

Recovery of Cobalt from the Wastewater produced during Malonate Process by Solvent Extraction

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The solvent extraction method was applied on the wastewater produced during malonate(malonic acid esters) process to recover cobalt. DEHPA and PC88A were used as organic solvent. From separation funnel experiment(batch experiment), the effects of various parameters (pH, cobalt concentration, reaction rate, and stripping temperature) on solvent extraction were examined and these data were used to derive equilibrium curve. A mixer-settler experiment (continuous experiment) of bench scale was also carried out for the plant construction and a McCabe-Thiele diagram was obtained. The results of these experiments indicate that cobalt is recoverable above 99 % and that its purity as cobalt sulfate is higher than 99.9 wt %.

Key Words : cobalt, solvent extraction, malonates, wastewater

1. Introduction

The rapid growth of industry caused a series of environmental problems and the nature has been losing its self-recovering capability over the recent years. As our desire to live in a healthy environment is increasing, the environmental problems becomes social sensitive issues.

Chemical plants can release substantial amounts of pollutant. Malonate can be synthesized with urea and carbon monoxide occurring from homogeneous catalyst of octacarbonyldicobalt. This homogeneous catalyst is synthesized by contacting cobalt oxide and carbon monoxide under high temperature and pressure. After the end of synthesis reaction of malonate, sulfuric acid solution is added to the reaction solution to separate malonate solution, and cobalt is discharged as mixture of acid solution. This wastewater is produced

at a rate of about 10 m³ a day in a malonate process and is dealt as a specific waste by domestic regulation. The disposal cost of wastewater is very expensive and becomes important in cost considerations. In Table 1, the compositions of wastewater is shown. About 5 g/l of cobalt is dissolved in wastewater and its COD(chemical oxygen demand) is over 20,000. If the wastewater is discharged directly into river or sea without proper treatment, it can cause serious environmental problems. So a number of various methods have been investigated to recover cobalt or malonate from the wastewater and to reduce toxicity of wastewater. The liquid incineration is one possibility, but this is very expensive and difficult technically due to: (1)the large amount of wastewater generated and/or (2) the occurrence of the high con-

Table 1. The composition of wastewater produced during malonate process

	NaCl	Malonates	Isopropanol	Na ₂ SO ₄	Toluene	H ₂ SO ₄	Cobalt
(wt %)	2~5	2~5	1~5	5~10	0.1~5	0.5~3	0.1~1
	Fe	Ni	Zn	Cu	Cd	Al	As
(ppm)	5~200	100~1000	1~100	0.1~10	0.1~1	0.1~5	0.1~0.3

centration of salts. Activated carbon can be used as an adsorbent to treat this waste components, but high organic content can reduce adsorption efficiency and the recovery of cobalt from activated carbon remains to be another problem. Alternative methods, (such as precipitation with hydrogen sulfide(H₂S), electrowinning, ion exchange and membrane separation), are possible but all the most of them suffer from a number of disadvantages.

In the present study, solvent extraction method was examined as a method to recover cobalt from wastewater. In hydrometallurgy the solvent extraction is popular in separating the metals with similar pyrometallurgical properties. Extensive researches have been carried out on the separation of rare earth metals having similar properties. The separation mechanism of solvent extraction can be accounted for in terms of ion exchange, formation of complex, and solvation. The solvents to be used for cobalt extraction by ion exchange are such as DEHPA (di-(2-ethylhexyl)phosphoric) acid, Lix 84(2-hydroxy-5-nonyl-acetophenon oxime), PC 88A(2-ethylhexyl hydrogen 2-ethylhexyl-phosphoric acid), Versatic acid(carboxyl acid), Cyanex(phosphoric acid), Kelex(8-hydroxyquinoline). Among these solvents, DEHPA and PC88A were selected for this study.

2. Experimental

2.1 Separation funnel experiment

The composition formula for the wastewater are shown in Table 1: one liter of wastewater contains about 5 g of

cobalt, 70 g of sodium sulfate, 20 g of sulfuric acid, and a small amount of valuable malonates. It is desirable that organic substance be removed from wastewater to prevent the contamination of organic solvent.

