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## Extraction and separation of zinc, lead, silver, and bismuth from bismuth slag

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**Abstract:** The present paper deals with the extraction and separation of zinc, lead, silver, and bismuth from a refractory bismuth refining slag via a hydrometallurgical route. The process consists of a preliminary leaching of zinc with water, followed by the selective leaching of lead and silver with a calcium chloride solution, leading to the crystallization of lead chloride and the cementation of silver. The diagrams of the total concentrations of  $[Pb]/[Ag]$  versus  $[Cl^-]$  and temperature in the Pb/Ag-Cl-H<sub>2</sub>O system were drawn, respectively, to determine the optimum concentration of leaching agent and leaching temperature. The potential-pH diagram of the Pb/Ag/Bi-H<sub>2</sub>O system indicates that the preferential leaching of lead and silver could be achieved. Finally, 98.8% of lead and 90.4% of silver were selectively removed by further leaching the water leaching residue with 400 g/dm<sup>3</sup> of CaCl<sub>2</sub> solution at pH 4.5 and 80 °C, while only 3.7% of bismuth was leached in this stage. Fifty-nine percent of lead in the leach liquor was separated out as PbCl<sub>2</sub> by natural cooling. Ninety-five percent of silver in mother liquor was recovered by cementation with a lead sheet. The depleted CaCl<sub>2</sub> solution can be sent to the leaching step again to close the loop.

**Keywords:** bismuth, zinc, lead, silver, extraction and separation

### 1. Introduction

Bismuth is now widely used in chemicals (including pharmaceuticals, pigments, and cosmetics), metallurgical additives for casting and galvanizing, alloys, solders, and photocatalytic materials (Zhang et al., 2006; Pistofidis et al., 2007), and is applied as an anode in Na-ion batteries in recent studies (Su et al., 2015). Bismuth is mostly a byproduct of lead smelting (Ojebuoboh, 1992), along with silver, zinc, antimony, and other metals, and also of tungsten production, along with molybdenum and tin, and copper production (Warren, 1996). Taking lead smelting as an example, bismuth is generally concentrated in the smelting slag of lead anode mud. The slag is treated in the converter by carbothermal reduction to produce crude bismuth, which is then refined by chlorination to remove the impurity metals lead, zinc, and silver. Consequently, a refining waste slag is generated during the refining of the crude bismuth by chlorine (Xiong and Xiao, 2005). This slag is unacceptable to lead smelters because the lead in the slag mainly exists in the form of lead chloride, which is volatile at temperature of lead smelting and thus refractory. World refinery production of bismuth is tens of thousands of tons per year (Anderson, 2014). As a result, huge quantities of bismuth refining slag are dumped continuously and pose a potential environmental threat due to entrained considerable amounts of heavy metals (lead, bismuth, and silver).

Recycling associated bismuth from the lead slag is difficult primarily because of the scattering of bismuth. Almeida and Amarante (1995) studied the simultaneous leaching of valuable metals silver, lead, and bismuth from sulfide residues with cyanide, thiourea and chloride. Most research focused on the selective leaching of bismuth from bismuth bearing materials with an H<sub>2</sub>SO<sub>4</sub>-NaCl solution (Yang et al., 2009a; Yang et al., 2009b; Chen et al., 2012; Zhang et al., 2012; Ha et al., 2015). Mostly, lead and

silver associated with bismuth remain in the leaching residue and the bismuth is leached into the solution. The mechanism is that the dissolution of bismuth is much larger than lead and silver in the  $\text{H}_2\text{SO}_4\text{-NaCl}$  medium. The leaching process generally requires sulfuric acid solution with a high concentration (1–2 M). Cementation, hydrolysis, solvent extraction, ion-exchange and electrodeposition are subsequently used to extract the bismuth from the solution (Argekar and Shetty, 1995; Sarkar and Dhadke, 1999; Campos et al., 2008; Yang et al., 2009a; Chen et al., 2012; Navarro et al., 2014; Ha et al., 2015). In addition, Cao et al. (2010) investigated the leaching of lead anode slime in an  $\text{HCl-Cl}_2$  system; similarly, the bismuth and some metals, like antimony and copper, were preferentially leached while the lead and silver were concentrated in the residue in the form of  $\text{PbCl}_2$  and  $\text{AgCl}$ . Liu et al. (2010) studied the leaching behavior of lead in the  $\text{H}_2\text{SO}_4\text{-NaCl}$  medium, which shows that the lead is more likely to precipitate in the form of  $\text{PbCl}$  when  $[\text{Cl}^-]$  is 2.4 M and  $[\text{H}^+]$  is 3.0 M. Although the separation of bismuth from lead and silver can be achieved in  $\text{H}_2\text{SO}_4\text{-NaCl}$  medium by the preferential leaching of bismuth, the treatment of leaching residue rich in lead chloride is still a problem.

