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Trans. Nonferrous Met. Soc. China 23(2013) 1179-1183

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

Thermodynamics of leaching roasted jarosite residue from zinc hydrometallurgy in NH₄Cl system

Shao-hua JU^{1,2,3}, Li-bo ZHANG^{1,2,3}, Jin-hui PENG^{1,2,3}, Zhe SHI³, Sheng-hui GUO^{1,2,3}, Bin-guo LIU^{1,2,3}, Ya-jian WANG¹

 Key Laboratory of Intensification Metallurgy in Yunnan Province, Kunming 650093, China;
 Key Laboratory of Unconventional Metallurgy, Ministry of Education, Kunming University of Science and Technology, Kunming 650093, China;
 Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

Received 6 January 2012; accepted 3 December 2012

Abstract: The thermal decomposition process of jarosite residue and the solubility of various oxides presented in the decomposed residue in NH_4Cl-H_2O system were studied. The results of heat decomposition of jarosite residue show that the insoluble $ZnFe_2O_4$ phase in the residue can be decomposed at temperatures ranging from 500 °C to 650 °C for 1 h. The OLI Systems software was used to study the thermodynamics of the solubility of various metal oxides existing in the decomposed residue in NH_4Cl-H_2O system. The results show that the solubility of ZnO, PbO, CdO, CuO and Ag₂O is high, while the solubility of Fe₂O₃ is less than 10^{-4} mol/L in the pH range from 4.0 to 9.0. The calculated data are in accordance with the experimental results. **Key words:** jarosite residue; zinc hydrometallurgy; thermodynamics; NH_4Cl system

1 Introduction

In China, the production capacity of zinc was reported to be more than 4.4 million tons in 2009, and it was expected to be more because a lot of new plants were built up in 2009–2012. About 70% of the zinc production was yielded by hydrometallurgy process, which will averagely produce 0.3 t of waste jarosite residue for yielding 1 t of zinc cathode. Thus, about one million tons of such jarosite can be produced in China every year.

This kind of residue contains not only some valuable metals such as Fe, Zn, Cu and Ag, but also some toxic elements such as Pb, Cd and As. Thus, it is very hard to treat the residue efficiently and profitably.

In our earlier study [1], a process of roasting, leaching and reduction using NH_4Cl media was reported. The merits of the process are that: 1) $ZnO \cdot Fe_2O_3$ can be decomposed during roasting; 2) Cl^- ion or/and NH_3 can form stable complexes with Zn, Pb, Ag, Cd and Cu;

3) Fe and As will not be dissolved due to the near neutral pH value of the solution.

FROST et al [2] studied the thermal decomposition of jarosites of potassium, sodium and lead, and found that mass loss of K-jarosite occurs in the temperature range of 130-330 °C and 500-622 °C and is attributed to dehydroxylation and desulphation. STOPIĆ and FRIEDRICH [3] studied the thermal decomposition of leach residue after neutral leaching process from zinc winning in a nitrogen atmosphere using DTA and TGA techniques, and found that ZnO·Fe₂O₃ would be decomposed to ZnO and Fe₃O₄ when the temperature is higher than 1100 °C.

Chemical modeling of aqueous electrolyte solutions is of great importance to the development, analysis, design, and control of hydrometallurgical processes. Thermodynamic model is extremely useful since it can accurately describe the behavior of electrolyte solutions over wide ranges of temperature, pressure, concentration and predict the solution properties up to saturation levels. There are a number of tools available for thermodynamic

Foundation item: Project (51090385) supported by the National Natural Science Foundation of China Corresponding author: Jin-hui PENG; Tel: +86-871-5147924; Fax: +86-871-5192076; E-mail: jhpeng72@hotmail.com DOI: 10.1016/S1003-6326(13)62581-9

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modeling of aqueous systems.

In general, Debye–Hückel model and its extensions [4], which have been presented by the Davis equation and the B-dot equation, are the most widely applied models. But these models are applicable only to dilute solutions. For the concentrated solutions, Bromley model and its extensions, Bromley–Zemaitis model [5,6], PITZER model [7], Electrolyte NRTL model [8], and UNIQUAC model [9–11], are applied successfully. The Bromley–Zemaitis model embedded within OLI Systems software [6], and the Electrolyte NRTL model in AspenPlusTM [9] are being utilized for modeling in industry.

