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Ultra fast microwave-assisted leaching for recovery of platinum from spent catalyst

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Abstract

The platinum/rhenium bimetallic catalyst is widely used in reforming process for the production of high octane fuels. This spent catalyst contains 0.2% Pt, 0.43% Re and other impurities. This work has investigated two alternative methods for leaching spent catalyst sample. In the first method the sample was refluxed with aqua regia at a liquid/solid ratio of 5 for 2.5 h. In the second case, microwave radiation was used at a power of 150 W with aqua regia at a liquid/solid ratio of 2 for 5 min. After leaching, the platinum was separated from rhenium and recovered as diammonium hexachloroplatinate with recoveries of 96.5% and 98.3%. Rhenium was recovered as potassium perrehenate by recovery of 94.2% and 98.9%, respectively in these methods.
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1. Introduction

The catalytic reforming process in petrochemical refining and manufacturers has significant commercial application. The original function of this process was to upgrade low octane naphtha to higher octane aromatic hydrocarbons. A significant step in the catalyst development was made by commercialization of bimetallic catalysts. The platinum/rhenium bimetallic catalyst is widely used throughout the world due to its activity, stability and selectivity (Kluksdahl, 1971; McCoy and Munk, 1971).

Different authors have investigated the recovery of platinum group metals from spent catalysts. Platinum recovery from spent reforming and isomerzing catalysts has been studied by selective dissolution of base metals in 50% H_2SO_4 and treating the insoluble residue with aqua regia from which platinum was recovered (Jeliyaskova et al., 1982). Platinum was also recovered from a spent Pt-aluminosilicate catalyst by slurrying in sulfuric acid to give an aluminum sulfate solution and platinum residue. The latter was leached with concentrate hydrochloric acid and chlorine gas at 95 °C to dissolve the platinum

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(Eugenia et al., 1983, 1984; Okuda, 1989; Ezawa, 1989). An aluminum chloride leaching process was developed for the recovery of both platinum and palladium from an alumina pellet catalyst (Letowski and Distin, 1985, 1987, 1989). The leachant was an aqua regia type solution in which the part of the hydrochloric acid content was replaced with aluminum chloride to reduce the acid consumption. Barakat and Mahmoud (2004) investigated a method of platinum recovery from spent catalyst dust by refluxing with aqua regia at a liquid/solid ratio of 7.5 for 1.5 h to solubilise platinum. Platinum was separated from the leach liquor by direct precipitation and by solvent extraction using trioctylamine in kerosene.

Microwave-assisted leaching has been investigated in an attempt to improve the yield of extracted metal and to reduce process time, especially with the increasing demand for more environmental-friendly processes. Unique microwave heating characteristics are the main drivers for the potential implementation in metal extraction. These include low processing time, direct, selective and volumetric heating, and a more controllable heating process. Various authors have suggested potential applications of microwave energy in mineral extraction and several review papers can be found in this area (Xia and Pickles, 1997; Kingman and Rowson, 1998; Kingman and Al-Harahsheh, 2004; Haque, 1999). It was indicated that microwave energy could have potential application in comminution, drying, pre-treatment of refractory gold ores, coal desulphurisation, leaching, roasting, carbon reactivation, carbothemic reduction of oxides, waste and slag management.

The aim of this study is to investigate the leaching, separation and recovery of platinum and rhenium from the spent catalyst from a reforming plant. Acid leaching and microwave-assisted leaching followed by chemical precipitation were examined. Parameters affecting leaching and separation processes such as time, temperature, acid concentration, liquid/solid ratio, microwave radiation power and time were also studied.

2. Experimental

A representative sample of spent catalyst was obtained from aromatic plant of Bandar Imam Petrochemical Company, Iran. The sample was decoked by heating the pellets at 350 °C in air. X-ray fluorescence analysis (Philips X′ Unique II 1480) indicated that the sample contained 0.20% Pt, 0.43% Re and other impurities such as iron oxide, coke and large amount of aluminosilicate supporting carrier. Chemical analysis of the sample and products was determined by using an atomic absorption spectrometer (Perkin Elmer Model 4100 ZL) and XRF. The composition of the sample is shown in Table 1.

