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Leaching of zinc sulfide in alkaline solution via chemical conversion with lead carbonate

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Abstract

A novel hydrometallurgical process for recovering Zn from ZnS in alkaline solution via chemical conversion with $PbCO_3$ was developed in this work. The S originally present in ZnS can be converted into PbS, while the Zn can be converted into $Na_2Zn(OH)_4$ in the alkaline solution in the presence of $PbCO_3$. And then, the Pb in PbS deposited in the leach residues can be converted into $PbCO_3$ again in the Na_2CO_3 solution. It was found that over 90% of Zn can be extracted from ZnS when the leaching process is operated in 6 mol/L NaOH solution at 90 °C with $PbCO_3$ as additive, and over 95% of PbS in the leach residues can be converted into $PbCO_3$ by stirring the leach residues in Na_2CO_3 solution with air bubble at a temperature of 80 °C. The leaching solution can be used to produce metallic zinc powder by electrowinning after chemical separation of impurities.
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Keywords: Zinc sulfide; Alkaline leaching; Lead carbonate; Sphalerite

1. Introduction

Since 2001 world zinc consumption has grown annually by 3.6% in 2002, 3.9% in 2003, 7.2% in 2004 and 3.6% in 2005 (Brook Hunt, June 2006). Currently, most of zinc is produced from zinc sulfides ores because the sulfides can easily be separated from gangue and concentrated by conventional flotation techniques. Oxidized zinc ores, such as smithsonite ($ZnCO_3$), willemiye (Zn_2SiO_4), hydrozincite ($2ZnCO_3$ $3Zn(OH)_2$), zincite (ZnO), and hemimorphite ($Zn_2SiO_3H_2O$), have also long been an important source of zinc. However, their concentration was difficult. And, until relatively recently, only rich ores were exploited, using limited concentration by washing and gravity methods. For the low grade oxidized zinc ores, the exploitation and metallurgy is very limited.

In our previous work, a cost-effective alkaline leaching and electrowinning process for the extraction of zinc and lead from the oxidized zinc ore was developed (Youcai and Stanforth, 2000, 2001). It was found that over 85% of both Zn and Pb, and less than 10% of Al can be leached from the ore respectively when the leaching operation is conducted at over 95 °C using 5 mol/L NaOH solution as leaching agent. The dissolution of other elements such as Fe, Mg, Cu, Ca, Cd, Co, Ni, etc, was negligible, which had no effect on the electrowinning of zinc in alkaline solution. The typical composition of leach solution is in the range of 22–25 g/L Zn, 2.96–3.05 g/L Pb, and 0.5–0.7 g/L Al.

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The corresponding zinc and lead contents in the resultant leaching residue were found to be lower than 0.1–2% and 0.05–0.2% respectively. After the lead in leach solution is separated selectively and quantitatively by the addition of sodium sulfide, the Pb-free solution is then used for the electrowinning of metallic zinc using stainless electrodes as cathode and titanium alloy as anode. A zinc metal powder with purity of over 99.5% can be thus obtained. The specific energy for the zinc electrowinning in alkaline leach solution is around 2.5–2.6 kWh/kg Zn, which is much lower than the corresponding energy consumption of 3.3 kWh/kg Zn in the conventional process of zinc electrowinning in acidic zinc sulfate solution.

However, the oxidized zinc ores usually co-existed with sphalerite which cannot be leached by NaOH solution under atmospheric pressure. In the conventional method of extracting zinc from sphalerite, the ore is roasted at 850–950 °C, leached the resultant zinc oxides with sulfuric acid solution, purified the leaching solution by a complex flowsheet, and then electrowon the zinc flake in the purified sulfuric acid solution. The obstacle for this process is the generation and emission of SO_2 in the roasting process.

