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Liquid–Liquid Extraction Applied to Metals Separation from Waelz Oxide

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ABSTRACT

Metal recovery from "Waelz oxide," the product obtained from steel foundry dusts through a pyrometallurgical process, and the slag obtained in this process has been carried out by liquid–liquid extraction. For this purpose, leaching of the solid samples was attained by microwave digestion with HCl. The extraction of 13 elements in the leachates was studied using the alkylthiophosphinic acid Cyanex 302 in kerosene and varying the acidity conditions and the extractant concentration. The experimental results on the extraction of cadmium, lead, and zinc have been compared with the theoretical behavior obtained by taking into account equilibrium extraction data reported for the extraction of these elements from synthetic individual solutions.

INTRODUCTION

Steel foundry dust is the solid-phase exhaust from filtration units in steel industries. Zn and Pb are the most important elements in the solid composition, although significant amounts of other toxic metals (Cd, Cu, Cr etc.) are also present. The pyrometallurgical Waelz process recovers Zn and Pb from steel foundry dusts, generating the "Waelz oxide" which is used in the Imperial Smelting Ovens for Zn recovery.

Figure 1 shows a scheme of the Waelz Plant of the ASER Company in Vizcaya, Spain (1). In this plant the steel foundry dusts are introduced into the rotary oven together with auxiliary materials (coke and silica). Metals are sublimated from the solid and oxidized into the oven atmosphere during the

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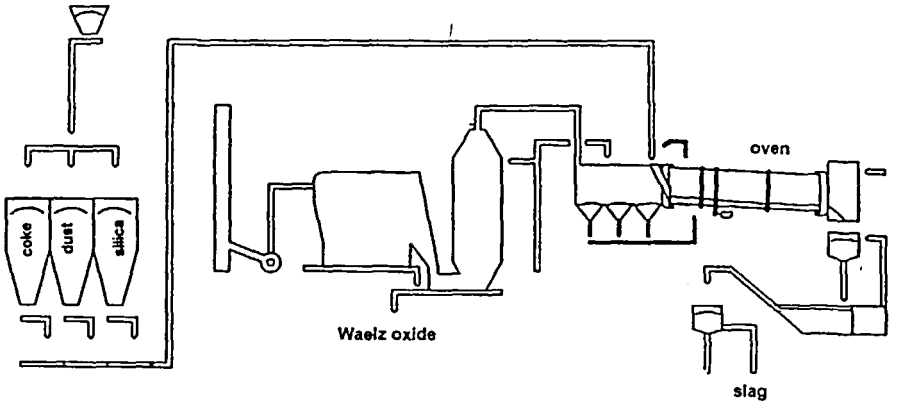

FIG. 1 Scheme of Waelz Plant in Asúa (Vizcaya, Spain).

process, so mainly zinc and lead oxides are obtained. A slag is obtained at the same time. Table 1 summarizes the composition of Waelz oxide and "slag" samples from the Waelz Plant of ASER. As can be seen, the major components in the Waelz oxide are Zn and Pb that can be recycled through fusion processes in the Imperial Smelting Ovens. However, significant

TABLE 1
Waelz Oxide and Slag Composition
Determined by X-Ray Spectrometry

Element	Waelz oxide (%)	Slag (%)
S	0.9	1.3
Mn	0.4	4.3
Si	0.2	15.6
Cu	0.3	0.7
Ni	<0.1	0.3
Cd	0.3	<0.1
Fe	4.8	26.3
Pb	9.2	0.2
Cr	0.1	0.8
Ca	0.6	7.4
Zn	54.5	1.2
Al	<0.1	1.9
Sn	0.1	<0.1
C	1.0	3.6
Cl	4.8	0.2
K	1.6	0.9

amounts of other elements, some of them toxic metals, are also present. On the other hand, the slag composition shows a large amount of iron and silicium. Slag is an inert solid and can be used for roadwork. However, slag samples contain significant amounts of such valuable elements as copper, manganese, chromium, etc. that could be recovered.

