Separation of Manganese and Cadmium from Cobalt Electrolyte Solution by Solvent Extraction

Shafiq Alam, Mirza Hossain, and Hesam Hassan Nejad

Abstract—Impurity metals such as manganese and cadmium from high-tenor cobalt electrolyte solution were selectively removed by solvent extraction method using Co-D2EHPA after converting the functional group of D2EHPA with Co^{2+} ions. The process parameters such as pH, organic concentration, O/A ratio, kinetics etc. were investigated and the experiments were conducted by batch tests in the laboratory bench scale. Results showed that a significant amount of manganese and cadmium can be extracted using Co-D2EHPA for the optimum processing of cobalt electrolyte solution at equilibrium pH about 3.5. The McCabe-Thiele diagram, constructed from the extraction studies showed that 100% impurities can be extracted through four stages for manganese and three stages for cadmium using O/A ratio of 0.65 and 1.0, respectively. From the stripping study, it was found that 100% manganese and cadmium can be stripped from the loaded organic using 0.4 M H_2SO_4 in a single contact. The loading capacity of Co-D2EHPA by manganese and cadmium were also investigated with different O/A ratio as well as with number of stages of contact of aqueous and organic phases. Valuable information was obtained for the designing of an impurities removal process for the production of pure cobalt with less trouble in the electrowinning circuit.

Keywords—Manganese, Cadmium, Cobalt, D2EHPA, Solvent extraction.

I. INTRODUCTION

IN the mineral processing of hydrometallurgical industries, the cobalt electrolyte solution comes as a byproduct along with the nickel/copper product stream.

The leaching of nickel sulphide ore/concentrate leads to these electrolyte solution that contains high tenor cobalt with trace amounts of impurities such as manganese (Mn) and cadmium (Cd). Over time, Mn accumulates in the electrowinning (EW) circuit which results in a significant decrease in the current efficiency. At the anode, Mn forms MnO2, which precipitates as sludge in the anode bags. These

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anode bags need to be removed from the electrowinning cells for periodic cleaning. Moreover, if any amount of Mn(III) is recycled back to the solvent extraction (SX) circuit with anolyte, it may oxidize and degrade the organic extractant [1]. Also Cd deteriorates the quality of the cobalt product. So, Mn and Cd need to be removed from the cobalt electrolyte solution. Several researchers found that D2EHPA is good for the removal of manganese from nickel-cobalt leach solution [1-3]. Some researchers examined Na-D2EHPA for manganese extraction [4, 5]. However, those processes require controlling pH of the solution as after extraction of metals, pH of the electrolyte is either dropped or increased because of releasing H+ or Na+ ions from D2EHPA or Na-D2EHPA, respectively. Since selective separation of Mn and Cd from a large amount of cobalt electrolyte solution is pH dependent, cobalt loaded D2EHPA was investigated in this research to avoid incoming of any foreign ions from the extractant. This paper describes different aspects of Co-D2EHPA for the selective removal of Mn and Cd that was tested for the Vale's real plant solution.

II. EXPERIMENTAL

A. Materials

In this study, the aqueous feed was the real plant solution (hereinafter referred to as "cobalt electrolyte solution") collected from the Vale's demonstration plant at Argentia, Newfoundland, Canada. The organic extractant, di-(2-ethylhexyl) phosphoric acid (D2EHPA), used in this study was purchased from Alfa Aesar. The organic solution was prepared by diluting the extractant in Escaid 110, which is a commercial aliphatic kerosene donated by Univar Canada Ltd., and 1-decanol was used as the phase modifier. To convert the functional group of D2EHPA with cobalt (Co) ions, a synthetic aqueous solution was prepared by dissolving cobalt sulphate heptahydrate ($CoSO_4.7H_2O$) in de-ionized water. Reagent grade sodium hydroxide (NaOH) was used to examine the effect of pH. The sulphuric acid (H_2SO_4) solution was used in the stripping study.