Methods based on direct leaching of sphalerite under hydrothermal conditions have been given considerable attention (Niederkorn, 1985; Forward and Veltman, 1959; Peters, 1976; Sato and Lawson, 1983). H_2SO_4, HCl, HNO_3, and $HClO_4$, and ammonia (Wend, 1963; Limp, 1997; Sarveswara Rao and Ray, 1998) solutions have been used, and reasonable leaching efficiencies are obtained. However, these processes are not considered environmentally friendly and cost-effective due to the uses of high temperature and oxygen pressure parameters. Ferric salts (Dutrizac, 1981; Lachmann and Pedlick, 1995; Jin et al., 1993; Massacci et al., 1998) and persulphate (Babu et al., 2002) were also used as leaching agents, but found difficult to separate zinc from ferrous.

Hydrometallurgical treatment of metal sulfide minerals by chemical conversion process has been proposed, such as the conversion of PbS in galena into $PbCO_3$ in ammonium or sodium carbonate solution (Lu and Chen, 1986; Gong and Chen, 1993). Ions of copper and lead are known to have a catalytic effect on the ammonia leaching of sphalerite at high temperature and oxygen pressure (Ghosh et al., 1989, 1990), however, the effect of lead on alkaline leaching of zinc sulfide is not explored.

The objectives of this work are to develop a novel hydrometallurgical process for recovering Zn from ZnS in alkaline solution via chemical conversion with lead compounds. The S originally present in ZnS can be converted into PbS, while Zn can be converted into $Na_2Zn(OH)_4$ in the alkaline solution in the presence of lead compounds. And then, the Pb in PbS deposited in the leach residues can be recycled by reacting with Na_2CO_3. The possible industrial application is discussed.

2. Experimental

2.1. Leaching of ZnS

All the chemicals used were of analytical grade. Leaching tests were carried out in a flask placed on a thermostatically controlled magnetic stirrer. To a 200 ml sodium hydroxide solution, zinc sulfide and lead compound was added and then leached at constant temperature of 60–100 °C. The volume was kept constant by adding water. After the leaching operation was terminated, the slurry was filtered and the zinc and lead contents in the filtrate were analyzed by titration with EDTA. The leaching efficiencies of zinc were calculated according to the following equation:

$$\text{Zinc extraction} = [(C_1 \times V_1)/(W_1 \times C_2)] \times 100\% \quad (1)$$

where W_1 (g) is the mass of ZnS, V_1 (L) the volume of leaching solution, C_1 (g/L) the zinc concentrations in the leaching solution, C_2 (%) the percent of zinc content in the ZnS.

2.2. Conversion of leach residue

The leach residue was thoroughly washed with NaOH solution and water, and then dried. For the conversion tests, a given quantity of leaching residues and catalysts such as ferrous and cupric ions was added into a flask containing Na_2CO_3 solution, and heated at required temperature while stirred with a magnetic stirrer. Air was bubbled into the reaction mixture through a flowmeter. The solid was separated from the solution by filtration, and the solid residue was treated with NaOH solution to dissolve the $PbCO_3$ formed in the conversion process. The lead and zinc in leaching residues or conversion residues after dissolution in NaOH solution were analyzed by ICP. The percent of lead converted was calculated according to the following equation:

$$\text{Pb conversion} = [1 - (W_3 \times m_2)/(W_2 \times m_1)] \times 100\% \quad (2)$$

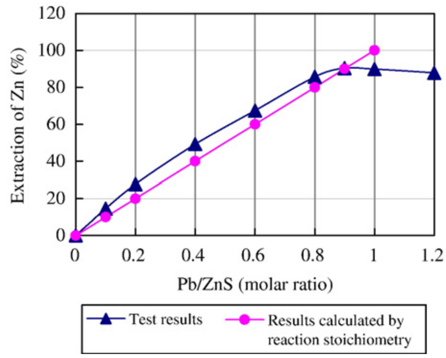

Fig. 1. Effect of the Pb/ZnS molar ratios on the zinc extraction (NaOH concentration 5 M, temperature 90 °C, phase ratios (v/w) 25, leaching time 120 min).

where W_2 (g) is the mass of leaching residue, W_3 (g) the mass of conversion residue after dissolution in NaOH solution, m_1 (%) the percent of lead content in the leaching residue, m_2 (%) the percent of lead content in the conversion residue after dissolution in NaOH solution.

