AN INNOVATIVE TECHNOLOGY FOR RECOVERY OF ZINC, LEAD AND SILVER FROM ZINC LEACHING RESIDUE

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Abstract: Zinc leaching residue is a good source of zinc and has a great potential to be utilized. However, it is very difficult to recover lead, zinc and silver from the residue by traditional technologies. In this study, a new technology based on conversions of $PbSO_4$ and $ZnSO_4$ in the residue to their respective sulfides by reduction roasting with coal powder followed by a flotation treatment was developed. The effects of roasting temperature, coal dosage, reaction time and pyrite dosage were investigated at a laboratory scale. The results showed that the conversion extent of $PbSO_4$ and $ZnSO_4$ under the optimal experimental conditions was 71.89 and 69.76%, respectively. A flotation concentrate containing 39.13% Zn, 6.93% Pb and 973.54 g/Mg Ag was obtained from the treated material, and the recovery of Zn, Pb and Ag was 48.38, 68.23 and 77.41%, respectively. The tailing containing $ZnFe_2O_4$ or Fe_3O_4 could be either stockpiled or further disposed.

Introduction

Currently, more than 70% of zinc is produced from zinc sulfide concentrates by a conventional roast-leach-electrowinning process (Ozverdi and Erdem, 2010; Peng et al., 2003). A drawback of this process is that considerable amounts of zinc leaching residue are generated. Although pyrometallurgical processes such as the Waelz and Ausmelt methods have been applied to treat these residues in industry, these methods are not economically feasible due to huge consumption of coal to provide the power

required for the high operating temperature (1100-1300 $^{\circ}$C). Therefore, the residues are usually stockpiled resulting in serious waste and environmental problems.

The generated residues commonly contain many valuable metals such as Zn, Pb, Au and Ag (Altundogan et al., 1998; Li et al., 2012). With decreasing the content of these valuable metals in the residues, some technologies for recovering them have been developed to create a new source as well as reduce the environmental problems. These are flotation, gravity separation combined with flotation and hydrometallurgy.
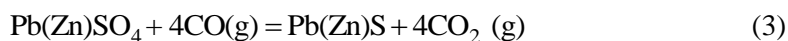
Fuerstenau et al. (1985) and Herrera-Urbina et al. (1999) found that the amount of collector needed to float anglesite or cerussite was several orders of magnitude more than that required for flotation of galena. They concluded that the main reason for large amount of collector consumed was that lead cations were dissolved from mineral lattice and then would precipitate with the collector as insoluble lead xanthate. In order to improve this situation, sulfidation of these oxides with Na_2S was proposed. Rastas et al. (1990) and Rashchi et al. (2005) studied the recovery of lead, silver and gold from zinc leaching residues by a sulfidation-flotation process. They found that collector consumption was reduced about three times in the presence of Na_2S. However, it will result in serious environmental pollution caused by H_2S. Besides, gravity separation combined with flotation was reported to recover $PbSO_4$ from an oxide lead-zinc ore. A lead concentrate containing 65.80% Pb was obtained with the recovery of 86.5% (Onal et al., 2005). However, it seems to be unsatisfactory for treating the residues due to the fine particle nature.

Considering comprehensive recovery of the valuable metals, hydrometallurgical process may be considered as an efficient way. Raghavan et al. (1998) extracted silver and lead from the residue by sulfuric acid leaching-brine leaching. The results showed that recoveries of lead, silver, zinc and sulfur were 90, 80, 80 and 87%, respectively. Patino et al. (1998) and Roca et al. (2006) investigated leaching of natrojarosite and silver ammonium jarosite by an alkaline decomposition–cyanidation route and it was proved to be a two-step process in series: a slow step of alkaline decomposition that controled the overall process, followed by a fast step of complexation of the silver from the decomposed solids. Furthermore, Vinals et al. (1991) reported leaching of noble metals in the $HCl-CaCl_2$ medium from plumbojarosite. The results presented that the extraction rates of gold, silver and lead were above 90%. However, operating environment is usually deteriorated during these processes, It is due to the release of various noxious gases and ions.

