Recovery of Platinum and Rhenium from the Spent Aromatization Catalyst of Naphta Using the Ion Exchange Method and Determining the Operational Parameters

Sara Sasani*, Giti Abolhamd
Chemical Engineering Department, University of Tehran, Tehran, Iran
P.O. Box 11365-4563
Alireza Mohammadrezai+, Ali Ranji
Research Institute of Petrochemical Industry, Tehran, Iran
+ E-mail: a.rezaee@npc-rt.ir

Abstract
This paper presents the recovery of the nobel metals, platinum and rhenium from the spent aromatization catalyst of naphta using anion exchange resins. The catalyst is solved in a mixture of sulphuric acid and aqua regia, and the produced solution is passed through the columns which contain the ion exchange resins. The platinum and rhenium that exist in the solution are adsorbed on the resin, then the resin is washed by the means of a suitable acid and platinum and rhenium are desorbed from resin. The different parameters which affect the process of desorption and adsorption are also considered and the best condition for the maximum efficiency is determined. The efficiency has been 100% in the adsorption process and over 95% in the desorption process.

Key words: Spent Catalyst, Ion exchange, Rhenium, Platinum, Anionic Resin.

Introduction
Catalysts are widely used in different processes related to petroleum and petrochemical industries. Usually the activity of these catalysts decreases after some operations. This is related to different factors like coke formation
on the active sites of the catalyst. In order to increase the activity, the catalyst should be regenerated. In order to regenerate the catalyst, it is usually heated in a high temperature and in the presence of an oxygen containing gas. The regeneration of the catalyst generally increases its activity to the level of a new catalyst. But after some operation, reduction has no effect on the activity and the catalyst should be replace by a new one. Platinum, rhenium, and other noble metals (PMGs) are the most essential active parts of aromatization, reforming, and dehydrogenation catalysts. Every year, oil and petrochemical industries expel a great amount of spent catalysts containing platinum, rhenium and other noble metals. These spent catalysts have many environmental dangers, because they contain contaminants such as coke, vanadium, nickel, .... On the other hand, the resources of these metals are limited and their production is costly [1]. Therefore, considering these factors and also the extended application of these metals in different industries like oil, and petrochemical industry, although the amount of these metals in the catalyst is as low as 1%, the processes used for the recovery of noble metals from spent catalysts would be worthy and considerable.

There are some methods for recovery of platinum, rhenium and other noble metals from catalysts [1-10]. One effective method for recovery of Pt and Re from spent catalysts containing these metals or from solutions containing the ions of these metals, is using appropriate ion exchange resins [1, 3, 5, 6, 9]. The noble metals are separated from the other impurities in solution in the columns containing ion exchange resins [3].

In this paper, separation of platinum and rhenium from spent aromatization catalyst using ion exchange method and ion exchange resin is studied.
Experiments

1-Materials

The spent catalyst is R-62 which is produced in UOP company. Its structure is Pt-Re / Al₂O₃ and is used for the aromatization of naphta. Its properties are mentioned in table (1).

Table 1 – Properties of catalyst R-62

<table>
<thead>
<tr>
<th>Catalyst support</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt , Re</td>
<td></td>
</tr>
<tr>
<td>Active metals</td>
<td></td>
</tr>
<tr>
<td>Particle shape</td>
<td>Spherical</td>
</tr>
<tr>
<td>Particle diameter (mm)</td>
<td>1.6</td>
</tr>
<tr>
<td>Bulk ( lb/ft³ )</td>
<td>44.3</td>
</tr>
<tr>
<td>density</td>
<td></td>
</tr>
<tr>
<td>Pt ( % wt )</td>
<td>0.22</td>
</tr>
<tr>
<td>( % wt )</td>
<td></td>
</tr>
<tr>
<td>Re ( % wt )</td>
<td>0.44</td>
</tr>
<tr>
<td>wt )</td>
<td></td>
</tr>
<tr>
<td>Cl ( % wt )</td>
<td>1-1.1</td>
</tr>
</tbody>
</table>

Sulphuric acid and aqua regia are used to solve the catalyst. In order to separate the noble metals from catalysts, different resins such as Diaion resins (Mitsubishi Company) [6], Dow resins (Dow Company) [3, 5], Amberjet, Amberlite and Duolite resins (Rohm and Haas Company) [1, 4] have been used. Based on the references, for both platinum and rhenium
recovery a strong anionic resin named Amberjet 4200 Cl (Rohm and Haas, France) is used. The structure of this resin is a copolymer of styrene divinylbenzene. Ionic form of this resin is Cl which in compare with the same resins, has high exchange capacity and is easily regenerated [11]. The properties of this resin is mentioned in table (2).

