



Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced during zinc hydrometallurgy

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ABSTRACT

A hydrometallurgical process for treating the hazardous jarosite residue from zinc hydrometallurgy was proposed, for not only detoxifying the residue, but also recovering the contained valuable metal components. The jarosite was initially activated and decomposed by sintering at 650 °C for 1 h. The sintered residue was leached in 6 mol L⁻¹ aqueous NH₄Cl solution at 105 °C, followed by filtration. The leaching extraction of Zn, Pb, Cu, Cd and Ag are more than 95%. During reduction with Zn powder, more than 93% of Pb, Cu, Ag and Cd can be simultaneously recovered. Then the NH₄Cl leaching residue were leached again in 30 wt% aqueous NaOH solution for 1 h at 160 °C, and about 94% of As and 73% of Si were removed from the residue. The final residue was almost completely detoxified, and contains about 55 wt% Fe, which can be used as an iron concentration.

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1. Introduction

Vast jarosite residue was produced from traditional zinc hydrometallurgy process in China. And most of the residue was stored up. According to rough calculation, no less than one million tons of this kind of residue was stored up in China per year. This residue not only takes massive land, but also comes forth great risk of environmental pollution, as it contains significant zinc and lead, as well as some arsenic, cadmium, and such toxic ingredients have the potent of being solved in rain water, as demonstrated [1,2].

The residue has three main phases: jarosite, zinc ferrite and anglesite. Jarosite mainly contains XFe₃(SO₄)₂(OH)₆, in which X can be replaced by K⁺, H₃O⁺, Ag⁺, Pb²⁺, Na⁺, NH₄⁺, or 1/2Pb²⁺, and some impurities such as Zn, Cd, Ni and Co can replace Fe in the crystal lattice of jarosite as demonstrated. Zinc ferrite (ZnO·Fe₂O₃) and anglesite (PbSO₄), which are difficult to be dissolved in sulfuric medium, also presented in the residue.

Usually, pyrometallurgical and hydrometallurgical processes are employed for treating such secondaries. Onsan Refinery of Korea Zinc used a Top Submerged Lancing (TSL) Technology to recover the valuable metals in the residue. About 82% Zn, 92% Pb, 86% Ag and 61% Cu in the residue can be recovered by the process [3]. In China, some factories adopt rotary kilns to fume Zn, In and Pb in the residue, using a mass of coal as heat source. About 75% Zn,

68% Pb, and 80% Ge in the residue can be recovered. However, these processes have some shortcomings such as high fixed investment, high operation cost and the air pollution during fuming.

Until now, many researchers are still making great efforts to develop cleaner processes. Ruşen et al. [4] developed a process of acid leaching and brine leaching to reclaim Zn and Pb, respectively. About 71.9% Zn and 98.9% Pb can be recovered. Turan et al. developed a process of H₂SO₄ blending, roasting, water leaching, and finally NaCl leaching to recover Zn and Pb, respectively. About 86% Zn, 89% Pb can be extracted from the residue. These studies had not showed how to recover Cd and Cu presented in the waste.

In India and Italy, some researchers intend to produce construction and ceramic materials with these jarosite as demonstrated [5–8]. The problems could be valuable elements lost and underlying pollution risk.

The recovery of lead and silver from zinc leach residues (as PbSO₄) by flotation is also one of the study direction [9].

In China, Chen et al. developed a process first leaching with alkali to decompose the jarosite into Fe₃O₄, then leaching the decomposed jarosite with dilute hydrochloric acid to extract Zn and In, finally recovering Fe₃O₄ by magnetic separation. Some other researchers try to treat jarosite residue directly with sulfuric acid, then separating Fe and Zn from the solution, and making them into magnetic ferrite or iron oxide yellow as demonstrated. However, these attempts encountered great difficulties of impurities removal.

This work presents a hydrometallurgical route, as shown in Fig. 1, for processing potassium jarosite residue.

