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Leaching and recycling of zinc from liquid waste sediments

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Abstract: The selective leaching and recovery of zinc in a zinciferous sediment from a synthetic wastewater treatment was investigated. The main composition of the sediment includes 6% zinc and other metal elements such as Ca, Fe, Cu, Mg. The effects of sulfuric acid concentration, temperature, leaching time and the liquid-to-solid ratio on the leaching rate of zinc were studied by single factor and orthogonal experiments. The maximum difference of leaching rate between zinc and iron, 89.85%, was obtained by leaching under 170 g/L H_2SO_4 in liquid-to-solid ratio 4.2 mL/g at 65 ℃ for 1 h, and the leaching rates of zinc and iron were 91.20% and 1.35%, respectively.

Key words: zinciferous sediments; leaching; zinc; recovery

1 Introduction

A lot of tailing dumps from zinc smelting industry are produced around the world. These dumps consist of casting scum, zinciferous dust, calcine leaching sediment, zinciferous wastes generated in hot-dip melting bath and zinc oxide slag produced in lead fume furnace, zinc rotary kiln and ore rotary kiln, etc[1−2]. It is not economical for them to prepare a zinc concentrate, which makes an increasing interest in the research of zinc recovery[3−4]. The main components of casting scum and zinciferous wastes are zinc and zinc oxide with over 60% zinc content[5], which are commonly treated for zinc separation followed by sulfuric acid leaching with zinc recovery ratio over 97%[6]. The main components of zinciferous dust and zinc oxide slag are zinc oxide with zinc content of 15%−40%[7], which are commonly treated with sulfuric acid leaching with the zinc recovery of about 95%[8−9]. The main components of calcine leaching sediment are zinc oxide and zinc ferrite with the content of 16%−25%, which are usually treated with rotary kiln fuming[10−11].

The zinciferous sludge investigated in this study is a sediment from the wastewater treatment, which consists of several kinds of metals such as zinc, calcium, and iron. The rotary kiln fuming and hot acid jarosite method are generally adopted to treat the low-grade zinciferous sludge. Zinc ferrite forms during the process due to the high content of iron and large quantity of slag deposited in the bottom of rotary kiln, which increases the burden of rotary kiln and reduces the zinc recovery[12]. The hot acid jarosite method is mostly used for the calcine leaching of zinc sulfate but a great deal of manganese powder or manganese dioxide ore must be consumed in this process[13−14]. Therefore, the process of sulfuric acid selective leaching without any other addition of oxidant or neutralization agents is adopted to recover zinc by controlling the acidity of solution on the basis of conventional sulfuric acid leaching in this study. This method is an improvement of the conventional sulfuric acid leaching by avoiding the limitation of the rotary kiln fuming and solves the low-usage of sulfuric acid problem of conventional sulfuric acid leaching.

2 Experimental

2.1 Raw materials

The zinciferous sludge sample was generated from synthetic wastewater treatment process and it contained about 90% moisture. The sample was filtered and dried at 104 ℃ in vacuum oven and then was analyzed by energy spectrometry. The main composition of sample with zinc, iron and calcium was detected by chemistry titration analysis and the result is shown in Table 1.

95%−98% sulfuric acid made by Institute of Chemical Industry in Zhuzhou, China and self-made

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Table 1 Main components of slag sample (mass fraction, %)

Ca	Zn	Fe	Mg	Al	Mn	Cu	Si	S	O	C
26	6	8.2	2.33	2.67	0.83	0.9	1.23	1.04	35.69	10.65

ultrapure water with electrical resistivity of about 18.0 MΩ·cm were used in the experiments.

2.2 Equipments

AB204-N electronic balance made by Shanghai Jinghong Laboratory Instrument Co. Ltd., China and SHA-C water-bath thermostatic vibrator made by Beijing Dongxia Scientific Instrument Co. Ltd., China were used in the experiments. DZF-2 vacuum oven made by Beijing Yongguang Instrument Co. Ltd., China, conical flask and volumetric flask with capacity volume 250 mL were also used in the experiments.