In this context, a novel hydrometallurgical process was proposed to achieve the preferential leaching of valuable metals zinc, lead, and silver from bismuth refining slag while minimizing the extent of bismuth dissolution. In addition, the separation of leached metals was studied. The process consists of a preliminary leaching of zinc with water, followed by the selective leaching of lead and silver with calcium chloride solution, the crystallization of lead chloride and the cementation of silver. As the leaching of bismuth was inhibited, bismuth was finally concentrated in the leaching residue, which could be returned to smelting system for recovery. The optimum conditions for leaching, crystallization, and cementation were investigated in the present work.

## 2. Materials and methods

### 2.1. Material

The contents of the main metal elements of slag are listed in Table 1. The elemental composition is dominated by lead and bismuth. The concentration of silver is also substantial. The X-ray diffraction (XRD) pattern (Fig. 1) shows that the main phases of bismuth refining slag are bismuth (Bi), bismoclite ( $\text{BiOCl}$ ), and cotunnite ( $\text{PbCl}_2$ ). Because of the low content, zinc and other metals are not found in the pattern.

Table 1. Contents of the main metal elements of the bismuth refining slag

Pb, %	Bi, %	Zn, %	Cu, %	Fe, %	Sb, %	Ag, g/Mg
40.85	26.08	1.86	1.50	1.03	0.25	1080

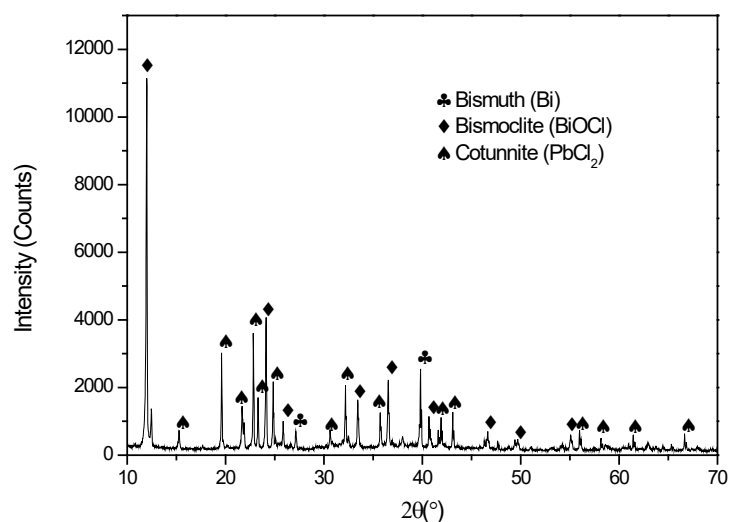


Fig. 1. XRD pattern of the bismuth refining slag

## 2.2. Experimental procedure

The tests on the dissolution of lead chloride and silver chloride in calcium chloride and sodium chloride solutions, respectively, were carried out in a beaker, heated and stirred by a magnetic stirring-heating device (RCT basic, IKA, Germany) at 500 rpm. Excessive amounts of lead chloride and silver chloride were added into the solutions and dissolved partly at a predetermined temperature for 4 h. To prevent the hydrolysis of lead and silver, the pH of the solutions was maintained at 4.5 with hydrochloric acid. After the dissolution, 1 mL solution was collected and diluted by 400 cm<sup>3</sup> 400 g/dm<sup>3</sup> CaCl<sub>2</sub> solution (pH 4.5) or 300 g/dm<sup>3</sup> NaCl solution (pH 4.5) to analyze the concentration of lead and silver. All reagents used in this work were of analytically pure grade.

The batch tests of the leaching and precipitation of zinc and the leaching of lead and silver were conducted in a beaker, stirred by a mechanical stirrer (RW20 digital, IKA, Germany) at 500 rpm in a water bath (HH-2, Guohua Electric Appliance Co. Ltd., China). After the leaching, slurry was filtered rapidly using a small centrifuge (SS150, Bluebird Machinery Co. Ltd., China) and the filter cake was washed with distilled water. The pH and potential of the solutions were determined by a pH-potential meter (PHS-3E, Shanghai REX Instrument Factory, China).

The leaching liquor of lead and silver was treated by natural cooling crystallization at ambient temperature (25 °C). Lead chloride crystallization was carried out in a beaker, stirred by the mechanical stirrer at 100 rpm. The solution and lead chloride crystals were separated by filtration.

The silver in the lead-silver leach liquor was cemented with a lead sheet (55 mm × 60 mm × 2 mm). The cementation was carried out in a 0.5 dm<sup>3</sup> beaker under stirring by the magnetic stirring-heating device at 100 rpm. The lead sheet was suspended in solution. 5 cm<sup>3</sup> aliquots of solution were collected at certain time intervals for analysis. The solution after cementation was filtered to obtain the silver deposits.

## 2.3. Analytical methods

The chemical compositions of the slag, leaching residue and solutions were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Chemical compositions of the zinc hydroxide precipitate, lead chloride crystals and cemented deposits were analyzed by X-ray fluorescence (XRF). Furthermore, except for the cemented deposits, the silver in abovementioned materials was analyzed by atomic absorption spectrometry (AAS).