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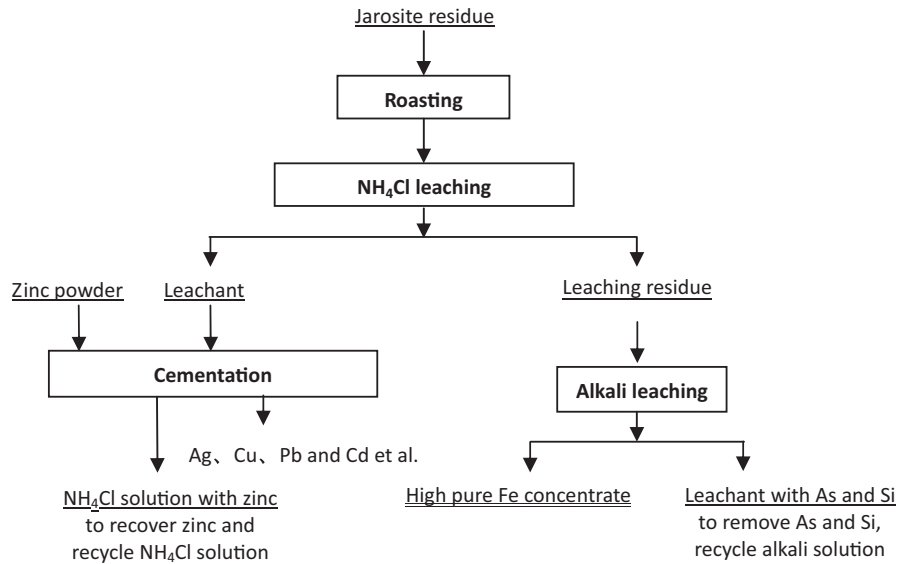


Fig. 1. General scheme for treating potassium jarosite residue in this process.

The main feature of this process is that using NH_4Cl solution as a leaching medium to dissolve the valuable metals presented in the residue, while obtained a kind of residue mainly containing Fe, which can be used as iron concentrate. In this work, the procedures of roasting, NH_4Cl leaching, alkali leaching and Zn cementation were mainly researched. The procedures of recycling NH_4Cl solution and recovering zinc. One is the process of CENIM-LNETI for treating sphalerite as demonstrated [10], the recovery of zinc from NH_4Cl medium by solvent extraction and electrodeposition was studied thoroughly. The other is EZINEX process, a procedure of direct-electrodepositing was used to recovery electrolytic zinc production and to recycle the NH_4Cl leaching solution.

For the As & Si removal from alkali medium, the process of precipitating Si with CaO from solution in the field of alumina production can be used as a reference.

2. Experimental

2.1. Jarosite residue

The fresh sample of potassium jarosite residue was taken from Baiyin Nonferrous Metals Group, one of the biggest smelter of copper, zinc and lead in China. After dried for 12 h at 80°C , the chemical analyses of the sample is presented in Line 2 of Table 1. Its XRD pattern is shown in Fig. 2.

According to Fig. 2, The main phases of the residue are jarosite ($\text{K}_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}$), zinc ferrite ($\text{ZnO}\cdot\text{Fe}_2\text{O}_3$), PbSO_4 , $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$ and SiO_2 .

2.2. Experiment approach

A serial of sintering experiments were conducted to find out the optimal roast condition. Each 10 g of the dried samples were

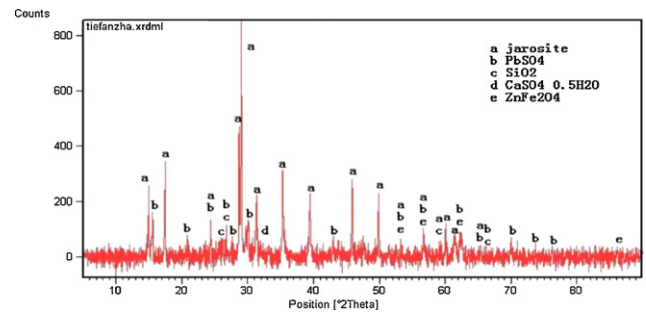


Fig. 2. XRD analyses of Baiyin jarosite residue after drying.

put into a ceramic crucible, which was then loaded into a muffle. The temperature of the muffle was set at a certain temperature, varying for $350\text{--}950^\circ\text{C}$, with a intervening step of every 50°C . XRD analyses of each sintered sample were detected to find out the decomposition effect.