Table 2 – Properties of Amberjet 4200 Cl resin [12]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Styrene divinylbenzene copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix</td>
<td>-N(CH₂)₂</td>
</tr>
<tr>
<td>Functional groups</td>
<td>Insoluble, white translucent beads</td>
</tr>
<tr>
<td>Physical form</td>
<td>Cl</td>
</tr>
<tr>
<td>Ionic form as shipped</td>
<td>≥ 1.30 val/L (Cl⁻ form)</td>
</tr>
<tr>
<td>Total exchange capacity*</td>
<td>49 to 54 % (Cl⁻ form)</td>
</tr>
<tr>
<td>Moisture holding capacity*</td>
<td>1.06 to 1.08 (Cl⁻ form)</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>670 g/L</td>
</tr>
<tr>
<td>Bulk density</td>
<td>≤ 1.5</td>
</tr>
<tr>
<td>Uniformity coefficient</td>
<td>cl - OH⁻ : 30 %</td>
</tr>
<tr>
<td>Mean diameter</td>
<td>600 - 800 μm</td>
</tr>
<tr>
<td>Maximum reversible swelling</td>
<td></td>
</tr>
</tbody>
</table>

* Test methods available upon request

<table>
<thead>
<tr>
<th>Suggested operating conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum bed depth</td>
<td>800 mm</td>
</tr>
<tr>
<td>Service flow rate</td>
<td>5 to 50 BV/hr</td>
</tr>
<tr>
<td>Maximum service velocity</td>
<td>60 m³/hr max.</td>
</tr>
<tr>
<td>Regenerants</td>
<td>NaOH</td>
</tr>
<tr>
<td>Concentration (%)</td>
<td>2 to 5</td>
</tr>
<tr>
<td>Flow rate (BV/hr)</td>
<td>2 to 8</td>
</tr>
<tr>
<td>Level</td>
<td>40 to 100 g/L</td>
</tr>
<tr>
<td>Minimum contact time</td>
<td>30 minutes</td>
</tr>
<tr>
<td>Slow rinse</td>
<td>2 BV at regeneration flow rate</td>
</tr>
<tr>
<td>Fast rinse</td>
<td>3 to 6 BV at service flow rate</td>
</tr>
</tbody>
</table>

*1 BV (Bed Volume) = 1 m³ solution per m³ resin

The preliminary experiments for determining the best operational condition have been done by using PtCl₄ (Platinum (IV)-Chloride 57.5% ) (Merck) and Re₂O₇ (Rhenium (VII)-Oxide 77% ) (Merck).
To desorb the ions from resin, different acids are used like nitric acid (Merck) 95%, perchloric acid (Merck) 70%, hydrochloric acid (Merck) 37%.  
2- Equipments

Separation of the ions from the solution was carried out in a glass fixed-bed column with a length of 40 cm and diameter of 7 mm. A control value is placed at the column exit to control the flow of the solution leaving the column. All the column length is made double-layered, because the solution inside the column should be heated.

The solution, entering the column are entered through a dosing pump. Calcination of the catalyst is done in a furnace with maximum temperature of 1200°C.

3- Experiments

To solve the catalyst, the required amount of the calcined spent catalyst was solved in the appropriate amount of sulphuric acid 50%wt and then in aqua regia. After around 5 hours, the catalyst was completely solved and a yellowish solution was formed. Then the solution was diluted and filtered several times so that all the sediments in the solution were separated and the solution has become transparent.

The amount of platinum and rhenium in the solution were determined by using the ICP analysis.

The existing platinum and rhenium in the catalyst solution are separated from other parts of the spent catalyst in a column containing ion exchange resins. The ion exchange resin is Amberjet 4200 Cl which is a strong anionic resin. The glass column was filled by the resin up to 10 cm and then some glasswool is entered the column to avoid the dislocation of resins, when the solution is entered. Before putting the resins in column, they were washed by distilled water and HCl 0.1 normal to ensure replacement of all anions of resin with Cl. After preparation of the column, the solution
containing platinum and rhenium is entered the coloumn to adsorb the platinum and rhenium on resins. After the complete evacuation of the coloumn from solution, three times as much as the volume of the entered solution, distilled water is added to the coloumn and then it is washed with HCl 0.1 normal to remove the interfering ions and those ions entrapped mechanically by the resin [3]. Resin is not able to adsorb the ions after it is saturated. At this state the ions which have not been adsorbed gradually increase in the effluent [3].