## 3. Results and discussion

### 3.1. Leaching and precipitation of zinc

As the zinc in the bismuth refining slag existed mainly as zinc chloride, which was readily soluble in water, a water leaching was chosen to treat the slag first. 100 g ground slag (<0.15 mm) was leached at a liquid/solid ratio of 4:1 and a temperature of 25 °C for 2 h. The leaching liquor contained 4.5 g/dm<sup>3</sup> Zn, 0.82 g/dm<sup>3</sup> Pb, 0.2 g/dm<sup>3</sup> Cu, and 1.2 mg/dm<sup>3</sup> Ag with a pH of 5.0. The leaching ratio of zinc was calculated to be 96.8%, which shows that the leaching of zinc was almost complete. The leaching ratios of lead, silver and copper were calculated to be 0.8%, 0.4% and 5.3%, respectively. Owing to its low concentration (<5 mg/dm<sup>3</sup>), the leaching of bismuth was negligible.

Except for the main metal, zinc, other metals in the solution have relatively low concentrations, so the recovery of zinc is a prime consideration. The solvent extraction method has been explored by researchers for extracting zinc from spent solutions and was shown to have a good separation effect (Sinha et al., 2016). However, the direct hydrolysis precipitation method is still an easy and economical way to recover zinc from solution. Hence, it was employed in the present work. As the pH is the key factor affecting the precipitation efficiency, the experiment was carried out at various pH values. The pH of the solution was adjusted by adding readily available calcium oxide. Fig. 2 shows the effect of pH on the precipitation efficiency of zinc. The maximum precipitation of zinc was obtained at pH 7.0 with a value of 99.9%. The chemical composition of the zinc hydroxide precipitate is shown in Table 2. The zinc hydroxide precipitate can be used for extraction of zinc.

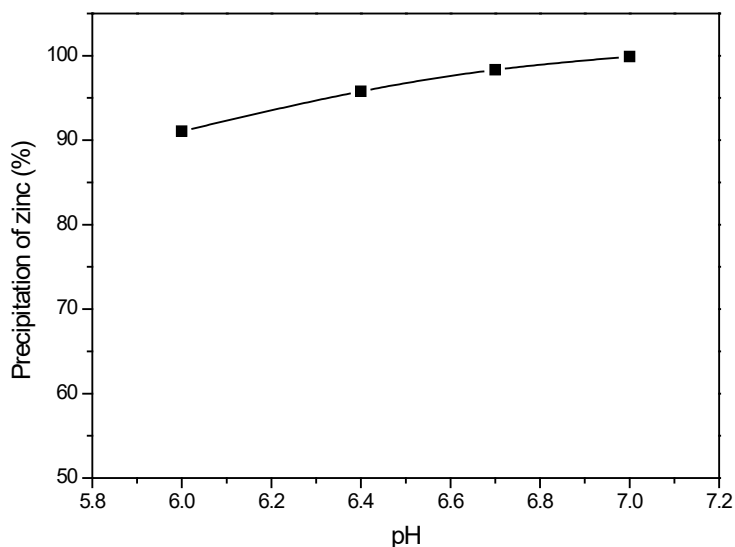


Fig. 2. The effect of pH on the precipitation of zinc (temperature: 25 °C; time: 2 h; pH: 6.0, 6.4, 6.7, and 7.0)

Table 2. Chemical composition of the zinc hydroxide precipitate (wt% -XRF)

ZnO	CaO	PbO	CuO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
68.90	17.77	6.81	3.14	0.56	0.16

### 3.2. Leaching of lead and silver

#### 3.2.1. Selection of leaching agent and determination of concentration of leaching agent and leaching temperature

As the main phase of lead in the slag is cotunnite, chloride was the preferred leaching agent. Sodium chloride has been employed as a leaching agent to extract lead from various materials in the past (Raghavan et al., 2000; Exposito et al., 2001; Chmielewski et al., 2017). In addition, research on the leaching of lead by hydrochloric acid has been reported (Nagib and Inoue, 2000; Adebayo and Olasehinde, 2015). In systems with high chloride concentrations, metal ions exist mainly in the form of chlorocomplexes. The total concentration of [Pb]/[Ag] in chloride solutions can be described as follows:

$$[\text{Pb}]_{\text{T}} = [\text{Pb}^{2+}] + [\text{PbCl}^+] + [\text{PbCl}_2] + [\text{PbCl}_3^-] \quad (1)$$

$$[\text{Ag}]_{\text{T}} = [\text{Ag}^+] + [\text{AgCl}] + [\text{AgCl}_2^-] + [\text{AgCl}_3^{2-}] \quad (2)$$

The function of the total concentration of [Pb]/[Ag] with [Cl<sup>-</sup>] was established by means of the ion solubility product (K<sub>sp</sub>) and complex constant (logK) of PbCl<sub>2</sub> and AgCl in Table 3, as shown below:

$$[\text{Pb}]_{\text{T}} = K_{\text{sp}} (1/[\text{Cl}^-]^2 + K_1/[\text{Cl}^-] + K_2 + K_3[\text{Cl}^-]) \quad (3)$$

$$[\text{Ag}]_{\text{T}} = K_{\text{sp}} (1/[\text{Cl}^-] + K_1 + K_2[\text{Cl}^-] + K_3[\text{Cl}^-]^2) \quad (4)$$