Recently, transformation of sulfates, especially $PbSO_4$, to sulfides has received considerable attentions as a promising method for managing the heavy metals. On the one hand, the sulfides obtained are less soluble than sulfates (Pacholewska, 2004; Wolthoorn et al., 2007), which lowers risk of pollution of the heavy metals. On the other hand, the sulfides generated can be recovered by some conventional techniques. Karnachuk et al. (2002) investigated conversion of $PbSO_4$ to PbS with lactate bacteria in acid mine drainage, and found that the concentration of Pb^{2+} was decreased in the solution with increasing in the amount of PbS. Weijma et al. (2002a) applied the

biological reduction technology to convert $PbSO_4$ in spent car batteries to PbS, which was recovered by electrochemical processes. The biological conversion process was based on biological reduction of a sulfur component, followed by a reaction of Pb^{2+} with HS^- produced (Van-Houten et al., 1994; Weijma et al., 2002b).

However, there are only a few papers which report conversion of sulfates in the zinc leaching residue to sulfides by reduction roasting. The related reactions could be described as (Habashi et al., 1976; Malinowski et al., 2004):

$$Pb(Zn)SO_4 + 4C = Pb(Zn)S + 4CO \text{ (g)} \tag{1}$$

$$Pb(Zn)SO_4 + 2C = Pb(Zn)S + 2CO_2 \text{ (g)} \tag{2}$$

$$Pb(Zn)SO_4 + 4CO(g) = Pb(Zn)S + 4CO_2 \text{ (g)} \tag{3}$$

The goal was to convert the sulfates in the residues to sulfides which could be easily recovered by conventional flotation techniques.

Experiment

Materials

The zinc leaching residue (<74 μm) was provided by a zinc hydrometallurgical plant in Hunan province, China. The XRD pattern of the material is shown in Fig. 1. The chemical composition obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES) is listed in Table 1 and the phase ratios of the primary elements distribution are shown in Table 2. It can be seen that the $PbSO_4$ accounts for 79.74% of total lead and $ZnSO_4$ accounts for 19.52% of total zinc. $ZnSO_4$ is a soluble form, whereas $PbSO_4$ is an insoluble component and both of them present great risks on the environment.
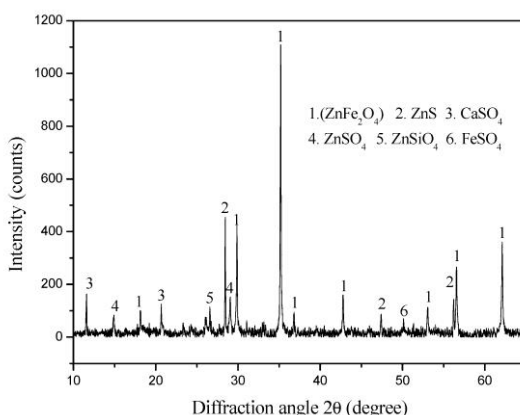

Fig. 1. XRD pattern of zinc leaching residue

Table 1. Major chemical composition of zinc leaching residue (wt.%)

Element	Pb	Zn	Fe	Ag (g/t)	S	Si	Cu	Ca
Content	2.47	20.88	23.74	326.16	6.38	1.89	0.76	1.96

Table 2. Phase composition of lead, zinc and silver in residue (%)

Constituent	Metal	Oxide	Sulfate	Sulfide	Ferrite	Others	Total
Lead	0	4.77	79.74	6.20	0	9.29	100.00
Zinc	0	2.25	19.52	27.42	50.81	0	100.00
Silver	34.24	0.30	1.30	41.97	0	22.19	100.00

Coal with a fixed carbon content of 53.0% was used as the reductant and the pyrite containing 47% Fe and 47.9% S was applied as the vulcanizing agent. Sodium carbonate, sodium hexametaphosphate, ammonium dibutyl dithiophosphate and sodium diethyldithiocarbamate were used in flotation experiments.
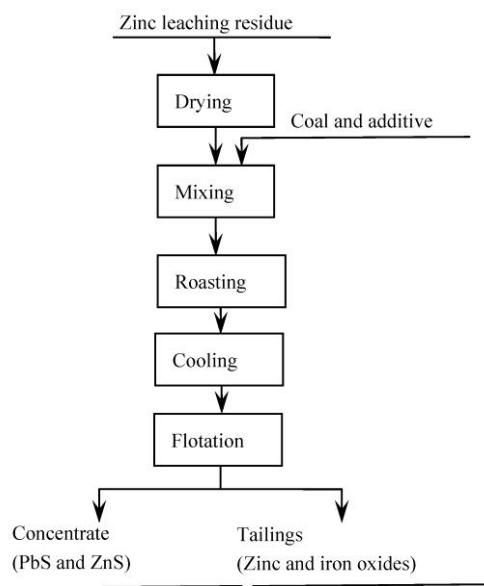