To determine the appropriate solution for washing the resin and desorb the ions from resin, according to references, three acid solutions, nitric acid, hydrochloric acid and perchloric acid were used [4, 6, 9]. These acids were used with different normality 3, 5, 7 and 8 normal [4, 6, 9]. After determining the appropriate acid with optimum concentration, the effect of residence time and temperature were also examined. Then according to these results, the obtained conditions were used to desorb the ions from coloumn containing resin.

To determine the saturation capacity of resins, five areas are determined based on the described capacity in the table of the resin properties. Then some experiments are done to obtain the saturation capacity of resins. The areas of 50, 100, 150, 200 and 250 $\frac{m g r \text{ metal}}{g r \text{ resin}}$ are considered and some experiments were done. Two standard solutions $\text{Re}_2\text{O}_7$ (77% Re) and $\text{PtCl}_4$ (57.5% Pt) are used in these experiments. Saturation ranges are tested for $\text{Re}_2\text{O}_7$, $\text{PtCl}_4$ and the mixture of these two.

**Results and discussion**

1 – Adsorption
The results of the experiments for determining the saturation capacity, with solutions containing chloroplatinate ions, perhenate ions and solutions containing both ions and also the solution of solved spent catalyst are shown in figures (1) and (2).

**Figure 1 – Saturation capacity of Amberjet 4200 Cl for Pt and Re at 25 °C**

- **Amount of Pt and Re in the solution leaving the resin (wt%)**

\[ \text{Saturation capacity} \text{ mg metal / gr resin} \]
According to these results, when the volume of the solution entering the column increases, the amount of Pt and Re leaving the column increase simultaneously. In the other hand the amount of Pt and Re which are adsorbed on resin are increased and the resin is saturated.

According to the results of figures (1) and (2), the saturation capacity of the resin is $100 \frac{\text{mgr metal}}{\text{gr resin}}$. In order to consider the effect of time that solution is contacted with resin, the adsorption operation is tested at different periods.

At the adsorption stage, some solutions with completely similar conditions and with saturation capacity of $100 \frac{\text{mgr metal}}{\text{gr resin}}$, are in contact with similar resins, for 5, 10, 12, 14, 15, 17 and 20 hours. The results are shown in figure (3).

According to figure (3) when residence time increases, adsorption recovery of both Pt and Re increase too. When the maximum recovery is obtained (this
is when the saturation capacity of resin is reached, increasing the residence time has no effect on recovery.

The saturation capacity of the resin is also tested for the dissolved spent catalyst for five resin saturation capacities 50, 100, 150, 200 and 250. The results are shown in figure (4).

Same as the resin saturation capacities which have been obtained in the last experiments, the saturation capacity for the spent catalyst is $\frac{\text{mgr metal}}{\text{gr resin}} = 100$

Also the comparison of figures (2) and (4) shows that interfering ions in the solution of dissolved spent catalyst have no effect on adsorption of Pt and Re. It means that the resin is very selective with relation to Pt and Re in the solution.

Figure 3 – Effect of residence time of the solution containing Pt and Re on adsorption recovery at 25 °C
Amount of Pt and Re in the solution leaving the resin (wt%)  

Figure 4 – Saturation capacity of Amberjet 4200 Cl for the solution of dissolved spent catalyst at 25 °C

To study the parameters that affect the adsorption process – flow rate of the interring solution and temperature (residence time) – some experiments in saturation capacity $100 \frac{\text{mgr metal}}{\text{gr resin}}$ at different temperatures (25, 55 and 70 °C) and different flow rates (5, 10 and 15 $\frac{\text{cc}}{\text{min}}$) were done and their effects on the process were tested. The results are shown in figure (5).
Flow rate of interring solution to the column

Figure 5 – Effect of different flow rate of interring solution on Pt and Re adsorption recovery at different temperatures 25, 55 and 70 °C

According to figure (5), adsorption of Pt and Re on resin at 70 °C and flow rate 5 \( \frac{cc}{min} \) has the maximum adsorption recovery. Also, this figure shows that when the flow rate of interring solution to the column increases, the adsorption ability for Pt and Re of the resin decreases, because of deduction of residence time of the solution on resin.

Now, at the presence of the best condition, the solution of dissolved spent catalyst is passed through the column.

In this state as well, the adsorption recovery of both metals is maximum. The adsorption recovery is 100% for Pt and 99.91% for Re.

2 - Desorption

To determine the appropriate material for rinsing the resin to desorb the platinum and rhenium ions, some experiments were done which are shown...
in table (3) and the results for HCl, HNO₃, and HClO₄ are reported in figures (6) and (7), (8) and (9), (10) and (11) respectively.

