



Recovery of zinc and lead from zinc plant residue

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Abstract

Zinc and lead recovery from zinc plant residue (ZPR) has been investigated. The residue is discarded as a cake from a Waelz kiln processing zinc–lead carbonate ores. The zinc plant residue containing 11.3% Zn, 24.6% Pb, and 8.3% Fe was blended with H₂SO₄ and subjected to a process comprising roasting, water leaching, and finally NaCl leaching. The effect of roasting and leaching parameters on the zinc recovery was first studied. About 86% Zn was recovered after roasting at 200 °C for 30 min with an equal weight ratio of H₂SO₄/ZPR followed by leaching at 25 °C for 60 min with a pulp density of 20% solids. For lead recovery, the residual solid after zinc extraction was subjected to NaCl leaching. At a pulp density of 20 g/L, about 89% Pb was dissolved in 200 g/L NaCl at 25 °C in 10 min.

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1. Introduction

Zinc is primarily produced from sulphidic ores; however, some zinc is produced from oxide-carbonate ores and different secondary resources such as zinc ash, zinc dross, flue dusts of electric arc furnace, leach residues, etc. Pyrometallurgical and hydrometallurgical routes or their combination can be employed for treating secondary materials. The hydrometallurgical processes are regarded as more eco-friendly for treating

such materials having a low zinc content (Jha et al., 2001).

In the most common hydrometallurgical zinc process, ZnO-rich calcine is first produced from sulphide or oxide-carbonate concentrates and then leached with hot sulphuric acid solution. After liquid/solid separation, the pregnant solution is purified and electrowon for metallic zinc production. In some plants (e.g., Çinkur, Kayseri, Turkey), the zinc leach residue is stockpiled for future lead recovery. These residues are considered as hazardous wastes due to their significant zinc, lead, and cadmium content. In fact, it has been shown that residues left after zinc extraction pose potential

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environmental risks because they exhibit significant heavy metals solubilization (Altundoğan et al., 1998).

Due to the extraction of zinc and formation of insoluble lead sulphate during sulphuric acid leaching, lead is concentrated in this residue. However, a significant part of zinc remains in the form of zinc ferrite ($\text{ZnO}\cdot\text{Fe}_2\text{O}_3$) in the leach residue that accounts for the high zinc losses in such processes. In the studies of metal recovery from the wastes containing zinc ferrite, efforts have focussed mainly on the decomposition of the ferrite structure. Different industrial wastes containing zinc ferrite have been subjected to various recovery methods such as carbothermic reduction (Nakamura et al., 1995), caustic leaching with and without microwave (Xia and Pickles, 1999a; Xia and Pickles, 2000), fusion with caustic soda (Xia and Pickles, 1999b; Youcai and Stanforth, 2000a,b), and leaching with various acids (Abdel Basir and Rabah, 1999; Rabah and El-Sayed, 1995; Zeydabadi et al., 1997; Barakat, 1999; Nagib and Inoue, 2000). Lead recovery from such metallurgical wastes and lead acid battery residues has also been studied.

Besides the alkaline and acid extraction techniques mentioned above, some pyrometallurgical recovery processes (Boyanov and Dimitrov, 1998; Guerrero et al., 1997) and chloride leaching processes have been employed using either NaCl (Raghavan et al., 1998; Raghavan et al., 2000; Andrews et al., 2000), or MgCl_2 and CaCl_2 (Sinadinovic et al., 1997), or FeCl_3 (Andrews et al., 2000; Leclerc et al., 2003). It has also been reported that the extraction of lead from acid batteries is possible by leaching with ammoniacal ammonium sulphate solution (Schwartz and Etsell, 1998).

In this study, zinc and lead recovery from zinc plant residue (ZPR) obtained from a plant using a Waelz kiln was investigated. For this purpose, optimum conditions for zinc and lead extraction using a two-stage process were determined. In the first stage, ZPR was roasted, after blending with concentrated H_2SO_4 , and then leached with water to bring zinc into solution. In the second stage for lead recovery, residual material from the first stage was leached using sodium chloride solution.

2. Experimental

2.1. Materials

Zinc plant residue (ZPR) was obtained from Çinkur Plant located at Kayseri, Turkey. Prior to use in this study, the ZPR sample was washed, homogenized, dried, and sieved to obtain a $-74\text{-}\mu\text{m}$ (-200 mesh) fraction. Its mineralogical structure was identified by X-ray diffraction analysis.