Among them, OLI has the most comprehensive database and solver engine available for simulation of aqueous chemistry. A simple interface gives power to the nonexperts, enabling quick evaluation of process chemistry issues and significant savings in laboratory testing. It has been successfully used to simulate a number of systems, including the dissolution behavior of Fe, Co, and Ni from nonferrous smelter slag in aqueous sulphur dioxide [12], thermodynamic equilibrium of the O_2 -ZnSO₄-H₂SO₄-H₂O system from 25 to 250 °C [13], and the thermodynamic equilibrium of monometallic sulphate solutions Al₂(SO₄)₃-H₂SO₄, MgSO₄-H₂SO₄, NiSO₄-H₂SO₄, Fe₂O₃-H₂SO₄, ternary Al-Mg-H₂SO₄ solutions and real laterite leaching solutions at 230-270 °C [14].

The solubility of pure ZnO or pure CuO in NH₄Cl solution has been studied separately [15]. However, no simulation of such a complicated system of jarosite residue in NH₄Cl has been studied.

The present work attempts to investigate the basic theory of NH₄Cl leaching through application of thermodynamic modeling. Firstly, the XRD patterns of the roasted jarosite residue at different temperatures, from 300 °C–850 °C with an interval of 50 °C, were obtained to analyze the phase transition at each temperature. Then, the OLI Systems software was utilized to estimate the thermodynamics of leaching jarosite in NH₄Cl media.

2 Basic theory of roasting

The fresh sample of potassium jarosite residue was obtained from Baiyin Nonferrous Metals Group, China. After being dried for 12 h at 80 °C, the chemical composition of the sample was analyzed and the result is shown in Table 1. A series of roasting experiments were conducted to obtain the optimal roasting conditions.

10 g of the dried jarosite sample was put into a ceramic crucible, and then was placed into a muffle

Table 1 Chemical composition of jarosite residue (massfraction, %)

State	Zn	Pb	Fe	Ag	Cu	As	Cd	SiO_2	S _{tot}
Before roasting	7.05	4.00	19.92	0.009	0.21	0.18	0.11	10.12	12.72
After roasting	8.97	4.84	23.1	0.011	0.24	0.18	0.14	12.02	11.18

furnace. The temperature of the muffle furnace was set at a desired temperature ranging from 300 to 850 °C, at an interval of 50 °C. XRD analyses for each roasted sample were performed to investigate the decomposition of the residue.

The XRD results of main phases in the original and roasted residues at each temperature are shown in Fig. 1.

It is shown in Fig. 1 that the main phases of the original residue are $K_2Fe_6(SO_4)_4(OH)_{12}$ and $ZnFe_2O_4$. When the roasting temperature is below or equal to 350 °C, the main phases do not change, while the diffraction intensity of $K_2Fe_6(SO_4)_4(OH)_{12}$ phase decreases quickly, indicating that the jarosite begins to decompose. In the temperature range of 400–450 °C, the main phases change to Fe_2SO_4 and $ZnFe_2O_4$. In the temperature range of 550–650 °C, the main phase is Fe_2O_3 , showing that $Fe_2(SO_4)_3$ and $ZnFe_2O_4$ have decomposed in this temperature range. In the temperature range of 700–850 °C, the main phases are $ZnFe_2O_4$ and Fe_2O_3 , indicating the formation of $ZnFe_2O_4$ again at higher temperature.

This explains that the concentration of zinc leaching is high with NH_4Cl solution for the residue roasted in the temperature range of 500–650 °C, while the Zn concentration is low at other temperatures.

3 Thermodynamic modeling using OLI Systems software

The equilibrium solubility of various metal oxides such as ZnO, CuO, PbO, Ag_2O , CaO, MgO and Fe_2O_3 in NH₄Cl media, is the main concern during the thermodynamic modeling of leaching.

