Galvanic sludge metals recovery by pyrometallurgical and hydrometallurgical treatment

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Abstract

This paper reports a study, on laboratory scale, of sulphating roasting to perform a treatment for a selective recovery of valuable metals from galvanic sludge. The target metals were copper, zinc and nickel and the sulphating agent used was pyrite, from coal wastes. The particularity of this treatment is the use of two hazardous wastes as raw material. They are generated in large quantities at coal extraction sites (coal wastes) and at plating shops (galvanic sludge).

The wastes were characterized by X-ray fluorescence (XRF), particle size distribution and water contents. The chemical characterization showed sludges with high copper concentration, with more than 14% (dry base). In the roasting step, the galvanic sludge was mixed with pyritic waste and the parameters evaluated were galvanic sludge/pyrite ratio, roasting temperature and roasting time. After roasting, the product of reaction was leached with water in room temperature for 15 min. Considering that other studies have already demonstrated that the pyrometallurgical step determines the process efficiency, this paper only reports the influence of pyrometallurgical parameters. Hydrometallurgical processes will be better evaluated in further studies.

The conditions that best reflect a compromise between the valuable metal recover and the economical viability of the process were achieved for 1:0.4 galvanic sludge/pyrite ratio, 90 min of roasting time and 550 °C of roasting temperature. These conditions lead to a recovery of 60% zinc, 43% nickel and 50% copper.

1. Introduction

Considering the present natural resources depletion, several researchers are looking for alternatives that treat industrial wastes and post use products with the objective to transform them in secondary raw material. The second relevant aspect of this kind of research, but not less important, is that, metallic scraps and sludges, when not correctly managed, are promising sources for environmental disasters.

Galvanic processes are based on metal plating baths and rinsewaters. They generate effluents with a metal concentration varying with the installed process. Traditional systems reduce the toxicity of wastewater by aggregating disposed aqueous solutions of various concentrations, followed by treatment with chemicals to coagulate, flocculate, and settle out solid wastes for off-site disposal [1]. This solid waste is listed on Brazilian Standard NBR10004 as hazardous and classified as F006 [2]. This code is also found in the Code for Federal Regulations, used by EPA agency [3]. This classification is based on heavy metals contents, as published by Magalhães et al. [4] and Bernardes et al. [5], like copper, zinc, lead, nickel, etc.

Medium and large plating shops generate, monthly, between two and three tons of this solid waste, also called galvanic sludge (GS) and, in southern of Brazil, the number of plating shops or industries that work with surface finishing is more than 500. Nowadays the majority of the waste generated is disposed on landfill sites [6].

Galvanic sludges presents chemical compounds like hydroxides, hydrate oxides and metal salts used in finishing operations (of chromium, nickel, zinc, cadmium, tin, lead, copper, etc.). Calcium carbonates, sulphates and phosphates are usually

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present when the neutralization of the stream is done with lime [6].

There are several treatment routes proposed in the literature to avoid dumping, or in other words, recycle the wastes. They can be divided into three processes: hydrometallurgical, pyrometallurgical and a mixed of both. The examples of hydrometallurgical processes are reported by Vegliò et al. [7], Odle et al. [8], Rajcevic [9] and Silva et al. [10]. Their works are related with acid leaching and metal separations with precipitation, solvent extraction or electrowinning. The main characteristic of acid leaching is low selectivity among valuable metals and impurities. There is also a study with alkaline leaching in ammoniacal media, followed by solvent extraction, developed by Park [11]. This author concluded that alkaline leaching is much more selective, but the overall efficiency in valuable metals extraction is low. Silva et al. [12] published a comparison between acid and alkaline media in galvanic sludge leaching and the conclusions were similar.

In the pyrometallurgical process, the majority of researches just treat wastes with restricted chemical composition of selected elements or maximum and minimum concentrations [13,14]. Another use of high temperature reactions is the solidification/stabilization systems with clinker [15,16], calcium carbonate [17] and silica and feldspar [18]. These processes related with solidification and/or stabilization are not focused on metals recovery.