The ZPR samples were analyzed for zinc, lead, iron, calcium, cadmium, copper, chromium, and cobalt using an atomic absorption spectrometer (Perkin-Elmer, 370) after LiBO_2 fusion and HNO_3 dissolution (Bailey and Woods, 1974). Also, the ZPR sample was subjected to a series of zinc extraction tests suggested by Addemir et al. (1995) in order to determine the amount of zinc in various forms such as sulphate, oxide plus metal, silicate, and ferrite. The sulphur content of ZPR was determined gravimetrically (Vogel, 1989).

2.2. Preliminary acid leaching study

Initially, H_2SO_4 leaching of ZPR was studied to provide reference results. The effects of H_2SO_4 /ZPR weight ratio (0.25–3.0), leaching temperature (25–80 °C), and temperature of pre-roasting (200–800 °C) on metal recovery were investigated. All preliminary leaching experiments were carried out in flasks that were magnetically stirred using a pulp density of 200 g/L. After leaching, the filter cakes were washed with distilled water and the wash solutions were added to main extracts. The leachates were acidified with nitric acid to prevent precipitation of metals. The solutions were analyzed by AAS for Fe, Pb, and Zn.

2.3. Roasting of ZPR– H_2SO_4 mixture and water leaching for zinc recovery

An appropriate amount of H_2SO_4 was mixed with 5.0 g of ZPR in a porcelain dish and placed in a muffle furnace preheated to the required temperature. At the end of the predetermined heating period, the sample was removed from the furnace, cooled in a desiccator, weighed, ground, and leached with water under predetermined conditions. Leach residues were

dried, weighed, and preserved in closed vessels to await analysis.

The effects of various parameters such as roasting temperature (50–900 °C), roasting time (5–240 min), H₂SO₄/ZPR ratio (0.25–3.0), leaching time (15–240 min), and leaching temperature (25–80 °C) on the leaching of metals were examined.

2.4. NaCl leaching for lead recovery

After water leaching, the secondary zinc plant residue (SZPR) was subjected to NaCl leaching to investigate the recovery of lead. The effects of NaCl concentration (50–300 g/l), SZPR pulp density (5–300 g/L), leaching temperature (25–80 °C), and time (5–120 min) were investigated. All experiments were performed in duplicate and the mean values were considered. Some of the experiments were repeated several times in order to ascertain the reproducibility. The results were found to vary within $\pm 5\%$.

3. Results and discussion

The chemical composition of ZPR is given in Table 1. Anglesite (PbSO₄) was identified in the ZPR sample as a major component by X-ray diffraction analysis whereas gypsum (CaSO₄·2H₂O) was determined as a minor component. Any knowledge about Zn and Fe mineralogy in ZPR could not be obtained from XRD results. For that reason, a series of selective leaching tests were applied to ZPR, as proposed for zinc containing wastes by Addemir et al. (1995). Selective leaching tests indicated that 0.24% Zn was present as sulphate, 0.21% as silicate, 5.65% as oxide plus zinc metal, and 5.2% as ferrite forms. Therefore, zinc is mostly in amorphous oxide and ferrite forms in the ZPR sample.

Table 1
Chemical composition of zinc plant residue (ZPR)

Constituents	w/w (%)	Constituents	w/w (mg/kg)
Pb	24.6	Cd	370
Zn	11.3	Cu	400
Fe	8.3	Cr	380
Ca	1.5	Co	170
S	5.2		
LOI (900 °C)	20.0		

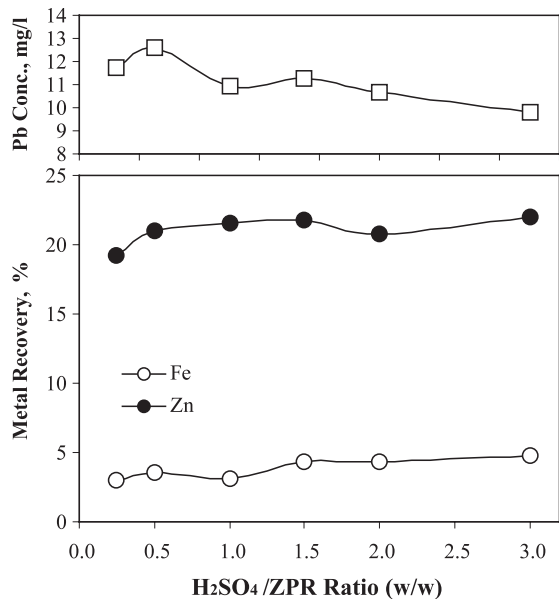


Fig. 1. Effect of H₂SO₄ on the leaching of metals from ZPR (pulp density, 20%; leaching temperature, 25 °C; leaching time, 30 min).

