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Short communication

Mixer-settler operation for the recovery of platinum, iron and hydrochloric acid from the leaching solution of spent petroleum reforming catalysts



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ABSTRACT

Bench scale mixer-settler was employed to recover Pt, Fe and HCl from the hydrochloric acid leaching solution of spent catalysts. The number of stages and flow rate ratio of the aqueous to organic was estimated from the McCabe–Thiele plots for the extraction and stripping of the elements. In mixer-settler operation, Fe was first completely extracted by TBP and then the most of Pt was extracted by Aliquat336. Finally, HCl was recovered by extraction with TEHA and by stripping with water. From mixer-settler operation, most of the Pt and Fe were recovered and the recovery percentage of HCl was 95%.

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1. Introduction

Spent catalysts are valuable secondary resources for the platinum group metals (PGMs) [1]. Lots of work have been done on the recovery of the PGMs from spent catalysts. In the hydrometallurgical treatment for the recovery of the PGMs from spent catalysts, chloride based solution is used for the dissolution of the PGMs [2–5]. Solvent extraction and ion exchange are widely employed to separate the PGMs from the leaching solution [6–16].

In our work on the recovery of Pt from the spent petroleum reforming catalysts, use of a mixture of hydrochloric acid and hydrogen peroxide led to 99% leaching percentage of Pt from the spent catalysts. The leaching solution contains 129 mg/L of Pt, 4917 mg/L of Al, 268.8 mg/L Fe and negligible amount of Si and Ni. From these leaching solutions, ferric iron was first extracted by TBP and then the Pt was extracted by Aliquat336 [17]. After the extraction of iron and Pt, HCl was recovered by extraction with TEHA (Tri 2-ethylhexyl amine). The optimum conditions for the extraction and stripping obtained are summarized in Table 1.

In developing a solvent extraction process for the recovery of metals from solutions, experimental results should be obtained by employing bench or pilot scale continuous extractor to justify the construction of full scale extractor. However, few works have been

reported on the results from mixer-settler operation to recover platinum group metals from strong HCl solution. Therefore, for small scale continuous work on a solvent extraction process, mixer-settler has been used due to its efficiency and the ease of handling high flow ratio [18–20]. In this study, bench scale mixer-settler was employed to test the possibility of recovering Pt and HCl from the chloride leaching solution of spent petroleum catalysts. The flow rate ratio of aqueous to organic together with the number of stages in the mixer-settler operation was obtained from the McCabe–Thiele plots. Recovery and purity percentages of Fe, Pt and HCl obtained from the mixer-settler operation are reported.

2. Experimental

2.1. Materials

TBP (Tri-n-butyl phosphate, 99%, Yakuri Pure Chemical), Aliquat336 (Aliphatic quaternary ammonium salt, 90.6%, Cognis Co.) and TEHA (99%, BASF Corp.) diluted in toluene were used as extractants. In continuous mixer-settler operation, large amount of leaching solution is needed. However, it is difficult to prepare large amount of leaching solution with uniform composition by using small scale leaching vessel. Therefore, the synthetic leaching solution was employed in this study and prepared by dissolving the necessary amount of PtCl_4 (Aldrich, 98%) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical Co., Inc., 97%) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Daejung Chemicals

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Table 1

The optimum experimental conditions obtained from batch solvent extraction experiments.

	Process	Reagent	Condition	Purity (%)	Recovery (%)
Fe	Extraction	0.3 M TBP	O/A = 1, extraction % = 99.4	99.7	99.4
	Stripping	0.1 M HCl	O/A = 1, stripping % = 99.9		
Pt	Extraction	0.3 M Aliquat 336	O/A = 1, extraction % = 99.2	98.6	98.2
	Stripping	1 M HClO ₄	O/A = 1, stripping % = 99.9		
HCl	Extraction	1.5 M TEHA	O/A = 4, 2 stages extraction % = 95.0	99.9	95.0
	Stripping	H ₂ O	A/O = 4, 2 stages stripping % = 100		

& Metals Co., Ltd., 97%) in doubly distilled water. The acidity of the solution was adjusted by adding HCl (35%, Junsei Chem.). The composition of the leaching solution is shown in Table 2.

2.2. Batch experiments

In batch experiments, the aqueous and organic phases were mixed in a 100 mL screwed cap bottle with needed O/A ratio and shaken for 30 min with a wrist action shaker. The aqueous phase was separated after the two phases were well separated. The organic phase was stripped with selected stripping agent at desired A/O ratio. All the extraction and stripping experiments were carried out at ambient temperature.