B. Analysis of Cobalt Electrolyte Solution

The concentrations of manganese, cadmium and cobalt in the feed electrolyte solution were determined using Perkin

Elmer ELAN DRCII ICP-MS (Inductively Coupled Plasma Mass Spectrometer). The pH of the aqueous solution was found to be about 3 and measured by an Orion pH meter.

C. Extraction Experiments

All the tests (extraction and stripping) were conducted in a programmable air bath shaker (Innova-43 Incubator Shaker from New Brunswick Scientific) to control the temperature, time and shaking speed of the mixtures (except for the kinetic study, which was done in a magnetic stirrer for the convenience of controlling the pH of the solution). The shaking speed was maintained at 300 rpm with a shaking time varied from 1 ~ 3 hours to attain equilibrium. All tests were carried out at 25 ^{o}C, unless otherwise stated. During solvent extraction, to measure the equilibrium distribution of metals between the aqueous and organic phases, equal volumes of the two phases of known concentrations were shaken. Once equilibrium was reached, the phases were separated in a separatory funnel. A centrifuge (Eppendorf Model: 5810) was used to remove any trace amount of emulsified organic from the aqueous raffinate. After separation of the two phases, the metal concentration in the raffinate was measured by ICP-MS (Model: Elan DRCII). The metal concentration in the organic phase was calculated from the difference in metal concentrations in the aqueous feed and the raffinate solution. In this study, no third phase formation was found during any of the extraction experiments.

D. Preparation of Co-D2EHPA

Co-D2EHPA was prepared by pre-loading cobalt ion (Co^{2+}) into D2EHPA. This was done by mixing a 200 mL cobalt sulphate synthetic solution with 150 mL of D2EHPA (25 vol.%) at pH 6.7 to get maximum cobalt loading [6].

III. RESULTS AND DISCUSSION

A. Metals Extraction with Co-D2EHPA

Fig. 1 shows the results of Mn and Cd extraction with Co-D2EHPA, where it was found that 70 – 80% manganese and 57 – 60% cadmium were extracted within the pH range of 3.5 – 5.5. The extraction percentage was improved by controlling the equilibrium pH of the solution. The co-extraction of cobalt was negligible at pH 3.5, however, about 10% cobalt was extracted at pH greater than 5. From this figure it is clear that more than 70% Mn and 57% Cd can be removed at pH 3.5 without losing any cobalt in the extraction stage. This would be a suitable condition for the selective removal of manganese and cadmium from the cobalt electrolyte solution. Zhang and Cheng [2] also found that the optimum pH was 3 for the selective separation of Mn from Co as the co-extraction of cobalt occurs at higher pH in the extraction stage. The choice of equilibrium pH is crucial, as the extraction of Mn is pH dependent. Therefore, to separate manganese from cobalt, it is important to maintain the extraction pH to avoid the co-extraction of cobalt. The advantages of using the Co-D2EHPA are:

During extraction only Co^{2+} ion is transferred into the cobalt electrolyte solution rather than transferring H^+ or Na^+,

and hence it is easy to control the pH of the solution at the desired level in the main process stream.

Manganese and cadmium could be selectively removed at pH 3 – 3.5 without losing any cobalt through co-extraction.
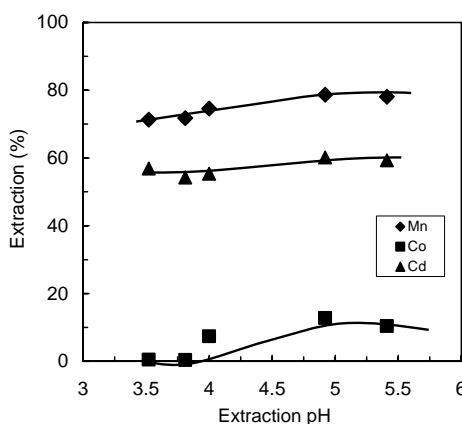

Fig. 1 Mn, Cd and Co extraction at different pH range with 25 vol.% Co-D2EHPA. Feed: Mn = 760 mg/L, Cd = 55 mg/L, Co = 55668 mg/L, A/O = 1