Two methods for leaching the catalyst sample were investigated. In the first method, leaching experiments were performed with 1500 g of spent catalyst in freshly prepared aqua regia. The 2-L glass balloon flask was equipped with a mechanical stirrer and a return-flow cooler (glass condenser) was used to recover HCl and NO_x gases and any escaped gases were scrubbed in water. In the second leaching method essentially identical experiments were performed in a 2-L Teflon container with microwave heating.

The reactions were occurred as below:

$$18HCl + 4HNO_3 + 3Pt \rightarrow 3H_2[PtC1_6] + 4NO + 8H_2O \quad (1)$$

$$7HNO_3 + 3Re \rightarrow 3HReO_4 + 7NO + 2H_2O. \quad (2)$$

In both cases, after the leaching process, the reaction mixture was filtered and washed. The solution was then heated and purged with N_2 to destroy the nitric compounds and drive off nitric gases, the escaped gases were scrubbed in water. This was continued until no further gas was evolved since residual nitric gases will reduce the yield during precipitation. The solution was then evaporated in order to reduce the volume and to distill any HCl remaining from the dissolution process. In this solution the concentration of Pt was approximately 30 g/L. Aqueous solution ammonium chloride was added to the metal solution and diammonium hexachloroplatinate immediately precipitated. The

Table 1
Chemical analysis of catalyst sample

Element	Weight percent	Element	Weight percent
Pt	0.20	Fe	0.19
Re	0.43	Al	95.5
Ca	0.31	Si	1.3
Mg	0.27	C	1.8

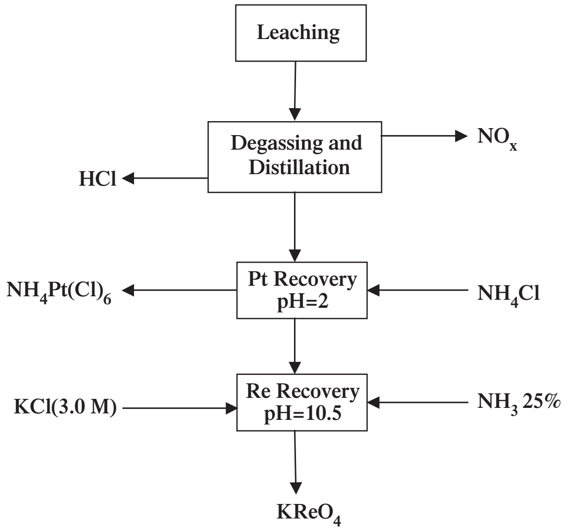

Fig. 1. Process flow chart for recovering platinum and rhenium from mother liquors.

precipitate was filtered, washed with saturated ammonium chloride solution, dried and finally calcined at 400 °C in a furnace with a fused silica muffle (Disam et al., 1997). Calcination gave a platinum sponge of high purity (>99.30%) with particle sizes in the range of 1–10 μm. The sponge was washed several times with hot distilled water in order to remove any residues of reaction products. In this process, the sponge disintegrated into a fine powder which was then dried to constant weight and characterized by X-ray fluorescence.

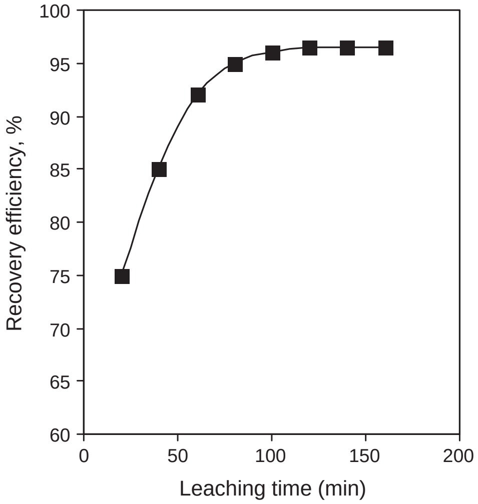

Fig. 2. Influence of leaching time on platinum recovery (liquid/solid ratio=10, *T*=aqua regia boiling point (109 °C)).

