Adsorption of Pt from Chloride Leaching Solution of Spent Catalyst with Anionic Resins

Pan-Pan Sun, Tae-Young Kim, Byoung-Jun Min, Hyoung-Il Song, and Sung-Yong Cho

Abstract— **Adsorption of platinum from the leaching solution of spent catalyst with anionic resins, such as AG1-x8, Diaion SA20A, and Diaion PA308, has been investigated. Pt and Fe were separated from the leaching solution by adsorption with Diaion SA20A and Diaion PA308 resins, leaving Al and Si in the solution. Iron loaded on the resins can be removed by selective elution with diluted HCl, while Pt was recovered by elution with 0.1 mol/L thiourea. The results suggested SA20A and Diaion PA308 resins can be utilized in developing a process to recover Pt from the chloride leaching solution of the spent catalyst containing Al, Fe and Si.**

***Index Terms*— AG1-x8, Diaion SA20A, Diaion PA308, ion exchange, Pt**

I. INTRODUCTION

Spent catalysts from the petroleum industries are valuable secondary resources for platinum group metals (PGMs).[1] Recovery of PGMs from these resources is an important way to manufacture materials due to economical as well as environmental considerations. [2] In hydrometallurgical treatment processes, the valuable metals are first dissolved by a leaching process using various lixiviants.[3] In order to recover Pt from the leaching solution, Pt must first be separated from the base metal ions.

Ion exchange was recognized to be a powerful method to selectively recover low concentrations of PGM ions from solutions containing high amounts of base metals, particularly aluminum. [4] Moreover, the operation of ion exchange is simple and the production of high purity Pt is possible through this method. Therefore, when the concentration of Pt in the hydrochloric acid solution is not high, ion exchange resins can be selected to separate Pt from other metal ions.

In our previous study, the spent reforming catalyst (Pt/Al_2O_3) was roasted at 800 °C to eliminate volatile substances. Platinum and part of the base metals (Al, Fe, Si) in the roasted spent catalyst were dissolved using a mixture of 20 vol% HCl and 3 times the stoichiometric ratio of H_2O_2. [5] The leaching solution contained Pt 127 mg/L, Fe 23.7mg/L, Al 4870 mg/L, Si 5.42 mg/L and HCl 6 mol/L.

In this study, the possibility of recovering Pt from the chloride leaching solution by using anionic resins, such as AG1-x8, Diaion SA20A and Diaion PA308 was investigated. The ion exchange condition effect on the loading of metals was studied. The optimum condition to separate Pt from the leaching solution was obtained.

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II. EXPERIMENTAL

A. Materials

The chloride leaching solution was obtained by dissolving a spent reforming monometallic catalyst (Pt/Al_2O_3) under optimum leaching conditions, which were reported in our previous study.[5] The leaching solution contained Pt 127 mg/L, Fe 23.7 mg/L, Al 4870 mg/L, Si 5.42 mg/L and HCl 6 mol/L. The elution solutions were prepared by dissolving NaCl, HNO_3, Na_2CO_3, thiourea, $Na_2S_2O_3 \cdot 5H_2O$ and NaOH in double distilled water. All the chemicals used in this study were analytical pure grade.

Commercial ionic resins, AG1-x8 (Aldrich), Diaion SA20A and Diaion PA308 (Mitsubishi chemical) were employed to adsorb platinum from the leaching solution. Their physicochemical characteristics are presented in Table 1. In the present study, the resin was used as received, without any treatment.

B. Adsorption procedure

Batch experiments were carried out in a shaking incubator (VS-8480SF, Vision Scientific Co., LTD) using a 100 mL screwed cap bottle at 25 °C. Twenty mL of leaching solution was bottle rolled for 24 hours, together with resin in the concentration range of 0.5-100 g/L. After the solution was separated by filtration, the concentration of metal ions in the solution was measured by using ICPS-7500 (Shimadzu). The concentration of metals loaded onto the resin was obtained by mass balance. The elution experiments were carried out by mixing the loaded resin with eluent in the same manner.