2.3 Procedure

The effects of sulfuric acid concentration, temperature, leaching time and liquid-to-solid ratio on the leaching rate of zinc were investigated. The orthogonal experiments were carried out to optimize the parameters of leaching process. The dried slag sample was accurately weighed and decanted to the conical flask with corresponding amount of sulfuric acid according to the defined liquid-to-solid ratio, and then the thermostatic vibrator was turned on and the slurry gained after vibrating was filtered, finally the leaching rates of zinc and iron were calculated by detecting the content of zinc and iron in the filtrate.

2.4 Analytical methods

The contents of zinc and iron were analyzed by EDTA titration by using 1 000 W/220 V-AC electronic universal furnace (Oersted Instrument Co. Ltd, China) and acidic burette[15]. The microcontent of iron was detected by using a VIS-7220 spectrophotometer (Raylpc Instrument Co. Ltd., Beijing, China)[16].

2.5 Fundamentals

The zinciferous sludge mainly contains zinc, iron and calcium. Sulfates are formed at different hydrolysis pH value for Zn^{2+} and Fe^{3+} during the leaching process. The reactions are as follows:

$$CaCO_3(s)+H_2SO_4(aq)═CaSO_4 \text{ (slightly soluble)}+H_2O+CO_2(g)$$

$$2Zn^{2+}(aq)+2H_2O═2Zn(OH)_2(s)+4H^+(aq) \quad (pH>5.6)$$

$$2Fe^{3+}(aq)+3H_2O═2Fe(OH)_3(s)+6H^+(aq) \quad (pH>1.8)$$

Therefore, zinc can be selectively recovered by controlling the acidity of leaching solution.

3 Results and discussion

3.1 Single factor experiment

3.1.1 Effect of sulfuric acid concentration on leaching rate

During the investigation on the effect of sulfuric acid concentration on the leaching rate, the concentration of sulfuric acid was set at 100, 130, 150, 180 and 200 g/L respectively and the leaching temperature, leaching time and liquid-to-solid ratio were set at 50 ℃, 30 min and 5 mL/g, respectively. The leaching solutions gained in different sulfuric acid concentrations were colorless, shallow orange, orange, yellow and yellowish green respectively and the results are shown in Fig.1.

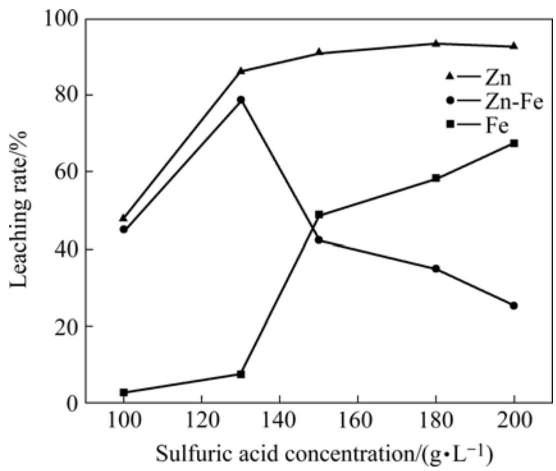

Fig. 1 Effect of sulfuric acid concentration on leaching rate

It can be seen from Fig.1 that as the sulfuric acid concentration increases from 100 g/L to 130 g/L, the leaching rate of zinc increases distinctly while the leaching rate of iron increases slowly, but the result is reversed as the sulfuric acid concentration rises from 130 g/L to 200 g/L. The pH value of leaching solution with sulfuric acid concentration of 100 g/L is 6.23 and the hydrolysis pH values of Fe^{2+} and Fe^{3+} are 6.0 and 1.8 respectively. The reactions are as follows.

$$2Fe^{2+}(aq)+2H_2O═2Fe(OH)_2(s)+4H^+(aq) \quad (pH>6.0)$$

$$2Fe^{3+}(aq)+3H_2O═2Fe(OH)_3(s)+6H^+(aq) \quad (pH>1.8)$$

It can be concluded that iron is transformed to hydroxide sediments under the sulfuric acid concentration of 100 g/L, which indicates that there is no Fe^{2+} or Fe^{3+} in the leaching solution and the solution. When the sulfuric acid concentration exceeds 130 g/L, the increase of zinc leaching rate is slower than that of iron leaching rate because reactions between calcium carbonate and sulfuric acid occur. The leaching rates of zinc and iron are 86.12% and 7.47% respectively when the concentration of sulfuric acid is 130 g/L and the difference of the leaching rate between zinc and iron is the greatest. Therefore, the efficiency of sulfuric acid is higher than that in other leaching conditions.