This wastewater is washed with kerosene by stirring vigorously in a mixer to remove the organic substance from the wastewater. To investigate the extraction behavior at a wide range of cobalt concentrations, some amount of pure cobalt sulfate was added in the washed wastewater. The prepared solution was neutralized by mixing with sodium carbonate to various pH conditions. The standard organic solvents were composed of 15 (v/v) % of PC88A(or DEHPA), 10 (v/v) % of isodecanol and 75 (v/v) % kerosene. Kerosene acts as diluent, and isodecanol acts as modifier to enhance the phase separation [Bailes et. al. 1976]. At the extraction step, 700 ml of the wastewater and 700 ml of the prepared organic solvent were shaken vigorously by hands for 5 minute in 2 liter of separation funnel at room temperature. Organic phase and aqueous phase was separated after about 10 min. storage. The pH of raffinate (extracted wastewater) was dropped to about 2, because cobalt ion was replaced with hydrogen. The lucid organic solvent was changed to blue color and was washed out with purified water to eliminate contaminants from organic solvent. At stripping step, 15 (wt) % of sulfuric acid solution was added to the organic solvent to strip cobalt like as extraction manner. The stripped organic solvent was washed again with purified water to remove sul-

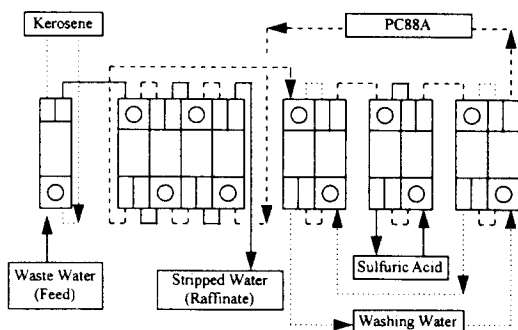


Fig. 1. A flow diagram of solvent extraction for cobalt.

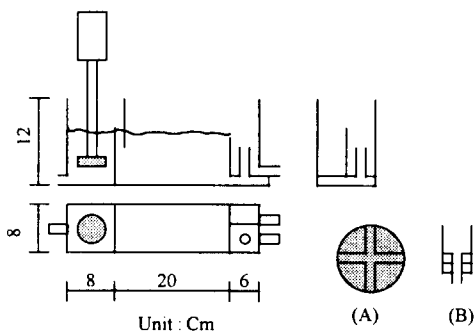


Fig. 2. A schematic diagram of mixer-settler.

furic acid which is capable of weakening the extraction efficiency of organic solvent. Then organic solvent was refreshed and recycled to extraction step. In separation funnel experiment, we examined mainly both (1)the effect of pH on the cobalt extraction and (2)the temperature effect on stripping.

2.2 Mixer-Settler experiment

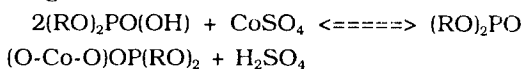
The continuous operation is generally favored in solvent extraction if without special purpose[Kim, B.N., 1994]. In continuous operation, several methods are used like as column, mixer-settler, vertical mixer-settler. In this study, a typical mixer-settler was used. The procedures include (1)one stage for washing the wastewater with kerosene, (2)4 stages for extraction of cobalt, (3)2 stages for wash-

ing the impurity, (4)2 stages for stripping of cobalt from organic solvent with sulfuric acid solution and (5)another 2 stages for removing sulfuric acid from organic solvent. The flow diagram for continuous mixer-settler is depicted in Fig. 1.