Table 3. The activity product (K<sub>sp</sub>) and complex constant (logK) of PbCl<sub>2</sub> and AgCl (Speight, 2004)

Reaction	K <sub>sp</sub>	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>3</sub>
PbCl <sub>2</sub> = Pb <sup>2+</sup> + 2Cl <sup>-</sup>	1.6×10 <sup>-5</sup>			
Pb <sup>2+</sup> + iCl <sup>-</sup> = PbCl <sub>i</sub> <sup>2-i</sup> i = 1,2,3		1.42	2.23	3.23
AgCl = Ag <sup>+</sup> + Cl <sup>-</sup>	1.8×10 <sup>-10</sup>			
Ag <sup>+</sup> + jCl <sup>-</sup> = AgCl <sub>j</sub> <sup>1-j</sup> j = 1,2,3		3.04	5.04	5.3

The diagram of the total concentration of [Pb]/[Ag] versus [Cl<sup>-</sup>] in the Pb/Ag-Cl-H<sub>2</sub>O system was drawn by taking the logarithm of the Eqs. (3) and (4), as shown in Fig. 3.

Due to the complexation of Pb/Ag with  $\text{Cl}^-$ , the dissolution of  $\text{PbCl}_2/\text{AgCl}$  in chloride aqueous solution increased obviously with the increase in  $[\text{Cl}^-]$  in the range of 0.8–7.2 M. Measured values of  $\log[\text{Me}]_T$  in  $\text{CaCl}_2$  and  $\text{NaCl}$  solutions (pH 4.5) verified this law. As shown in Fig. 3, there are small differences between  $\text{NaCl}$  and  $\text{CaCl}_2$  systems; nevertheless, as the solubility of  $\text{CaCl}_2$  is larger than that of  $\text{NaCl}$  in water ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ : 100;  $\text{NaCl}$ : 36.1, at 30 °C (Speight, 2004)), the former can provide more chloride ions and thus dissolve more lead and silver.

The dissolution of lead chloride in 400  $\text{g}/\text{dm}^3$  of  $\text{CaCl}_2$  and 300  $\text{g}/\text{dm}^3$  of  $\text{NaCl}$  solutions at pH 4.5 and different temperatures was measured. The concentration of lead versus temperature is shown in Fig. 4. The dissolution of  $\text{PbCl}_2$  increases with the increasing of temperature in both chloride solutions, but there is a larger increment in  $\text{CaCl}_2$  solution. On the basis of the results of Figs. 3 and 4,  $\text{CaCl}_2$  was selected as the optimal leaching agent and the concentration of  $\text{CaCl}_2$  was set to 400  $\text{g}/\text{dm}^3$ . The  $\Delta C$ , saturation concentration value difference, for lead between 25 °C and 80 °C in  $\text{CaCl}_2$  solution was also found to be larger than that in  $\text{NaCl}$  solution. Because of the large  $\Delta C$  for the  $\text{CaCl}_2$  solution, a process of leaching lead from refining slag at high temperature and recovering it by crystallization at ambient temperature was proposed. In view of this, the leaching temperature was set to 80 °C and the liquid/solid ratio (v/w) was set to 8:1.

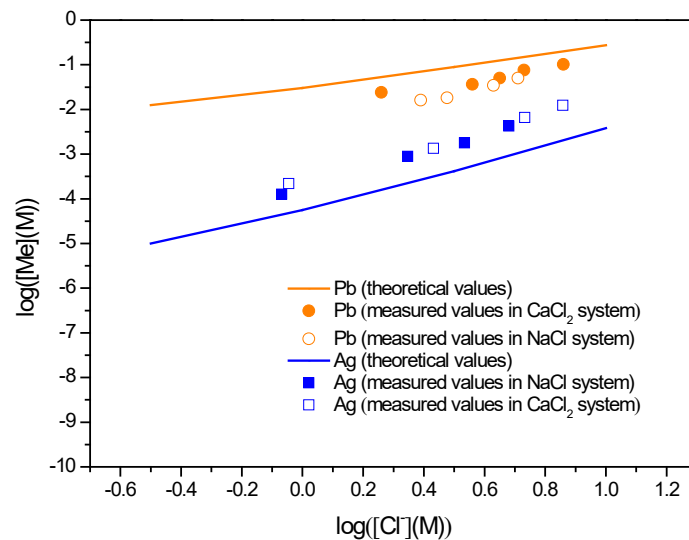


Fig. 3. Diagram of the total concentration of  $[\text{Pb}]/[\text{Ag}]$  versus  $[\text{Cl}^-]$  in the  $\text{Pb}/\text{Ag}-\text{Cl}-\text{H}_2\text{O}$  system (25 °C)

