above the saturation limit (>38%), after 120 min of reduction. The acidity index of the final slag becomes higher than 1.8.

In the case where the coal is added to the molten slag, the optimum conditions for the direct reduction of the slag using a metallurgical coal, especially with the aim to maximise metal recovery and reduce Fe contamination, is to apply low ratios of coal-to-slag weights (*w*). The *w* ratio of between 3.5% and 4% should be considered for a reduction time of about 60 min. Recoveries of higher than 70% for zinc and 80% for copper and cobalt from the slag can be achieved under these conditions.

The chemistry of the zinciferrous dust is not dependent on the ratio *w*.

The process temperature should imperatively be kept lower than 1400 °C as the thermodynamics predicts a predominant reduction of the FeO above this temperature.

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