3.1. Preliminary experiments with sulphuric acid leaching

The effect of increasing the weight ratio of sulphuric acid/ZPR in the slurry on the extraction of metals from ZPR at 25 °C is shown in Fig. 1. The results show that increasing the amount of H₂SO₄ has no significant effect. For the H₂SO₄/ZPR ratio of 3, about 22% Zn and 4% Fe were leached, respectively; while lead concentrations in the leachates were in the range of 9.8–12.6 mg/L Pb. This is consistent with part of the zinc in a refractory zinc ferrite phase and the limited solubility of lead sulphate in a sulphuric acid solution.

Fig. 2 shows the leaching of zinc and lead increases with temperature, with 36% Zn and 10.6% Fe extracted at 80 °C. Temperature has little effect on the lead concentration in solution. The effect of pre-roasting the ZPR over a range of temperatures on the leach recovery of metals is given in Fig. 3. The figure also includes the weight losses observed on pre-roasting due to dehydration of hydrated minerals. In this case, the recovery of zinc increases slightly up to 400 °C and thereafter decreases. This behavior may be attributed to increasing surface area and porosity of ZPR by dehydration. Decreasing zinc recovery from ZPR

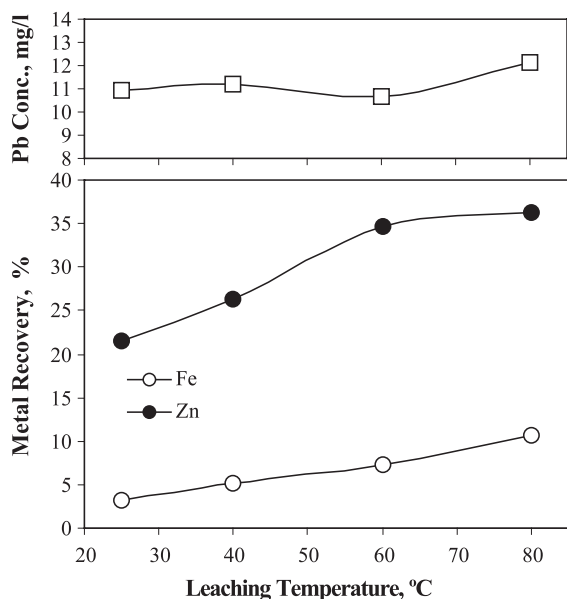


Fig. 2. Effect of temperature on the leaching of metals from ZPR by H_2SO_4 (H_2SO_4/ZPR ratio, 1; pulp density, 20%; leaching time, 30 min).

roasted at higher temperatures may be due to sintering/agglomeration or further reaction to form zinc ferrites.

As a result of these preliminary studies, it can be concluded that zinc could not be efficiently leached from ZPR or pre-roasted ZPR by using an ordinary sulphuric acid leaching process and that decomposition of zinc ferrite appears necessary for satisfactory metal recovery. Also, encapsulation of zinc oxide or zinc ferrite in a lead sulphate matrix may be another reason for poor zinc recovery.

3.2. Recovery of zinc

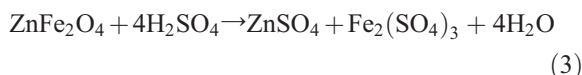
In order to decompose the ferrite structure and thus obtain high zinc recovery, the ZPR was subjected to roasting after mixing with H_2SO_4 . For this purpose, the effect of roasting temperature on the recovery of metals was initially investigated over a wide range of 50–900 °C as summarized in Fig. 4.