3. Results

3.1. Effect of Pb/ZnS ratios

The following leaching tests were carried out at 90 °C, NaOH concentration of 5 mol/L, phase ratios (v/w) of 25:1, and leaching time of 120 min, otherwise indicated elsewhere. Only 0.1% zinc can be leached in the absence of lead compounds (PbO), as shown in Fig. 1. However, the leaching efficiency increased considerably as the lead compounds added, with a maximum leaching efficiency of around 90% at a Pb/ZnS molar ratio of over 0.9:1 which was used in the following tests.

It was found that PbS phase predominated in the leaching residue as shown in the XRD pattern, indicating that most of the S in the ZnS had been converted into PbS (Fig. 2).

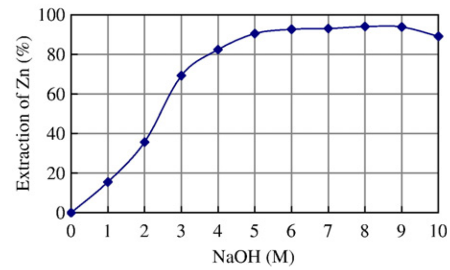

Fig. 3. Effect of the sodium hydroxide concentration on the zinc extraction (temperature 90 °C, phase ratios (v/w) 25, leaching time 120 min, Pb/ZnS molar ratios 0.9).

3.2. Effect of NaOH concentrations

The zinc extraction increased with the increase of sodium hydroxide concentrations and 94% of zinc can be leached at over 8 mol/L NaOH solution, as shown in Fig. 3. In practical

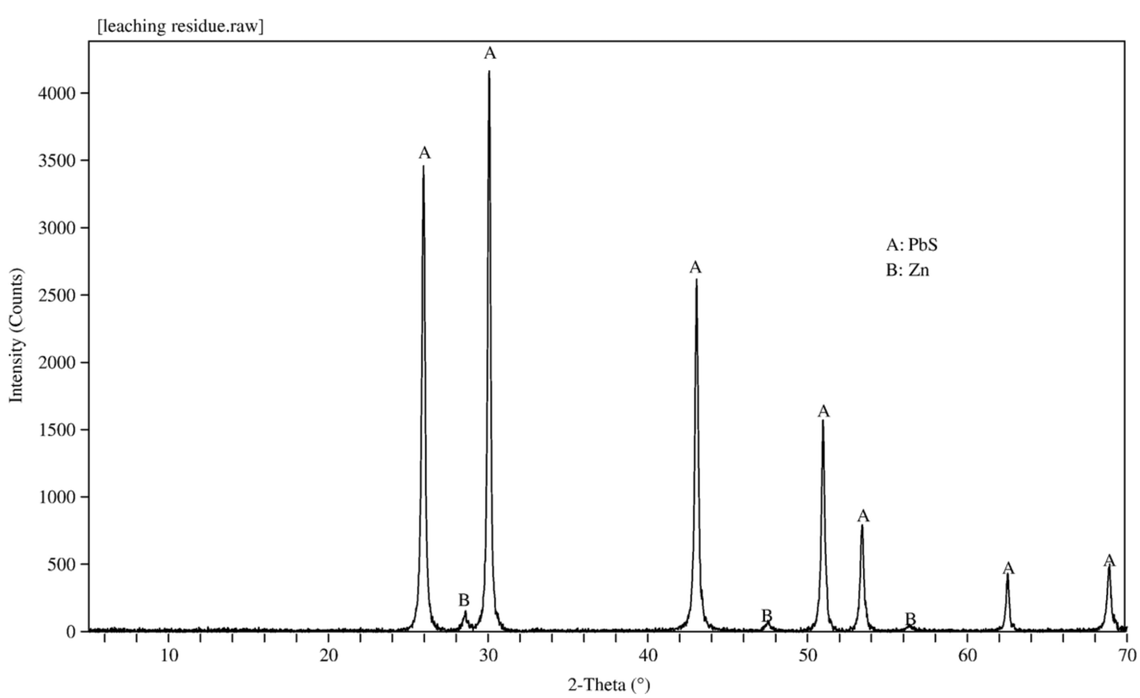

Fig. 2. XRD pattern of the leaching residue (temperature 90 °C, NaOH concentration 6 M, phase ratios (v/w)25, leaching time 120 min, Pb/ZnS molar ratios 0.9).