3.1.2 Effect of leaching temperature on leaching rate

The leaching temperatures were controlled at 20, 30, 50, 65, 80 and 90 ℃ respectively, and the sulfuric acid concentration, leaching time and liquid-to-solid ratio were set at 130 g/L, 30 min and 5 mL/g, respectively. The results are shown in Fig.2.

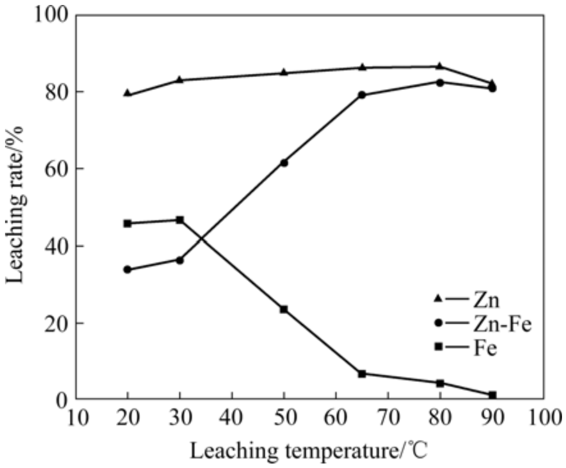

Fig.2 Effect of leaching temperature on leaching rate

As shown in Fig.2, the effect of leaching temperature on leaching rate of zinc is unobvious while the effect on the leaching rate of iron is very distinct. The leaching rate of zinc increases from 79.52% to 86.47% with leaching temperature rising from 20 ℃ to 80 ℃ and decreases to 82.10% with leaching temperature rising to 90 ℃. The leaching rate of iron increases slightly with leaching temperature rising from 20 ℃ to 30 ℃ and decreases sharply with leaching temperature increasing gradually. The leaching rate of iron is only 6.88% at leaching temperature of 65 ℃ and 1.19% at 90 ℃ respectively. This is because the final acidity of solution reduces due to the strengthened reactions between sludge and sulfuric acid with the increase of temperature. The pH value of the leaching solution is 5.7 when the temperature increases to 90 ℃. The leaching rate of zinc is reduced because a little Zn^{2+} enters into the final sludge as precipitate due to the Zn^{2+} hydrolysis at pH value of 5.6[23], while all the irons enter into the final sludge as the form of hydroxide.

The leaching rate of zinc and the difference of leaching rate between zinc and iron are 86.47% and 82.24% respectively at 80 ℃, while the leaching rate of zinc at 65 ℃ is only 0.3% lower than that at 80℃ and the difference of leaching rate between zinc and iron is 79.22%. The rational leaching temperature is 65 ℃ because high temperature leads to high evaporation speed and energy consumption.

3.1.3 Effect of leaching time on leaching rate

The leaching time was varied and the sulfuric acid concentration, leaching temperature and liquid-to-solid ratio were set at 130 g/L, 65 ℃ and 5 mL/g, respectively. The results are shown in Fig.3.

