

Separation of Cobalt and Nickel from Sulfate Solutions

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Abstract. Separation of cobalt and nickel from sulfate solutions was studied, using the sodium hypochlorite solution as the oxidant of Co^{2+} . The cobalt removal rate reached 98% while Ni^{2+} was hardly oxidized at 80°C, 1h, pH 2.3 and $\text{Co}^{2+}/\text{ClO}^-$ molar ratio of 1:15. Solution pH and the amount of ClO^- had more significant influences on oxidation of Co^{2+} and Ni^{2+} . Increasing temperature could improve the filtration performance of the solid product. The Co^{2+} oxidation product was CoOOH . Adding the sodium hypochlorite solution in more than one times could inhibit the Ni^{2+} oxidation to NiOOH .

Introduction

Cobalt and nickel often coexist in cobalt or nickel ores and are leached together into the liquors during acid leaching of cobalt or nickel ores. In the leach liquors, cobalt and nickel are difficult to separate because of their similar physical and chemical properties[1-3]. Solvent extraction is the main technology for separating nickel and cobalt [4-6], but needs many stages of extraction procedures and is easy to be influenced by the Mg^{2+} ions in the solutions.

Cobalt and nickel can react with some oxidants and are oxidized to trivalent compounds of cobalt and nickel. In this study, sodium hypochlorite was selected as the oxidant. The possibility of separation of cobalt and nickel using sodium hypochlorite was investigated. The oxidation products of cobalt and nickel in sulfate solutions were studied. The results may be helpful for the separation of cobalt and nickel in sulfate solutions.

Experimental

Materials. The feed solution containing Co^{2+} and/or Ni^{2+} used in this study was prepared by dissolving cobalt sulfate, nickel sulfate (analytical grade) with distilled water, with Ni^{2+} and/or Co^{2+} concentrations of 5g/L and 0.4-2g/L. The industrial sodium hypochlorite (10%) solution was used directly. The solution pH was adjusted using the dilute sulfuric acid.

Methods. Leaching experiments were carried out in a 500ml Erlenmeyer flask. The feed solution and the sodium hypochlorite solution were placed in the Erlenmeyer flask. The Erlenmeyer flask was placed in a magnetic stirrer, heated to the desired temperature, and then leached for a set time at 450rpm. The slurry was filtered and the leach residues were washed with distilled water and dried for 4h at 100°C.

The solution pH was measured using a pH meter (PHS-3E, Shanghai INESA Scientific Instrument Co., Ltd., China). The filtrate was analyzed for nickel and cobalt by a Hitachi Z-5000 atomic absorption spectrometer. The amount of metal ion entering into solid products was the difference between mass of metal ion in the feed solution and in the filtrate. The removal rate of metal ion was calculated as the ratio of the amount of metal ion entering into solid products to that in the feed solution. Some solid products were analyzed using a D/max 2550 X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation between 10° to 80° (2θ).

Results and discussion

Reaction of Co^{2+} and ClO^- . The feed solution containing 0.4g/L Co^{2+} was selected to react with the sodium hypochlorite (10%) solution. The results are shown in Tables 1-4.

Table 1 Effect of solution pH on cobalt oxidation
(20°C, 1h, $\text{Co}^{2+}/\text{ClO}^-$ molar ratio 1:13)

Feed solution pH	Phenomena	Cobalt removal rate (%)
5.7	difficult to be filtered	78.6
4.4	difficult to be filtered	86.1
2.6	difficult to be filtered	69.4
1.1	traces of products	1.3

Table 1 shows that the cobalt removal rate increases with the increase of solution pH, but the most solid products are extremely fine and difficult to be filtered.

Table 2 Effect of temperature on cobalt oxidation
(feed solution pH 5.7, 1h, $\text{Co}^{2+}/\text{ClO}^-$ molar ratio 1:13)

Temperature(°C)	Phenomena	Cobalt removal rate (%)
15	difficult to be filtered	88.4
25	difficult to be filtered	84.5
35	easy to be filtered	85.8
55	easy to be filtered	86.4
70	easy to be filtered	86.9

Table 2 shows that the cobalt removal rate keeps at about 85% within the temperature range of 15-70°C, but the oxidation products became easy to be filtered with the increase of temperature.

Table 3 Effect of reaction time on cobalt oxidation
(feed solution pH 5.7, 15°C, $\text{Co}^{2+}/\text{ClO}^-$ molar ratio 1:13)

Reaction time(min)	Cobalt removal rate (%)
15	85.6
30	85.2
60	88.3

It can be seen from Table 3 that the cobalt removal rate increases with the increase of reaction time, but the increasing extent is low, indicating the cobalt oxidation is a rapid reaction.