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In continuous experiments, a glass column(250mm×10 mm) was used. One gram of Diaion PA308 resin was poured into the column to obtain a packed column. Throughout the entire operation process, the temperature of the column was controlled at 25 °C using a water circulator bath (Scientific Co., Vs-1902WF). The flow rate of the feed solution/elution solution was controlled at 1.5 mL/min using a pump (QG20 lab pump, FMI). The effluent was fractionated into portions of desired volume, and the concentration of metal ions in each fraction was measured using an ICPS-7500 (Shimadzu).

Table 1. Physical properties of resins used in this study.

	AG1-x8	Diaion SA20A	Diaion PA308
Total capacity meq/mL resin bed	1.2	1.3	1.0
Density (g/mL)	0.75	0.7	0.7
Moisture	48%	44%	67%
Ionic forms	Chloride	Chloride	Chloride

III. Results and Discussions

A. Adsorption of Pt and Fe

In order to determine the effect of resin concentration on the loading of metals from leaching solutions, batch experiments were carried out by varying the concentration of resin from 0.5 to 100 g/L. The chloride leaching solution containing Pt, Fe, Al and Si was used as the feed solution.

The results in Figs. 1-3 show that Diaion SA20A and Diaion PA308 resin have good selectivity on both Pt and Fe, compared with the other ions (Al, Si) in the leaching solution. The loading percentage of both Pt and Fe increased with increasing the concentration of resin. When the concentration of resin was higher than 20 g/L, most of the Pt and Fe were loaded onto the resin simultaneously, leaving Al and Si in the effluent. Thus there is possibility to separate Pt and Fe from other metals ions in the leaching solution by varying the concentration of Diaion resins. In the case of loading metals with AG1-x8 resin, 40% of Si was co-adsorbed with Pt and Fe, the selectivity of Pt and Fe was lower than that of Diaion SA20A and Diaion PA308 resin.

The adsorption of Pt and Fe can be explained by the nature of the predominant species of each element. Since the predominant species of platinum in the leaching solution is $PtCl_6^-$, and the adsorbable iron species is $FeCl_4^-$, the general reaction for the adsorption of Pt and Fe can be represented as follows,

$$2RCl + PtCl_6^{2-} = R_2PtCl_6 + 2Cl^- \quad (1)$$

$$RCl + FeCl_4^- = RFeCl_4 + Cl^- \quad (2)$$

where RCl represents the chloride form of DiaionSA20A, Diaion PA308 and AG1-x8 resin.

B. Removal of Fe

In ion exchange processes, elution of metals from the loaded resin is an important step to obtain the metal solution. In the reported literature, Fe was easily removed from various loaded organics, such as TBP and Aliquat336, using distilled water and diluted acid, respectively.[6,7] Since iron may precipitated when the solution PH value is higher than 4, in

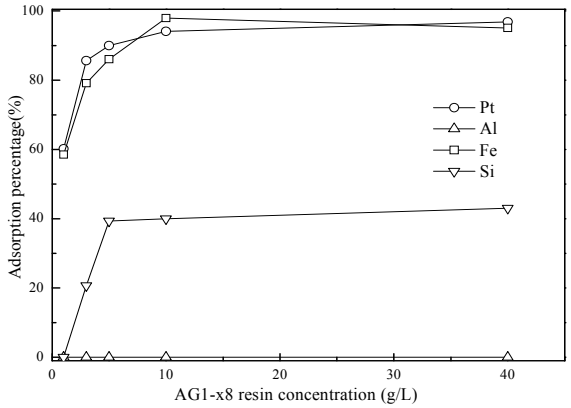

Fig. 1. Effect of AG1-x8 resin concentration on adsorption of metals.

