

廢觸媒 鹽酸浸出液에서 컬럼형 抽出器에 의한 白金 回收

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Recovery of Pt from the Chloride Leaching Solution of Spent Catalysts by using Column Extractor

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요 약

폐촉매 염산 침출액으로부터 백금을 회수하기 위해 벤치규모의 Karr 왕복 추출기를 사용하였다. 최적의 유량속도와 진동 빈도에
서 철과 백금은 TBP와 Aliquat 336에 의해 모두 추출되었다. 같은 진동 빈도에서 유량을 조절함으로써 염산과 과염소산을 사용하
여 철과 백금을 모두 탈거하였다. TEHA를 사용하여 추출액으로부터 염산을 추출하는 경우 컬럼 추출기의 안정성을 유지하기 어
려웠다. 컬럼 추출기와 mixer-settler에 의한 작업 결과를 비교하였다.

주제어 : 백금, 철, 염산, Karr 왕복추출기

Abstract

In order to recover Pt from the hydrochloric acid leaching solution of spent catalysts, bench scale Karr reciprocating column
was employed. At an optimum flow rate and vibration frequency, iron and Pt was completely extracted by using TBP and Aliquat
336. At the same vibration frequency, iron and Pt was completely stripped by HCl and HClO₄ after adjusting the flow rate. In
the case of extraction of HCl from the raffinate with TEHA, it was difficult to maintain the stability of the column extractor.
A comparison of the operation results between column extractor and mixer-settler is reported.

Key words : Pt, Fe, HCl, Karr reciprocating column

1. Introduction

Spent catalysts are valuable secondary resources
for the platinum group metals (PGMs). Much work

has been done on the recovery of PGMs from spent
catalysts by hydrometallurgical method. First, PGMs
are dissolved by chloride based solution and then
are separated by employing solvent extraction or

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Table 1. The optimum experimental conditions obtained from batch solvent extraction and stripping experiments.

	Process	Reagent	Condition
Fe	Extraction	0.3 M TBP	A/O = 2, 2 stages
	Stripping	0.1 M HCl	O/A= 2, 1 stage
Pt	Extraction	0.3 M Aliaquat336	A/O=2, 2 stages
	Stripping	1 M HClO ₄	O/A=1, 2 stages
HCl	Extraction	1 M TEHA	O/A=5, 3 stages
	Stripping	H ₂ O	A/O=2.5, 3 stages

ion exchange.¹⁻³⁾ In our previous study, spent catalysts were first roasted at 800°C to eliminate volatile matters and use of a mixture of hydrochloric acid and hydrogen peroxide resulted in 99% leaching percentage of Pt from the spent catalysts. In the obtained leaching solution, the concentration of Pt, Fe and Al was 124 mg/L, 269 mg/L and 4917 mg/L. Besides, 5 mg/L of Si and 0.4 mg/L of Ni were also detected. The concentration of HCl in the leaching solution was 5.9 M. In order to recover Pt from the leaching solution, Fe(III) was first separated by extraction with TBP and then Pt was extracted by Aliquat 336. Moreover, HCl was recovered from the raffinate by extraction with TEHA (tri 2-ethylhexyl amine). The optimum conditions obtained from batch experiments are summarized in Table 1.

There are no versatile contacting equipments suitable for all solvent extraction operations.⁴⁾ For small scale continuous work on a solvent extraction process, mixer-settler has been used.⁵⁻⁷⁾ In our previous continuous experiments, mixer-settler was successfully operated. In this study, Karr reciprocating plate column was employed to test the possibility of recovering Pt and HCl from the chloride leaching solution of spent petroleum catalysts containing Fe and Al. The flow rate ratio of aqueous to organic in the continuous operation was obtained from the batch experimental results.⁸⁻⁹⁾ Recovery and purity percentages of Pt obtained from the Karr reciprocating plate column operation together with the comparison with the results obtained from the mixer-settler operation are reported.