Fig. 2. A general process flowsheet for treating zinc leaching residue

Experimental setup

The general process flow sheet is shown in Fig. 2. About 200 g of the zinc leaching residue was mixed with coal with different weight ratios, and then loaded into an Alundum crucible equipped with a cover, which was then placed in the muffle furnace heated in a temperature range of 600–900 $^{\circ}$C. The roasted sample was cooled, analyzed (Zhang., 1992; Liang et al., 2012) and floated. Flotation was performed in a

XFG flotation machine using a 1.0 dm^3 glass cell. Assuming that the content of Pb(Zn) was constant before and after reduction roasting, the conversion extent of Pb(Zn)SO$_4$ to Pb(Zn)S was calculated using the formula:

$$\varepsilon = \frac{\beta_2 - \beta_1}{\alpha} \times 100\% \tag{4}$$

where ε is the conversion extent of Pb(Zn)SO$_4$, β_2 and β_1 are percentages of Pb(Zn)S accounting for total Pb(Zn) for the roasted product and raw material, respectively, α is percentage of Pb(Zn)SO$_4$ accounting for total Pb(Zn) in the raw material.

Results and discussion

Effect of roasting temperature

It is well known that temperature plays a very important role in reduction roasting. Therefore, the effect of roasting temperature was investigated under the reaction time of 90 minutes and coal dosage of 10%, and the results are shown in Fig. 3. It can be seen that both of the conversion extents were fast and increased as the temperature was increased from 600 to 700 $^{\circ}$C. With a further increase in temperature, the conversion extent of ZnSO$_4$ slightly increased, but PbSO$_4$ sharply decreased. This explained that the increasing temperature caused fast decomposition of PbSO$_4$ (Habashi et al., 1976; Malinowski et al., 1996). Considering the simultaneous recovery of lead and silver as well as energy consumption, the optimum reduction temperature was determined to be 700 $^{\circ}$C and all further experiments were carried out at this temperature.
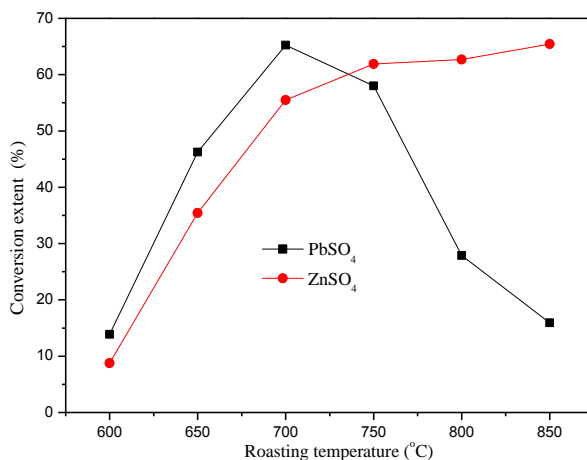

Fig. 3. Effect of roasting temperature on conversion extent

Effect of coal dosage

Coal powder plays an important role in maintaining a reducing atmosphere. Therefore, the effect of coal dosage was investigated. The experiments were conducted for 90 minutes and the roasting temperature was 700 $^{\circ}$C. Figure 4 shows that both of the conversion extents of $PbSO_4$ and $ZnSO_4$ increased as the coal dosage increased from 4 to 8%. With a further increase in dosage of coal, extents of $PbSO_4$ and $ZnSO_4$ were changed only slightly or remained constant (Fig. 4). Thus, the optimum coal dosage was determined to be 8% and all further experiments were carried out at this dosage.
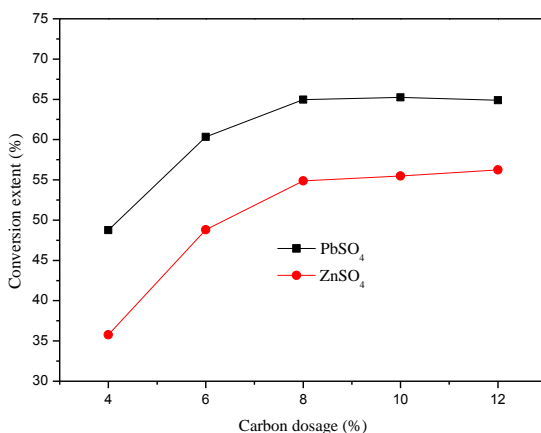