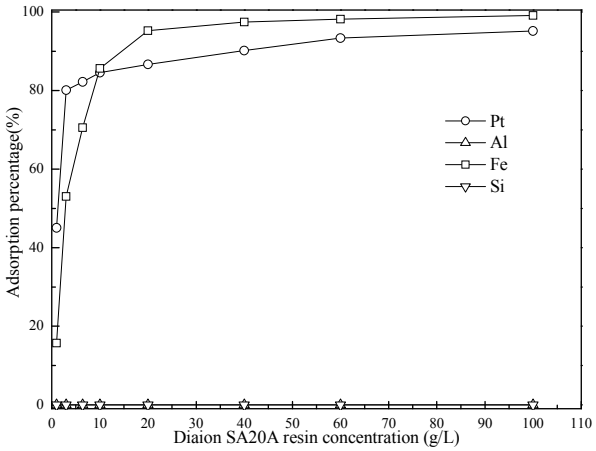

Fig. 2. Effect of Diaion SA20A resin concentration on the adsorption of metals.

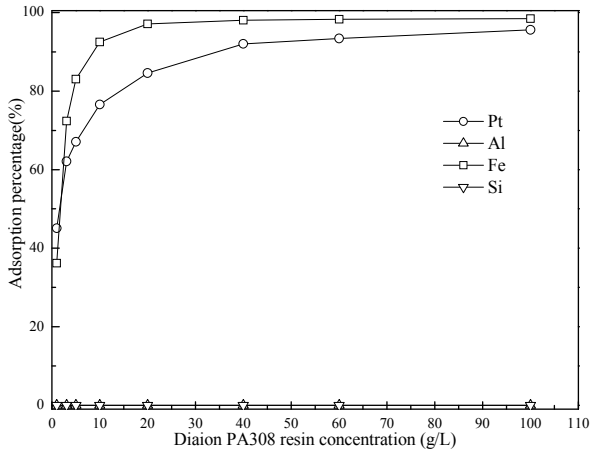

Fig. 3. Effect of Diaion PA308 resin concentration on the adsorption of metals.

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this study, in order to remove iron from the loaded resin, 0.0001 mol/L of HCl was tested as eluent. The loaded resins were obtained from the batch experiments by loading the leaching solution with 40 g/L of resin. The results (Table 2) suggest that when an equal volume of 0.0001 mol/L of HCl is employed as eluent, iron was quantitatively eluted from the loaded resin. Complete elution was obtained using DiaionPA308 resin. Under these elution conditions, the elution percentage of Pt was zero. Therefore, it can be concluded that Fe can be selectively removed from the loaded resin using 0.0001 mol/L of HCl.

Table 2.Elution of Fe from the loaded resin with H_2O.

	Fe (%)		Pt(%)	
	Loading	Elution	Loading	Elution
AG1-x8	97.93	90.67	98.52	Nil
Diaion SA 20A	98.45	89.89	99.04	Nil
Diaion PA 308	98.37	100	99.3	Nil

C. Elution of Pt

It is reported that acidic solutions can elute platinum from some loaded resins, depending on the experimental conditions.[8] Na_2CO_3, NaCl, NaOH, thiourea, and $Na_2S_2O_3$ have each shown the ability to elute platinum from several basic anion exchange resins.[9, 10] In this study, elution of platinum from the loaded AG1-x8, Diaion SA20A and DiaionPA308 resin, after removal of iron, were tested using all of the above agents. Loading experiments were carried out by loading the leaching solution with 40 g/L of resins. Co-loaded iron was removed using 0.0001 mol/L of HCl before the elution tests of Pt. For all these three resins, similar results (<15%) were obtained using these agents, except that using thiourea. when 0.1 mol/L of thiourea was used as eluent, quantitative Pt was eluted from loaded AG1-x8, Diaion SA20A and DiaionPA308 resins. The results are summarized in Table 3. This fact could be explained by the hard and soft acid and base theory (HSAB theory).[11] Thiourea is a soft ligand, which was also reported to be effective in stripping Pt/Pd from a loaded organic phase, such as DEHTPA and Alamine336.[10,12] The elution reaction might be explained by the following reaction:

$$R_2PtCl_6 + 6Tu = Pt(Tu)_6^{4+} + 4Cl^- + 2RCl \qquad (3)$$

where RCl and Tu represent the chloride form of DiaionSA20A/ Diaion PA308/ AG1-x8 resin and thiourea, respectively.