During NH_4Cl leaching procedure, experiments were carried out using 50 mL NH_4Cl solution with a concentration of between 4 and 7 mol L^{-1} . Leaching was performed at temperature varied between 50 and 105°C , under mechanical stirring (300 rpm) in a 3-jaw-bottle heated in an oil bath for a time of 1–4 h. The residue was separated from the liquid phase by filtration, then washed with dilute NH_4Cl solution and deionized water, respectively, and then dried at 80°C for 12 h and finally weighed and analyzed.

During reduction by zinc powder, the experiment is conducted in a 250 mL 3-jaw-bottle, a quantity of zinc powder, 0.2, 0.5, 0.8, 1.0, 2.0 or 3.0 multiples of the total mole number of Ag, Cu, Pb and Cd presented in the NH_4Cl solution in a 3-jaw-bottle, stirred at a speed of 300 r/m, was adding. The reaction temperature is kept at 20°C , 30°C , 40°C or 50°C by a oil-bath in each experiment. NH_4Cl leached solution containing Zn, Ag, Cu, Pb and Cd ions. A certain quantity of Zn powder was put into this solution to reduce Ag, Cu, Pb and Cd ions.

Table 1
Element contents (wt% dry basis) of jarosite residue.

Element	Zn	Pb	Fe	Ag	Cu	As	Cd	SiO_2	SO_4^{2-}
Before roasting	7.06	4.00	19.92	0.009	0.21	0.18	0.11	10.12	38.17
After roasting	8.97	4.84	23.1	0.011	0.24	0.18	0.14	12.02	33.54

Note: roasting for 1 h at 650°C .

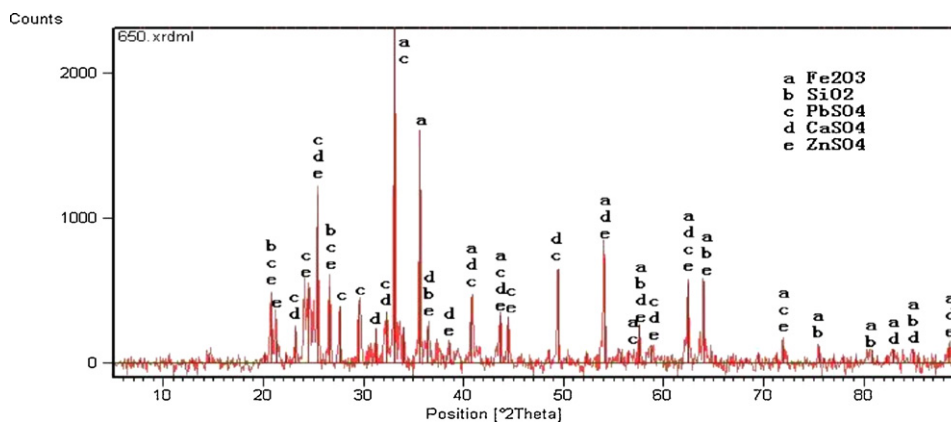


Fig. 3. XRD analyses of jarosite after sintering at 650 °C for 1 h.

Table 2

The reducing experiment result.