As seen from Fig. 4, recovery of zinc and iron significantly increases with roasting temperature up to 200 °C. While the recoveries of zinc and iron were 31% and 9% at 50 °C, they increased to 80% and 43% at 200 °C, respectively. Further increasing the temperature up to 500 °C had no significant effect on the

leaching of these metals. But above this temperature, the recovery of these metals sharply decreased. Below the boiling temperature of H_2SO_4 (~330 °C), it can be considered that leaching is accomplished by means of a sulphation reaction as follows:



and/or,



It can be stated that the liquid H_2SO_4 is more effective for sulphation up to boiling temperature of H_2SO_4 . Above the boiling temperature, H_2SO_4 will partially decompose, producing SO_3 (or $SO_2 + 1/2O_2$) that can also sulphate metals. But rapid escape of SO_3 at higher temperatures may reduce the degree of sulphation and thus the recovery of zinc and iron

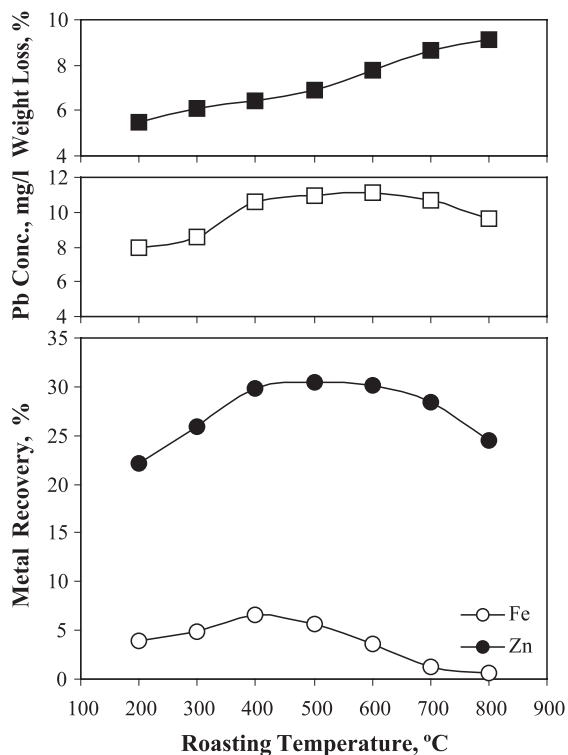


Fig. 3. Effect of pre-roasting temperature on H_2SO_4 leaching of metals from ZPR (pre-roasting time, 60 min; H_2SO_4/ZPR ratio, 1; pulp density, 20%; leaching temperature, 25 °C; leaching time, 30 min).

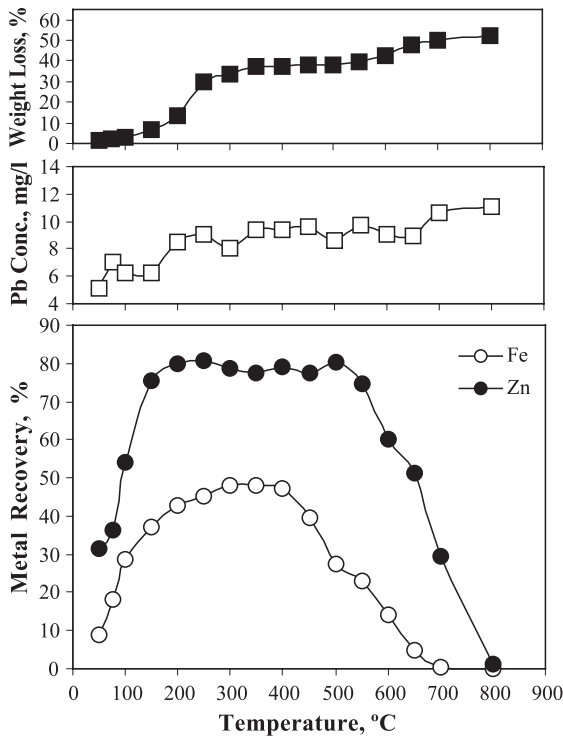
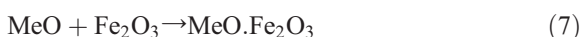
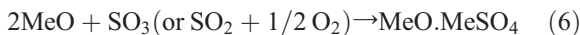
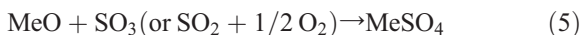
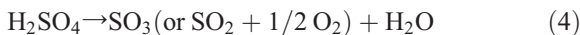


Fig. 4. Effect of roasting temperature on the leaching of metals from ZPR–H₂SO₄ mixtures (H₂SO₄/ZPR ratio, 1; roasting time, 60 min; pulp density, 20%; leaching temperature, 25 °C; leaching time, 30 min).

decreases. Another reason for the decreasing recovery is the decomposition of metal sulphates and formation of some insoluble compounds such as oxy-sulphates and even ferrites. It has been reported that the decomposition of iron and zinc sulphates initiates at about 500 and 650 °C, respectively (Weast, 1978; Siriwardane et al., 1999; Olszak-Humienik and Mozejko, 2000). Decomposition and sulphation reactions can be described as follows:



where Me represents metals such as Zn and Fe.