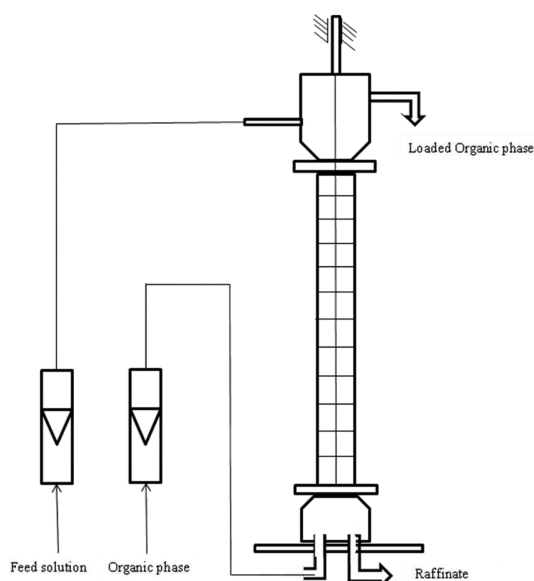


Fig. 1. Schematic diagram of a Karr reciprocating plate column.

2. Experimental

TBP (Tri-n-butyl phosphate, Yakuri Pure Chemical, 99%), Aliquat 336 (Aliphatic quaternary ammonium salt, Cognis co., 90.6%) and TEHA (BASF corp., 99%) diluted in toluene were used as extractants in the extraction of Fe, Pt and HCl, respectively. The acidity of the solution was adjusted by adding HCl (35%, Junsei Chem.).

The column consists of a glass tube (the diameter is 3 cm) and a central shaft on which 25 evenly spaced open-type perforated plates are mounted. This central shaft is reciprocated by means of a simple drive mechanism at the top of the column. The amplitude was fixed at 2.5 cm by adjusting the length of a cam arm. The speed of reciprocation could be controlled over of 60-480 rpm by using a speed controller. The schematic diagram of a Karr reciprocating plate column and its dimensions are shown in Fig. 1 and Table 2, respectively.

The feed solution and organic phase are flowed into the column from the top and bottom of the column. Agitation was provided by the plates

Table 2. The dimensions of the Karr reciprocating plate column used in this study.

	Parameters	Value
Reactor	Height of main column(h/D)	80 cm/3 cm
	Top container (h/D)	30 cm/5 cm
	Bottom container(h/D)	30 cm/5 cm
Plate	Number of plate	25
	Spacing between plates	2 cm
	Free area	34 %
Operating condition	Amplitude of reciprocating	2.5 cm

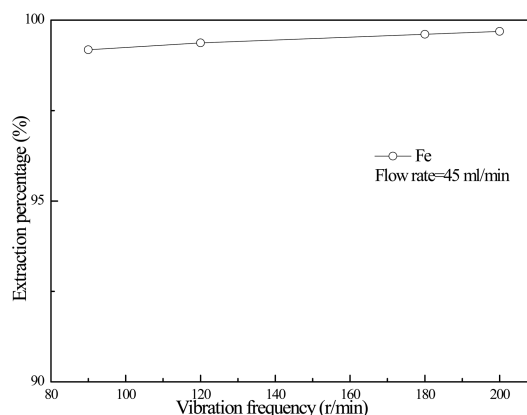
moving through the solution, thus providing the necessary mass transfer. The mixture of the two phases was separated in the top and bottom container by virtue of the difference of gravity. The aqueous and organic phase after reaction was collected from the bottom and top container, respectively.