There is also the third option, which uses pyrometallurgical and hydrometallurgical processes associated. One alternative is the case of Nickelhütte Aue [19]. This commercial process is designed to the treatment of galvanic sludge with high copper, nickel and cobalt contents. Initially the sludge is mixed with pyrite (iron sulphide) and introduced in a furnace with oxidant atmosphere, in order to oxidize the pyrite to iron oxide and release sulphur dioxide, what changes the furnace atmosphere. The target metals are transformed in sulphide and then processed in primary metallurgy.

This work proposes a similar solution, but with atmosphere and temperature conditioned to produce selective sulphating roasting of target metals. Other authors [20,21] show the use of similar procedure to remove metals from primary and secondary copper slags. The proposed reaction, responsible to metals extraction in sulphate form, is presented below [21]:

$$MeO + SO_3 \leftrightarrow MeSO_4,$$
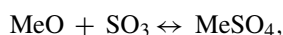
At this work, the source of sulphur dioxide is a coal waste containing pyrite, abundant in coal extraction sites. This waste can also cause impact to the environment with the possibility of presenting acid mine drainage if not carefully disposed of [22].

2. Experimental procedure

Four kinds of galvanic sludge from three different industries located in the southern of Brazil were collected at the effluent treatment plant and labeled as GS1, GS2, GS3 and GS4. The first industry works with jewellery, the second produces appliance controls and the third one acts in several areas, from manual tools to electric engines. All plating shop have a conventional effluent treatment station. They use a physico-chemical process with the consequent generation of these kind of sludges. The coal waste (CW), containing pyrite, was collected at Mina do Recreio, southern of Brazil too.

The GS samples were dried at 110 °C for 24 h in a muffle furnace and then crushed in a ball mill. The coal waste was received in dry form, so it was just crushed, first in a jaw mill and on a second step in a ball mill too. The particle size distribution was analyzed with a laser diffraction equipment (Mod. Cilas 1180).

The CW was submitted to a pre-leaching step with 25% HCl solution in order to remove limestone. This calcium compound is sulphur consumer and its presence causes a decrease in the efficiency of sulphating roasting reaction [23]. After leaching, the CW was filtered, washed and dried at 110 °C for 24 h.

After materials preparation, they were characterized by X-ray fluorescence (Mod. Shimadzu XRF 1800). The results of particle size and chemical analyses are shown in Tables 1 and 2, respectively.

The mixture of leached coal waste (LCW) and GS was placed in an alumina crucible and the sulphating roasting was carried out on a muffle furnace, which was preheated to the required temperature. The amount of GS in the samples was 3 g. The roasting variables were LCW mass (0.3–3 g), roasting time (30–120 min) and roasting temperature (450–700 °C).

After roasting, the samples were removed from the furnace, cooled off at room temperature and leached with distilled and deionized water. The volume added was 50 mL. The pulp was magnetically stirred (100 min^{-1}). After 15 min the pulp was filtered, using a Whatman no. 42 filter paper, and the volume was completed to 100 mL with consecutive washes. The leachates were then acidified to prevent metals precipitation and analyzed by atomic absorption spectrophotometry (Mod. CG AA7000 SBC).

3. Results and discussions

The chemical analyses of the leachates were used to relate the samples extractions to roasting variables. The experimental errors, determined by different experiments were ±3.5%. The results are presented in Figs. 1–12. Figs. 1–3 show the graphics related to the influence of the mass of LCW in the sulphating roasting and consequently extraction of target metals. The first figure, related to the copper extraction, shows an increase in extraction with LCW mass until the value 0.6 g. After this point there is no remarkable tendency. Although the amount of copper in the wastes GS1 and GS2 is almost the same, the extraction of this metal in the second waste, was almost zero. The following figure (Fig. 2) shows the zinc behavior and its extraction raises until 1.8 g. However, the extraction value with 1.8 g of LCW, is not considerably higher than the value extracted when the mass of LCW is 1.2 g. The nickel behavior, which is only present in GS1, was similar to zinc with a maximum value obtained with 1.8 g of LCW. Again, this value is not higher than the value obtained with 1.2 g (Fig. 3).