Item	Unit	Zn	Pb	Ag	Cu	Cd	Mg	Ca
Liquor before reducing	g/L	6.803	2.434	0.0851	0.9913	1.646	0.868	3.778
Liquor after reducing	g/L	9.836	0	0.0036	0.0014	0.1081	0.856	3.78
Reducing residue	%	18.7	39.21	1.3	13.1	24.5	–	–
Extraction fraction	%	–	100	95.77	99.86	93.43	0	0

NH₄Cl leached residue was leached by NaOH solution (30 wt%, 1 h) at 160 °C with a pressure of 0.41 MPa, in an autoclave made of 316L steel to remove Si and As.

2.3. Analytical methods

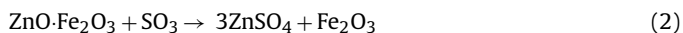
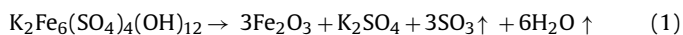
The residue samples were dissolved in HCl, HNO₃, HF and HClO₅ sequentially at 80 °C for chemical analysis, the leaching liquor was diluted for chemical analysis, wash water was analyzed directly.

Metal concentrations in solution were determined by Perlivn-Elmer ICP-OES (Optima5300DV type). A LECO analyzer determined sulfur contents. Crystalline phases in solid samples were identified by X' Pert PROMPD Panalytical, and the result was analyzed by the software of X' Pert Highscore. pH was measured by a digital pH meter.

3. Results and discussion

3.1. Thermal decomposition

The result showed that after sintering at 650 °C for 1 h, the residues are decomposed into four crystalline phases: Fe₂O₃, ZnSO₄, PbSO₄ and SiO₂, and ZnO·Fe₂O₃ phase disappeared, as shown in Fig. 3. According to XRD result, the reaction at 650 °C can be concluded as following:



The weight loss of residue after roasting at 650 °C for 1 h is about 10%, and the chemical analysis result is shown in Line 2 of Table 1.

Table 3

Chemical composition of residue the residues before and after alkali leached.

Item	Zn	Pb	Fe	Ag	As	Al	Ca	Mg	SiO ₂	
Residue before alkali leaching	%	0.41	0.15	41.53	0.000	0.33	0.60	0.42	0.01	21.81
Residue after alkali leaching	%	0.27	0.00	53.84	0.000	0.02	0.55	2.64	0.12	5.80
Extraction fraction	%	49.29	100	0.15	–	93.93	–	–	–	72.91

It is mainly H₂O and SO₃ were released at this temperature, and Cd, Zn, Pb and As would not be released. This means that the gas given off during roasting in this condition can be easily dissolved in water, and no air pollution could take place.

3.2. NH₄Cl leaching

Four serials of the experiments were performed. One is the concentration of NH₄Cl, varied between 4 and 7 M, the second is the ratio of liquid to solid, varied between 10:1 and 10:3, the third is the reaction temperature, varied between 50 and 105 °C, and the fourth is the leaching time of the reaction, varied between 1 and 4 h. The extraction fraction of Zn, Pb, Ag, Cu and Cd is shown in Fig. 3(a–d). The extraction of both Fe and As in each experiment is very low, so that their extraction results are not shown in Fig. 3.

Fig. 4 shows that (1) the extraction of the valuable metals increases as the concentration of NH₄Cl increased, but when the concentration increased to more than 6 M, the extraction fraction increased little, as shown in Fig. 4(a); (2) the ratio of liquid to solid has a big effect to metal extraction, when it is lower than 10:2, the valuable decreased quickly, and when it increased to more than 10:2, the valuable extraction increased little, as shown in Fig. 4(b); (3) the metal extraction increases as the temperature increased, when the temperature goes up to 105 °C, the metal extraction increased to more than 93%, as shown in Fig. 4(c); (4) it is shown in Fig. 4(d) that the extraction of Cd is very fast, after leaching for 1 h, the extraction reached to nearly 100%; and the extraction of other metals increases as the leaching time increased, but when the leaching time is more than 2 h, the extraction fraction increased little. So, the optimized leaching condition could be: NH₄Cl 6 M, the ratio of liquid to solid is 10:2 at 105 °C for 2 h.