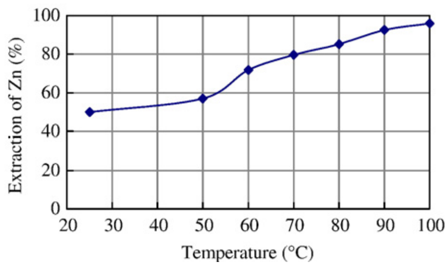

Fig. 4. Effect of temperature on the zinc extraction (NaOH concentration 6 M, phase ratios (v/w) 25, leaching time 120 min, Pb/ZnS molar ratios 0.9).

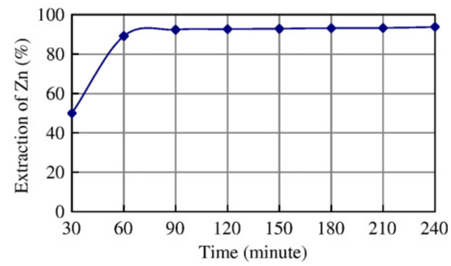

Fig. 6. Effect of leaching time on the zinc extraction (temperature 90 °C, NaOH concentration 6 M, phase ratios(v/w) 20, Pb/ZnS molar ratios 0.9).

application, a NaOH solution of 5–6 mol/L may be selected. It should be noted that no zinc sulfide can be dissolved in water medium in the presence of lead compounds.

3.3. Effect of temperature

The effect of temperature on the zinc extraction at NaOH concentration of 6 mol/L was shown in Fig. 4. The leaching efficiencies increased with the increase of leaching temperatures from 25 to 100 °C. At 100 °C, 96.92% zinc extraction can be obtained.

3.4. Effect of phase ratios

The effect of phase ratios on the zinc extraction was shown in Fig. 5. Higher phase ratios of NaOH solution to ZnS facilitated dissolution of Zn and Pb, and improved surface contact between solution and ZnS particles thus increasing the extraction efficiencies of Zn. But higher phase ratios would increase the amount of NaOH required and reduced the Zn concentrations in the resultant leach solutions. Therefore, a phase ratio of 20 can be employed in order to optimize the leaching process.

3.5. Effect of leaching time

The effect of leaching time on the zinc extraction was shown in Fig. 6. As expected, the rate of zinc leaching increased with the increase of leaching time. Around 90 min was sufficient to reach the maximum extraction and leaching equilibrium.

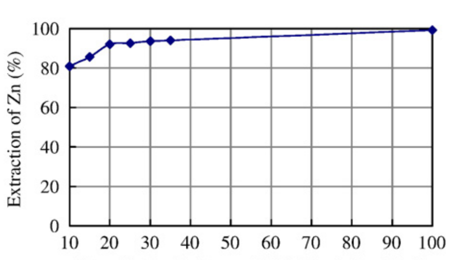

Fig. 5. Effect of phase ratios on the zinc extraction (temperature 90 °C, NaOH concentration 6 M, leaching time 120 min, Pb/ZnS molar ratios 0.9).

3.6. Effect of type of initial lead content

Leaching tests were also carried out with $Pb(NO_3)_2$, $PbSO_4$, PbO_2, $PbCO_3$, Pb_3O_4 as additives to compare with PbO. The results were shown in Table 1. It was found that the effects of Pb compounds on the leaching of Zn from ZnS were comparable, with an exception of PbO_2 which was more effective for zinc recovery because of its strong oxidation efficiency. However, in order to recycle the lead content cost-effectively, $PbCO_3$ was considered suitable as additive.

3.7. Conversion of leach residue

The lead sulfide formed thus in leaching residue should be recycled. Much work has been done on the conversion of galena to lead carbonate in ammonium or sodium carbonate solution (Lu and Chen, 1986; Gong and Chen, 1993). It has been shown that the conversion of lead is effective and cost-effective. In this work, the conversion of lead sulfide into lead carbonate was also tested. Experimental results were shown in Table 2. Over 95% of lead in leaching residue can be converted again into $PbCO_3$, which can dissolve completely in NaOH solution and be recycled for leaching reaction.