The solubility values of the low commercial valuable metals (Fe, Ca and Cr) are presented in Fig. 4 and Table 3. These

Table 1
Materials particle size after crushing

	Galvanic sludge (%)				Leached coal waste, LCW (%)
	GS1	GS2	GS3	GS4	
$D_{average}$ (μm)	22.26	17.49	66.7	164.17	70.22
$D_{10\%}$ (μm)	1.74	2.14	3.09	3.14	3.78
$D_{50\%}$ (μm)	16.79	12.54	36.29	71.09	28.69
$D_{90\%}$ (μm)	51.51	40.02	189.87	461.73	206.42

D = diameter.

Table 2
Solid wastes elementary chemical composition (dry base)

	Galvanic sludge (%)				Leached coal wastes, LCW (%)
	GS1	GS2	GS3	GS4	
Fe	9.6	0.8	0.16	0.2	43.2
Cu	14.7	13.9	60.2	37.8	ND
Zn	7.2	7.5	3.22	21.2	ND
Ni	3.08	ND	ND	ND	ND
Ca	0.2	10.8	ND	0.35	1.8
Al	2.35	0.11	0.19	0.46	0.6
Si	0.66	0.1	0.14	0.13	1.2
P	1.22	ND	ND	0.15	ND
Na	0.16	0.8	0.6	ND	0.4
Sn	0.26	1.01	ND	ND	ND
S	1.13	2.04	0.38	0.17	37.8
Cr	0.25	18	ND	ND	ND
H_2O	67.5	60.2	59.2	89	0.5

ND: not detected.

metals are considered as contaminants in the process, so their concentration should be as low as possible. In the figure, it is observed that iron concentration on lecheate is proportional to the increasing of LCW mass, and this tendency is explained by the increase of the iron amount available to be leached, since the LCW has high iron content. It is possible to see that solutions from GS1/LCW samples have the highest iron content and this fact is explained by the amount of iron present in the initial waste GS1 composition, as seen in Table 2. The lowest concentration value was observed in GS2/LCW samples.
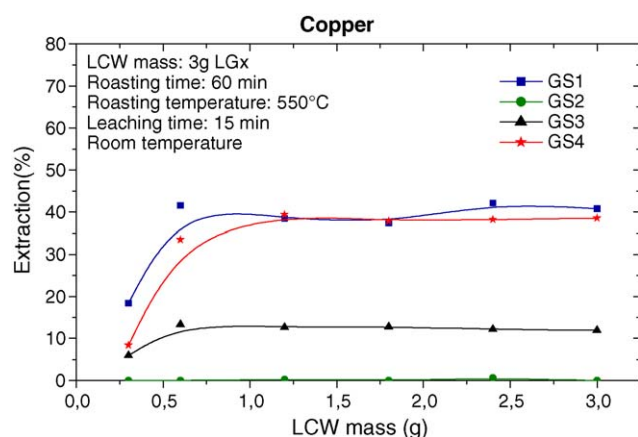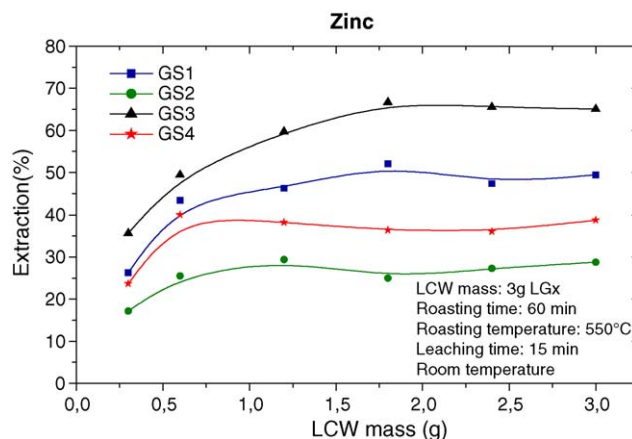

Fig. 2. LCW mass influence on zinc extraction.