The concentration of metal in the aqueous phase was measured by ICP-OES (Spectro arcs). The concentration of metal in the organic phase was obtained by mass balance. The concentration of HCl was determined by volumetric titration with standard Na_2CO_3 solution.¹⁰⁾

3. Results and discussion

3.1. Selection of flow rate and vibration frequency

In order to get an optimum condition for the column operation, the vibration of the column was investigated by varying the vibration frequency from 90 to 200 r/min. The effect of vibration frequency on the extraction of Fe at a flow rate of 45 ml/min is shown in Fig. 2. According to Fig. 2, the extraction percentage of Fe increased slightly with increasing the vibration frequency from 90 to 200 r/min. Considering that the extraction percentage of Fe has direct effect on the purity of Pt, the vibration frequency of 180 r/min was selected in the subsequent extraction experiments. Further increase of the flow rate in the vibration frequency range from 90 to 180 r/min led to a failure in the operation of the

**Fig. 2.** Effect of vibration frequency on the extraction of Fe from FeCl_3 solution.

column due to the difficulty of maintaining the stability of the system. Therefore, in the following experiments, the flow rate of 45 ml/min and vibration frequency of 180 r/min was employed, respectively.

3.2. Removal of Fe from the leaching solution

Removal of Fe from the leaching solution by 0.3 M TBP was carried out using Karr reciprocating plate column. Based on the batch experimental results shown in Table 1, the continuous extraction experiment was carried out at an O/A ratio of 0.5. Two liters leaching solution was used as the feed solution, and its flow rate was adjusted to 45 ml/min, while the vibration frequency was fixed at 180 r/min. The concentration of metals in the feed solution and raffinate was analyzed before and after extraction experiment. The extraction percentage of Fe was 99.6% and the co-extracted Pt and Si was 8 and 0.7 ppm, respectively. The co-extraction of Al and Ni was negligible.

In the case of stripping of Fe from the loaded TBP, 2 L of 0.1 M HCl was used as a stripping agent. When the flow rate of the loaded TBP was 45 mL/min, stripping of Fe at an O/A ratio of 2 with vibration frequency of 180 r/min led to a failure of the operation due to the severe entrainment phenomena. Therefore, the same operation condition

as the extraction condition was employed. The flow rate of 0.1 M HCl was adjusted to 45 ml/min, while that of loaded TBP was adjusted to 22.5 ml/min. The concentration of metals in the collected stripping solution was measured after all of the HCl solution was flowed into the column. Fe was completely stripped, and the co-stripped Pt and Si was 0.5 and 0.3 ppm, respectively. Since the concentration of Pt in the loaded TBP was only 0.5 mg/L, there was no merit in employing scrubbing stage to recover Pt from the loaded TBP.

3.3. Recovery of Pt from the raffinate after removal of Fe

Based on the batch experimental results shown in Table 1, extraction of Pt from the raffinate after removal of Fe was carried out with 0.3 M of Aliquat336 using Karr reciprocating plate column at an A/O ratio of 2. The vibration frequency was kept at 180 r/min.

When the flow rate of feed solution was 45 mL/min, the mixture could not be maintained in the column long enough for the two phases to be separated well before they flow out of the column. Therefore, the flow rate of the feed solution was decreased to 34 mL/min, while the flow rate ratio of the two phases and the vibration frequency was kept the same.

After the feed solution was flowed into the column, the concentration of metals in the collected raffinate was analyzed. The extraction percentage of Pt was higher than 99.9%, and the co-extracted Fe and Si were only 0.47 and 0.2 ppm, respectively. In this operation, the co-extraction of Al and Ni was negligible.

In stripping process, 1 M HClO₄ was used as a stripping agent (Table 1). Considering the same difficulty as the stripping of Fe from the loaded TBP, the flow rate of 1 M HClO₄ was adjusted to 45 mL/min and the flow rate ratio was fixed at an A/O of 2. Pt in the loaded Aliquat336 was completely stripped together with the co-extracted Fe and Si. The concentrations of metals in the

stripping solution were 140 mg/L, 0.4 mg/L, 0.2 mg/L for Pt, Fe and Si, respectively. The purity of Pt in stripping solution was 99.6%. Considering that the concentration of Fe and Si in the loaded Aliquat 336 was only 0.86 and 0.38 mg/L, it is not economical to employ scrubbing process to remove Fe and Si.