In this work the liquid–liquid extraction technique is applied to samples of both Waelz oxide and slag in order to remove metal impurities. A previous leaching of the solid samples has been carried out by microwave digestion. Although some other methods for steel foundry dust leaching have been reported (2–4), for analytical purposes the microwave process provides good results as well as an important time reduction (5).

Cyanex 302 is a commercial reagent manufactured to recover metals from acidic media. Its active component, bis(2,4,4-trimethylpentyl)thiophosphinic acid (6), has been used as an extractant. Since studies on Cd, Pb, and Zn extraction by Cyanex 302 from synthetic chloride media have been reported (7–9), the experimental results have been compared with the theoretical behavior obtained by taking into account the corresponding extraction equilibrium constant values.

EXPERIMENTAL

Waelz oxide and slag samples were supplied by ASER S.A. from the Waelz Plant in Asúa (Vizcaya). Leaching of these solids was carried out using a microwave digestor CEM MDS-2000 with HCl (Merck, p.a.).

Half a gram of solid and 10 mL of concentrated HCl were put in each microwave vessel. The solid digestion was achieved in 20 minutes at 160 psi. After this procedure a solid residue remained in each digestion vessel.

Elements in the solid phase were measured by x-ray fluorescence spectroscopy using a Siemens SRS 303 spectrometer.

Elements in the aqueous phase were measured by inductively coupled plasma spectroscopy (ICP) using an ARL 3410 spectrometer equipped with a mini-Torch. The experimental procedure included the refinement of the spectral lines, the calibration of the elements, the calibration of the interferences, and the analysis of the samples. Thirteen elements were analyzed, and in each case standard solutions of the elements (Merck) were used.

The extraction procedure of metal ions from leachates of both Waelz oxide and slag was carried out using Cyanex 302 (supplied by Cytec Canadá Inc) in kerosene (Fluka p.a.) at different concentrations (1.48–7.72% w/v) prepared daily. The acidity of the aqueous solutions was modified by adding KOH. Equal volumes of both phases (10 mL) were shaken in special stoppered tubes for 30 minutes. After phase separation using a high-speed centrifuge (Centaur 2 MSE), the composition of the aqueous phase was measured by ICP.

RESULTS AND DISCUSSION

Digestion of Solid Samples

A residue of 2.6% of the Waelz oxide sample was obtained with the microwave digestion, whereas the solid residue from the slag was near 33%. This difference can be attributed to the different compositions of the two solids, and mainly to the high content of Si in the slag sample which makes the leaching process more difficult in the conditions of the assay.

Figure 2 shows the comparison between the composition of the Waelz oxide and its residue determined by its x-ray fluorescence spectroscopy. Si