Fig. 1. LCW mass influence on copper extraction.

Table 3
Influence of LCW mass in calcium and chromium concentration in GS2/LCW samples

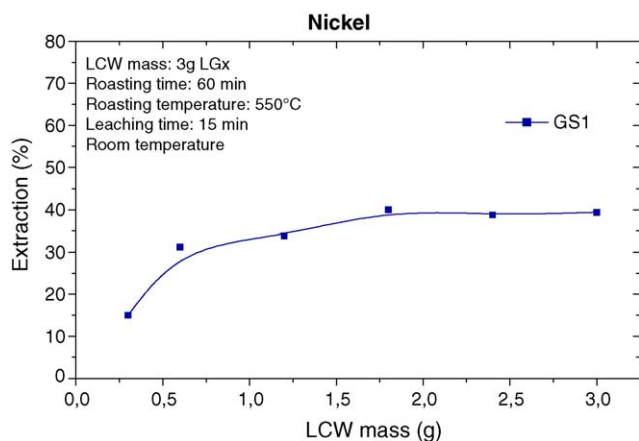|	Leached coal waste mass (g)					
Impurities	0.3	0.6	1.2	1.8	2.4	3.0
Calcium (g L^{-1})	1.1	2.1	2.5	2.4	2.5	2.6
Chromium (g L^{-1})	0.34	0.15	0.02	ND	ND	ND

ND: not detected.

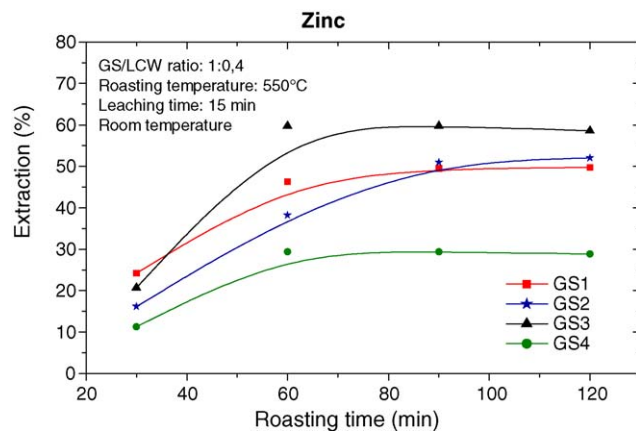Fig. 3. LCW mass influence on nickel extraction.

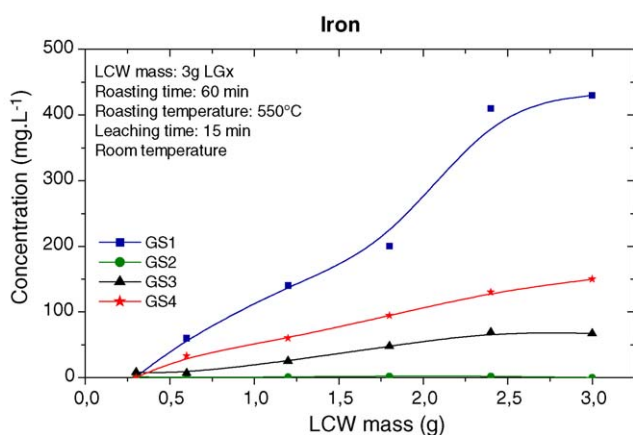Fig. 6. Roasting time effect on zinc extraction.

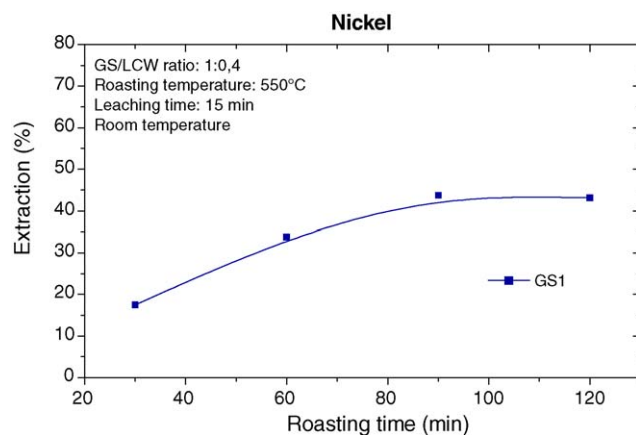Fig. 4. LCW mass influence on iron concentration in liquid samples.