It was found that the lead concentrations in all leaching solutions were low due to the limited solubility of lead sulphate. Because lead can be regarded as an impurity in zinc solutions, the low value of lead can be considered as an advantage. On the other hand, the residue obtained from the H₂SO₄ roasting–water leaching treatment (secondary zinc plant residue (SZPR)) can be utilized for lead recovery. This intermediate product was chemically analyzed, giving the results shown in Table 2.

As Table 2 shows, the zinc, iron, and lead contents of SZPR obtained from samples roasted at 200–550 °C are all about 2%, 5%, and 30%, respectively. As a consequence, 200 °C was selected as a most suitable roasting temperature. The effect of H₂SO₄/ZPR ratio on the recovery of metals from the samples roasted at 200 °C is shown in Fig. 5. In this case, the leaching of iron and zinc increases with the H₂SO₄/ZPR ratio, but the increase in zinc recovery was very low for ratios over 1. It can be concluded that a weight ratio of 1 is sufficient for a satisfactory recovery. Other tests showed that there was no significant change in the recovery of zinc when roasting more than 30 min although iron extraction fell slightly from 40% to 35% after 4 h.

After determining the optimum roasting conditions, the optimum leaching conditions on the recovery of metals from ZPR were investigated. It

Table 2

Chemical composition of residue left after the H₂SO₄ roasting–water leaching process

Roasting temperature (°C)	Composition % (w/w)		
	Fe	Zn	Pb
50	8.85	7.08	24.9
75	7.95	6.13	25.5
100	5.02	4.16	26.0
150	5.65	2.82	26.5
200	4.87	1.92	30.1
250	5.15	1.89	30.0
300	5.27	1.90	30.1
350	5.44	2.05	30.2
400	5.36	2.02	30.6
450	4.72	1.89	29.4
500	5.36	2.57	29.8
550	5.26	1.93	29.2
600	5.69	1.99	27.7
650	6.77	3.64	27.5
700	8.12	7.18	26.1
800	8.95	10.07	26.6

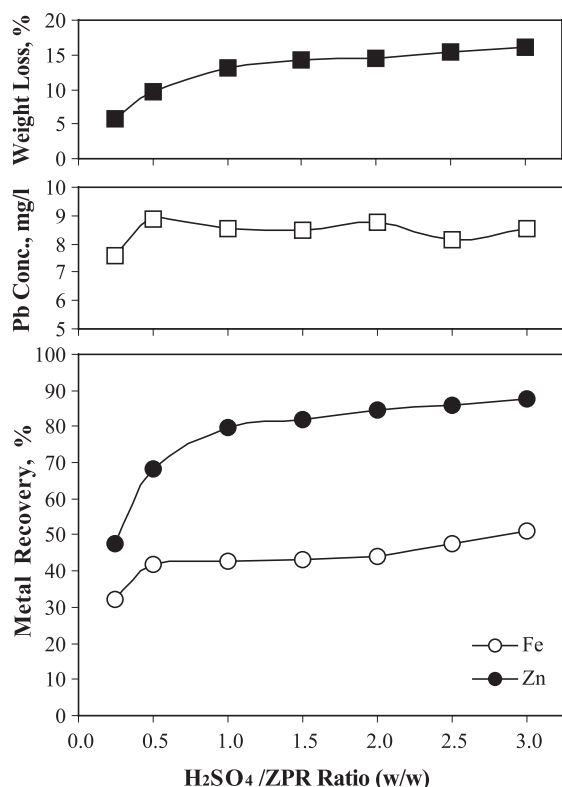


Fig. 5. Effect of H₂SO₄ on the recovery of metals from roasted ZPR–H₂SO₄ mixtures (roasting temperature, 200 °C; roasting time, 60 min; pulp density, 20%; leaching temperature, 25 °C; leaching time, 30 min).

was found that the recovery of zinc and iron increased to about 85% and 50%, respectively, with a contact time up to 60 min, and thereafter the extraction remained nearly constant. Similarly, the leaching temperature between 25 and 80 °C had no significant effect on the recovery of zinc or the solubility of lead sulphate.