Each stage consists mixer part, settling part and separation part as shown in Fig. 2. The impeller is a sphere-disk which is engraved with a half depth of disk at the bottom side with the cross-lined shape as shown in (A) of Fig. 2. When this disk-type of impeller is rotating at a rpm of 500, the engraved lines make a strong friction with solution. Thus the flow of centrifugal direction under the disk impeller sucks the organic and aqueous solution into mixer part without pumps. The retention time was set for 2 min. in mixer and 5 min. in settler. At separation part, the height of vertical tube for aqueous solution should be calculated by considering the density of organic phase and aqueous phase. However since the operation condition (such as the ratio of organic phase and aqueous phase) can be frequently changed, it is desirable to design the vertical tube which can be adjusted by screw, as shown in (B) of Fig. 2. For each extraction stage, the pH drops slightly because of cobalt exchange with hydrogen of organic solvent. Hence sodium carbonate solution (e.g., 1 mole/l) is added in each stage of extraction, hence to maintain the pH=4.

3. Results and Discussion

The mechanism of separation for DEHPA or PC88A is an ion exchange of hydrogen with metal ion as below.



DEHPA((RO)2PO(OH)) acts like as acid and 2 hydrogen atoms in DEHPA are exchanged by divalent cobalt ion in

wastewater. Thus this reaction is reversible and affected seriously by pH of reaction solution (Ritcey, G.M. and Asbrook, A.W., 1979)

3.1 Separation funnel experiment (batch experiment)

In separation funnel experiment a cobalt concentration is adjusted to 20 g/l by adding pure cobalt sulfate to wastewater. The effect of pH on cobalt extraction is shown in Fig. 3. Cobalt extraction occurred at pH=2 and reached maximum at about pH=5. DEHPA was able to extract cobalt in slightly lower range of pH than PC88A. The equilibrium loading of both DEHPA and PC88A is 11 g of cobalt at about pH=4. From Fig. 3 it appears that pH is a very important factor for extraction. Hence pH should be carefully adjusted about pH=4 to obtain high extraction efficiency. Cobalt can precipitate as cobalt hydroxide above pH=6 according to Pourbaix diagram (Pourbaix, 1966) but actually it precipitates around pH=5 because of impurities. Equilibrium loading of cobalt on DEHPA and PC88A were obtained by varying the concentration of cobalt in aqueous phase at pH=4 as shown in Fig. 4. DEHPA and PC88A are easily saturated with cobalt above 2 g/liter of cobalt in aqueous phase. DEHPA was able to extract cobalt at slightly lower concentration than PC88A. The shape of these equilibrium loading curves is like a Langmuir-Hinshelwood type in adsorption mode. The extraction rate of cobalt in organic solvents was measured and provided in Fig. 5. In this experiment, it was found that extraction saturation occurred within 2 min. Thus DEHPA and PC88A were able to extract cobalt easily from wastewater produced during malonate process. At stripping step, 15 (wt) % of sulfuric acid solution

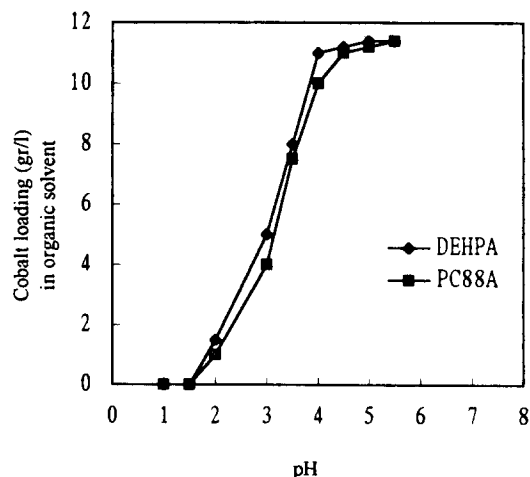


Fig. 3. Cobalt loadings of DEHPA and PC88A with pH variations.