As shown in Fig.3, the leaching rate of zinc and iron are 67.21% and 31.11% at 1 min, indicating that the leaching reactions proceed rapidly in the initial stage. The leaching rates of zinc and iron increase from 67.21% to 76.73% and from 31.11% to 34.57%, respectively, with leaching time increasing from 1 min to 5 min. The leaching rate of zinc increases from 76.73% to 86.85% while the leaching rate of iron decreases from 34.57% to 8.74% with leaching time increasing from 5 min to 30 min. With further increasing the leaching time, the leaching rate of zinc decreases slightly and keeps constant after 90 min while the leaching rate of iron decreases gradually. The leaching rate of iron at leaching time of 90 min and 120 min are 1.54% and 1.23% respectively. This is because the final acidity of solution reduces when the reactions between the sludge and sulfuric acid proceed with the increase of leaching time. The pH value of the leaching solution is 5.93 when the leaching time increases to 90 min. The leaching rate of zinc is reduced because a little Zn^{2+} ions enter into the final sludge as precipitates due to the Zn^{2+} hydrolysis at pH value of 5.6[17], while all the irons enter into the final sludge in the form of hydroxide. The analysis results indicate that the rational leaching time is 30 min with the leaching rates of zinc and iron of 86.85% and 8.74% respectively and the difference of leaching rate between zinc and iron is the greatest (78.11%), therefore the efficiency of sulfuric acid is the highest.

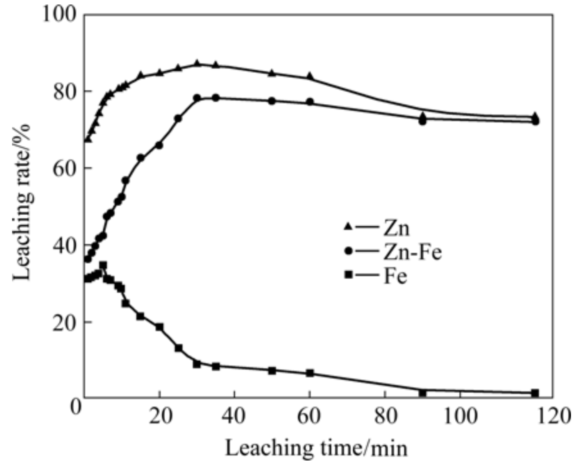

Fig.3 Effect of leaching time on leaching rate

3.1.4 Effect of liquid-to-solid ratio on leaching rate

The liquid-to-solid ratios were varied and the sulfuric acid concentration, leaching temperature and leaching time were set at 130 g/L, 65 ℃ and 30 min respectively. The results are shown in Fig.4.

As shown in Fig.4, the leaching rates of zinc and iron are very low when the liquid-to-solid ratio is between 3 and 4. They increase sharply from 16.03% to 86.03% with the liquid-to-solid ratio from 3 to 5 and increase slowly from 5 to 8, finally descend with the liquid-to-solid ratio over 8. The leaching rate of iron increases slightly from 0.31% to 6.92% with the liquid-

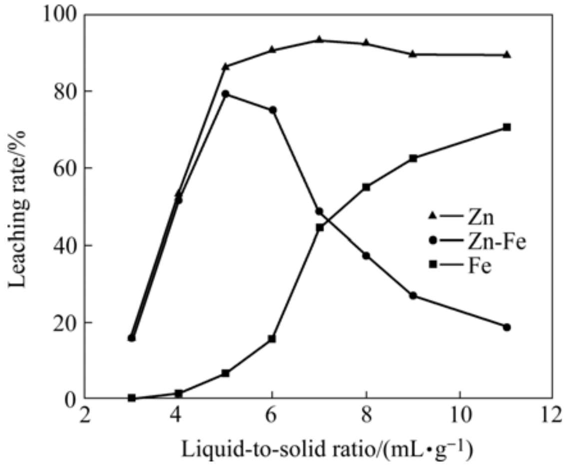

Fig.4 Effect of liquid-to-solid ratio on leaching rate

to-solid ratio rising from 3 to 5 and increases sharply with the liquid-to-solid ratio gradually increasing, finally the leaching rate of iron is 70.23% when the liquid-to-solid ratio increases to 11. The leaching rate of zinc increases slowly with the liquid-to-solid ratio over 5. This is because most of the zinc compounds dissolve with liquid-to-solid ratio rising from 3 to 5 and there are only a few indissolvable zinc compounds dissolved with the liquid-to-solid ratio over 5. The leaching rate of iron increases obviously because the reactions between iron compounds and sulfuric acid are strengthened with liquid-to-solid ratio gradually increasing. The analysis results indicate that the rational liquid-to-solid ratio is 5 with the leaching rate of 86.03% and the difference of leaching rate between zinc and iron is the greatest, therefore the efficiency of sulfuric acid is the highest(79.11%).