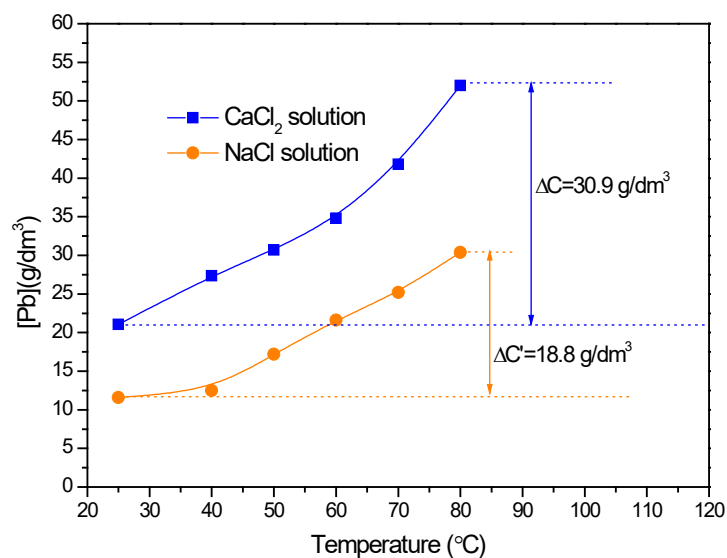


Fig. 4. Diagram of the dissolution of  $\text{PbCl}_2$  versus temperature ( $\text{CaCl}_2$  concentration: 400  $\text{g}/\text{dm}^3$ ;  $\text{NaCl}$  concentration: 300  $\text{g}/\text{dm}^3$ ; pH 4.5)

### 3.2.2. Influence of pH

A potential-pH diagram is a plot of the equilibrium potential (Eh) between a metal and its various oxidized species as a function of pH (Hinai et al., 2014), which provides comprehensive visual summaries of solubility relationships in aqueous process systems (Kim and Asare, 2012). Therefore, the potential-pH diagram of the Pb/Ag/Bi-H<sub>2</sub>O system (Fig. 5) was drawn in this work to assess the possibilities of the selective leaching of lead and silver. The thermodynamic data used in this work are listed in Table 4 (Speight, 2004).

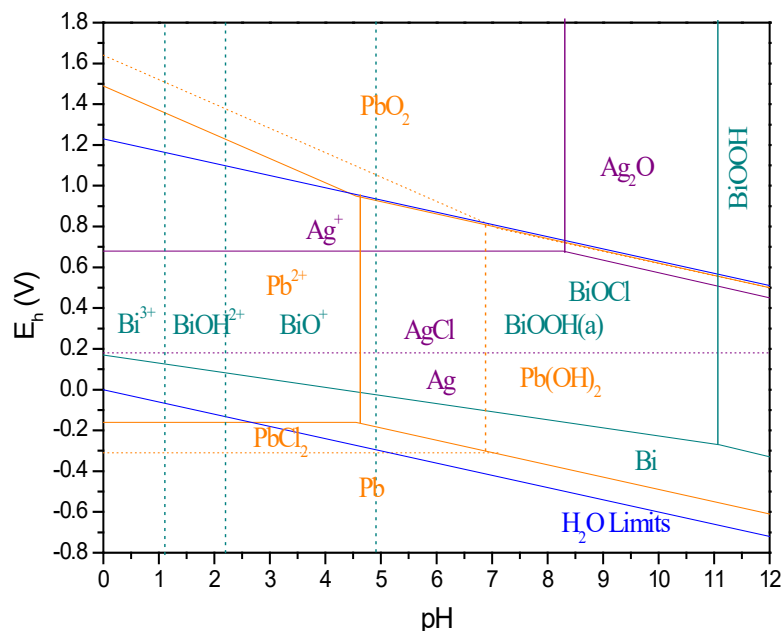


Fig. 5. Eh-pH diagram for the Pb-, Ag-, Bi-H<sub>2</sub>O systems at 25 °C ([Pb]=10<sup>-1</sup> M, [Bi]=10<sup>-1</sup> M, [Ag]=10<sup>-2</sup> M, [Cl<sup>-</sup>]=5 M)

Table 4. Thermodynamic data for Pb-, Ag-, Bi-H<sub>2</sub>O systems at 25 °C

Species	$\Delta_f G^\circ$ (kJ/mol)	Species	$\Delta_f G^\circ$ (kJ/mol)
Ag	0	Bi	0
Ag <sup>+</sup>	77.12	Bi <sup>3+</sup>	95.65
Ag <sub>2</sub> O	-11.21	BiOCl	-322.2
AgCl	-109.8	BiOOH	-368.4
Pb	0	BiO <sup>+</sup>	-146.5
Pb <sup>2+</sup>	-24.4	BiOH <sub>2</sub> <sup>+</sup>	-135.2
PbCl <sub>2</sub>	-314.1	BiOOH(a)	-331.8
Pb(OH) <sub>2</sub>	-452.5	H <sup>+</sup>	0
PbO <sub>2</sub>	-217.3	H <sub>2</sub> O	-237.14
		Cl <sup>-</sup>	-131.3

As shown in Fig. 5, owing to the low leaching potential of chloride and large stable pH range (0–7.1 for PbCl<sub>2</sub> and 0–12 for AgCl), the leaching of silver chloride and lead chloride becomes easier under the premise that there is a sufficient concentration of chloride ions in the solution. In addition, Fig. 5 indicates that BiOCl has a large stable area (pH 0–11.1), which means that the preferential leaching of lead and silver could be achieved. It should be noted that the predominance areas of bismuth ions show that Bi<sup>3+</sup>, BiOH<sub>2</sub><sup>+</sup>, BiO<sup>+</sup>, and BiOOH ions coexist with BiOCl successively in different pH ranges, and thus the real effect of pH on the leaching is well worth examining.