Thus, optimum conditions for zinc recovery from ZPR by a process comprising sulphuric acid addition–roasting–water leaching were determined as H₂SO₄/ZPR weight ratio=1; roasting temperature, 200 °C; roasting time, 30 min; leaching temperature, 25 °C; and leaching time, 60 min.

3.3. Recovery of lead

The chemical composition of secondary zinc plant residue (SZPR) obtained under optimum conditions of zinc recovery shows that it contains about 30.6% Pb,

1.6% Zn, 4.7% Fe, and 7.3% S. The effects of NaCl concentration and solid/liquid ratio on the recovery of zinc and lead from SZPR were investigated in a set of experiments whose results are given in Fig. 6. As the figure shows, the recovery of lead decreases significantly by increasing the SZPR solution ratio due to the limited solubility of PbCl₂. In 200 g/L NaCl solution, the recovery of lead is satisfactory up to a pulp density of 20 g/L SZPR, but above this level the extraction of lead decreases sharply. Although lead recovery increases with NaCl concentration, leaching with NaCl concentrations above 300 g/L seems practically impossible due to saturation. Since there was no significant difference between lead recoveries obtained with NaCl concentrations of 200 and 300 g/L, it was concluded that a concentration of 200 g/L NaCl is sufficient.

The reaction between lead sulphate in the SZPR and chloride ions in the solution can be depicted as



In the presence of high chloride concentrations, lead chloride subsequently converts to PbCl₃⁻ and

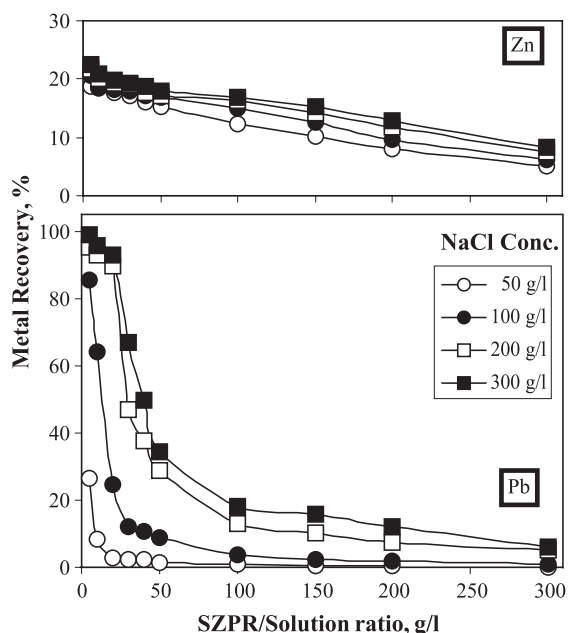


Fig. 6. Effects of NaCl concentration and SZPR pulp density on the recovery of metals from SZPR (leaching temperature, 25 °C; leaching time, 30 min).

PbCl_4^{2-} complexes having higher solubilities (Sinadinovic et al., 1997).

Leaching times up to 120 min and temperatures up to 80 °C did not influence lead and zinc recoveries significantly. Thus, leaching for 10 min at 25 °C was sufficient for >90% lead recovery.

4. Conclusions

Significant amounts of zinc and lead could be recovered from zinc plant residue (ZPR) by using a two-stage recovery process comprising (1) roasting

of the ZPR– H_2SO_4 mixture followed by a water leaching and (2) sodium chloride leaching of the residual solids. The production of metallic zinc from the first-stage leach solution would seem possible after appropriate purification and concentration. Lead from the second stage leach solution could be recovered by means of a sulphide precipitation as a rich lead sulphide concentrate suitable for pyrometallurgical treatment. Although SZPR produced after the recovery of zinc could be considered as a saleable commodity to lead smelters, it can be converted into a more concentrated and valuable product by a simple NaCl leaching–sulphide precip-

