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Effects of impurities ions on Zinc Electrowinning process in Alkaline Leaching

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***Abstract*—The effects of impurities ions on the quality of the metallic zinc powder in zinc alkaline leaching electrowinning process are researched. The experimental results indicated that the ions of CO_3^{2-},SO_4^{2-},SiO_3^{2-}、F^- have no influences on zinc Electrowinning and the maximum concentration of the chlorine ion should be controlled under 20g/L, the concentration of the sulfide ion has significant influence on electrowinning process, the quality of zinc decreased by 5% even under the slight amount of sulfide ion condition.**

Keywords-alkaline leaching; impurities ions; Electrowinning

I. INTRODUCTION

Zinc is the indispensable metal material of people's livelihood and country's development. China, as the world's second-largest zinc producing kingdom, its zinc raw material gap will get up to 600,000t by 2015[1] through forecasting according to GDP growth speed by 7 ~ 8%. So comprehensive disposal and processing the tailings with zinc and the lean zinc-oxide ore not only improve the degree of zinc, reduce the waste of resources and relieve the shortages of zinc at present, but also reduce the environmental pollution of smelting industry[2,3]

In China, the technology of producing high-purity zinc powder from the materials of tailings with zinc and the lean zinc-oxide ore has been studied and great successes have been achieved by Zhao You-cai of Tongji university by means of alkaline leaching and electrowinning. Smelting plants of zinc powder have been built successively in Guizhou, Yunnan and Zhejiang provinces[4].But in the actual process, because the continuous circulation of waste electrolyte will lead to CO_3^{2-},SO_4^{2-},SiO_3^{2-},F^-,Cl^-, S^{2-} and arsenic etc. impurities' accumulation, which will affect seriously the quality of zinc powder and the current efficiency.

In view of the above questions, in this paper CO_3^{2-},SO_4^{2-},SiO_3^{2-},F^-,Cl^-,S^{2-} and arsenic influencing on electrowinning zinc in the NaOH-Zn(Ⅱ) -H_2O system was studied systematically and at the same time the limited concentration of impurity ions was determined.

II. EXPERIMENTAL METHODS

A. . Confection of the electrolyte

Confected the electrolyte: Put 348g NaOH and 60g ZnO into the beakers, dissolved in distilled water with stirring, and then defined the constant volume of solution to 1200 ml, got the concentration of NaOH 240 g/l, the concentration of Zn 40 g/l. Put the different quality of Na_2CO_3, Na_2SO_4, $Na_2SiO_3\cdot 9H_2O$, NaF,NaCl,Na_2S and $Na_3AsO_4\cdot 9H_2O$ without water into the pure electrolyte respectively, dissolved with stirring, made different concentration containing CO_3^{2-}、SO_4^{2-}、SiO_3^{2-}、F^-、Cl^-、S^{2-}、$AsO_4^{3-}$and AsO_3^{3-} ions of the electrolyte.

B. Experimental devices

The volume of electrolytic cell was 1.2l. The cathode board was alloy plate, anode board was stainless steel plate, effective area was 8.00cm×6.00cm. In addition, equipped with stainless steel cathode electrode plate and stainless steel anode electrode board, 7.00cmx6.40cm. Figure 1 is experimental device.

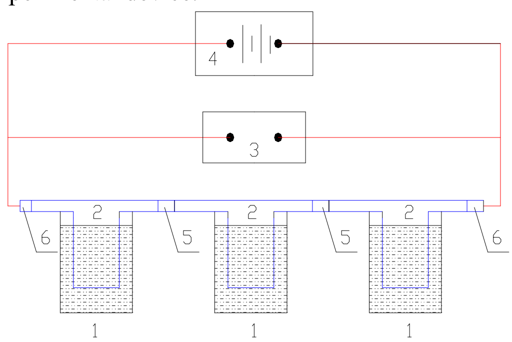

Figure 1. Effect of impurities ions on zinc electrowinning process in alkaline leaching

1—electrolytic cell; 2—polar plate; 3—digital multimeter; 4—DC stabilized power supply; 5—the joint of polar plate; 6—the joint of power line and polar plate.

