

Journal of Hazardous Materials B131 (2006) 229-237

*Journal of* Hazardous Materials

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# Improved and selective platinum recovery from spent $\alpha$ -alumina supported catalysts using pretreated anionic ion exchange resin

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Received 20 July 2005; received in revised form 11 September 2005; accepted 15 September 2005 Available online 2 November 2005

### Abstract

Improved and selective recovery of platinum from a spent dehydrogenation platinum  $\alpha$ -alumina supported catalyst using a strong basic ion exchange resin is reported. Platinum and other precious metal group (PMG) complexes are leached using concentrated hydrochloric acid along with about 0.20 vol.% nitric acid as an oxidizing agent from de-coked and crushed spent catalyst. Effects of hydrochloric acid concentration, time, and temperature in leaching stage are investigated. The strong basic anionic resin is treated by sodium hydroxide solution to replace chloride anion by hydroxyl group ion. The supernatant of the leaching process is passed through a fixed column of hydroxylated strong base anionic resin. The treated resin on which the platinum complex is adsorbed is dried and burned in an oxidizing atmosphere at 750–800 °C. The recovered gray metallic powder is mainly platinum. Results compared with those obtained from untreated anionic resin show that adsorption of platinum complexes onto the treated anionic resin is more selective and the yield of separation is considerably improved. The breakthrough curves of the pretreated anion exchanger and that of untreated exchange resin reveals that the capacity of the hyroxilated resin is decreased by about 14%. These breakthrough curves can be used for calculation of height of a practical exchange plate (HPEP) for design purposes.

Keywords: Platinum recovery; Ion exchange; Spent catalyst; Precious metals; Dehydrogenation catalyst; Strong basic resin (SBR); Breakthrough curve

# 1. Introduction

The environmental catalysis and its pertinent technologies have attracted much attention in the past decade. Strong demand for diesel vehicles, more stringent emissions legislation, and the rapid shift from palladium- to platinum-rich catalytic converter systems in gasoline powered vehicles has increased the demand for platinum consumption worldwide. Automotive CO and NOx emission control catalysts used in catalytic converters are usually guaranteed for 40,000–80,000 km depending upon the quality of the product. During the course of use, the catalyst content of the converter is thermally shocked and disturbed by going through repeated low and high temperature cycles. This leads to gradual loss of activity of the catalyst because active surface area of the catalyst in the converter is diminished, and there would be a need for replacement of the used catalytic converter. Several million

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spent catalytic converters are disposed annually worldwide, each containing about 0.5–1 g of platinum and 1–2 g of all platinum group metals (PGMs) [1].

Demand for improved and/or new polymer, petrochemical, chemical, and refining catalysts is also increasing. In the fluid catalytic cracking (FCC), hydrodesulfurization (HDS), residue fluid catalytic cracking (RFCC), dehydrogenation, reforming, hydrogenation, and other catalytic processes in petroleum, petrochemical, pharmaceutical and chemical industries vast variety and voluminous amounts of catalysts are used.

In 1991 the catalyst demand in the USA was 190,000 metric tons and the produced catalyst waste was 12,000 metric tons/year. In the same year in Europe alone, 60,000 metric tons of spent FCC/RFCC catalyst, and 105,000 metric tons of the same catalyst waste were produced in Japan. The catalyst demand of FCC and RFCC catalyst has been in the order of 570,000 metric tons in 1998 [2]. In 1990s more than 130 new catalysts or improved catalysts were introduced within the USA for catalytic chemical, petroleum, biochemical, and environmental processes [3]. These statistics show that catalytic technology will con-

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tinue to be a key player in process industries for many years to come.