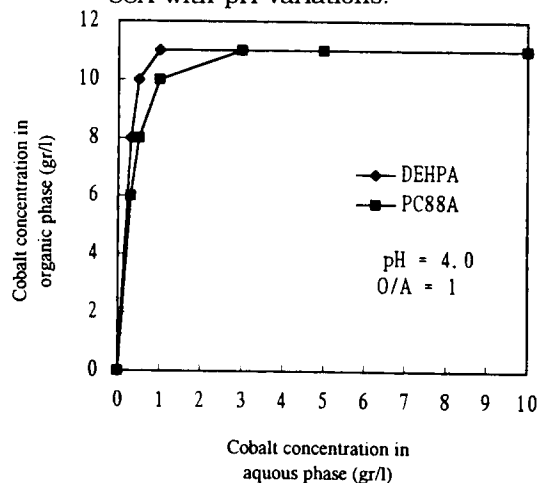


Fig. 4. Cobalt loadings of DEHPA and PC88A with cobalt concentration in aqueous phase.

was added. PC88A is easily stripped by sulfuric acid solution at room temperature, whereas DEHPA was not. The stripping efficiency of DEHPA is dependent on temperature. It can be fully stripped above 40 °C as shown in Fig. 6. These results thus indicate that DEHPA can extract cobalt more strongly than PC88A. In industrial aspects, PC88A is however recommended for it can easily be stripped without heating procedures.

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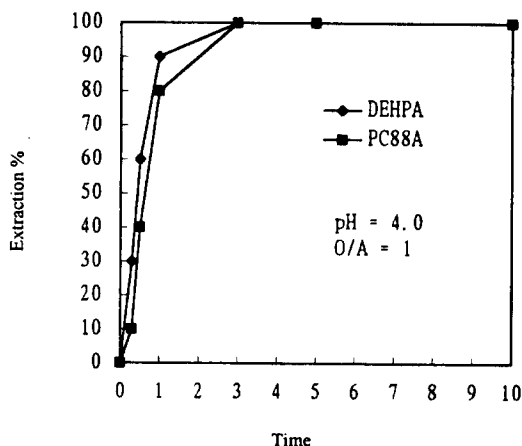


Fig. 5. Cobalt extraction rate of DEHPA and PC88A at room temperature and pH=4.

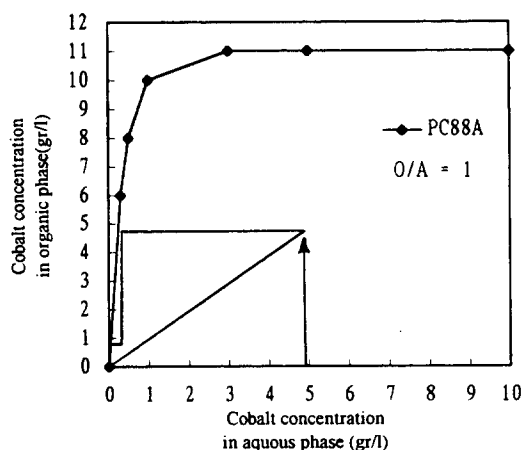


Fig. 7. McCabe diagram for cobalt extraction of PC88A.

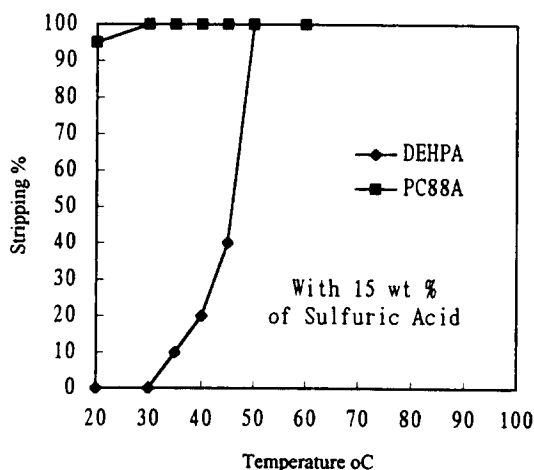


Fig. 6. The effect of temperature on the stripping of DEHPA and PC88A.