4. Discussion

The solubility product constant of ZnS and PbS is 2×10^{-23} and 1×10^{-28}, respectively; PbS is much more

Table 1
Effect of type of initial lead content on the leaching of Zn (temperature 90 °C, NaOH concentration 6 M, phase ratios (v/w) 25, leaching time 120 min)

Type of initial lead content [a]	Zn extraction (%)
PbO	92.81
$Pb(NO_3)_2$	92.90
$PbSO_4$	90.52
PbO_2	95.21
$PbCO_3$	92.67
Pb_3O_4	93.25

[a] The stoichiometric requirement of Pb was used in the experiments.

Table 2
Typical conditions for the conversion of Pb from leaching residues

Na_2CO_3/Pb (molar ratios)	Phase ratio (V/W)	Temperature (°C)	Flow rate of air (L/min)	Time (h)	Concentration of cupric ions (M)	Pb conversion (%)
1–3	4–5	60–80	0.5	3–5	0.001–0.01	95.0–99.0

insoluble than ZnS. This relative insolubility accounts for one reason why zinc sulfide can be dissolved preferably in alkaline solution with lead compound as additive. The non-dissolution for zinc sulfide in water showed that the solid–solid reaction cannot take place between ZnS and $PbCO_3$. The main forms of lead and zinc in strongly alkaline solution may be $Na_2Pb(OH)_4$ and $Na_2Zn(OH)_4$. The dissolution of zinc sulfide by reacting with $PbCO_3$ in alkaline solution can be represented as:

$$PbCO_3(s) + 2NaOH(aq.) + H_2O(l) = Na_2Pb(OH)_4(aq.) + Na_2CO_3(aq.) \quad (3)$$

$$Na_2Pb(OH)_4(aq.) + ZnS(s) = Na_2Zn(OH)_4(aq.) + PbS(s) \quad (4)$$

The experimental results of leaching of Zn from ZnS via conversion by lead compound were in agreement with the theoretical results calculated by reaction stoichiometry as shown in Fig. 1.

The conversion of PbS into $PbCO_3$ by reacting with Na_2CO_3 catalyzed by cupric ion in the presence of air can be summarized as follow:

$$PbS(s) + Na_2CO_3(aq.) + 2O_2(g) = PbCO_3(s) + Na_2SO_4(aq.) \quad (5)$$

The ΔG_{298} and ΔH_{298} for the conservation reaction are −752.9 kJ/mol and −829.29 kJ/mol, showing that the reaction can take place in standard reference states.

A flowsheet was suggested for an alkaline hydrometallurgical process for zinc sulfide ores on the results of this work as shown in Fig. 7. The leach solution can be used to produce metallic zinc powder by electrowinning after chemical separation of impurities. The NaOH solution is recycled to the next leaching operation after most of the Zn is electrowon. The high-purity zinc powder