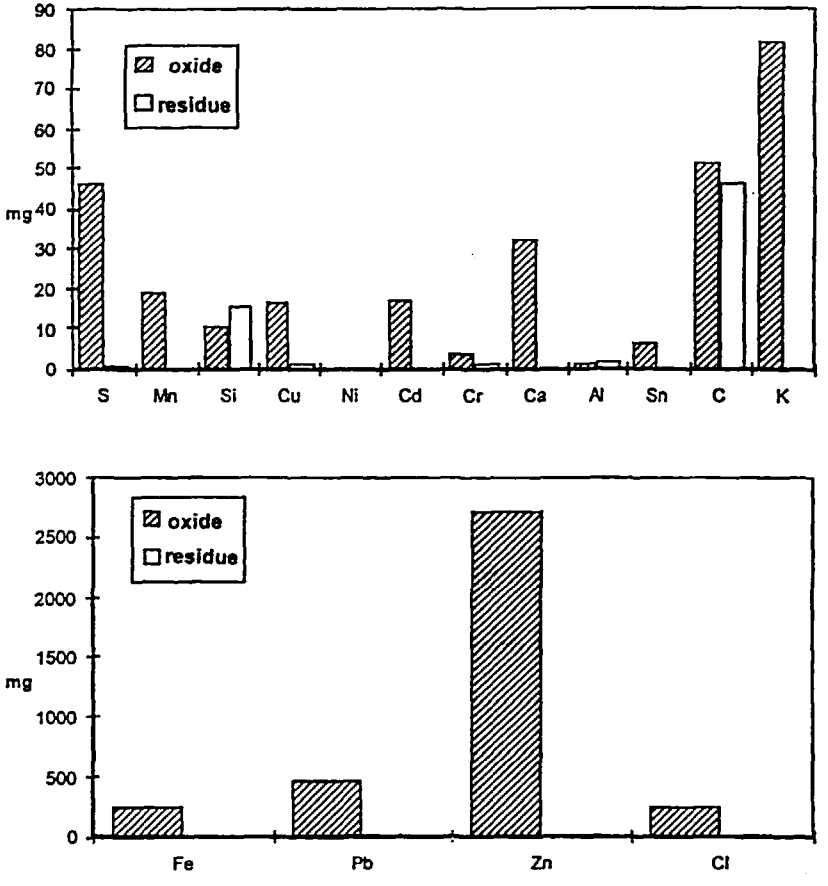

FIG. 2 Comparison between the composition of Waelz oxide and its digestion residue.

TABLE 2
Composition (ppm) of Hydrochloric Leachates of Waelz Oxide and Slag, Measured by ICP

Element	Waelz oxide	Slag
S	94 ± 4	11.4 ± 0.1
P	57 ± 2	5.8 ± 0.7
Mn	31 ± 1	360 ± 3
Cu	33.3 ± 0.1	87.9 ± 0.8
Ni	1.3 ± 0.1	30.4 ± 0.3
Pb	859 ± 4	197.7 ± 0.3
Cd	30.7 ± 0.4	0.73 ± 0.01
Fe	315.6 ± 0.9	2797 ± 17
Mg	15.2 ± 0.4	93.5 ± 0.4
Cr	3.0 ± 0.1	17.2 ± 0.2
Ca	54.4 ± 0.4	483 ± 3
Zn	5253 ± 62	98 ± 1
Al	13.9 ± 0.1	153 ± 1

and C remain in the solid residue, whereas practically all the metal content is present in the aqueous solution.

Table 2 summarizes the composition of both hydrochloric leachates (Waelz oxide and slag) measured by ICP. Together with the major components of the Waelz oxide (zinc and lead), other elements, some of them toxic metals, are present in the leachates. On the other hand, leaching of the slag revealed a high iron concentration and significant quantities of manganese, calcium, copper and aluminum.

Liquid–Liquid Extraction of the Leachate of the Waelz Oxide

Several extraction experiments were performed using different Cyanex 302 concentrations (1.91, 4.06, and 7.72%) in kerosene at various acidity conditions in the aqueous phase. The composition of the aqueous phase was always measured before and after the extraction process. The results obtained indicated that the elements manganese, nickel, magnesium, calcium, and aluminum did not change their concentration during the extraction process in any of the conditions studied. On the other hand, P and S increased their concentration after the extraction process. This increase was larger when high extractant concentrations and strong acidic conditions were used. This fact can be attributed to the solubilization of some extractant impurities, probably short-chain organophosphorus acids.