3.2 Mixer-settler experiment(continuous experiment)

Another type of experiment was also carried out continuously at bench scale using a mixer settler with PC88A as an organic solvent, based on the separation funnel experiment data. Huges and Parker(1985) reported a simulation method to calculate the heavy metal concentration of aqueous and organic phase, using the equilibrium curve data and the ratio of organic over aqueous phase. However in

this research, the cobalt concentration of organic and aqueous phase was directly analyzed by atomic absorption spectroscopy. It appears that cobalt extraction of organic solvent is almost at equilibrium state at each stage because the reaction rate is very fast as shown in Fig. 5. The McCabe-Thiele triangle shows that cobalt can be almost extracted within 2 stages as shown in Fig. 7. The cobalt concentration of each stage is listed at Table 2. The cobalt concentration at the third stage was below 0.1 g/l. To drop the cobalt concentration of aqueous phase below 10 ppm, the fourth stage was additionally attached. Although cobalt is not included in the heavy metals prohibited in environmental regulations, it is desirable to remove cobalt from wastewater because of its pink color.

Between extraction and stripping step, the washing step was inserted to remove other pollutants from organic solvent. At the first and second extraction stage, cobalt was extracted above 95 % as shown in Fig. 7 and the pH in these stages dropped to about 2. Thus Na_2CO_3 solution of 1 mole/l was continuously added in the first and second mixer to keep

Table 2. The cobalt concentration at each extraction stage

	Waste water (Feed)	Stage #1	Stage #2	Stage #3	Stage #4	Organic solvent
Organic phase	-	4.9 g/l	0.3 g/l	0.1 g/l	100 ppm	0.0
Aqueous phase	4.9 g/l	0.3 g/l	0.1 g/l	100 ppm	5 ppm	-

Table 3. The composition of cobalt sulfate($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$)

	Co	Ni	Cu	Fe	Zn	Cd,Al,As
Content	20.9 wt%	50 ppm	2 ppm	3 ppm	3 ppm	trace

pH=4 by the action of pH controller. In mixer-settler experiment, the organic phase and aqueous phase were easily separated in settler. This was due to the fact that a large amount of salts (such as Na_2SO_4) is dissolved in aqueous phase. The stripping solution was recycled, and cobalt was accumulated continuously on it. When concentrated sulfuric acid solution is added in stripping solution, cobalt sulfate precipitates due to the salting out effect. The cobalt sulfate precipitates were washed slightly in centrifugal and used mainly for raw material of magnetic tape. The purity of obtained cobalt sulfate was higher than 99.9 % corresponding to 20.9 (wt) % of cobalt in heptahydrated cobalt sulfate as shown in Table 3.

4. Conclusion

Form wastewater produced during malonate process, cobalt was recovered by solvent extraction method. Both DEHPA and PC88A can be used as organic solvent, but PC88A is recommended because it can easily be stripped at room temperature. One liter of prepared organic solvent, which consists of 15 (v/v) % of PC88A, 10 (v/v) % of isodecanol and 75 (v/v) % kerosene, extracted 11 g of cobalt at about pH=4. In the continuous experiment, we used 1 stage for washing with kerosene, 4 stages for extraction, 2

stages for washing, 2 stages for stripping and 2 stages for another washing. Cobalt was recovered above 99 % and its purity as cobalt sulfate was higher than 99.9 (wt) %

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말로네이트 제조 공정 폐수로부터 코발트 회수: 용매추출법 적용

문영환

삼성지구환경연구소

(1996년 9월 3일 접수)

말로네이트 제조 공정에서 발생하는 폐액으로부터 용매추출법을 적용하여 코발트 회수 연구를 하였다. 용매 추출에서의 주요 변수는 용매의 선택, pH, 코발트 농도, 역추출 온도 등이며 이러한 변수들의 영향을 조사하였다. 용매로써 DEHPA와 PC88A가 사용되었으며 이들 용매의 평형추출 곡선을 구하였다. 공장설계 조건을 찾기 위하여 McCabe-Tiele 선도를 작성하였고, 연속 공정인 믹서-세틀러 장치를 가동하였다. 본 연구 결과 폐액 중에서 코발트는 99.9% 이상 회수되었고, 회수된 황산코발트의 순도는 99.9% 이상이었다.