Fig. 7. Roasting time effect on nickel extraction.

Chromium and calcium are present in highest concentration in GS2/LCW samples. Their concentrations in solution, related to the LCW mass, are shown in Table 3. The increase of LCW mass decreases the concentration of chromium in solution and with 1.8 g or more, there is no chromium detected.

The explanation of this fact may be related with the chromium oxidation, that is related to the amount of oxygen available. As shown in the reaction below, each 3 mol of iron sulphide

(present in LCW) needs 8 mol of oxygen gas to oxidize and release sulphur dioxide

$$3FeS_2 + 8O_2 \leftrightarrow Fe_3O_4 + 6SO_2$$
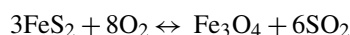
Chromium is present, in the galvanic sludge, in the trivalent form. It can be thermally transformed to its hexavalent form in oxidant atmospheres, as observed by Apte et al. [24]. So, increasing the iron sulphide amount, the oxygen available to
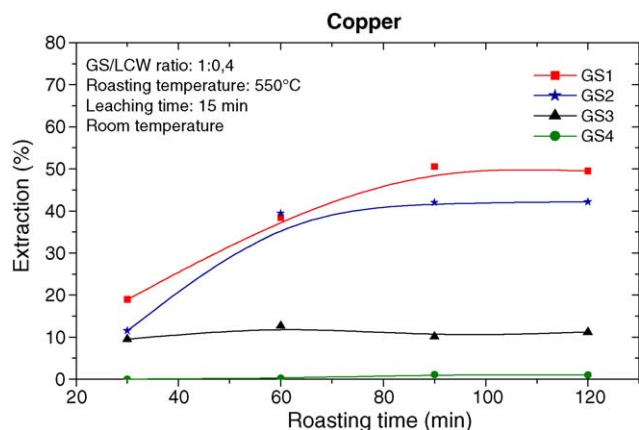

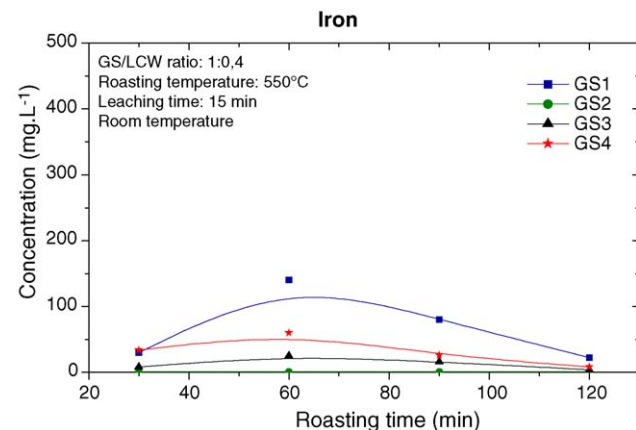Fig. 5. Roasting time effect on copper extraction.

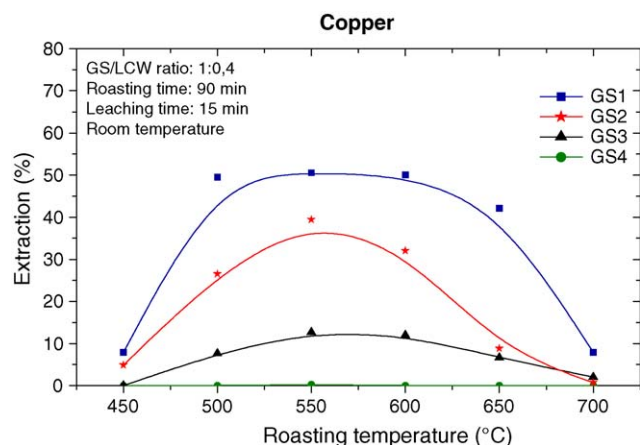Fig. 8. Roasting time effect on iron concentration in liquid sample.