Table 4

The chemical content of the materials in each step of the overall process.

Procedure	Unit	Zn	Pb	Fe	Ag	Cu	As	Cd	Al	Ca	Mg	SiO ₂	SO ₄ ²⁻
Before sinter	%	7.06	4.00	19.92	0.009	0.21	0.12	0.10	0.33	1.33	0.14	10.33	38.17
After sinter	%	8.97	4.84	23.1	0.011	0.24	0.18	0.14	0.33	1.33	0.14	12.02	33.54
NH ₄ Cl leach residue	%	0.41	0.15	41.53	0.000	0.02	0.33	0.00	0.6	0.42	0.01	21.81	6.24
NH ₄ Cl leach solution	g/L	7.78	4.31	0.00	0.01	0.21	0.00	0.13	0.00	0.87	0.12	0.00	28.20
NH ₄ Cl leach extraction	%	97.26	98.14	0.00	100	95.00	0.00	100	0	–	–	–	88.84
reduction solution	g/L	11.99	0.00	0.00	0.003	0.015	0.00	0.03	0.00	0.65	0.26	0.00	28.14
Reduction extraction	%	–	100	–	70.00	92.86	–	76.92	–	–	–	–	–
Alkali leach residue	%	0.27	0.00	53.83	0.000	0.04	0.02	0.00	0.55	0.44	0.02	5.46	6.43
Alkali leach extraction	%	49.29	100	0.15	–	–	93.93	–	–	–	–	75.23	–

Operating conditions: (a) sintering at 650 °C for 1 h; (b) NH₄Cl leaching with a concentrate of 6 M at 105 °C for 2 h; (c) reducing with 1.4 multiple of zinc powder at 50 °C for 1 h; (d) Alkali leaching with 30% NaOH at 160 °C for 1 h.

At the optimized condition, the extraction of Zn, Pb, Cu, Cd and Ag can reached to 97.5%, 95.3%, 95.4%, 100% and 100%.

3.3. Zinc powder reduction

A simulated leaching solution with a composition listed in the first line of Table 2 in 6 M NH₄Cl, was used in this reduction experiment. Finally, the optimized reducing condition is found to be 1.5 multiple zinc powder of the total mol number of Pb, Cu, Cd and Ag, at 40 °C, which showed the reducing extraction of each valuable metal is more than 93%. The chemical containing of liquor after reducing were showed in the second line of Table 2. The result showed that about 1.1 multiple mole of Zn powder was dissolved into NH₄Cl solution. The reducing residue gained was analyzed and its composition is showed in the third line of Table 2.

Table 2 shows that more than 93% of Pb, Ag, Cu and Cd can be extracted by zinc power.

3.4. Alkali leaching

Alkali leaching was performed in an 500 mL autoclave made of 316L. The optimal leaching condition is NaOH solution (30 wt%) at 160 °C for 1 h, with a pressure of 0.41 MPa. The pressure of the autoclave is about 73% of Si and 94% of As were removed from the NH₄Cl leached residue, and the content of iron increased from 41.53% to 53.84%, as shown in Table 3.

3.5. Overall process study

For checking the effect of this overall process for treating potassium jarosite, under the optimized experimental condition, the result was shown in Table 4.

The apparent data in Table 4 showed that the direct recovery of Zn, Pb, Cu, Cd, Ag and Fe, respectively, are about 97%, 98%, 87%, 77%, 70% and 95%, and the As removal fraction can reach to 94%. The content of sulfur in the final residue is about 2.1%. After commingling