C. experiment methods

Electrolyzed the electrolyte containing different concentration of ions in series under the condition of temperature 25℃, current density 1000 A/m^2, Polar distance 3cm, electrolysis time 3h. In the process of electrolysis, stainless steel cathode board was used in electrolysis containing CO_3^{2-}ion electrolyte, other experiments adopted alloy plates as cathode board, electrolysis time of containing SO_4^{2-} was 4h. After the electrolysis, washed the zinc powder with 20% NaOH solution once or twice and then used water to clean the zinc powder to neutral condition, dried it under the condition of vacuity 0.06 to 0.08Mpa, temperature 120℃, then weighed zinc and metal zinc. Used Na_2EDTA to measure the quality of zinc and used permanganate itration method to measure the quality of metal zinc (GB/T6890－2000).

Calculated the current efficiency according to the ratio of actual quality of zinc by electrolysis and theoretical numerical value,such as formula 1.

$$\eta = {m}/{q \bullet I \bullet t \bullet n} \times 100\% \quad (1)$$

Where, η is current efficiency(%), m is precipitation actual production of zinc in t time(g), I is electrolysis current(A),t is electrolysis time(h),n is the number of electrolytic cell；q is the electrochemical equivalent of zinc，1.220g/(A·h).

III. RESULTS OF EXPERIMENT AND DISCUSSION

A. *Influence* of CO_3^{2-}、$SO_4^{2-}$and SiO_3^{2-} on electrolytic zinc powder metal

In raw materials containing zinc such as the tailings with zinc and the lean zinc-oxide ore, zinc existing forms of zinc oxide, zinc carbonate,zinc silicate(hemimorphite, Zn_2SiO_4 or $Zn_4Si_2O_7(OH)_2·H_2O$). The experimental results were recorded in table 1 to 3 about influence of CO_3^{2-}、$SO_4^{2-}$and SiO_3^{2-} on electrolytic zinc powder metal.

TABLE I. EFFECT OF CO_3^{2-} ON ZINC ELECTROWINNING PROCESS

No	Concentration of CO_3^{2-} (g/l)	Quality of Zinc powder (g)	Current efficiency (%)	Zinc (%)	Metal Zinc (%)
1	0	13.3855	93.58	99.91	95.76
2	5.66	14.6725	95.45	99.45	96.50
3	11.32	14.2188	92.50	99.23	96.48
4	16.98	14.3417	93.30	99.73	96.28
5	22.64	15.1181	98.35	99.34	95.28

Annotation, electrolytic current was 4.2 A, electrolytic voltage was 14.2 V.

TABLE II. EFFECT OF $SO4^{2-}$ ON ZINC ELECTROWINNING PROCESS

No	Concentration of SO_4^{2-} (g/l)	Quality of Zinc powder (g)	Current efficiency (%)	Zinc (%)	Metal Zinc (%)
1	0	21.6150	92.28	99.06	92.07
2	1	22.0331	94.06	98.45	92.63
3	5	21.7283	92.76	98.05	91.94
4	10	21.1878	90.45	98.14	92.99
5	20	21.8718	93.37	98.45	92.9

Annotation, electrolytic current was 4.8 A, electrolytic voltage was 15.3 V.

TABLE III. EFFECT OF SIO_3^{2-} ON ZINC ELECTROWINNING PROCESS

No	Concentration of SiO_3^{2-} (g/l)	Quality of Zinc powder (g)	Current efficiency (%)	Zinc (%)	Metal Zinc (%)
1	0	16.4426	93.59	97.96	92.93
2	1.65	16.4777	93.80	98.24	92.33
3	3.3	16.6376	94.70	97.92	91.44
4	6.6	16.6302	94.66	97.7	92.22

Annotation, electrolytic current was 4.8 A, electrolytic voltage was 12.4 V.