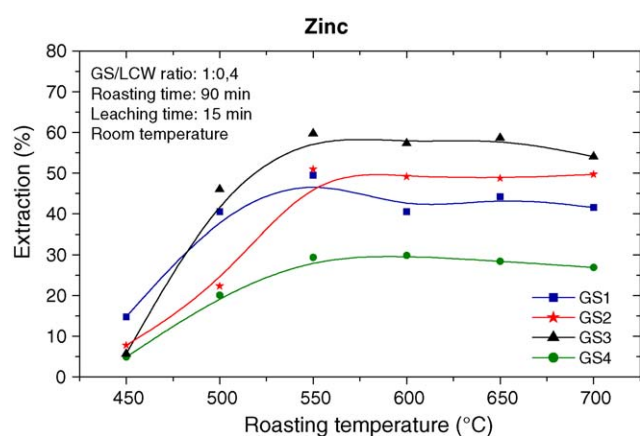Fig. 9. Roasting temperature influence on copper extraction.

Fig. 10. Roasting temperature influence on zinc extraction.

trivalent chromium oxidation decreases, inhibiting the oxidation reaction. The reaction related to trivalent chromium oxidation is shown below
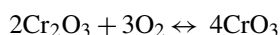
$$2Cr_2O_3 + 3O_2 \leftrightarrow 4CrO_3$$

Table 3 also shows calcium in high concentration, compared with other impurities (Fe and Cr). Thermodynamic data, present in Table 4, shows that calcium sulphate has the lowest free energy
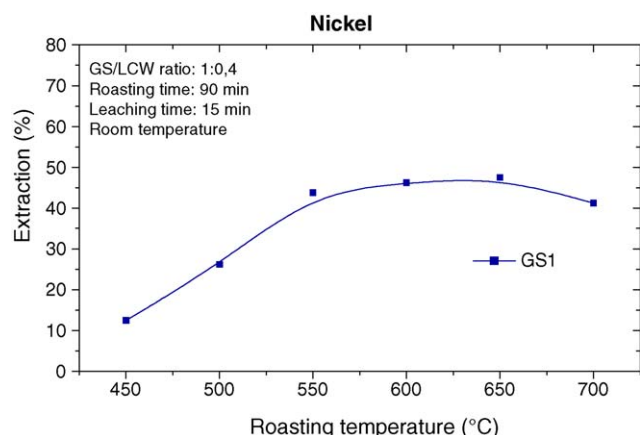

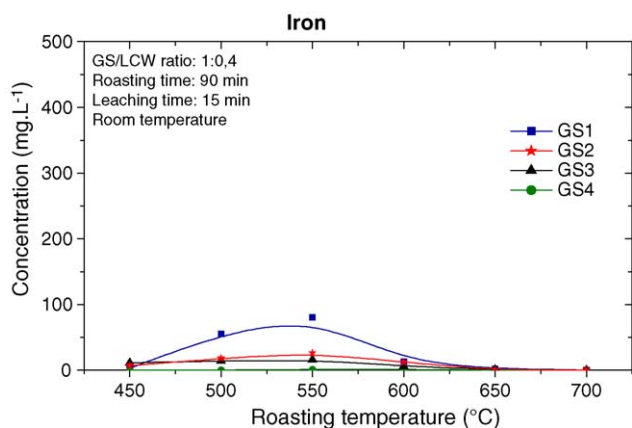Fig. 11. Roasting temperature influence on nickel extraction.

Fig. 12. Roasting temperature influence on iron concentration in liquid samples.

if compared with other metals present in the system (Cu, Zn and Fe) [25]. Since GS2 has the highest calcium concentration, the low extraction of target metals and also low iron concentration, in GS2/LCW samples, can be associated to the fact mentioned above.