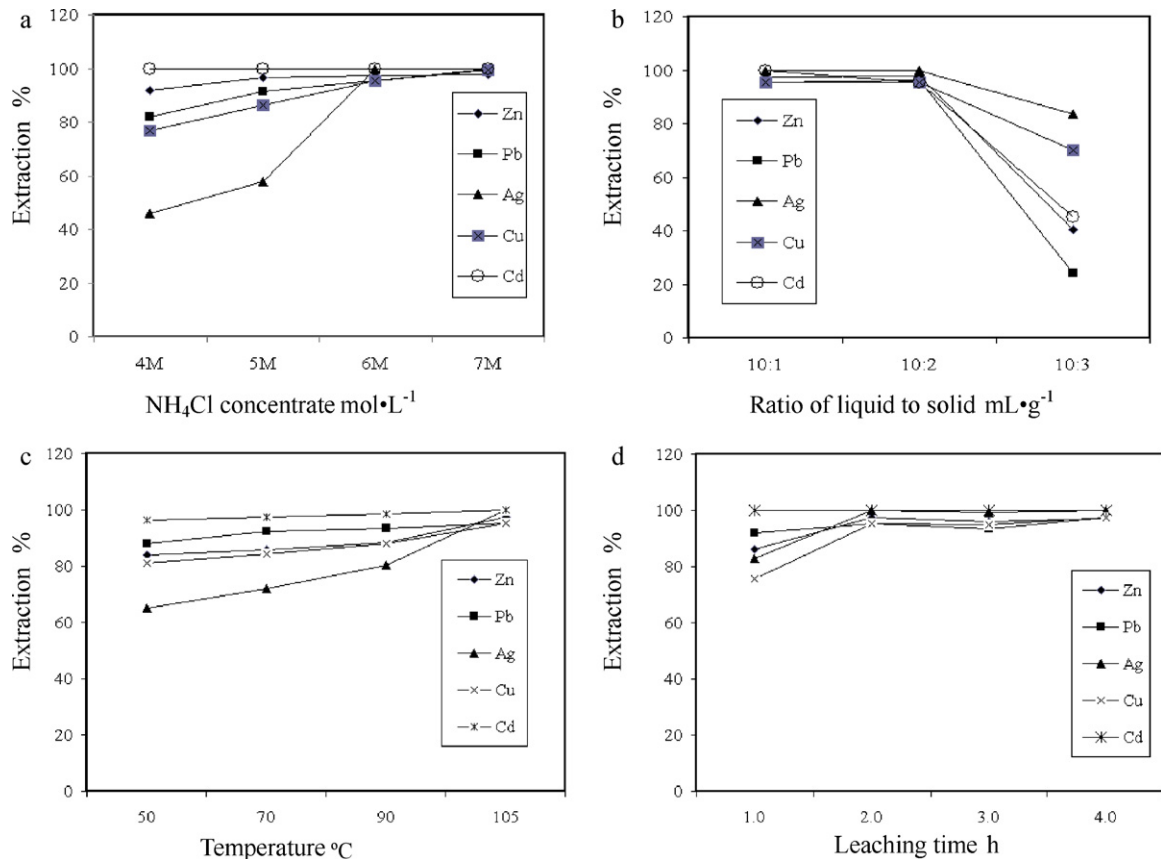


Fig. 4. NH₄Cl leaching extraction result: (a) varying with NH₄Cl concentrate when the ratio of liquid to solid equals to 10:1, at 105 °C for 2 h; (b) varying with the ratio of liquid to solid, when NH₄Cl concentration equals to 6 M at 105 °C for 2 h; (c) varying with temperature, when the ratio of liquid to solid equals to 10:1, NH₄Cl concentration equals to 6 M for 2 h; (d) varying with leaching time, when the ratio of liquid to solid equals to 10:1, NH₄Cl concentration equals to 6 M at 105 °C.

with some iron concentrate of low sulfur, it has the potential to be used in the field of iron concentrate.

4. Conclusions

The process presented in this work for treating jarosite presents the following merits: the leaching extraction of valuable metals in the NH_4Cl medium from sintered jarosite were higher than 95% under the optimal case, while Fe remained in the residues. Then alkali leaching can release most of As from the residue, which detoxified the residue completely.

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