Table 3. Elution of Pt from the loaded resin.

	Resin concentration(g/L)	Elution (%)
AG1-x 8	1 mol/L$Na_2S_2O_2$	1.1
	1 mol/L NaOH	nil
	1 mol/L Na_2CO_3	11
	0.1 mol/L thiourea	94
Diaion SA 20A	1 mol/L$Na_2S_2O_2$	5
	1 mol/L NaOH	Nil
	1 mol/L Na_2CO_3	9
	0.1 mol/L thiourea	85.7
Diaion PA 308	1 mol/L$Na_2S_2O_2$	2
	1 mol/L NaOH	nil
	1 mol/L Na_2CO_3	10
	0.1 mol/L thiourea	>99.9

D. Breakthrough curves of Pt and Fe

Based on the selectivity of Pt and Fe, and efficiency removal of Fe from the loaded resin, DiaionPA308 was selected in the further study of adsorption in column experiment. In order to obtain the breakthrough curves for Pt and Fe, column experiments were carried out by passing the leaching solution through a column containing 1 g of Diaion PA308 resin. The effluent was fractionated into portions of 50 mL (24 bed volume). The obtained results are represented as a function of concentration fraction (C/C_0, a ratio of the concentration of metal ions in the effluent to that in the feed solution) to bed volume in Fig. 4. The adsorption of Al and Si were nil in the column experiment. The breakthrough curves of Pt and Fe were obtained. These breakthrough curves can be utilized to calculate the height of a practical exchange plate (HPEP) for design intentions and validation of mathematical models for the behavior of ion exchange beds.[13]

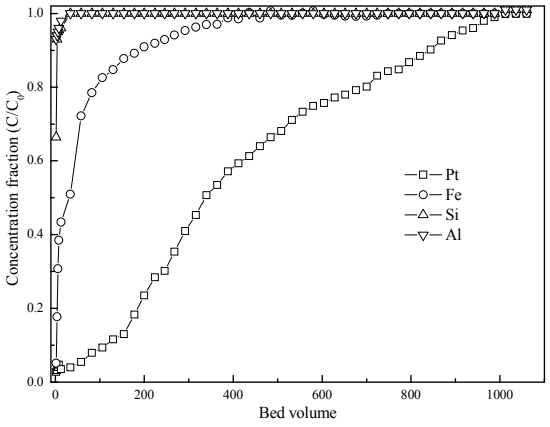

Fig. 4 Breakthrough curves of adsorption of Pt and Fe on the Diaion PA308 resin.

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IV. Conclusion

Recovery of Pt from chloride leaching solution by adsorption with anionic resins has been investigated. In the present experiments condition, Pt and Fe could be absorbed with Diaion resins simultaneously, leaving Al and Si in the effluent. AG1-x8 adsorbed 40% of Si together with Pt and Fe. Iron could be selectively removed from the loaded resins by using diluted HCl. After removal of Fe, 94% and 85.7% of Pt loaded in AG1-x8, and Diaion SA20A resin could be eluted by using 0.1 mol/L of thiourea. While more than 99.9% of Pt loaded on Diaion PA308 could be eluted with 0.1 mol/L thiourea. The breakthrough curves of Pt and Fe on Diaion PA308 was obtained. Diaion SA20A and Diaion PA308 can be utilized in developing a separation process to recover Pt from the chloride leaching solution of the spent catalyst containing Pt, Al, Fe and Si.

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