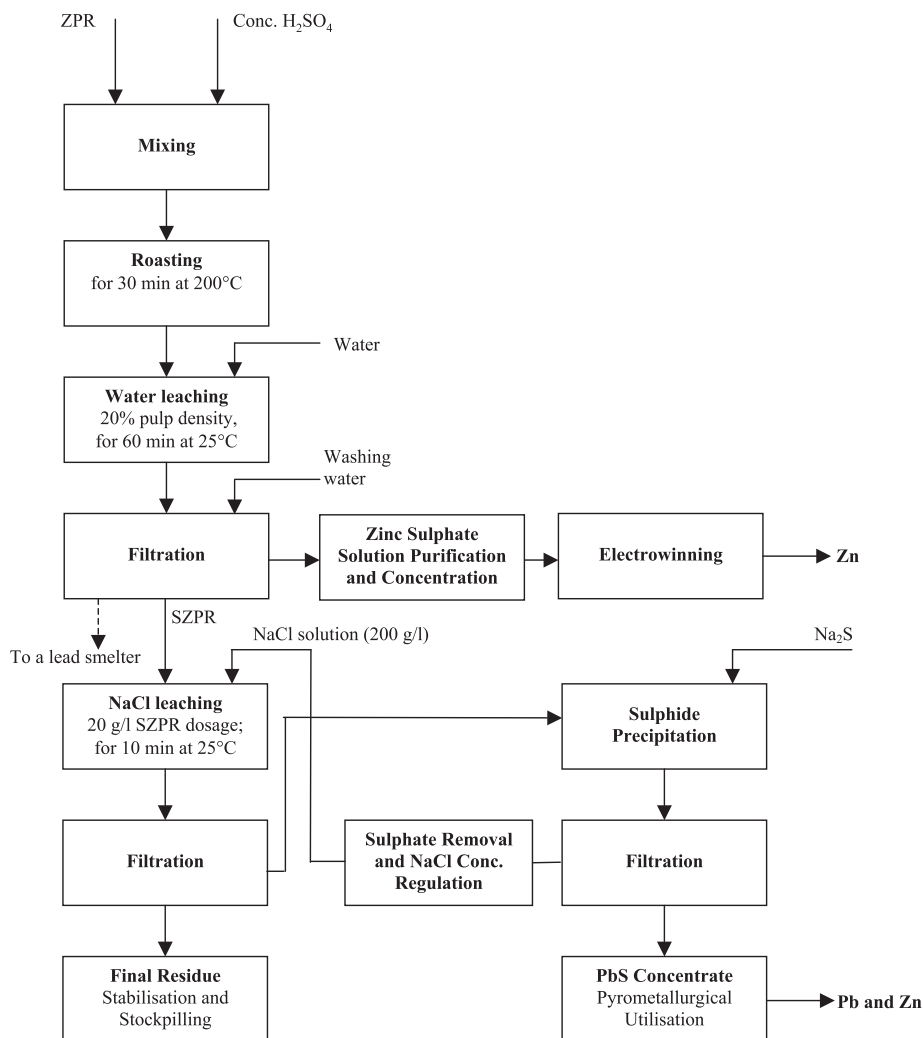


Fig. 7. Proposed flow sheet for metal recovery from ZPR.

itation process. The solution obtained after sulphide precipitation can be reused for brine leaching but may require a sulphate removal treatment prior to recycling. A proposed process flow sheet is illustrated in Fig. 7.

Further investigation is needed on the chemical and mineralogical characterization and stabilization of the final residue before it can be disposed.