3.4. Recovery of HCl from the raffinate after removal of Fe and Pt.

The concentration change of HCl in raffinate after separation of Pt was negligible (5.9 M). Based on the result shown in Table 1, 1 M TEHA was used for the extraction of HCl from the raffinate after removal of Fe and Pt by using Karr reciprocating plate column at an O/A ratio of 4. The flow rate of 1 M TEHA was adjusted to 45 ml/min. When the vibration frequency was 180 r/min, the flooding phenomena appeared. Therefore, the vibration frequency was decreased to 120 r/min, while the other experimental conditions were kept to the same. After half an hour, the raffinate solution was collected, and the concentration of HCl was 0.34 ± 0.02 M. In the extraction of HCl by TEHA, it has been reported that there is a minimum concentration of HCl (0.3 M) below which extraction of HCl does not occur.⁹⁾ Analysis of the raffinate after the extraction of HCl revealed that most of Pt after the extraction with Aliquat336 (0.9 mg/L) was co-extracted by TEHA but the extraction percentage of Si, Ni and Al by TEHA was nil. In order to collect more loaded TEHA for further stripping experiments, the extraction process was repeated. However, the experiment was stopped due to the difficulty in keeping the stability of the system.

The effect TEHA concentration on the extraction of HCl was further investigated by varying the concentration of TEHA from 0.1 to 1.5 M. The results in Fig. 3 show that the extraction percentage of HCl with TEHA was between 3 to 53% with increasing the concentration of TEHA from 0.1 to 1.5 M. When the concentration of TEHA was lower

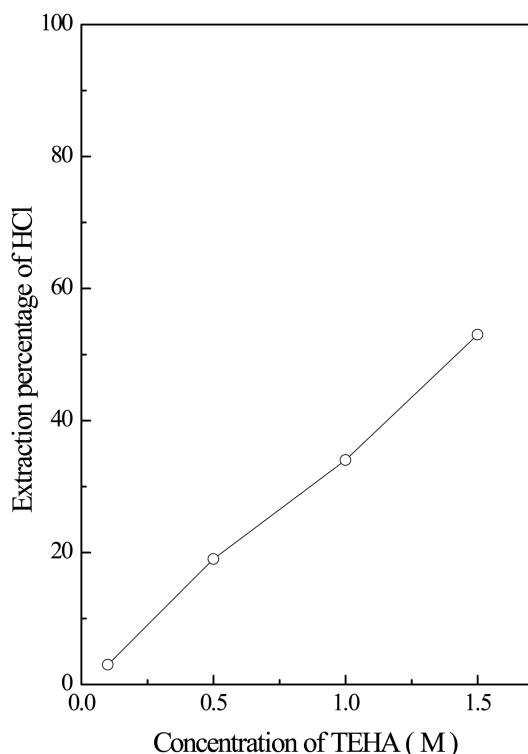


Fig. 3. Effect of TEHA concentration on the extraction of HCl.

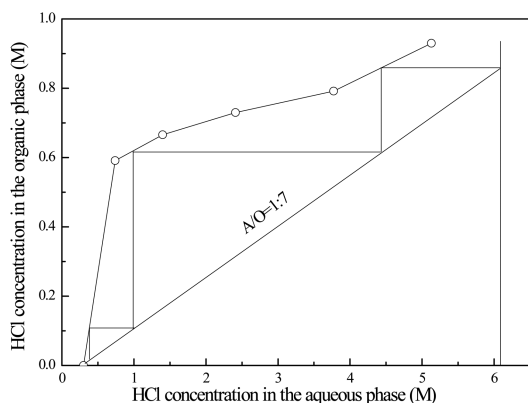


Fig. 4. McCabe-Thiele plot for HCl extraction with 0.75 M TEHA.

than 1 M, the extraction percentage of HCl was very low (<35%). Therefore, 0.75 M TEHA was selected and the McCabe-Thiele plot for HCl extraction by 0.75 M TEHA was constructed. As shown in Fig. 4, when the concentration of TEHA

was 0.75 M, 3 stages are needed to achieve complete extraction of HCl at an O/A ratio of 7.