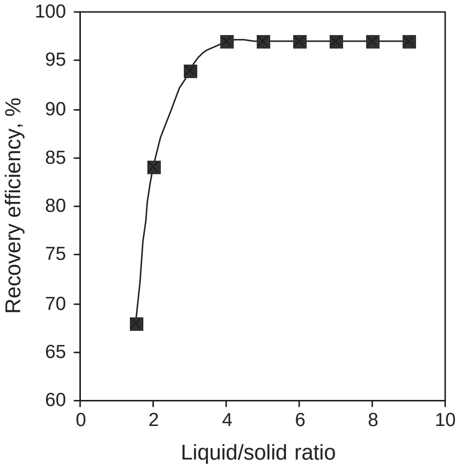

Fig. 3. Influence of liquid/solid ratio on platinum recovery (time=3 h, *T*=109 °C).

After the recovery of platinum the pH was raised to 10.5 using 25% NH_3. The solution was partly evaporated and 3.0 M KCl solution added to precipitate potassium perrhenate (Eckstein et al., 1985; Pauls et al., 1988). High recoveries in both alternative leaching methods were seen. The effect of solid/liquid ratio, leaching time, and influence of pH on precipitation of Re salt was investigated. The details of Re recovery method will be described in our forthcoming paper. Fig. 1 shows the Pt and Re recovery process method.

3. Results and discussion

The leaching and precipitation steps have the main influence on the purity and yield of metal. Solid/liquid ratio, time and temperature affect the leaching whilst NH_4C1 concentration and temperature affect the precipitation yield.

Table 2
Chemical analysis of platinum powder produced by acid leaching process

Element	Weight percent	Element	Weight percent
Pt	98.8	Fe	0.06
Re	0.06	Al	0.77
Ca	0.11	Si	0.15
Mg	0.05	C	Nil

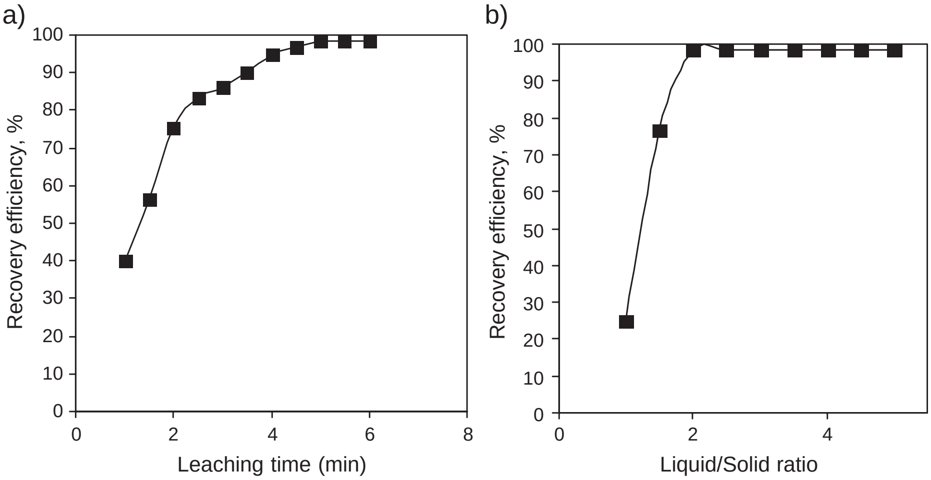

Fig. 4. Optimization of leaching conditions. (a) Dependence of recovery efficiency of platinum on leaching time (liquid/solid ratio=5, power=150 W). (b) Effects of liquid/solid ratio on recovery efficiency of platinum (time=5 min, power=150 W).