The effect of the pH on the leaching of lead, silver, and bismuth was investigated in the range of 0.5–6.0. The pH of the solution was adjusted by adding hydrochloric acid. Other constant operation conditions are as follows:  $\text{CaCl}_2$  concentration  $400 \text{ g/dm}^3$ , temperature  $80 \text{ }^\circ\text{C}$ , and time 2 h. The potential of the solution was spontaneously around 0.4 V. Lead, silver, and bismuth extractions versus pH are shown in Fig. 6. It was found that the leaching of bismuth increased rapidly with the decrease in pH when the pH was below 3.0, while the extractions of lead and silver basically achieved balance when the pH was below 4.5. The experimental results confirm the conclusions from the Eh-pH diagram. In order to obtain high extractions of lead and silver and low extraction of bismuth, so as to achieve the selective leaching of lead and silver, the optimum pH was determined to be 4.5.

The batch test results show that the optimum conditions for the selective leaching of lead and silver are:  $\text{CaCl}_2$  concentration  $400 \text{ g/dm}^3$ , temperature  $80 \text{ }^\circ\text{C}$  and pH 4.5. The extraction yields of lead, silver and bismuth under optimum conditions are 98.8%, 90.4% and 3.7%, respectively. The X-ray diffraction pattern (Fig. 7) shows that the main phases of the leaching residue are bismuth and bismoclite. It is revealed that the main phases of bismuth were concentrated while the main phase of lead was almost entirely dissolved after the  $\text{CaCl}_2$  leaching. The second leaching residue containing 87.46% of Bi, 1.58% of Pb and 361 g/Mg of Ag could be returned to the bismuth smelting system to recover bismuth and silver.

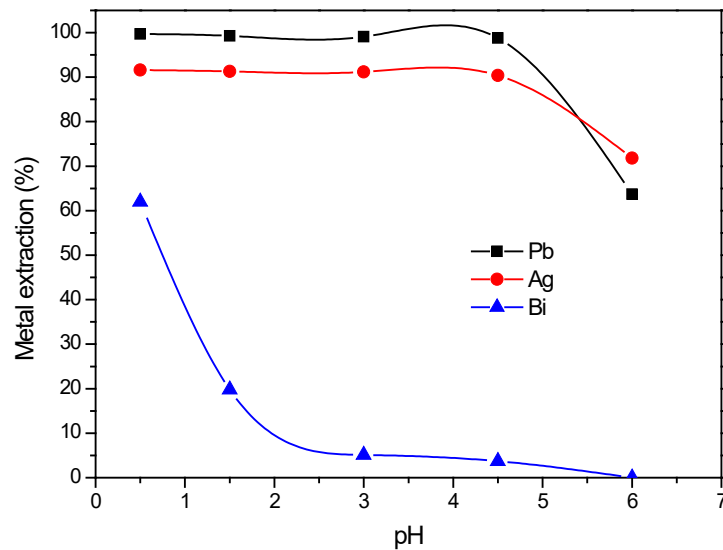


Fig. 6. Influence of pH on the leaching of lead, silver and bismuth ( $\text{CaCl}_2$  concentration:  $400 \text{ g/dm}^3$ ; temperature:  $80 \text{ }^\circ\text{C}$ ; pH: 0.5, 1.5, 3.0, 4.5, and 6.0)

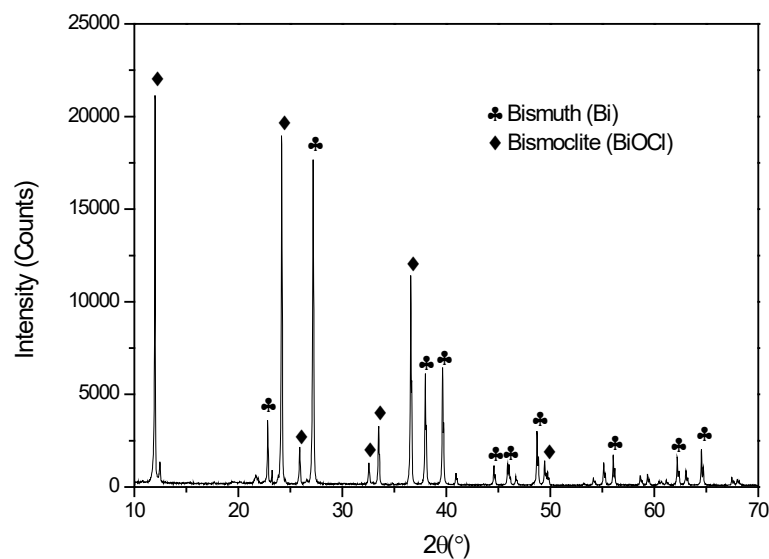


Fig. 7. XRD pattern of the leaching residue

### 3.3. Crystallization of lead chloride

The cooling crystallization process is a useful method to separate metals with different solubilities from the aqueous solution (Han et al., 2017). As the concentration of silver in the leaching liquor was lower than its solubility (Fig. 3), a cooling crystallization process was performed to separate silver and lead in the leaching liquor.