By the results presented in Figs. 1–4 and Table 3, the suitable condition, related with selectivity of valuable metals over impurities and for samples with low calcium concentration is 1:0.4 GS/LCW ratio.

The effect of roasting time parameter is presented from Figs. 5–8. It is clear to see that copper extraction raises until 90 min and there is no necessity to spend more time in the roasting. One more time the waste GS2 has no copper extraction and again this behavior is related to calcium extraction.

The behavior described to copper showed to be coherent for the other two target metals (Zn, Fig. 6 and Ni, Fig. 7). So, the suitable roasting time condition is 90 min.

The amount of iron leached on the roasting time dependence is present in Fig. 8. The maximal leaching occurs with samples roasted for 60 min. From this time, the values decrease with the increasing time, probably because the thermal sulphate decomposition. With 90 min, the iron concentrations are 80, 1, 16 and 26 mg L^{-1}, respectively to wastes GS1, GS2, GS3 and GS4.

The effect of roasting temperature in metals extraction, evaluated to all studied wastes, seems to be very important to copper. This metal shows an increasing extraction until 550–600 °C and then the extraction diminishes drastically (Fig. 9). Zinc (Fig. 10) and nickel (Fig. 11) did not suffer the same influence. Tümen and Bailey [21] observed similar thermal behavior and explained through the basic copper sulphate thermal decomposition to copper oxysulphate (CuSO$_4$·CuO) and its further decomposition

Table 4
Thermodynamic data of sulphating reactions

Reactions	$\Delta G_{800\,K}$ (10^6 J)
$CaO + SO_3 \leftrightarrow CaSO_4$	−0.25
$NiO + SO_3 \leftrightarrow NiSO_4$	−0.1
$ZnO + SO_3 \leftrightarrow ZnSO_4$	−0.09
$CuO + SO_3 \leftrightarrow CuSO_4$	−0.07

Table 5
Extraction results compared with Tümen and Bailey [21]

Elements	Galvanic sludge, GS1			Copper slag		
	Initial waste (%)	Extraction (%)	Mass over 100 g (g)	Initial waste (%)	Extraction (%)	Mass over 100 g (g)
Cu	14	50	7	4.1	98	4.01
Ni	3.08	47	1.4	0.66	35	0.23
Zn	3.22	49	1.57	1.37	29	0.39
Total (g)			9.94			4.63

product, copper oxide. Both of them have limited solubility in water.

Iron leaching is also highly temperature dependent in the studied range and above 650 °C there is no more iron present in liquid samples (Fig. 12). Arslan et al. [20] and Sulka et al. [26] used the iron sulphate thermal decomposition above 650 °C to diminish the high amount of iron present in lecheates samples.

Comparing the results achieved in this work with the results obtained by Tümen and Bailey [21], the roasting temperature is the same but roasting time and pyrite/waste slag are slightly different. Extraction values in Table 5 shows that Tümem et al. [18] obtained higher percentual extraction but lower total mass extraction.

4. Conclusions

Although the target metals extraction did not reach expressive values, i.e., higher than 90%, the results are relevant. Sulphating roasting, in selected conditions, shows to be selective over process impurities, like iron and chromium, which remains in the solid waste while target metals are extracted.

Calcium proved to be harmful to metals extraction. This is explained to the higher affinity with sulphur dioxide than target metals.

Optimum sulphating roasting conditions, reflecting the compromise with valuable metals recovery and economical viability of the process were achieved with 550 °C of roasting temperature, 90 min. of roasting time and 1:0.4 GS/LCW ratio.

With proposed parameters, the results achieved in target metal extraction were 60% zinc, 50% copper and 43% nickel. The maximum iron concentration in solution was 80 mg L^{-1}.

Further studies are going to be done related to suitable conditions in hydrometallurgical step, i.e., pulp density, leaching temperature, leaching time, etc. Besides this, probably better recoveries could be achieved in a rotary roasting furnace.

Acknowledgment

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