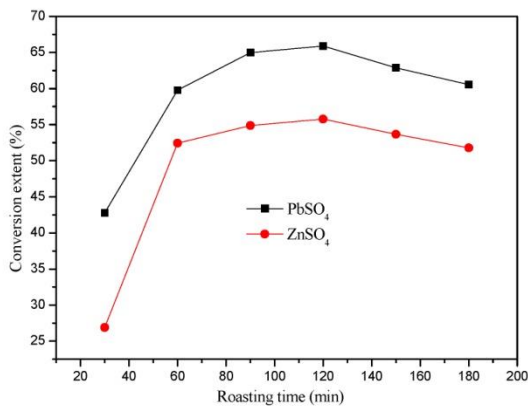Fig. 4. Effect of coal dosage on conversion extent
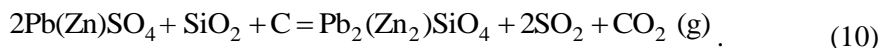

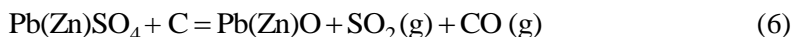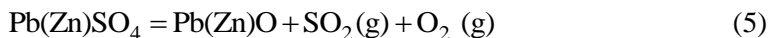Fig. 5. Effect of roasting time on conversion extent

Effect of roasting time

Figure 5 shows that the conversion extents of $PbSO_4$ and $ZnSO_4$ increased from 42.78 to 64.97% and 26.89 to 54.87%, respectively, as the roasting time increased from 30 to 90 minutes. With a further increase in time, both of the conversion extents were

fluctuated and then slightly decreased. The most likely reason for this is that the sulfides produced were oxidized with constant consumption of coal. Accordingly, the optimum roasting time was determined to be 90 min.

Effect of pyrite dosage

The results presented above indicated that conversion of $Pb(Zn)SO_4$ to $Pb(Zn)S$ was insufficient. This may be ascribed by the following reactions (Morgan et al., 1986; Peng et al., 2003; Abdel-Rehim, 2006):

$$Pb(Zn)SO_4 = Pb(Zn)O + SO_2(g) + O_2 \ (g) \tag{5}$$

$$Pb(Zn)SO_4 + C = Pb(Zn)O + SO_2(g) + CO \ (g) \tag{6}$$

$$Pb(Zn)SO_4 + CO = Pb(Zn)O + SO_2 + CO_2 \ (g) \tag{7}$$

$$2PbO + C = Pb(l) + CO(g) \tag{8}$$

$$2PbO + SiO_2 = Pb_2SiO_4 \tag{9}$$

$$2Pb(Zn)SO_4 + SiO_2 + C = Pb_2(Zn_2)SiO_4 + 2SO_2 + CO_2 \ (g) \ . \tag{10}$$

In order to improve conversion extents, pyrite as a vulcanizing agent was applied to convert the oxides. The reactions involved are (Lambert et al., 1998; Li et al., 2010).
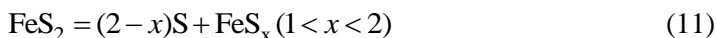
$$FeS_2 = (2 - x)S + FeS_x \ (1 < x < 2) \tag{11}$$