2.3. Continuous experiments

In continuous experiments, a 10-stage box-type mixer-settler was employed. The mixer-settler units are made of PVDF and have a counter-current flow scheme. Each of the mixer-settler unit has a total hold up volume of 1 L with a mixer volume of 172 mL (5.5 × 6 × 5.2 cm) and settler volume of 593 mL (19 × 6 × 5.2 cm). For one unit, the aqueous and organic phase was flowed into the bottom of the mixer by pumps. They were well mixed and transported by the pumping action of the impeller in the mixer. The flow rate of the aqueous/organic solution was adjusted by metering pumps. All the extraction and stripping experiments were carried out at ambient temperature.

2.4. Analysis

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 Na₂CO₃ solution [21].

3. Results and discussion

3.1. Removal of Fe from the solution

The number of theoretical stages required for quantitative extraction and stripping of metal ions in mixer-settler operation is determined from McCabe–Thiele diagram. In batch solvent extraction experiment, the extraction percentage of Fe with 0.3 M TBP was 99.4% at unit phase ratio (Table 1). Since the extraction percentage of iron was high, two extraction stages may be enough to extract iron completely. This was verified by the McCabe–Thiele plot for Fe extraction (Fig. 1), where it is seen that two stages are needed for complete extraction of Fe from the solution containing 213 mg/L of Fe at an A/O ratio of 2.

Table 2

Chemical composition of synthetic leaching solution (Unit: mg/L).

Pt	Al	Fe	HCl
123.1	4583	254.2	6.0M

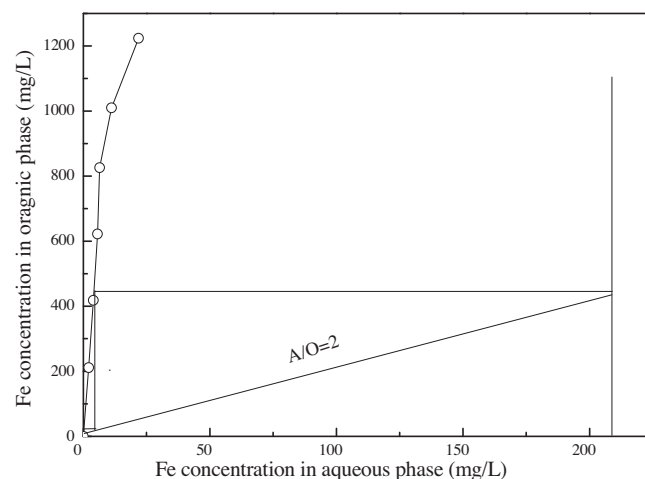
Therefore, the continuous count-current extraction of Fe from the solution was carried out at an A/O ratio of 2. The flow rate of aqueous feed was controlled to 30 mL/min. The concentrations of metals in the raffinate from each stage were measured. The results show that when the flow rate ratio of two phases (A/O) was 2, the extraction percentage of Fe was 99.9% after 2 stages, while complete extraction of Fe was obtained after 3 extraction stages. Further increase of the extraction stage to 5 had no effect on the extraction of Fe from the feed solution. In each mixer-settler unit, the two phases were separated very well. During the extraction of Fe with TBP by using mixer-settler, the co-extraction of Pt and Al was negligible.

In the case of Fe stripping process, 0.1 M HCl was found to be efficient to strip Fe from the loaded TBP (Table 1). A McCabe–Thiele plot for the stripping of Fe with 0.1 M HCl was constructed (Fig. 2), which suggest that one stage is sufficient for quantitative stripping of Fe from the loaded TBP at an A/O ratio of 0.5. The continuous 3 stage counter-current stripping experiment was carried out with 0.1 M HCl at an A/O ratio of 0.5. It was observed that separation of these two phases took a little longer time than that of extraction of Fe by using TBP. Therefore, the flow rate of loaded TBP was reduced to 25 mL/min and the flow rate ratio A/O was kept at 0.5.

The results show that after 2 stripping stages, only 46.6% of Fe was stripped by 0.1 M HCl from the loaded TBP, while complete stripping of Fe was obtained after 3 stages. The low stripping percentage of Fe after 2 stages might be due to the insufficiency of residence time or the residence time distribution caused by the vigorous mixing during the continuous experiment [22]. In the stripping solution, the concentration of Fe was 1016.9 mg/L, and Fe was completely recovered from the solution.

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

Batch experimental results suggested that 0.3 M Aliquat336 was enough to extract Pt from the solution after removal of Fe

**Fig. 1.** McCabe–Thiele plot for the extraction of Fe with 0.3 M TBP.

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