B. Separation Factor

Separation factor, which is the ratio of distribution coefficients of two metals, is an important consideration for the selective separation of metals which is significantly dominated by the equilibrium pH as found from this study. Higher separation factor of two metals leads to the more selective separation of metals. The effect of equilibrium pH on the separation factors of Mn/Co and Cd/Co were examined in this study and it was found that at lower pH, separation factor for both Mn/Co and Cd/Co are at a maximum. With the increase of equilibrium pH, the separation factor decreased significantly. Separation factor (as shown in Table I) in this study provided more favorable results of the extraction of manganese from cobalt (without co-extraction of cobalt) at equilibrium pH 3.5, using the extractant Co-D2EHPA.

TABLE I
SEPARATION FACTOR AT DIFFERENT PH

Separation Factor of	Equilibrium pH		
	3.5	4	5.4
Mn/Co	498.00	36.30	29.58
Cd/Co	264.00	15.30	12.58

C. Kinetics of Mn and Cd Extraction

The kinetics study was conducted using Co-D2EHPA in an open beaker placed on a magnetic stirrer, where the solution was continuously stirred. Fig. 2 shows the results of the kinetic studies where it was found that the kinetics for the extraction of manganese and cadmium were very fast and equilibrium was reached within 5 minutes. On the other hand, the kinetics of cobalt extraction was not faster compared to

that of Mn and Cd. From these experimental results it was observed that based on the difference of the extraction rate, the selective separation of manganese and cadmium over cobalt is also possible using Co-D2EHPA.
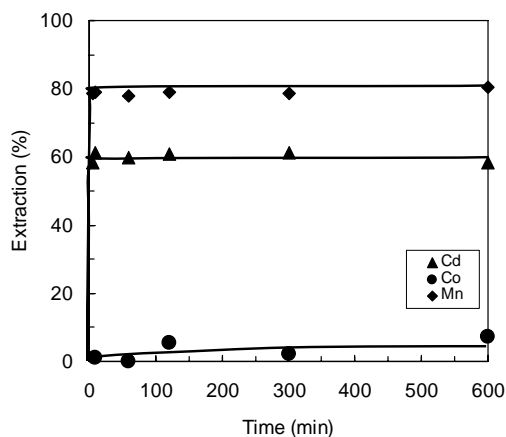

Fig. 2 Kinetics of the extraction of metals with 25 vol.% Co-D2EHPA. Feed: Mn = 760 mg/L, Cd = 52.23 mg/L, Co = 55668 mg/L, pH = 5.5, A/O = 1
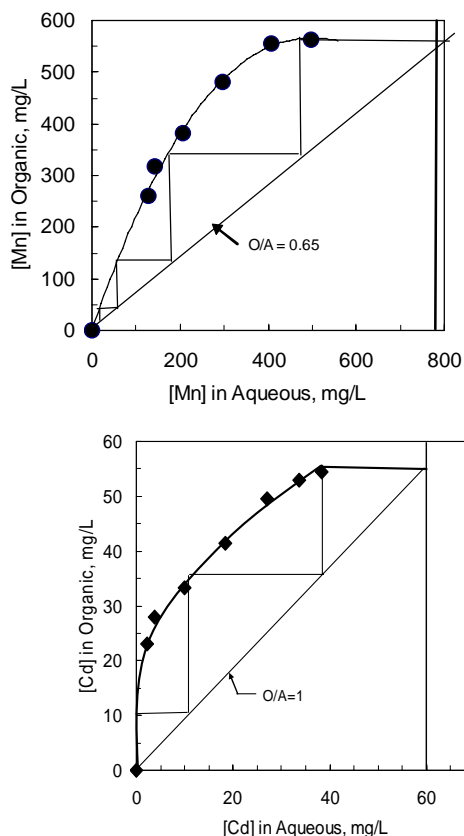
D. Extraction Isotherm