Heterogeneous catalysts contain appreciable amounts of precious metals. In petroleum and chemical industries the deactivated catalysts are replaced periodically by fresh catalysts. The cycle time of replacement is usually short because of catalyst decay induced by fouling, poisoning and/or thermal degradation/sintering. Deposition of coke, which is various forms of carbonaceous materials that vary widely from a graphitic wellordered molecular structure to insoluble high molecular weight aromatic and/or polymeric compounds, is the most common catalyst fouling process. Poisoning occurs because of strong chemical bounds between a feed component, such as sulfur, or catalytic reaction products with active sites on the heterogeneous catalyst surface. Thermal degradation is provoked by high temperatures and/or thermal shocks due to heating and cooling in presence of a suitable physicochemical environment. Numerous workers have reviewed causes and methods of prevention or alleviation of different deactivation processes and we do not intend to overview them in this communication (e.g., see [4–9] among others).

The lifetime of all catalysts is limited and it could be in order of 1 min to several years, and even if the in situ regeneration of the catalyst is possible, eventually it must be replaced by fresh catalyst. Although regeneration and reuse of the spent catalysts are always preferred, however, if economics of the precious metals recovery from spent catalysts is not justifiable, then spent catalyst must be disposed. Trimm [10] has treated the criteria for disposal of spent catalysts. Platinum along with some other platinum group metals are the main active ingredients of these catalysts, and these precious metals will remain imbedded in the matrix of the support of the spent catalysts, which is usually some type of ceramic, such as alumina and the like. In addition to auto-catalysts, the petroleum, petrochemical, and chemical industries produce considerable amounts of the spent catalysts

#### Table 1

Platinum supply and demand, 1997-2002 [12]

containing platinum and other precious and rare metals annually.

The spent catalyst is considered an environmentally hazardous waste because it commonly contains contaminants such as coke, vanadium, nickel to name but a few. Therefore, there exist serious environmental concerns with regard to spent catalysts.

The world's reserve of precious group metals was estimated to be about 78,000 metric tons in the year 2000 [11]. The platinum supply and demand statistics from 1997 to 2002 is listed in Table 1 [12]. Comparison of the total supply and demand figures in a time span of five consecutive years shows that with the exception of 1998 that there has been a week surplus/balance in supply and demand, the platinum demand always has exceeded the platinum supply. Also, from 1997 to 2002 the platinum demand has increased about 24%, and there has been a gradual growth in the share of the amount of the platinum recovery in auto-catalyst sector (from 7.2% in 1997 up to 9% in 2002). The most recent market analyses also show that demand for platinum in 2003 and 2004 increased by about 1% to 202,791 kg and 0.75% to 204,657 kg, respectively. Supply in 2003 and 2004 was less than the demand for about 4.5 and 1.2%, respectively [13,14].

Natural resources of platinum and platinum group metals are limited and because of their extensive use in catalysis, electronic devices, and space materials, biomedical devices, etc., their demand is increasing. Therefore, low rate of production of these metals due to their low concentration in related ores, and their high costs of production from naturally occurring supplies has made precious metals recovery from spent catalysts a viable and cost effective alternative of their preparation. Regarding the outlook of increasing demand versus limited global reserves of platinum group metals in general, and platinum in particular, mandates a revision of the consumption and utilization of these strategic metals. Furthermore, the potential environmental haz-

	Year						
	1997	1998	1999	2000	2001	2002	
Supplier	Supply (kg)						
South Africa	115100	114500	121300	118200	127500	138100	
Russia	2800	40400	16800	34200	40500	29600	
North America	7500	8900	8400	8900	10900	1100	
Others	3700	4200	5000	3300	3400	4200	
Total	154300	16800	151500	164600	182300	182900	
Application	Demand (kg)						
Autocatalyst:gross	56900	56000	50000	58800	78400	78400	
Recovery	-11500	-12600	-13100	-14600	-16200	-17800	
Chemical	7300	8700	10000	9200	9000	9300	
Electrical	9500	9300	11500	14200	12000	12000	
Glass	8200	6800	6200	7900	8900	8100	
Bars and bullion coins for investment	7500	9800	5700	-1900	2500	2800	
Jewelry	67200	75600	89600	88000	79300	86500	
Petroleum	5300	3900	3600	3400	3900	4200	
Other	9200	9500	10400	11700	13500	14600	
Total	159600	167000	173900	176700	191300	198100	

ards of spent industrial and automotive catalysts call for putting an emphasis on recovery and recycling policies for these commodities.

