Vol. 10 №. 2 **Trans. Nonferrous Met. Soc. China** Apr. 2000

Article ID: 1003 - 6326(2000)02 - 0267 - 03

Treatment of cadmium dust with two-stage leaching process ①

WANG De-quan(王德全), JIANG Lan(姜 澜), LIN Mao-shen(林茂森)
School of Materials and Metallurgy, Northeastern University, Shenyang 110006, P. R. China

Abstract: The treatment of cadmium dust with a two-stage leaching process was investigated to replace the existing sulphation roast-leaching processes. The process parameters in the first stage leaching were basically similar to the neutral leaching in zinc hydrometallurgy. The effects of process parameters in the second stage leaching on the extraction of zinc and cadmium were mainly studied. The experimental results indicated that zinc and cadmium could be efficiently recovered from the cadmium dust by two-stage leaching process. The extraction percentages of zinc and cadmium in two stage leaching reached 95 % and 88 % respectively under the optimum conditions. The total extraction percentage of Zn and Cd reached 94 %.

Key words: cadmium dusts; neutral leaching; hot acid leaching **Document code:** A

1 INTRODUCTION

Cadmium dust is produced from the secondary roasting of roast dust of zinc sulphide concentrate in Huludao Zinc Plant. According to the result of X-ray diffraction analysis, cadmium dust typically contains zinc oxide, zinc ferrite and sulphides of zinc, cadmium and lead. The existing technological process treating cadmium dust includes sulphation roasting and water leaching. Thermodynamic analysis of the sulphation roast and chemical composition of the flue gas from the roasting indicate that following reactions occur in the sulphation roast process of cadmium dust:

$$MeS + H_2SO_4 = MeSO_4 + H_2S\uparrow \quad (1)$$

$$MeS + 2H_2SO_4 = MeSO_4 + 0.5S_2\uparrow + SO_2\uparrow + 2H_2O\uparrow \quad (2)$$

$$MeO + H_2SO_4 = MeSO_4 + H_2O\uparrow \quad (3)$$

$$2H_2SO_4 = 2SO_2\uparrow + O_2\uparrow + 2H_2O\uparrow \quad (4)$$

It can be seen from reactions (1) ~ (4) that the flue gas from the sulphation roast mainly consists of hydrogen sulphide, sulphur, sulphur oxide and steam. The flue gas, therefore, results in environment pollution, bad operation condition and corrosion of equipments for dust system.

The purpose of the present study is to treat the cadmium dust with two-stage leaching in place of the existing sulphation roasting-water leaching process. The main chemical reaction in the first stage leaching is the dissolution of zinc oxide in the cadmium dust by sulphuric acid:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O \quad (5)$$

According to the principle of hot acid leaching in zinc hydrometallurgy[1~4], the dissolution of zinc ferrite in the cadmium dust occurs during the second stage leaching:

$$ZnO\cdot Fe_2O_3 + 4H_2SO_4 = Fe_2(SO_4)_3 + ZnSO_4 + 4H_2O \quad (6)$$

Sulphides of zinc, cadmium and lead in the cadmium dust will be oxidated by ferric sulphate produced in the dissolution of zinc ferrite[5,6]:

$$MeS + Fe_2(SO_4)_3 = MeSO_4 + 2FeSO_4 + S^0 \quad (7)$$

where Me represents Zn, Cd and Pb. Since iron in the cadmium dust may be not enough for the oxidation of MeS in Reaction (7), the addition of manganese oxide as an oxidant is required in the second stage leaching. The oxidation process of MeS with MnO_2 is slow but can be accelerated by the catalysis of $FeSO_4$[7~9] produced in Reaction (7).

$$MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + 2H_2O + Fe_2(SO_4)_3 \quad (8)$$

The two stage leaching process has a considerable advantage over the existing sulphation roasting-water leaching process because it eliminates environment pollution, bad operation condition and equipment corrosion. The most satisfactory feature of the two stage leaching process is the behaviour of iron in the second stage leaching. Firstly, the dissolution of zinc ferrite makes zinc and iron be leached simultaneously. Secondly, Fe^{3+} from the dissolution of zinc ferrite can oxidize MeS to Me^{2+} and S^0, and Fe^{3+} itself becomes Fe^{2+} ion. Finally, Fe^{2+} ion can be used as catalyzer of the oxidation of MeS by MnO_2.

The first stage leaching in which the main reaction is the dissolution of zinc oxide is analogous to the neutral leaching in zinc hydrometallurgy. Emphases in this study were put on the second stage leaching.

2 EXPERIMENTAL

The cadmium dust used in this study was provided by Huludao Zinc Plant. The chemical composition of the cadmium dust is listed in Table 1. The cadmium dust size is smaller than 0.074 mm being up to 90 %. Reagent-grade sulphuric acid was used in all

① **Received date:** Sep.18, 1999; **accepted date:** Jan.17, 2000

experiments. MnO_2 used in the second stage leaching was added in the form of anode mud from zinc electrolysis process. The main composition of the anode mud is listed in Table 2.