Fig. 3 and 4 McCabe-Thiele diagram for distribution isotherm of Mn (Fig. 3) and Cd (Fig. 4). Feed: Mn = 779 mg/L, Cd = 60 mg/L, Equilibrium pH = 3.5, Org. conc. = 25 vol.% Co-D2EHPA, O/A ratio: 2.5/1 – 1/ 2.5, Temp. = 25 °C

It is important to make a decision regarding the staging requirements, as it is directly related to the cost of operation and maintenance. The McCabe-Thiele diagram helps to set the number of extraction stages needed in a mixer-settler for the extraction of Mn and Cd from the cobalt electrolyte solution. The McCabe-Thiele diagram (Figs. 3 and 4) indicates that 4 and 3 stages of extraction would be sufficient to remove 100% Mn and Cd, respectively, from the cobalt electrolyte solution having starting Mn and Cd concentration of 779 and 60 mg/L, respectively, at an O/A ratio of 0.65 for Mn and 1.0 for Cd.

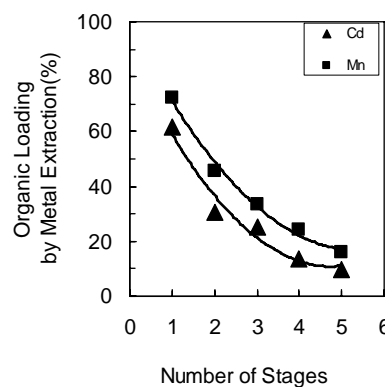### E. Extraction Isotherm with Same O/A Ratio and Repeated Contacts

Fig. 5 Mn and Cd extraction with number of contacts at O/A ratio = 1. Feed: Mn = 779 mg/L, Cd = 60 mg/L, pH = ~ 3.5, Org. conc. = 25 vol.%, Temp. = 25 °C
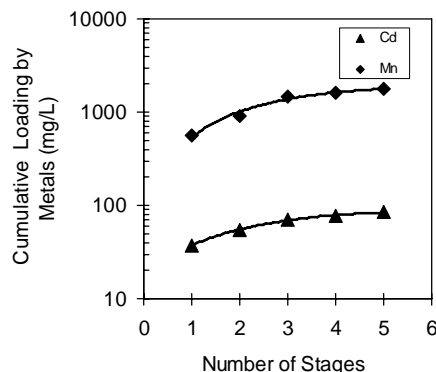

Fig. 6 Cumulative loading of Mn and Cd with number of contacts

Extraction studies were also carried out for loading of Co-D2EHPA by Mn and Cd with O/A ratio = 1 and at pH about 3.5, where the same Co-D2EHPA was repeatedly contacted up to 5 stages with fresh aqueous solution. It is seen that the extraction capacity of organic decreases significantly with the increasing number of contact. Loading capacity of Co-D2EHPA for Mn and Cd was decreased from 73% to 16% and 61% to 10%, respectively (Fig. 5), where the cumulative concentration of Mn and Cd in the extractant increased conversely as shown in Fig. 6.

F. The Effect of O/A Ratio on Metals Extraction

The effect of O/A ratio was studied for the extraction of Mn and Cd with 25 vol.% Co-D2EHPA at pH about 3.5. The initial concentrations of Mn and Cd were 779 mg/L and 60 mg/L, respectively. It was found that the extraction of Mn and Cd were increased from 53% to 89% and 39% to 91%, respectively, with an increase in O/A ratio from 0.4 to 2.5 (Fig. 7).
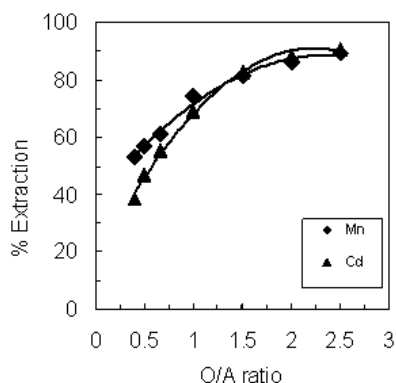

Fig. 7 Effect of variation of O/A ratio on the extraction of Mn and Cd with 25 vol.% Co-D2EHPA at pH about 3.5. Feed: Mn = 779 mg/L, Cd = 60 mg/L, Temp. = 25 °C