Since the maximum flow rate of the feed solution for this column was 45 ml/min, it is difficult to operate the column at a flow rate ratio of 7. Therefore, the flow rate of 0.75 M TEHA was adjusted to 45 ml/min and the flow rate ratio was kept as an O/A ratio of 4. The vibration frequency was varied from 120 to 90 r/min. After 2 L feed solution was flowed into the column, the concentration of HCl in the raffinate was measured. About 92.6 and 90.5% extraction percentage of HCl was obtained from 120 and 90 r/min operation, respectively. The concentration of HCl in the raffinate was 0.45 ± 0.02 M and 0.57 ± 0.02 M, respectively. The extraction experiments were operated well when the volume of the feed was 2 L. Further increase of solution volume led to the difficulty in the operation of the column because the system became unstable.

The loaded TEHA was tested for the stripping HCl with distilled water by Karr reciprocating plate column. The flow rate of the loaded TEHA was adjusted to 11 ml/min, and the flow rate ratio (A/O) was varied to be 4, 2.5 and 2. Even if the operating conditions were changed, it was difficult to maintain the stability of the system. Therefore, it might be concluded that it is difficult to apply Karr reciprocating plate column to the extraction of HCl with 1 M TEHA.

3.5. Comparison with mixer-settler operation

Operation of a mixer-settler requires high solvent inventory, and is effective for solvent extraction systems requiring a few stages. By contrast, Karr reciprocating plate columns need intermediate solvent inventory and are useful for systems requiring many stages. Comparison of the two extractors is listed in Table 3. Generally, mixer-settler is simple to scale up and provides the most economical equipment when only the capital cost is considered. In terms of solvent residence time, mixer-settler results in long residence time of solvent.

The results obtained by using Karr reciprocating

Table 3. Comparison of the operation between mixer-settler and column extractor.

Mixer-settler	Karr Column
Good contacting of phases	Good dispersion
Handle wide range flow rate(with recycle)	Cannot handle high flow ratio
Low headroom; Large floor space	Low floor space; Large headroom
Many stages (few stages are preferred)	Many stages possible
Low cost	Reasonable cost
Reliable scale-up	Relatively easy scale-up
Intermediate throughput	Limited throughput with small gravity difference
Inter stage pumping may be necessary	/

Table 4. Comparison of results obtained by using mixer-settler and reciprocating plate column.

	Mixer-settler		Column	
	Purity	Recovery	Purity	Recovery
Pt	>99.98%	99.18%	99.60%	99.90%
Fe	>99.99%	>99.99%	99.64%	99.64%
HCl	>99.90%	95%	/	/

column in this study is compared with that of mixer-settler operation in our previous experiments. The results are represented in Table 4. According to Table 4, the extraction and stripping of Fe and Pt were accomplished using both equipments, while the recovery of HCl from the raffinate was only possible using mixer-settler. The purity of Pt and HCl after the continuous mixer-settler operation was higher than 99.9%. Although the purity of Pt was a little lower with column operation, the recovery of Pt by column was higher than that by mixer-settler operation. The operating condition of column extractor was much stringent in the control of the flow rate of the two phases. Therefore, mixer-settler is recommended to scale up for further research.

4. Conclusions

In order to develop a process to recover Pt and HCl from the leaching solution of spent petroleum catalysts, continuous counter current extraction and stripping experiments have been performed by using

bench scale Karr reciprocating column. The flow rate ratio of aqueous to organic was obtained from the McCabe-Thiele plots which had been chosen from the batch experimental results. TBP and Aliquat 336 were employed to extract Fe and Pt from the leaching solution, respectively. The recovery of Pt and Fe was 99.9% and 99.6% by the Karr reciprocating column operation. It is difficult to recover HCl with TEHA using reciprocating column operation due to the difficulty in maintaining the stability of the system. The purity of Pt obtained from the Karr reciprocating column under the specific conditions was 99.6%.

감사의 글

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