Table 1 Chemical composition of cadmium dust (%)

Zn	Cd	Pb	Fe	S
33.14	4.51	22.57	4.55	7.89

Table 2 Chemical composition of anode mud (%)

Zn	Pb	Mn
0.58	7.63	41.97

The leaching tests using 100 g cadmium dust each run were carried out in a 500 mL beaker, which was held in the thermostatted water bath in order to control temperature of leach solution (The precision of controlling temperature is ±1 ℃). Agitation of leach solution was provided by a paddle stirrer, and the stirring velocity was fixed at 400 r·min^{-1}. At the end of the experiment, leach slurry was filtered and the filter cake was washed with hot water and then dried at 110 ℃ prior to chemical analysis.

3 RESULTS AND DISCUSSION

3.1 The first stage leaching

The purpose of the first stage leaching is to leach zinc oxide in the cadmium dust. The process parameters in the first stage leaching, with reference to neutral leach in zinc hydrometallurgy, were selected as follows:

Concentration of H_2SO_4	110 g/L
Operation temperature	60 ℃
L/S	4∶1
Retention time	1 h

The experimental results showed that the extraction percentage of zinc and cadmium reached 79% under the above test conditions. Also, the extraction percentage of iron reached 65%. This illustrated some of zinc ferrite and sulphides in the cadmium dust dissolved in the first stage leaching.

3.2 The second stage leaching

The leaching residue of the first stage was treated in the second stage leaching for dissolution of zinc ferrite and sulphides in cadmium dust. It has been demonstrated in zinc hydrometallurgy that the dissolution of zinc ferrite must be conducted at more than 85 ℃[10]. Therefore, the leaching temperature of the second stage was controlled at 90 ℃ as a fixed parameter. The effects of the other operation conditions, including concentration of H_2SO_4, addition of oxidant and retention time, on the leaching of zinc and cadmium were studied in the second stage leaching.

3.2.1 Effect of anode mud addition

The effect of anode mud addition was examined over the range of anode mud amount 0 ~ 40 g. Fig.1 illustrates that the anode mud addition has a very important effect on the leaching of zinc and cadmium. The extraction percentage of zinc and cadmium is lower, only 6.5%, without addition of anode mud, but increases with increasing anode mud amount.

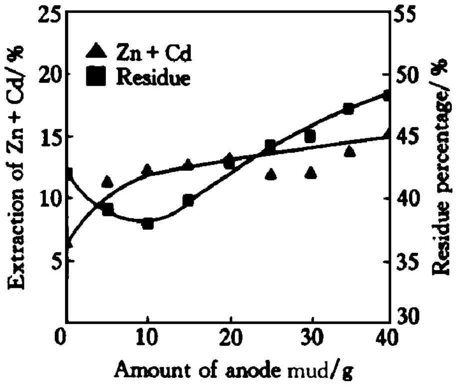

Fig.1 Effects of anode mud amount on leaching of zinc and cadmium
($\rho(H_2SO_4)$ = 200 g/L; 90 ℃; L/S = 4∶1; t = 2 h)

The extraction percentage of zinc and cadmium reaches 13.5% when 10 g anode mud were added. However, further increasing anode mud amount only slightly increases the extraction percentage of zinc and cadmium. On the other hand, it can be seen from Fig.1 that the residue percentage of leaching decreases as anode mud addition being less than 10 g but increases as anode mud addition being more than 10 g. The above results demonstrate that iron in cadmium dust is not enough for oxidation of MeS in accordance with Reaction (7) and MnO_2 in anode mud can oxidize MeS in cadmium dust in the presence of Fe^{2+} and Fe^{3+}. For 100 g cadmium dust, 10 g anode mud is enough and further increasing anode mud amount can only increase residue percentage of leaching.

3.2.2 Effects of H_2SO_4 concentration

The concentration of sulphuric acid is one of the important control parameters in dissolution of zinc ferrite. Fig.2 shows that the extraction percentage of zinc and cadmium increases with the increase of H_2SO_4 concentration in leach solution over range of 80 ~ 200 g/L, and do not increase beyond 200 g/L. On the other hand, the residue percentage of leaching decreases with the increase of H_2SO_4 concentration.

The reason for the strong effect of H_2SO_4 concentration on leaching of zinc and cadmium is that the rate of zinc ferrite dissolution increases with the increase of H_2SO_4 concentration. It has been reported[4] that the dissolution rate of zinc ferrite in sulphuric acid solution can be written as follows.

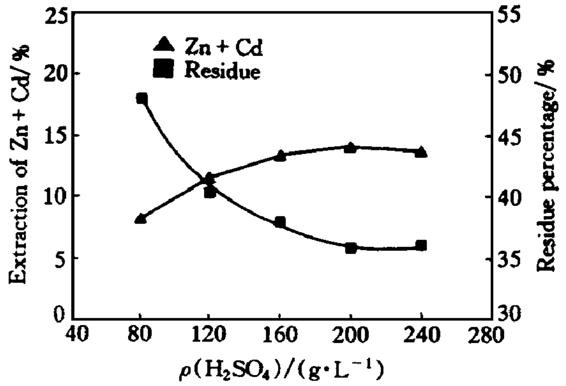

Fig.2 Effect of H_2SO_4 concentration on leaching of zinc and cadmium
(10 g anode mud; 90 ℃; L/S = 4∶1; t = 2 h)

For $[Fe^{3+}] < 0.216\ mol·L^{-1}$:

$$v = 3.8 \times 10^4 \exp(-63.6/RT)(a_{H^+})^{0.57}$$

For $[Fe^{3+}] > 0.216\ mol·L^{-1}$:

$$v = 1.16 \times 10^4 \exp(-69.2/RT)\frac{(a_{H^+})^{0.57}}{[Fe^{3+}]^{0.5}}$$

It is quite evident that the dissolution rate of zinc ferrite depends on the value of hydrogen ion activity in leach solution.