Obtained conclusion from the above three tables, electrolyzed the electrolyte which contained different concentrations of CO_3^{2-}、SO_4^{2-}、SiO_3^{2-},the quality of zinc powder has little difference, electrolytic rate of zinc was more than 98%,metal zinc was more than 98%,which could be achieved level 3 of national standards (GB/T6890－2000), electrolytic efficiency was more than 90%.The results show that CO_3^{2-}、SO_4^{2-}、SiO_3^{2-} has no significant effect on electrolytic zinc in the alkaline solution, the reason could be that three ions have no oxidation and deoxidization and do not suffer electronic gain or loss during electrolysis process, so it will not affect zinc deposition process. The results of experiment also show that the technology of leaching zinc from zinc-oxide materials by NaOH solution and electrolysis is applied in many fields.

B. *Influence* of F and Cl on electrolytic zinc powder

Fluorine and chlorine are harmful impurities to leaching zinc by acid, such as corroding electrode, decreasing the quality of electricity zinc and current efficiency, which makes exfoliate zinc from electrode difficult. So it is necessary to purify them when the concentration of fluorine and chlorine are more than 100mg/l in electrolyte by acid leaching[5]. Therefore, this experiment mainly studied the influence of fluoride and chlorine to zinc deposit in alkaline medium. The experimental results were recorded in table 4 to 5 about influence of CO_3^{2-}、$SO_4^{2-}$and SiO_3^{2-} on electrolytic zinc powder metal.

TABLE IV. EFFECT OF F^- ON ZINC ELECTROWINNING PROCESS

No	Concentration of F^- (g/l)	Quality of zinc powder (g)	Current efficiency (%)	Zinc (%)	Metal Zinc (%)
1	0	16.0695	91.47	98.73	92.96
2	0.05	16.0447	91.85	96.24	92.04
3	0.1	16.1600	91.99	98.34	92.03
4	5	16.1683	92.03	97.67	92.07

Annotation, electrolytic current was 4.8 A, electrolytic voltage was 14.3 V.

TABLE V. EFFECT OF CL^- ON ZINC ELECTROWINNING PROCESS

No	Concentration of Cl^- (g/l)	Quality of zinc powder (g)	Current efficiency (%)	Zinc (%)	Metal Zinc (%)
1	0	16.7009	95.06	98.62	92.02
2	0.5	16.4216	93.47	98.84	92.56
3	0.1	16.6330	94.68	98.83	91.17
4	1	16.5149	94.01	98.89	91.84
5	5	16.6994	95.63	98.46	91.60

Annotation, electrolytic current was 4.8 A, electrolytic voltage was 15.2 V.

It can be concluded from table 4 and table 5 that Fluorine and chlorine have no obvious impact on the quality of zinc powder metal even the concentration of them is at 5g/l[6].

QiuYuanYuan etc. [7] had done the experiments, the results of experiment also show that Fluorine and chlorine have no obvious impact on the quality of zinc powder metal even the concentration of them is at 25g/l. The reason is that chlorine and hypochlorite conversion reaction does not occur, in the same way fluoride and hydrofluoric acid of transform reaction is unlikely to happen. in alkaline medium.

According to the experimental results and producing practice of several smelters, the licensing concentration of chlorine was determined by 20 g/l.

C. Influence of sulfur on electrolytic zinc powder

In order to precipitate the impurities such as lead etc. in the purification process Na_2S used as purifying agent.Na_2S with lead and zinc in the leaching solution generate chemical reaction to produce precipitation, but there was a little residue sulfur elements in the solution inevitably. Therefore, it was necessary to research this part the traces of the sulfur elements on the influence of electrolytic zinc powder.

Prepared two beakers of pure electrolyte, put 0.5g Na_2S into the No.2 beaker, then white precipitation generated, filtered the precipitation, and then electrolyzed two beakers of electrolyte in series. The experimental results were recorded in table 6 about influence of sulfur on electrolytic zinc powder metal and the current efficiency.