$$2Pb(Zn)O + 3S = 2Pb(Zn)S + SO_2(g) \tag{12}$$

$$8Pb(Zn)O + 9/2\,FeS_2 = 8Pb(Zn)S + SO_2(g) + 3/2\,Fe_3O_4 \ . \tag{13}$$

Figure 6 illustrates that the conversion extents of $PbSO_4$ and $ZnSO_4$ increased from 64.97 to 71.89% and from 54.87 to 69.76%, respectively, as the pyrite dosage was increased from 0 to 2%. With a further increase of the dosage, the conversion extent of $PbSO_4$ remained constant, while $ZnSO_4$ constantly increased. It was known that other reactions given in Eqs. 11 to 13, involving zinc ferrite, can also take place with either sulfur or pyrite, resulting in the increase of the conversion extent of $ZnSO_4$. However, this will degrade the flotation concentrate due to difficult liberation of iron from marmatite formed by grinding. Therefore, the optimal pyrite dosage was determined to be equal to 2%.
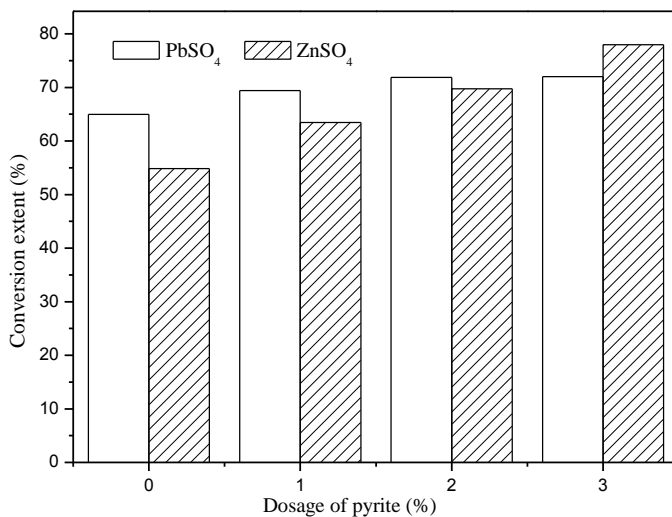
Fig. 6. Effect of pyrite dosage on conversion extent

The phase compositions of lead and zinc in the treated materials are shown in Table 3 and the XRD pattern is shown in Fig. 7. The obtained results confirmed that $PbSO_4$ and $ZnSO_4$ could be simultaneously converted to their respective sulfides by reduction roasting and even if, conversion degree of $PbSO_4$ and $ZnSO_4$ under the optimal experimental conditions was only 71.89 and 69.76%, respectively, the process can be considered as a promising method of solid residue processing.

Table 3. Phase composition of lead and zinc in the residue (%)

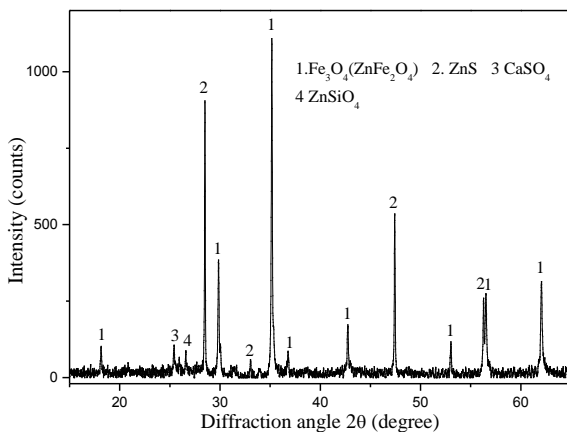| Constituent	Oxide	Sulfide	Others	Total
Lead	13.77	65.12	21.11	100.00
Zinc	14.07	41.04	44.89	100.00