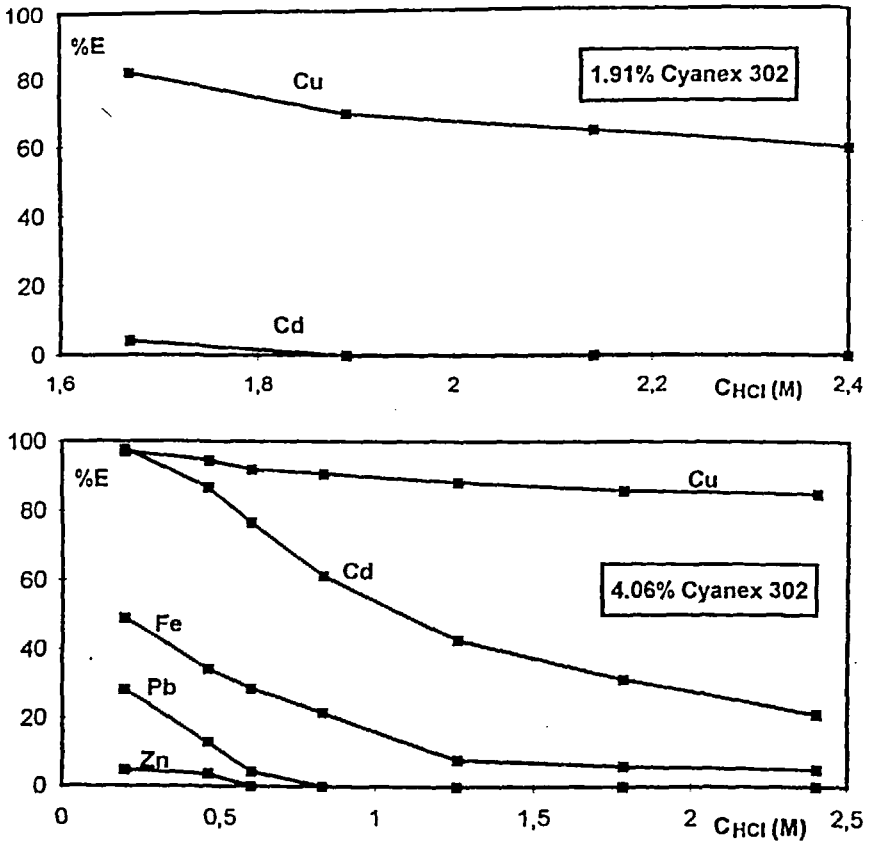

FIG. 3 Experimental results of metal extraction from leachate of Waelz oxide with different Cyanex 302 concentrations.

Only the elements copper, cadmium, iron, lead, and zinc were extracted by Cyanex 302 in the experimental conditions used. Figure 3 illustrates the results for the extraction of these metals when the extractant concentration and the acidity conditions were varied.

From these results it can be said that the extraction order using Cyanex 302 in hydrochloric media is Cu > Cd > Fe > Pb > Zn the selective extraction of copper from the rest of these elements is possible by using 1.91% Cyanex 302 in the organic phase. Only a small percentage of cadmium is extracted when the sample acidity is decreased with 2 M HCl. If 4.06% Cyanex 302

and 1.26 M HCl are used, 88% Cu, 43% Cd, and 8% Fe can be removed, with the rest of the elements remaining in the leachate. This situation is interesting because Pb and Zn (the major components of Waelz oxide) remain in the aqueous solution and the above impurities can be removed. At the same extractant concentration and 0.2 M HCl (pH ≈ 0.77), quantitative Cu and Cd extraction together with significant amounts of Fe, Pb, and Zn are obtained. However, when higher Cyanex 302 concentrations were used, significant quantities of Pb and Zn are extracted in all the acidity conditions.

On the other hand, the above results indicate that after a first stage for copper removal, it is possible to remove cadmium quantitatively which is interesting because of the high toxicity of this element. The iron coextracted with cadmium could be removed from the extracted solution by precipitation.

The experimental results of the extraction of Cu(II), Cd(II), Fe(III), and Pb(II) were fitted to Freundlich isotherms within the experimental range. The extraction of Zn(II) was not considered since it is not significant in the conditions of the study.

Consider the expression

$$C_{org} = \beta C_{aq}^{n}$$

C_{org} and C_{aq} are the equilibrium concentrations of the metals in the organic and the aqueous phases, respectively, and n is the Freundlich exponent, which in this case is a function of the acidity in the aqueous phase (C_{HCl}) according to

$$n = 1/[1 + \alpha(C_{HCl} - C_{HCl}^{0})]$$

where α and β are parameters of the fit, characteristic for each metal, and C_{HCl}^{0} is the hydrochloric concentration taken as a reference. The obtained parameters were $\alpha = 1.25$, $\beta = 17.6$, and $C_{HCl}^{0} = 0.46$ for copper; $\alpha = 2.04$, $\beta = 6.61$, and $C_{HCl}^{0} = 0.46$ for cadmium; $\alpha = 0.49$, $\beta = 0.96$, and $C_{HCl}^{0} = 0.20$ for iron; and $\alpha = 1.30$, $\beta = 0.39$, and $C_{HCl}^{0} = 0.20$ for lead.