The Pb-Ag leaching liquor was naturally cooled at ambient temperature and aged for 2 h. The lead chloride crystals were analyzed by XRF and subsequently characterized by XRD. Only trace amounts of calcium, iron, and silver were found in the lead chloride crystal (Table 5). The XRD patterns of the lead chloride crystal (Fig. 8) show that all the diffraction peaks can be indexed for the structure of lead chloride without any identifiable impurities, and the sharp and strong peaks imply that particle growth takes place with high crystallinity. Table 5 and Fig. 8 both suggest that the lead chloride crystal is sufficiently pure. The concentration of lead in the crystal mother liquor was 20.6 g/dm<sup>3</sup>; accordingly, the crystallization yield of lead was calculated to be 58.9%. The loss of silver in the lead chloride crystal is almost negligible.

Table 5. Component of lead chloride crystal (wt% -XRF)

Pb	Cl	Ca	Fe	Ag
77.03	22.8	0.10	0.04	10.3 g/Mg

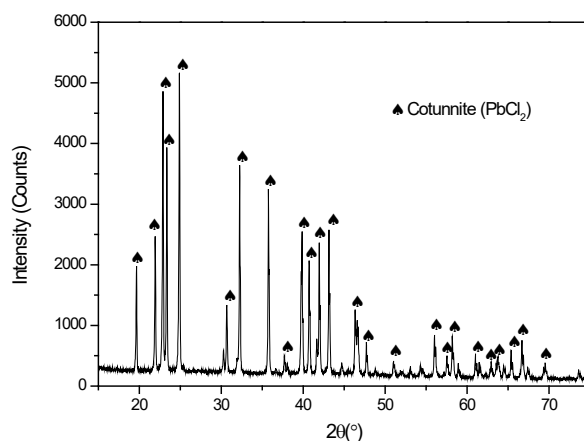


Fig. 8. XRD pattern of the lead chloride crystal

### 3.4. Cementation of silver

Cementation is an electrochemical process widely used in the industry for the removal of silver metal ions. Various metal cementing agents, such as zinc, copper, and iron, have been used in the silver recovery from leached solutions (Syed, 2016). Nevertheless, there are few studies reporting on the cementation of silver by lead. The  $E^0$  for the  $\text{Ag}^+$  and  $\text{Pb}^{2+}$  are 0.799 and -0.126 V (Speight, 2004), respectively, which indicates that the cementation of silver by lead will proceed. In order not to introduce impurity metals into the solution or increase the treatment cost of the solution, lead was used as cementing agent in the present work.

The overall reaction for the silver ion cementation by lead in the chloride solution can be expressed by the following equation:



The effect of temperature on the silver cementation was investigated at 25, 60, and 90 °C for 3 h, and cementation efficiencies of 76.2%, 95.3%, and 88.2% were obtained, respectively. The increase in temperature was obviously favorable for the cementation of silver. However, the highest temperature (90 °C) was counter-productive. This is in agreement with the research on noble metal cementation by Mpinga et al. (2014). The excessive temperature resulted in the decrease in cementation efficiency, the increase in the dissolution of cementing agent and evaporation of the solution. Thus, 60 °C is the optimum for the cementation of silver in the present work.



The variations in silver cementation with various cementing time (1–4 h) were also investigated at 60 °C. As shown in Fig. 9, the cementation efficiency of silver increased with the increasing of reaction time and gradually tended to stabilize at 4 h. The best (optimum) cementation result obtained is 95.3% removal of silver at 60 °C and reaction time of 4 h. The chemical composition of cemented deposits is shown in Table 6. The main impurities in deposits are bismuth, copper and lead. The silver deposits can be purified to produce silver ingots.

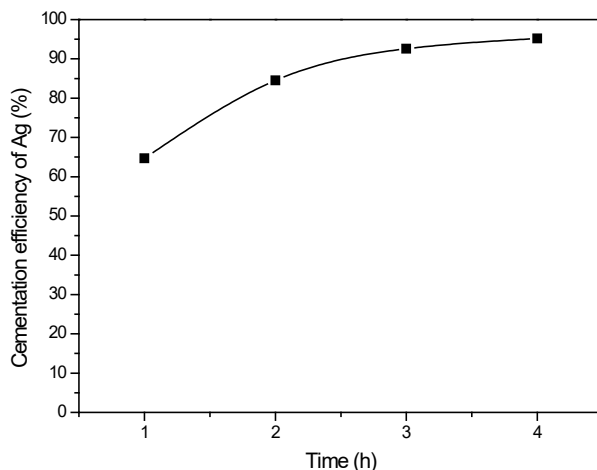


Fig. 9. Effect of reaction time on the cementation (temperature: 60 °C; time: 1, 2, 3, and 4 h)