The cobalt removal rate increased significantly with the decrease of $\text{Co}^{2+}/\text{ClO}^-$ molar ratio, and reached about 95% and 98% at $\text{Co}^{2+}/\text{ClO}^-$ molar ratios of 1:11 and 1:21, as seen in Table 4. This indicates that increasing the amount of ClO^- facilitates the Co^{2+} oxidation.

Table 4 Effect of $\text{Co}^{2+}/\text{ClO}^-$ molar ratio on cobalt oxidation
(feed solution pH 5.7, 80°C, 1h)

$\text{Co}^{2+}/\text{ClO}^-$ molar ratio	Cobalt removal rate (%)
1:3	49.2
1:6	79.8
1:11	95.1
1:21	98.4
1:31	98.4

Reaction of ClO⁻ and solution containing Co²⁺ and Ni²⁺. The feed solution containing 2g/L Co²⁺ and 5g/L Ni²⁺ was selected to react with sodium hypochlorite (10%) solution. The results are shown in Table 5.

Table 5 Effect of solution pH on oxidation of cobalt and nickel (80°C, 1h, Co²⁺/ClO⁻ molar ratio 1:1)

Feed solution pH	Cobalt removal rate (%)	Nickel removal rate (%)
2.7	18.5	0
2.5	20.8	0
2.3	23.2	0
2.1	22.1	0
1.9	24.4	0

In the pH range of 1.9-2.7, the nickel removal rate was essentially zero at Co²⁺/ClO⁻ molar ratio of 1:1, but the cobalt removal rate was only about 20%, as seen in Table 5. It was found in the experiments that the Ni²⁺ could react with ClO⁻ if increasing the amount of ClO⁻ or increasing feed solution pH to 3 or above, for example, the nickel removal rate reached about 5% when Co²⁺/ClO⁻ molar ratio was 1:3. In order to improve the cobalt removal rate and inhibit the oxidation of Ni²⁺, the following experiments were carried out at a decreased Co²⁺/ClO⁻ molar ratio, but the sodium hypochlorite solution was added in more than one times. The results are shown in Table 6 and Fig.1.

Table 6 Effect of Co²⁺/ClO⁻ molar ratio on oxidation of cobalt and nickel (80°C, 1h, feed solution pH 2.3)

Co ²⁺ /ClO ⁻ molar ratio	Adding manner of the ClO ⁻ solution	Cobalt removal rate (%)	Nickel removal rate (%)
1:3	adding in 5 times	52.6	0
1:6	adding in 6 times	76.1	0
1:9	adding in 9 times	89.4	0
1:15	adding in 12 times	98.8	0

When Co²⁺/ClO⁻ molar ratio was 1:15 and the sodium hypochlorite solution was added in 12 times, the cobalt removal rate reached about 98%, and the nickel removal rate was nearly zero. This indicates that the amount of ClO⁻ can be increased to improve the cobalt removal rate, but the sodium hypochlorite solution should add in more than one times to control the ClO⁻ amount for every time, and thus can inhibit the Ni²⁺ oxidation. XRD analysis of the solid product showed the oxidation product was CoOOH, as seen in Fig.1. Therefore, the Co²⁺ oxidation by ClO⁻ is as Eq.1:



As Ni²⁺ was not oxidized by ClO⁻, there was no NiOOH produced. Therefore, Co²⁺ and Ni²⁺ can be separated under this condition.

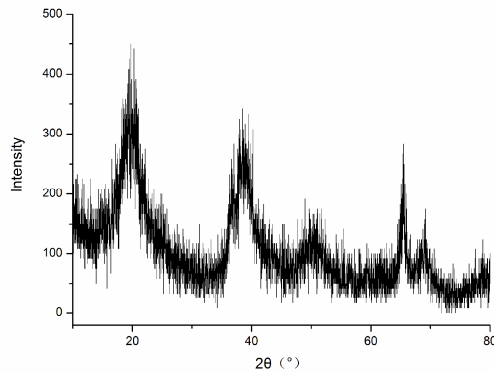


Fig.1 XRD pattern of solid product of Co^{2+} oxidation ($\text{Co}^{2+}/\text{ClO}^-$ molar ratio of 1:15, adding in 12 times)

Conclusions

Cobalt and nickel could be separated in sulfate solution through the reaction with sodium hypochlorite solution at 80°C , 1h, pH 2.3 and $\text{Co}^{2+}/\text{ClO}^-$ molar ratio of 1:15. Increasing temperature did not increase the speed of Co^{2+} oxidation obviously, but improved the filtration performance of the solid product. Increasing feed solution pH and the amount of ClO^- would increase the Co^{2+} removal rate, but resulted in the Ni^{2+} oxidation. The Co^{2+} oxidation product was CoOOH . The adding amount of the sodium hypochlorite solution should be controlled for every time to inhibit the Ni^{2+} oxidation to NiOOH .

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