The isotherms obtained for Cu, Cd, Fe, and Pb at two different acidity conditions (1.78 and 0.60 M HCl), when 4.06% Cyanex 302 in kerosene was used as the extractant and taking into account the above parameters, are shown in Fig. 4.

Comparison of the Theoretical and Experimental Behavior of Cd(II), Pb(II), and Zn(II)

Cd(II), Pb(II), and Zn(II) extraction equilibria data for Cyanex 302 from 1 M KCl medium are available (7–9). No equilibrium data for Fe(III) and Cu(II) extraction can be found, although the order of extraction, Cu > Cd > Pb > Fe > Zn, has been reported in chloride media (10).

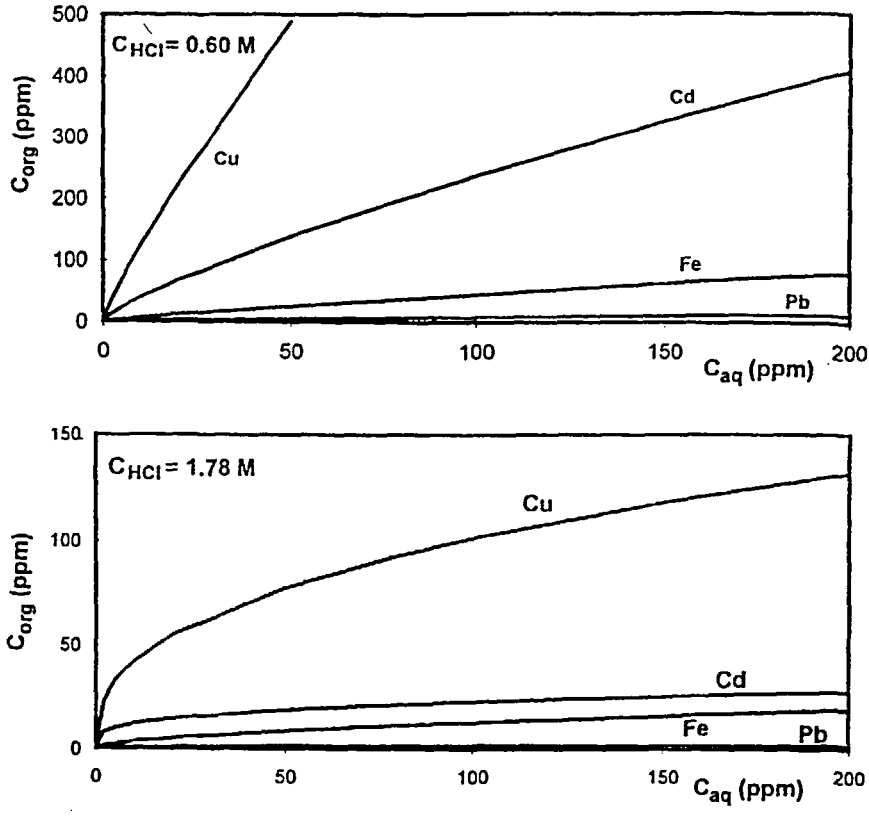

FIG. 4 Cu(II), Cd(II), Fe(III), and Pb(II) uptake isotherms at two different acidity levels.