G. Stripping of Metals from the Loaded Organic

In the present study, sulphuric acid (H_2SO_4) solutions with various concentrations (0.02 M to 1.0 M) were used as the stripping agent to strip both Mn and Cd from the loaded Co-D2EHPA. Different authors also used sulphuric acid solution

to strip manganese [7] and cadmium [8-10]. In this research, it was found that 100% Mn and Cd were stripped (Fig. 8) using 0.4 M concentration of H_2SO_4 in a single stage.
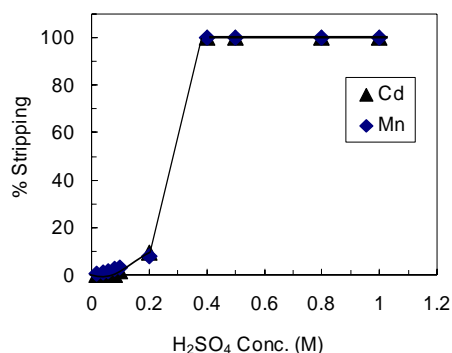

Fig. 8 Stripping (%) of Mn and Cd at different concentration of H_2SO_4

H. Extraction Mechanism

In cobalt electrolyte solution, metals stay as cationic species, such as Co^{2+}, Mn^{2+}. Cd^{2+}. Sastre and Muhammed [11] mentioned that practically all D2EHPA exists as dimmer. The following stoichiometric equation, Equation (1), is considered for the dimmer state of D2EHPA during the preloading of

cobalt. Here, H_2R_2 is the dimeric extractant, and subscript "org" is the organic phase.

$$Co^{2+} + H_2R_{2(org)} \Leftrightarrow CoR_{2(org)} + 2H^+ \qquad (1)$$
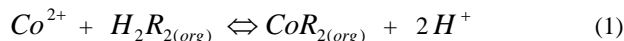
The above Co-loaded D2EHPA (i.e. CoR_2) extracts metals (Mn and Cd in this case) via cation exchange mechanism as shown in Equation (2), where, M^{2+} is the divalent manganese or cadmium in the cobalt electrolyte solution remains as impurity metal.

$$M^{2+} + CoR_{2(org)} \Leftrightarrow MR_{2(org)} + Co^{2+} \qquad (2)$$
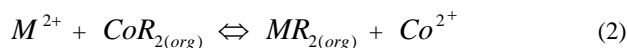
IV. CONCLUSION

A solvent extraction method was proposed to separate manganese and cadmium from a cobalt electrolyte solution using modified D2EHPA. The functional group of D2EHPA was converted to Co-D2EHPA by introducing Co^{2+} ions. Application of Co-D2EHPA for Mn and Cd removal from the cobalt electrolyte solution is new and it has several advantages as mentioned earlier. Experimental results revealed that 70% manganese and 57% cadmium can be selectively removed from the cobalt electrolyte solution using 25 vol. % Co-D2EHPA at an equilibrium pH of around 3.5, without losing any cobalt through co-extraction. It was found that the kinetics of Mn and Cd extraction were very fast and equilibrium was attained within 5 minutes of contact time. Stripping of manganese from the loaded organic shows that 100% both Mn and Cd can be stripped using 0.4 M H_2SO_4 in a single contact. The McCabe-Thiele diagrams were constructed for stage calculations for Mn and Cd removal. It was found that the number of stages for the complete removal of Mn and Cd is 4 and 3 with O/A ratio of 0.65 and 1.0, respectively. The loading capacity of Co-D2EHPA by Mn and Cd at different O/A ratio was studied. It was found that the extraction of both Mn and Cd increases with the increase of O/A ratio. The Mn and Cd extraction with number of contacts of fresh aqueous with the repeated use of organic shows that with the increase of the number of contacts, the extraction decreased significantly resulting in the cumulative increase of Mn and Cd in the organic. The above results will help for modeling and optimization of separation processes to purify cobalt electrolyte solution.

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