It can be concluded that the leaching ratio of zinc to iron are greatly affected by the final acidity of leaching solution, and all the irons dissolved enter into the final slag in the form of hydroxide precipitates because the acidity of Fe^{3+} hydrolysis is greater than that of Zn^{2+}. The investigation of single factor indicates that the optimal parameters are 130 g/L H_2SO_4, leaching temperature 65 ℃, leaching time 30 min and liquid-to-solid ratio 5 mL/g. The leaching rates of zinc and iron are 86% and 7% while the difference between them is about 79%.

3.2 Orthogonal experiments

The orthogonal experiments were carried out to optimize the conditions of leaching process in order to increase the leaching rate of zinc and the leaching ratio of zinc to iron, and finally increases the efficiency of sulfuric acid.

The effects of sulfuric acid concentration, leaching temperature, leaching time and liquid-to-solid ratio were investigated by orthogonal experiment. The factor level of the orthogonal experiment is shown in Table 2.

Table 2 Factor level of orthogonal experiment

Content	Factor	Level		
		1	2	3
H_2SO_4 concentration/(g·L^{-1})	A	130	150	170
Leaching temperature/℃	B	30	50	65
Leaching time/min	C	30	45	60
Liquid-to-solid ratio/(mL·g^{-1})	D	4	5	6

Each experiment was repeated three times and the final data are the average value of three results. The results of orthogonal experiments and range analysis are shown in Table 3.

As shown in Table 3, the effect significance sequence of each factor on leaching rate of zinc, iron and the difference between them are DACB, DABC and DCAB respectively. The better level combination for the former is $A_3B_3C_1D_3$, while the better level combination for the latter two is $A_1B_1C_3D_1$. Experiments were carried out according to the results of orthogonal experimental analysis and the results gained were compared with the result of the ninth experiment of orthogonal experiments. The results of each better experimental combination are shown in Table 4.

As shown in Table 4, the leaching rates of zinc and iron in Combination A are the highest among the three and the difference between zinc and iron leaching ratio is only 25.58%, which indicates the usage of sulfuric acid is low. Iron compounds in Combination B are nearly indissolvable and the leaching rate of iron is only 0.15% while the leaching rate of zinc is 56.68%, which indicates that the recovery of zinc is low. The leaching rate of zinc and the difference of leaching rates between zinc and iron are 89.23% and 88.67%, which are distinctly greater than those of the formers and the efficiency of sulfuric acid is also greater. Compared with the single factor experiments, the leaching rate of zinc and the leaching ratio of zinc to iron are increased to different extents, that is, the efficiency of sulfuric acid is effectively increased.

It can be concluded that the liquid-to-solid ratio (factor D) and sulfuric acid concentration (factor A) are leading factors influencing the results, which further testifies that the final acidity of leaching solution directly affects the leaching rates of zinc and iron.

3.3 Data fitting of orthogonal experiments

In order to study the effect of sulfuric acid concentration, leaching temperature, leaching time and liquid-to-solid ratio on the leaching rates of zinc and iron, data-handing software was used to optimize the conditions of leaching process by fitting the results gained in orthogonal experiments.