Menoyo et al. (8) reported that $PbR_2(HR)$, $PbL_2(HL)$, and PbLR(HR) are the species responsible for lead extraction from 1 M KCl by Cyanex 302 in toluene, with log k_{ex} = 2.95, 11.65, and 6.34, respectively. HR represents bis(2,4,4-trimethylpentyl)thiophosphinic acid, the major component of the extractant (79% purity), and HL stands for bis(2,4,4-trimethylpentyl)dithiophosphinic acid, a Cyanex 302 impurity (1.4%). On the other hand, Benito et al. (9) indicated that zinc extraction from 1 M KCl by Cyanex 302 in toluene is due to ZnClR(HL), $ZnR_2(HR)_2$, ZnL_2, and $ZnL_2(HL)(HR)_3$ formation, with log k_{ex} = 0.87, 2.23, 1.92, and 9.60, respectively. Finally, cadmium extraction from 1 M KCl by Cyanex 302 in kerosene has been explained through the formation of the species $CdR_2(HR)$ and $CdR_2(HR)_2$, with log k_{ex} values of 5.95 and 7.52, respectively (7).

Taking into account the formation constants of all the species involved in the three individual synthetic systems, distribution diagrams of the metallic species in the biphasic system consisted of a solution of 1 M KCl containing Cd(II), Pb(II), and Zn(II) in the concentration levels corresponding to the leachate of Waelz oxide and organic solutions of Cyanex 302 in kerosene were created by means of the SED computer program (11). From these diagrams the theoretical extraction percentage of the metals as a function of the aqueous pH was calculated for a Cyanex 302 concentration of 4.06% in the organic phase.

Figure 5 shows a comparison of the experimental and theoretical extraction percentages of Cd(II), Pb(II) and Zn(II) by Cyanex 302 in kerosene. There is an acceptable agreement between both type of data. However, there are some discrepancies. For example, the theoretical extraction of Cd(II) is slightly higher than the experimental one, probably due to the higher chloride concentration in the leachate of Waelz oxide (2.4 M). On the other hand, the deviations in Pb(II) extraction at high acidity levels can be attributed to the inactivation of the small alkyldithiophosphinic acid percentage present in the composition of the commercial extractant Cyanex 302, and which has been proved to be responsible for Pb(II) extraction in these conditions (8). Finally, the theoretical and experimental results of Zn(II) extraction are almost identical and not relevant in the conditions of the study.

Liquid–Liquid Extraction of the Leachate of the Slag

Several extraction assays were made using Cyanex 302 solutions at different concentrations (1.48, 4.56, and 6.02%) and modifying the leachate slag

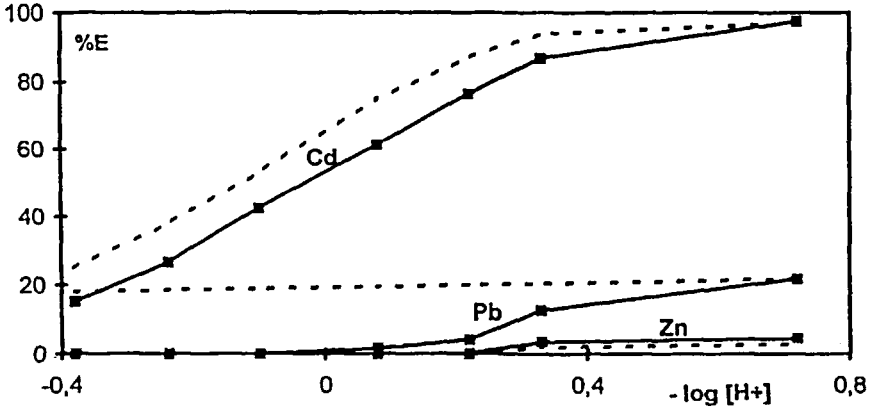

FIG. 5 Comparison of the theoretical (dotted lines) and experimental extraction results.