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References

- Abdel Basir, S.M., Rabah, M.A., 1999. Hydrometallurgical recovery of metal values from brass melting slag. *Hydrometallurgy* 53 (1), 31–44.
- Addemir, O., Açma, E., Arslan, C., 1995. Çinko. Sistem Yaynclık, Istanbul. In Turkish.
- Altundoğan, H.S., Erdem, M., Orhan, R., Tümen, F., 1998. Heavy metal pollution potential of zinc leach residues discarded in Çinkur plant. *Doğa, Turk J. Eng. Environ. Sci.* 22, 167–177.
- Andrews, D., Raychaudhuri, A., Frias, C., 2000. Environmentally sound technologies for recycling secondary lead. *J. Power Sources* 88 (1), 124–129.
- Bailey, N.T., Woods, S.I., 1974. A comparison of two rapid methods for the analyses of copper smelting slags by atomic absorption spectrometry. *Anal. Chim. Acta* 69 (1), 19–25.
- Barakat, M.A., 1999. Recovery of metal values from zinc solder dross. *Waste Manage.* 19 (7–8), 503–507.
- Boyanov, B., Dimitrov, R., 1998. DTA and TG study of PbSO₄ dissociation in the presence of solid fuels. *Thermochim. Acta* 322 (1), 69–75.
- Guerrero, A., Romero, A., Morales, R.D., Chaves, F., 1997. Thermodynamic analyses of the soda ash smelting of lead acid battery residues in a rotary furnace. *Can. Metall. Q.* 36 (2), 121–130.
- Jha, M.K., Kumar, V., Singh, R.J., 2001. Review of the hydrometallurgical recovery of zinc from industrial wastes. *Resour. Conserv. Recycl.* 33 (1), 1–22.
- Leclerc, N., Meux, E., Lecuire, J.-M., 2003. Hydrometallurgical extraction of zinc from zinc ferrites. *Hydrometallurgy* 70 (1–3), 175–183.
- Nagib, S., Inoue, K., 2000. Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching. *Hydrometallurgy* 56 (3), 269–292.
- Nakamura, T., Itou, H., Takasu, T., 1995. Fundamentals of the pyrometallurgical treatment of zinc leach residue. Proc. 2nd International Symposium of Quality in Non-Ferrous Pyrometallurgy. CIM, Montreal, pp. 341–355.
- Olszak-Humienik, M., Mozejko, J., 2000. Thermodynamic functions of activated complexes created in thermal decomposition process of sulphates. *Thermochim. Acta* 344 (1–2), 73–79.
- Rabah, M.A., El-Sayed, A.S., 1995. Recovery of zinc and some of its valuable salts from secondary resources and wastes. *Hydrometallurgy* 37 (1), 23–32.
- Raghavan, R., Mohanan, P.K., Patnaik, S.C., 1998. Innovative processing technique to produce zinc concentrate from zinc production residue with simultaneous recovery of lead and silver. *Hydrometallurgy* 48 (2), 225–237.
- Raghavan, R., Mohanan, P.K., Swarnkar, S.R., 2000. Hydrometallurgical processing of lead bearing materials for the recovery of lead and silver as lead concentrate and lead metal. *Hydrometallurgy* 58 (2), 103–116.
- Schwartz, L.D., Etsell, T.H., 1998. The cementation of lead from ammoniacal ammonium sulphate solution. *Hydrometallurgy* 47 (2–3), 273–279.
- Sinadinovic, D., Kamberovic, Z., Sutic, A., 1997. Leaching kinetics of lead from lead(II) sulphate in aqueous calcium chloride and magnesium chloride solutions. *Hydrometallurgy* 47 (1), 137–147.
- Siriwardane, R.V., Poston Jr., J.A., Fisher, E.P., Shen, M.-S., Miltz, A.L., 1999. Decomposition of the sulphates of copper, iron(II), iron(III), nickel and zinc: XPS, SEM, DRIFTS, XRD, and TGA study. *Appl. Surf. Sci.* 152 (3–4), 219–236.
- Vogel, A.I., 1989. *Vogel's Textbook of Quantitative Chemical Analyses*, Revised by Jeffery, G.H., et al., 5th ed., Longmans, London.
- Weast, R.C. (Ed.), 1978. *Handbook of Chemistry and Physics*, (58th ed.). CRC Press, Florida.
- Xia, D.K., Pickles, C.A., 1999a. Kinetics of zinc ferrite leaching in caustic media in the deceleratory period. *Miner. Eng.* 12 (6), 693–700.
- Xia, D.K., Pickles, C.A., 1999b. Caustic roasting and leaching of electric arc furnace dust. *Can. Metall. Q.* 38 (3), 175–186.
- Xia, D.K., Pickles, C.A., 2000. Microwave caustic leaching of electric arc furnace dust. *Miner. Eng.* 13 (1), 79–94.
- Youcai, Z., Stanforth, R., 2000a. Extraction of zinc from zinc ferrites by fusion with caustic soda. *Miner. Eng.* 13 (13), 1417–1421.
- Youcai, Z., Stanforth, R., 2000b. Integrated hydrometallurgical process for production of zinc from electric arc furnace dust in alkaline medium. *J. Hazard. Mater.* 80 (1–3), 223–240.
- Zeydabadi, B.A., Mowla, D., Shariat, M.H., Kalajahi, J.F., 1997. Zinc recovery from blast furnace flue dust. *Hydrometallurgy* 47 (1), 113–125.