Fig. 7. XRD pattern of roasted material

Close-circuit flotation tests

Close-circuit flotation tests of the roasted material were carried out by a bulk flotation process, as shown in Fig. 8. Table 4 shows that the flotation concentrate could be used as a commercial product containing 39.13% Zn, 6.93% Pb and 973.54 g/Mg Ag, with the Zn, Pb and Ag recoveries of 48.38%, 68.23% and 77.41%, respectively. The tailing could be stockpiled or further disposed. These results confirmed that the obtained artificial sulfides could be well recovered by conventional flotation technology. The XRD patterns (Fig. 9) also support this conclusion.
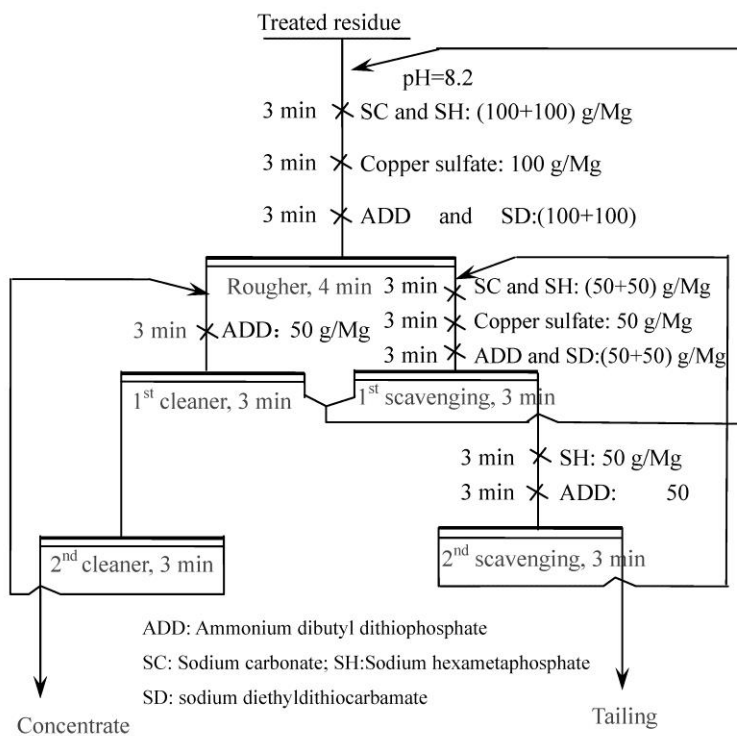
Fig. 8. Flow-chart of close-circuit flotation test

Table 4. Results of close-circuit flotation test

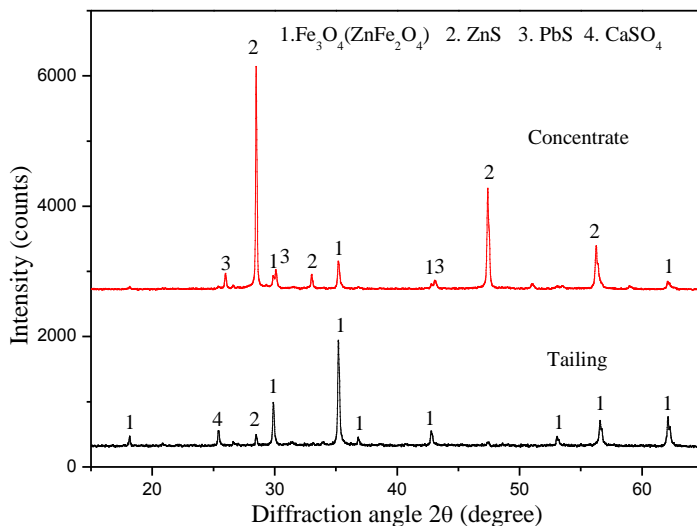| Products	Yield (%)	Grade			Recovery		
		Pb (%)	Ag (g/Mg)	Zn (%)	Pb (%)	Ag (%)	Zn (%)
Concentrate	30.86	5.88	973.54	39.13	59.59	77.41	48.38
Tailing	69.14	1.78	126.80	18.63	40.41	22.59	51.62
Feed	100.00	3.05	388.06	24.95	100.00	100.00	100.00

Fig. 9. XRD patterns of flotation concentrate and tailing

Conclusions

$PbSO_4$ and $ZnSO_4$ in the zinc leaching residue could be simultaneously converted to their respective sulfides by reduction roasting. The optimum operating process parameters for conversion were determined as: roasting temperature 700 ^{o}C, coal dosage 8%, reaction time 90 minutes and pyrite dosage 2%. Under these experimental conditions, the conversion extents of $PbSO_4$ and $ZnSO_4$ were 71.89 and 69.76%, respectively.

A flotation concentrate was obtained containing 39.13% Zn, 6.93% Pb and 973.54 g/Mg Ag from the treated material, and the recovery of Zn, Pb and Ag was 48.38%, 68.23% and 77.41%, respectively. The novel processing technology has a promising application. On the one hand, selective conversion of sulfates to sulfides could be carried out at lower temperature and the pollution caused by release of SO_2 was reduced. On the other hand, the novel treatment removed significant amounts of soluble metal ions, which made the consumption of flotation reagent decreased and the recoveries of valuable metals improved.

Acknowledgements

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