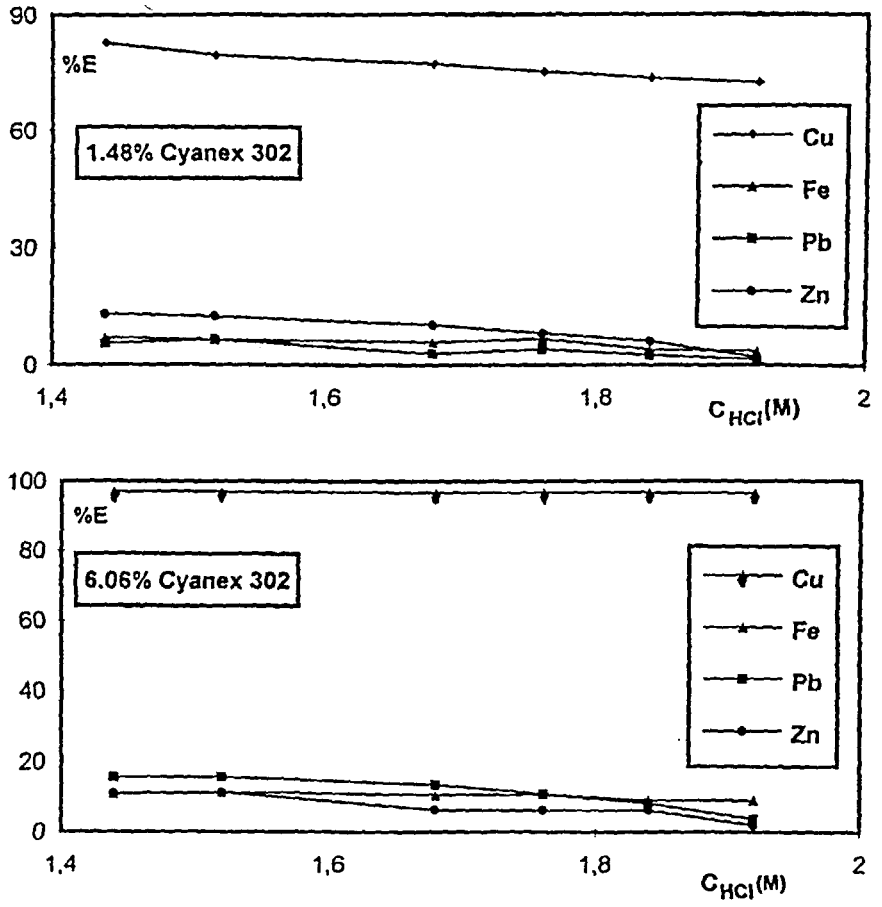

FIG. 6 Experimental results of metal extraction from leachate of the slag with different Cyanex 302 concentrations.

acidity between 1.4 and 2 M HCl. The results again showed that only Cu(II), Fe(III), Pb(II), and Zn(II) were extracted in the conditions of the study, whereas manganese, nickel, magnesium, calcium, and aluminum remained in the aqueous phase, as in the above case.

Figure 6 shows the extraction percentages of metals obtained for the different conditions. The results reveal that when strong acidic conditions are used (2 M HCl), high copper recoveries can be achieved and favorable selectivity for this metal is obtained. Copper extraction increases perceptibly when the

Cyanex 302 concentration increased, whereas no significant changes in Fe(III), Pb(II), and Zn(II) extraction are observed.

CONCLUSION

Microwave digestion with HCl of Waelz oxide leads to good results for analytical purposes, and practically all the metals of the solid sample go to solution. However, poorer results are obtained in slag leaching because an important percentage of silicium remains in the solid phase.

The use of Cyanex 302 allows the extraction of different percentages of Cu(II), Cd(II), Fe(III), Pb(II), and Zn(II) from hydrochloric acid solutions. In the conditions of our studies, no extraction of Mn(II), Ni(II), Cr(III), Ca(II), Mg(II), and Al(III) occurs. The selective recovery of Cu(II) from leachates of Waelz oxide and slag is possible without any modification of the aqueous acidity. However, Cd(II) recovery is not selective because a considerable percentage of Fe(III) is coextracted.

There is acceptable agreement between the experimental results obtained with industrial samples and the extraction percentages of Cd(II), Pb(II), and Zn(II) theoretically calculated from equilibrium extraction data of these metals in individual synthetic systems. This agreement can be useful for predicting theoretically the best conditions necessary to recover these elements using liquid–liquid extraction by Cyanex 302.

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