TABLE VI. EFFECT OF SULFUR ON ZINC ELECTROWINNING PROCESS

No	Concentration of Cl^- (g/l)	Quality of zinc powder (g)	Current efficiency (%)	Zinc (%)	Metal Zinc (%)
1	0	16.4943	93.89	99.22	92.68
2	trace	16.0278	91.23	98.96	87.76

Annotation, electrolytic current was 4.8 A, electrolytic voltage was 6.1 V.

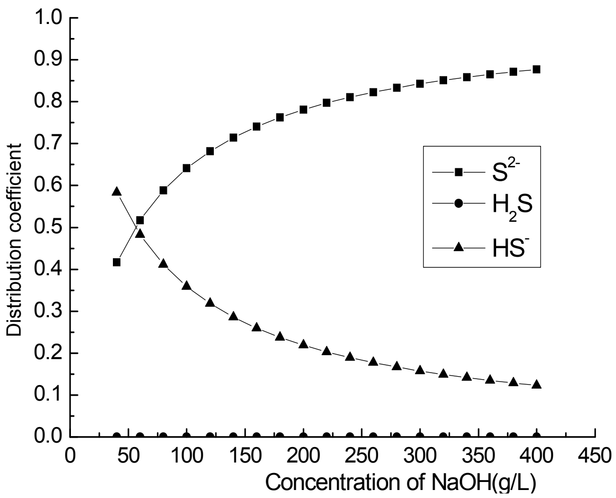

Figure 2. Distribution curve of Sulfur in alkali solution

Known from figure 2 that sulfur existed mainly in two kinds of S^{2-} and HS^- in alkali solution[8]. Got electronic and generated oxidation reaction in electrolytic process, thereby it affected the quality of zinc powder and current efficiency.

D. Influence of arsenic on electrolytic zinc powder

Prepared electrolyte, put sodium arsenate into four beakers respectively, the concentration of arsenic was 0, 100,200 and 300 mg/l, and then electrolyzed four beakers of electrolyte in series under the condition of electrolytic current 4.8 A and electrolytic voltage 2.2 V. After the start of electrolysis, observed the beaker of electrolyte rollover phenomenon at the concentration of arsenic was 300mg/l, zinc powder had no metal luster, zinc electrolysis balance was destroyed, electrolysis process was stopped.

The result shows that arsenic has obvious effect on electrolytic zinc in the alkaline solution, The reason is that AsO_4^{3-} and AsO_3^{3-} obtained electron and generated (2) and (3) reaction in the alkaline solution, broke zinc electrolysis balance, influenced precipitation of zinc seriously. Therefore, in practice the concentration of arsenic should be controlled under 200mg/l (the licensing concentration of arsenic should be determined by further experiments).

$$AsO_4^{3-} + 2H_2O + 2e^- \rightarrow AsO_2^- + 4OH^- \quad (2)$$

$$E^\theta = -0.71\text{V}$$

$$AsO_3^{3-} + 2H_2O + 3e^- \rightarrow As + 4OH^- \quad (3)$$

$$E^\theta = -0.68\text{V}$$

E. Electrolysis effect of production

Taken leaching agent from smelter production as electrolyte to do electrolytic experiment, electrolyte ingredients were recorded in following table 7. In the electrolytic product zinc accounted for 98.98%, mental zinc accounted for 95.9%,current efficiency was above 99% and electric energy consumption was 2.38kwh/kg, the quality of zinc powder got up to level 3 of national standards (GB/T6890－2000).

IV. CONCLUSION

In this work, the results show that CO_3^{2-},SO_4^{2-},SiO_3^{2-},F have no significant effect on electrolytic zinc in the alkaline solution, the licensing concentration of chlorine is determined by 20 g/l, sulfur and arsenic have obvious effect on electrolytic zinc in the alkaline solution.

The results also show that the technology of producing zinc powder by sodium hydroxide leaching and electrolysis can be adapted to all types of zinc oxide materials, particularly zinc raw materials containing fluorine and chlorine which can not be leached by acid method.

Sulfur and arsenic in the electrolyte can be purified by electrolyte aging or electrolyte deep purification to ensure the quality zinc powder.

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