Table 3 Results of orthogonal experiments and range analysis

Sample number	Factor				Leaching rate of Zn/%	Leaching rate of Fe/%	Difference of leaching rate between Zn and Fe/%
	A/($g\cdot L^{-1}$)	B/℃	C/min	D/($mL\cdot g^{-1}$)			
1	130	30	60	5	85.63	10.59	75.04
2	150	30	30	4	80.73	1.23	79.5
3	170	30	45	6	93.43	64.54	28.89
4	130	50	45	4	52.27	0.32	51.95
5	150	50	60	6	91.27	64.54	26.73
6	170	50	30	5	95.9	60.78	35.12
7	130	65	30	6	92.57	54.98	37.59
8	150	65	45	5	90.1	45.76	44.34
9	170	65	60	4	89.23	0.56	88.67
Leaching rate of Zn on each level/%	76.82	86.60	88.38	90.21			
	87.03	79.81	89.73	73.74			
	92.52	89.97	78.27	92.42			
Range/%	15.7	10.16	11.46	18.68			
Leaching rate of Fe on each level/%	21.96	25.45	39.00	0.70			
	37.18	41.88	36.87	39.04			
	41.96	33.77	25.23	61.35			
Range/%	20	16.43	13.77	60.65			
Difference of leaching rate between Zn and Fe/%	54.86	61.15	49.38	89.51			
	49.85	37.93	52.86	34.7			
	50.56	56.2	53.04	31.07			
Range/%	5.01	23.22	3.66	58.44			

Table 4 Results of each better experimental combination

Number	Experimental combination	Leaching rate of Zn/%	Leaching rate of Fe/%	Difference of leaching rate between Zn and Fe/%
A	$A_3B_3C_1D_3$	91.43	65.85	25.58
B	$A_1B_1C_3D_1$	56.68	0.15	56.53
9	$A_3B_3C_3D_1$	89.23	0.56	88.67

The difference between the leaching rates of zinc and iron gained in orthogonal experiments was investigated. The relationship between the difference (denoted with Y) and sulfuric acid concentration, leaching temperature, leaching time and liquid-to-solid ratio (denoted with X_A, X_B, X_C, and X_D respectively) is as follows.

$$Y=F(X_A, X_B, X_C, X_D)$$

The expression gained by fitting is

$$Y=-0.811X_A+0.069\,9X_A^2+0.248\,1X_B^2+0.262\,X_C^2-0.185\,1X_AX_B-0.212\,4X_AX_C-0.44X_AX_D+0.132\,9X_BX_C+0.854\,5X_CX_D$$

The fitting formula verified by T test of assumption is appropriate and its correlation coefficient is 0.971 2. The optimal values of X_A, X_B, X_C and X_D gained by least squares fitting are 170.31, 64.89, 59.36 and 4.12, respectively, which indicate that the optimal experimental parameters are 170 g/L H_2SO_4, leaching temperature 65 ℃, leaching time 60 min and liquid-to-solid ratio 4.1 mL/g. The experiments were carried out for three times based on the optimal experimental parameters gained by fitting and the results are shown in Table 5.

As shown in Table 5, the offsets of leaching rate of zinc, iron and the difference between them in the

Table 5 Results of repetitive experiments

Number	Leaching rate of Zn/%	Leaching rate of Fe/%	Difference of leaching rate between Zn and Fe%
1	90.92	1.05	89.87
2	91.24	1.23	90.01
3	91.46	1.78	89.68
Average value	91.20	1.35	89.85

repetitive experiments are very small, which indicates that the repeatability of experiments and the reliability of results are high. Simultaneously, the leaching rate of zinc and the difference of leaching rate between zinc and iron are increased within a narrow range compared to that of orthogonal experiments, which indicates that the data fitting of orthogonal experiment is successful and the leaching conditions are further optimized. The optimal leaching conditions are 170 g/L H_2SO_4, leaching temperature 65 ℃, leaching time 60 min and liquid-to-solid ratio 4.1 mL/g.

4 Conclusions

1) The improved sulfuric acid leaching method was carried out and selective recovery of zinc was realized by using low-grade zinciferous slag with complex component and phase as raw materials. The leaching rate of zinc, iron and the difference between them are 91.20%, 1.35% and 89.85% respectively, which avoids the limitation of rotary kiln volatilization and solved the low-usage of conventional sulfuric acid leaching.

2) The liquid-to-solid ratio and sulfuric acid concentration are leading factors influencing the leaching rate of zinc and iron. The optimal parameters are 170 g/L H_2SO_4, leaching temperature 65 ℃, leaching time 60 min and liquid-to-solid ratio 4.1 mL/g.