<table>
<thead>
<tr>
<th>acid</th>
<th>normality</th>
<th>Temperature(°c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>3-8</td>
<td>25, 55</td>
</tr>
<tr>
<td>HNO₃</td>
<td>3-8</td>
<td>25, 55</td>
</tr>
<tr>
<td>HClO₄</td>
<td>3-8</td>
<td>25, 55, 75</td>
</tr>
</tbody>
</table>

According to figure (7), for the mixture of Pt and Re, the maximum desorption recovery for HCl is 33% for Pt and 18% for Re at 25°C and 36% for Pt and 20% for Re at 55°C. SO this acid has a very low desorption ability for Pt and Re, even at high temperatures.

According to figures (6) to (11), 7 normal perchloric acid with 85% desorption recovery for Pt and 89% for Re at 25°C in comparison with the other acids, has the maximum desorption recovery for both Pt and Re. When the best concentration and also the suitable kind of acid is found, time and temperature were also tested. In order to consider the effect of time and temperature at this stage, desorption operation is examined by HClO₄ of 7 normal at different times and temperatures. The results are shown in figure (12).
HCl Normality

Figure 6 – Effect of different normality of HCl on desorption recovery of Pt and Re at 25 and 55°C

HCl Normality

Figure 7 – Effect of different normality of HCl on desorption recovery of mixture of Pt and Re (Re/Pt = 2/1) at 25 and 55°C
HNO₃ Normality

Figure 8 – Effect of different normality of HNO₃ on desorption recovery of Pt and Re at 25 and 55°c

HNO₃ Normality

Figure 9 – Effect of different normality of HNO₃ on desorption recovery of mixture of Pt and Re (Re / Pt = 2/1) at 25 and 55°c
Figure 10 – Effect of different normality of HClO₄ on desorption recovery of Pt and Re at 25°C

According to figure (12), when residence time decreases, desorption recovery of Pt and Re decreases simultaneously until the maximum desorption recovery is obtained. After this point, increasing the residence time has no effect on recovery.

To study the effect of temperature on desorption, some experiments were done and their results are shown in figure (13).

According to figure (13), 7 normal perchloric acid at 75 °C with 96.5% desorption recovery for Pt and 95% for Re has the maximum desorption recovery in comparison with two other acids.
Figure 11 – Effect of different normality of HClO₄ on desorption recovery of mixture of Pt and Re (Re/Pt = 2/1) at 25°C

Figure 12 – Effect of residence time for HClO₄ 7 normal on resin, on Pt and Re desorption recovery (Re/Pt = 2/1) at 25°C
Figure 13 – effect of temperature on desorption recovery of resin with HClO₄

Figure 14 – effective parameters on desorption recovery of column containing resin using HClO₄ 7 normal at 75 °C and saturation capacity
Now the results of these experiments should be examined for recovery of Pt and Re from the column containing resin which has adsorbed the Pt and Re from interring solution. The results of these experiments are shown in figure (14).

According to figure (14), when the flow rate of interring acid solution to the column (increasing the residence time) and also the volume of acid increases, the desorption recovery of Pt and Re increase too. In this state at 75 °C, 200 cc acid volume and 2 cc/min flow rate, the maximum desorption recovery is obtained.
**Conclusion**

Recovery of noble metals platinum and rhenium from spent aromatization catalyst using ion exchange resin was studied and following results were obtained:

- Ion exchange method using strong anion exchange resin Amberjet 4200 Cl can completely adsorb the platinum and rhenium from solution (100% for Pt and 99.91% for Re).

- Temperature and flowrate (residence time) of interring solution to the column are the main parameters which affect the adsorption and desorption process.

- Whatever the temperature is higher and the flowrate of interring solution to the column is lower, adsorption and desorption of ions from resin is better.

- Interfering ions in the solution of solved spent catalyst, have no effect on adsorbing Pt and Re on resin. In the other hand this resin is very selective in relation with Pt and Re.

- Perchloric acid 7 normal is the most appropriate material for separation of Pt and Re from resin Amberjet 4200 Cl. Desorption recovery with this acid for both Pt and Re at ambient temperature is higher than 85% and at 75°C higher than 95% for both metals.

- In the desorption stage of the column, the maximum separation recovery of Pt and Re is obtained at 75°C, 200 cc acid volume and 2 cc/min acid flow rate.

- In the adsorption stage of the column, the maximum adsorption recovery is obtained at 70°C and $5 \frac{cc}{min}$ interring solution flow rate.
References