3.1. Acid leaching process

The leaching of catalyst with aqua regia at different times, temperatures and liquid/solid (acid/catalyst) ratios were investigated. Fig. 2 shows the effect of leaching time on the recovery of platinum at a liquid/solid ratio of 10 at the aqua regia boiling point (109 °C).

It can be seen that even after 20 min, the extent of platinum recovery was relatively high with a recovery of 75%. The recovery increases with increasing time, reaching a maximum and constant value of 96.5% after 2.5 h. The effect of liquid/solid ratios at 109 °C for 3 h is shown in Fig. 3. The maximum recovery of 96.5% was attained with a liquid/solid ratio of 5. The boiling point of aqua regia (109 °C) was found to be the optimum temperature for leaching. It was obvious that the maximum platinum recovery was 96.5%, it is assumed the remaining Pt was not readily accessible to the aqua regia and a preliminary crushing of the pellets may be required for greater recovery.

In the precipitation stage, saturated ammonium chloride was added to the concentrated metal solution and diammonium hexachloroplatinate precipitated (Loewen, 1995; Schreier and Edtmaier, 2003). Due to the increased solubility of the platinum salt at higher temperatures, increasing the temperature resulted in lower recoveries. The optimum results were obtained at 20 °C with 99.5% Pt precipitated. The platinum precipitate was ignited to platinum powder in 400 °C according to:

$$(NH_4)_2PtC1_6 \rightarrow Pt + 2NH_4C1 + 2Cl_2 \qquad (3)$$

Table 2 shows the analysis of the produced powder after ignition at 400 °C. The product contains 98.8% platinum which is satisfactory for a commercial grade product.

Table 3
Chemical analysis of platinum powder produced by microwave-assisted leaching process

Element	Weight percent	Element	Weight percent
Pt	99.3	Fe	0.02
Re	0.03	Al	0.47
Ca	0.01	Si	0.15
Mg	0.02	C	Nil

Table 4
Comparision of two leaching methods results

Parameter	Acid leaching	Microwave-assisted leaching
Leaching time	2.5 h	5 min
Liquid/solid ratio	5	2
Platinum recovery (%)	96.5	98.3
Platinum powder purity (%)	98.8	99.3

3.2. Microwave-assisted leaching process

Fig. 4a shows the effect of leaching time on the recovery of platinum at a liquid/solid ratio of 5, and microwave power 150 W. It can be seen that platinum recovery was very rapid with >80% within 2.5 min reaching a maximum recovery of 98.3% after 5 min. The effect of liquid/solid ratios is shown in Fig. 4b. The maximum recovery of 98.3% was attained with a liquid/solid ratio of 2. The analysis of the platinum powder obtained from microwave leaching process is shown in Table 3. The purity is greater than with the more conventional leach process suggesting that less impurities were leached in the microwave process.

Table 4 compares the results obtained from the two leaching methods. As can be seen, microwave-assisted leaching is substantially faster and gives a higher recovery of higher purity Pt metal. The substantially lower acid:catalyst ratio used in the microwave process reduces reagent use and the associated environmental impacts.

4. Conclusion

The recovery of platinum from a platinum/rhenium bimetallic spent catalyst containing 0.2% Pt, 0.43% Re and other impurities was investigated by two leaching methods. In the first method, the sample was refluxed with aqua regia at a liquid/solid ratio of 5 for 2.5 h. In the second case, microwave radiation was used as the heating technique using a liquid/solid ratio of 2 for 5 min. After leaching, the platinum was precipitated as diammonium hexachloroplatinate at recoveries of 96.5% and 98.3%, ignition of the ammonium hexachloroplatinate produced platinum powder of 98.8% and 99.3% purity for conventional and microwave processes, respectively. The rhenium was subsequently precipitated from the filtrate as potassium perrehenate at recoveries of 94.2% and 98.9%, respectively.

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