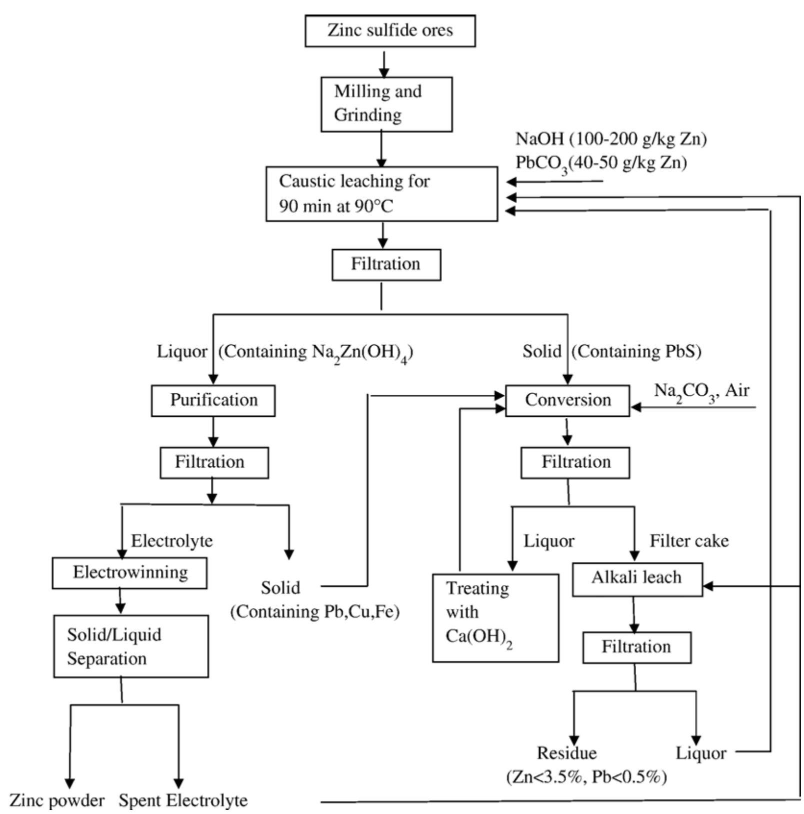

Fig. 7. Schematic flowsheet of hydrometallurgical process for zinc sulfide ores by alkaline leaching and electrowinning.

Table 3
Comparisons for different processes for the production of Zn from ZnS ores (based on the production of 1 kg Zn)

Processes selected	Alkaline process developed in this work	Acidic process
Energy for electrowinning	2.5–2.6 kWh	3.3–3.4 kWh
Energy for heating leaching system	0.9–1 kWh	1 kWh
Purification of leaching solution	Simple	Complex
Chemical consumption	Caustic soda (small quantity)	Sulphuric acid (large quantity)
Loss of Zn powder for impurity removal	None	Necessary
Transformation of S present in the ZnS ores	S is converted to sulfide and sulphate in the leaching residue	S is converted sulfur dioxide in the gaseous effluent

with metallic zinc over 96% can be obtained. The conversion solution of Na_2CO_3 for lead can be recycled into the leaching step or the next conversion step by reacting with the addition of $Ca(OH)_2$ to remove sulfate.

NaOH losses in the whole process are estimated to be around 100 g per kg of Zn from titration analysis. The presence and leaching of silicates, carbonates and phosphates in the ores would increase the loss of NaOH.

The Pb/ZnS molar ratio of 0.9:1is needed for chemical conversion of ZnS, and around 99% of Pb in PbS deposited in the leach residues can be recycled. Hence, the Pb_2CO_3 losses in the whole process are estimated to be 40–50 g per kg of Zn.

Table 3 compares the alkaline process developed in this work with the classical acidic process for the production of metallic Zn from ZnS and oxidized Zn ores. Around 20% of energy for electrowinning in the alkaline solution is reduced in comparison to that in the acidic solution (Youcai and Stanforth, 2000). The purification process in the alkaline process is simpler than the acidic process, as the undesired elements such as Fe, Mg, Cu, Cd, Co, Ni, etc, can hardly be leached out in alkaline solution. Moreover, the alkaline process is cleaner for sulfur in the zinc sulfide ores is converted to sulfide and sulphate, which remains in the leaching residue, rather than sulfur dioxide in the gaseous effluent to pollute the atmosphere in acidic process. The alkaline leaching via chemical conversion-electrowinning process can be considered as a cost-effective and environmentally friendly technology for extracting zinc from sphalerite or oxidized zinc ores co-existed with sphalerite.

5. Conclusions

The zinc in zinc sulfide can be extracted in NaOH solution with lead carbonate as additive, and the lead sulfide in the leach residues can be converted to lead carbonate by reacting with sodium carbonate solution using air as the oxidizing agent, and then the lead can be recycled in the whole process by dissolving the lead carbonate in NaOH solution. Over 90% of zinc can be extracted from the zinc sulfide, and over 95% of lead sulfide in leach residues can be converted. A new cleaner hydrometallurgical flowsheet for recovering zinc from sphalerite ores was proposed.

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