3) All the dissolved irons enter into the final sluge in the form of hydroxide because the acidity of Fe^{3+} hydrolysis is higher than that of Zn^{2+} hydrolysis with pH 1.8 and 5.6 respectively.

References

[1] JHA M K, KUMAR V, SINGH R J. Review of hydrometallurgical recovery of zinc from industrial wastes [J]. Resources, Conservation and Recycling, 2001, 33(1): 1−22.

[2] LECLERC N, MEUX E, LECUIRE J M. Hydrometallurgical extraction of zinc from zinc ferrites [J]. Hydrometallurgy, 2003, 70(1/3): 175−183.

[3] YU M Y, WANG H P, CHEN C Y, HSIUNG T L. Recovery of zinc in phosphor wastes via electrokinetic treatments [J]. Journal of Electron Spectroscopy and Related Phenomena, 2007, 156/158(1): 211–213.

[4] Van BEERS D, KAPUR A, GRAEDEL T E. Copper and zinc recycling in Australia: Potential quantities and policy options [J]. Journal of Cleaner Production, 2007, 15(8/9): 862−877.

[5] JHA M K, KUMAR V, BAGCHI D, SINGH R J, LEE J C. Processing of rayon waste effluent for the recovery of zinc and separation of calcium using thiophosphinic extractant [J]. Journal of Hazardous Materials, 2007, 145(1/2): 221−226.

[6] KINOSHITA T, YAMAGUCHI K, AKITA S, NII S, KAWAIZUMI F. Hydrometallurgical recovery of zinc from ashes of automobile tire wastes [J]. Chemosphere, 2005, 59(8): 1105−1111.

[7] SAFFARZADEH A, SHIMAOKA T. Chemical and mineralogical evaluation of slag products derived from the pyrolysis/melting treatment of MSW [J]. Waste Management, 2006, 26(12): 1443−1452.

[8] ABDEL-LATIF M A. Fundamentals of zinc recovery from metallurgical wastes in the Enviroplas process [J]. Minerals Engineering, 2002, 15(11): 945−952.

[9] DUTRA A J B, PAIVA P R P, TAVARES L M. Alkaline leaching of zinc from electric arc furnace steel dust [J]. Minerals Engineering, 2006, 19(5): 478−485.

[10] BUENO C C, de SOUZA M. Simultaneous recovery of zinc and manganese dioxide from household alkaline batteries through hydrometallurgical processing [J]. Journal of Power Sources, 2004, 136(1): 191−196.

[11] STROBOS J G, FRIEND J F C. Zinc recovery from baghouse dust generated at ferrochrome foundries [J]. Hydrmetallurgy, 2004, 74(1/2): 165−171.

[12] MOUSAVI S M, YAGHMAEI S. Zinc extraction from Iranian low-grade complex zinc-lead ore by two native microorganisms: *Acidithiobacillus ferrooxidans* and *sulfobacillus* [J]. Int J Miner Process, 2006, 80: 238−243.

[13] MOUSAVI S M, JAFARI A, YAGHMAEI S, VOSSOUGHI M, et al. Bioleaching of low-grade sphalerite using a column reactor [J]. Hydrometallurgy, 2006, 82(1/2): 75−82.

[14] MOORS E H M, DIJKEMA G P J. Embedded industrial production systems: Lessons from waste management in zinc production [J]. Technological Forecasting and Social Change, 2006, 73(3): 250−265.

[15] FU Bin. Metallurgical analysis of heavy metals [M]. Beijing: Metallurgical Industry Press, 2001: 123−126. (in Chinese)

[16] WEI Fu-sheng. Monitoring and analysis method of water and waste [M]. Beijing: Environmental Science Press, 1998: 38−42. (in Chinese)

[17] CHEN C K, YANG C Y. A study on the preparation of zinc ferrite [J]. Journal of Metallurgy, 2001, 30(4): 238−245. (in Chinese)

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