3.2.3 Effect of retention time

Fig.3 shows the leaching as a function of retention time. The extraction percentage of zinc and cadmium increases and the corresponding residue percentage of leaching decreases as leaching proceeds. The extraction percentage of zinc and cadmium in the second leaching stage is 15 % as leaching for 3 h, after which no evident change is observed. The results indicate that Reactions (6) ~ (8) are more rapid under the conditions of high temperature, high acidity and the presence of oxidant.

It should be noted that the extraction percentage of zinc and cadmium mentioned in results and discussion means the extraction percentage of Zn + Cd. Under the optimum conditions, the total extraction percentages of zinc and cadmium in two stage leaching reach 95 % and 88 % respectively if they are calculated respectively.

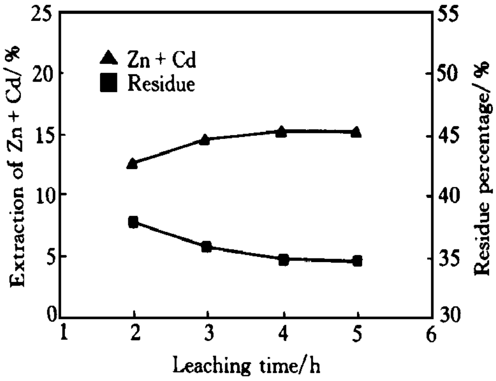

Fig.3 Effect of retention time on leaching of zinc and cadmium
(10 g anode mud; 90 ℃; L/S = 4∶1; $\rho(H_2SO_4)$ = 200 g/L)

4 CONCLUSIONS

A two stage leaching process is proposed for treatment of cadmium dust. The first stage basically similar to the neutral leaching in zinc hydrometallurgy is followed by hot acid leaching with the addition of anode mud as an oxidant for dissolution of zinc ferrite and sulphides of cadmium dust.

Experimental results indicate that the two stage leaching process is feasible. The extraction percentages of Zn + Cd in the first stage and the second stage reach 79 % and 15 % respectively and the total extraction percentage of Zn + Cd is 94 % under the optimum conditions. If the extraction percentages of zinc and cadmium are calculated respectively, they reach 95 % and 88 % respectively in two stage leaching. This result shows that the leaching of cadmium sulphide is more difficult than that of zinc sulphide under the conditions used in the present study.

REFERENCES

[1] Gordon A R and Pickering R W. Improved leaching technologies in the electrolytic zinc industry [J]. Metall Trans B, 1975, 6B: 43 ~ 53.

[2] Rastas J and Fuglebery S. Kinetics of ferrite leaching and jarosite precipitation [J]. Erzmetall, 1976, 32(3): 117 ~ 121.

[3] Filippon D, et al. A reaction kinetic model for the leaching of industrial zinc ferrite particulates in sulphuric acid media [J]. Can Metall Q, 1992, 31(1): 41 ~ 54.

[4] Filippon D and Demopoulos G P. Steady-state modeling of zinc ferrite hot acid leaching [J]. Metallurgical and Materials Transactions B, 1997, 28B: 701 ~ 711.

[5] Verbaan B and Crundwell F K. An electrochemical model for the leaching of a sphalerite concentrate [J]. Hydrometallurgy, 1986, 16(2): 345 ~ 359.

[6] Crundwell F K. Kinetics and mechanism of the oxidative dissolution of zinc sulphide concentrate in ferric sulphate solution [J]. Hydrometallurgy, 1987, 19(2): 227 ~ 242.

[7] Verbaan B and Mullinder B. The simultaneous electrowinning of manganese dioxide and zinc from purified neutral zinc sulphate at high current efficiencies [J]. Hydrometallurgy, 1981, 7(4): 339 ~ 352.

[8] Punde A M, et al. Single cell extraction of zinc and manganese dioxide from zinc sulphide concentrate and manganese ores [J]. Hydrometallurgy, 1982, 9(1): 57 ~ 68.

[9] Srinivasa K and Paramaguru R K. Dissolution of sphalerite (ZnS) in acidic solution in the presence of manganese dioxide [J]. Miner Metall Process, 1998, 15(1): 29 ~ 34.

[10] Monhemius A J. The electrolytic production of zinc [A]. In: Burkin A R ed. Topics in Non-ferrous Extractive Metallurgy [C]. Oxford, United Kingdom: Blackwell Scientific Publication, 1980: 104 ~ 130.

(Edited by YUAN Sai-qian)