Table 6. Chemical composition of the cemented deposits (wt%–XRF)

Bi	Ag	Cu	Pb	Sb	Fe	As	Cl	Ca	Si	Zn
28.80	24.87	23.01	17.28	2.85	1.17	0.66	0.52	0.36	0.22	0.10

### 3.5. Treatment of the solution after removal of silver

To assess the feasibility of the recycling of the solution after the removal of silver, the 0.4 dm<sup>3</sup> solution containing 5.7 mg/dm<sup>3</sup> of Ag and 20.8 g/dm<sup>3</sup> Pb was reused to leach the lead and silver from 30 g slag under the optimum conditions. The extraction yields of lead, silver, and bismuth were 98.3%, 90.1%, and 3.2%, respectively. This indicates that the depleted Pb-bearing CaCl<sub>2</sub> solution is recyclable and can be replenished with Pb<sup>2+</sup> by sending it back to lead leaching where it extracts Pb<sup>2+</sup> from the water leaching residue.

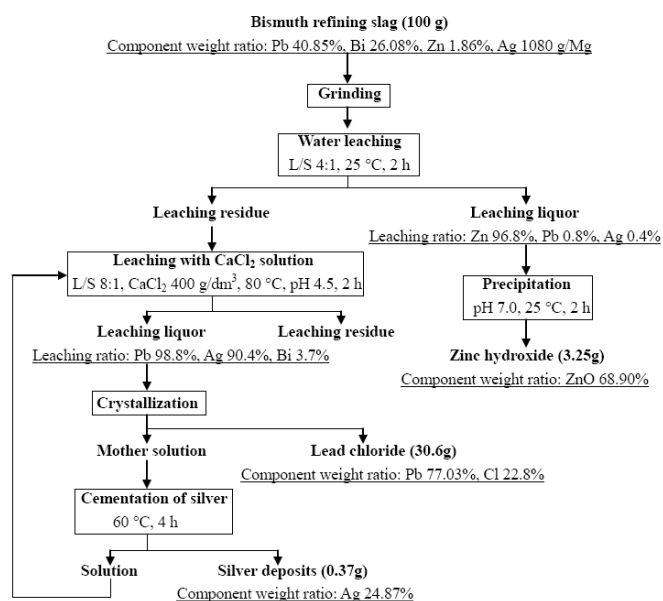


Fig. 10. Proposed flow sheet for the treatment of bismuth refining slag

Based on the present study, an integrated flow sheet (Fig. 10) has been developed for the extraction and separation of valuable metals zinc, lead, silver, and bismuth from bismuth refining slag.

#### 4. Conclusions

The process is an attractive solution for treating refractory bismuth bearing slag, comprehensively recovering the zinc, lead, silver, and bismuth from the slag. Distinguished from the existing processes, zinc, lead, and silver were preferentially leached from the slag while the bismuth remained in the residue in this process. The lead in the leaching liquor was recovered in the form of pure lead chloride by natural crystallization and the silver was recovered by cementation with a lead sheet. No liquid effluent is produced in the process and it has low reagent consumption. The process is simple, eco-efficient and environmentally friendly. In addition, it produces value-added products with a high metal recovery. Based on the experiments conducted, the following conclusions are drawn:

(1) The leaching of zinc was complete under the conditions of liquid/solid ratio 4:1, temperature 25 °C and leaching time 2 h. The maximum precipitation of zinc was obtained at pH 7.0 with a value of 99.9%. The zinc hydroxide precipitate can be used for extraction of zinc.

(2) The theoretical and measured values of the total concentration of [Pb]/[Ag] versus [Cl<sup>-</sup>] in the Pb/Ag-Cl-H<sub>2</sub>O system show that the dissolution of PbCl<sub>2</sub>/AgCl in chloride aqueous solutions increased obviously with the increase in [Cl<sup>-</sup>] in the range of 0.8–7.2 M. CaCl<sub>2</sub> was finally determined to be the optimum leaching agent and the optimum concentration of CaCl<sub>2</sub> was determined to be 400 g/dm<sup>3</sup>.

(3) The diagram of the dissolution of PbCl<sub>2</sub> versus temperature shows that the dissolution of PbCl<sub>2</sub> increases with increasing temperature, and there is a large saturation concentration difference for lead between 25 °C and 80 °C in CaCl<sub>2</sub> solutions. Based on this, the lead was leached at high temperature and recovered by crystallization at ambient temperature.

(4) The Eh-pH diagram indicates that the preferential leaching of lead and silver could be achieved. The optimum conditions for the selective leaching of lead and silver were found to be: CaCl<sub>2</sub> concentration 400 g/dm<sup>3</sup>, temperature 80 °C and pH 4.5. The extraction yields of lead, silver, and bismuth under optimum conditions are 98.8%, 90.4%, and 3.7%, respectively.

(5) The final leaching residue could be returned to bismuth smelting system to recover bismuth. The depleted Pb-bearing CaCl<sub>2</sub> solution can be sent to the leaching step again to close the loop.

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