In NH₄Cl system, the reaction is very complicated because NH₃ and Cl⁻ are both strong ligands for metal ions such as Zn^{2+} , Cu^{2+} , Pb^{2+} , Ag^+ and Cd^{2+} , as their coordination numbers are very high. Additionally, there are many insoluble solids produced during leaching procedures.

The data input to the OLI Systems for modeling and estimating the equilibrium conditions of leaching are listed in Table 2. The concentration of each species is got by the experiments and from the reported data in earlier work [1].

	- 1	• $ZnFe_2O_4$
	850 °C	• Fe_2O_3
		• $Fe_2(SO_4)_3$
	800 °C	• $K_2Fe_6(SO_4)_4(OH)_{12}$
	750 °C	* PbSO ₄
	700 °C	
	650 °C	•
	600 °C	•
	550 °C * * * * * * * * *	•
	500 °C the south the second	•
	450 °C	~
	400 °C	
	350 °C in mind in it is in	
	300 °C vi milinatione in interest	
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)	10 20 30 40 50 60	70 80 90
	$2\theta/(\circ)$	

Fig. 1 XRD patterns of jarosite residue after roasting at different temperatures for 1 h

 Table 2 Initial data input to OLI Systems for modeling of leaching

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Chemica	Concentration/(mol·L ^{-1})
NH ₄ OH	0.10
NH ₄ Cl	6.00
Zn(OH) ₂	0.05
Pb(OH) ₂	0.05
AgOH	0.01
Fe(OH) ₃	0.50
Mg(OH) ₂	0.02
$(NH_4)_2SO_4$	0.50
Cu(OH) ₂	0.05
Ca(OH) ₂	0.04
H_2O	55.51

4 Modeling result of leaching procedure

The solubility results of various metal oxides at different pH values estimated by the OLI Systems are

shown in Fig. 2.

Figure 2 shows that the solubilities of oxides of Zn, Cu, Ag and Pb are very high in this system in all pH ranges, and the variation rule of the concentration of their main complexes are also presented. However, iron oxide has a very low solubility in the pH range from 4.0 to 9.0; the oxides of Ca and Mg have a relatively high solubility in the pH lower than 10.0, and a relative low solubility when the pH is increased to more than 10.0.

5 Conclusions

The roasting of jarosite residue showed that $ZnFe_2O_4$ in the residue can be decomposed in the temperature range of 500 °C-650 °C for duration of 1 h.

OLI Systems was used to model the leaching process of valuable metal oxide in NH_4Cl system. The results showed that the solubility of oxides of Zn, Cu, Ag and Pb is very high, while the solubility of Fe_2O_3 is less than 10^{-4} mol/L in the pH range from 4.0 to 9.0. These data are in accordance with the experimental results.



Fig. 2 Solubility of oxides of Fe, Zn, Pb, Cu, Ag, Ca and Mg in NH₄Cl solution

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NH₄Cl 体系浸出焙烧后湿法炼锌铁矾渣的热力学

巨少华^{1,2,3}, 张利波^{1,2,3}, 彭金辉^{1,2,3}, 施哲³, 郭胜惠^{1,2,3}, 刘秉国^{1,2,3}, 王亚健¹

1. 云南省特种冶金重点实验室,昆明 650093;
 2. 昆明理工大学 非常规冶金教育部重点实验室,昆明 650093;
 3. 昆明理工大学 冶金与能源工程学院,昆明 650093

摘 要:研究湿法炼锌铁矾渣的热分解过程,及其分解后各种氧化物在 NH₄Cl-H₂O 体系中的溶解度。铁矾渣的 热分解实验结果表明,渣中不可溶物相 ZnFe₂O₄在 500~650 ℃ 下焙烧 1 h 后发生分解。采用 OLI System 软件研 究热分解得到的渣中各金属氧化物在 NH₄Cl-H₂O 溶液中的溶解度。结果表明,在 pH 为 4.0~9.0 范围内, ZnO、 PbO、CdO、CuO 和 Ag₂O 的溶解度较大,而 Fe₂O₃ 的溶解度仅为 10⁻⁴ mol/L。计算结果与实验结果相吻合。 关键词:铁矾渣;湿法炼锌;热力学;NH₄Cl 体系

(Edited by Sai-qian YUAN)