There are a large number of methods of recovery of platinum and the other platinum group metals from spent catalyst ([15–30], among others), and ores [31] reported in literature. Angelidis and Skouraki [29] have examined a spent Pt-NiO/Al<sub>2</sub>O<sub>3</sub> industrial catalyst with respect to platinum removal. They have used aluminum chloride solutions, with low concentrations of nitric acid as an oxidant instead of "aqua regia". Mhaske and Dhadke [30] have extracted precious metals from spent catalysts using Cyanex 921 in toluene. Our goal in this communication is not to review the extensive and voluminous information accumulated in this area. Interested readers can refer to the review article by Yoo [2], references cited by Mhaske and Dhadke [30], and the review article by Mishra [32] for further references.

Generally speaking, there is no universally acceptable method for classification of the precious metals recovery from spent catalysts. However, it is a common practice to classify the existing processes in hydro-metallurgical, electro-metallurgical, and pyro-metallurgical methods. Among the vast variety of the available methods, solid-liquid extraction of the spent catalyst by concentrated hydrochloric acid in presence of an oxidizing agent such as nitric acid, hydrogen peroxide, chlorine, or the like can be a viable wet recovery technique. In this technique the supernatant of the leaching process which is rich in precious metal complexes is passed through a fixed bed of an anionic resin, and the contained PGMs of the bed are subsequently separated by ashing. This technique is particularly useful when iron and iridium are present in the spent catalyst matrix, either as a constituent or as an added component in the reacting system during processing time [16]. In this method, however, the ion exchange process is the time limiting step, and improved efficiency of separation, ion exchange capacity and selectivity, and possibility and ease of regeneration of the ion exchanger resin is more desirable, and will make the method much more attractive. These issues, however, because of the complexity of the system are poorly understood, and there is a great need for finding better ways to improve the selective separation of different PGMs commonly used in industrial and automotive catalysts after their regular life cycle. As was mentioned earlier, although there are a number of routes for separating PGMs from ores and spent industrial and auto-catalysts, to the best of our knowledge, there is not enough reliable data available in open literature for using in process selection as well as design purposes. Therefore, as a sequel of our previous work [33], our goal in this research effort has been parametric study of platinum recovery by acid leaching and comparison of the results by those of cyanide leaching and improving on the selectivity of platinum adsorption onto the ion-exchange bed, and collecting realistic data for unit operation and design purposes. To these ends, we have studied effects of some parameters such as hydrochloric acid concentration, time, temperature, spent catalyst particle size in leaching stage using hydrochloric acid along with nitric acid as the oxidizing agent. These parameters play significant roles in unit operation equipment design. Also, we report that by pretreatment of a strong base resin (SBR) with mobile anion in form of  $Cl^-$  by 4% sodium hydroxide solution and replacement of chlorine anion by hydroxyl group ion (hydroxylation), improved purity in separation and ion exchange selectivity with respect to hexachloroplatinic anion are achieved. Breakthrough curves of the pretreated anion exchanger and intact resin are obtained for capacity calculations.

# 2. Experimental

### 2.1. Materials

The spent catalyst was a highly selective platinum alumina dehydrogenation catalyst whose chemical composition in fresh form is reported in a previous communication [33]. Analytical grade sodium hydroxide (Merck) was used for hydroxylation experiments and analytical grade sodium hydroxide and hydrochloric acid (Merck) was utilized for pH adjustment. A strong anionic resin (AMBERTJET 4200 Cl, an industrial grade strong base anion exchanger, Rohmhaas, France) was used for separation of platinum complexes produced in leaching process. Industrial hydrochloric acid (31%) and nitric acid (57%) were used in leaching stage.

### 2.2. Apparatus and procedures

Following Grosboi et al. [16] with minor modifications, 280 g of a sample of spent dehydrogenation catalyst was decoked at 400–450 °C, and crushed to the desired particle size. The particle size distribution of the samples was determined using standard mesh size sieves. The crushed and de-coked catalyst was then leached with 3850 g of a mixture of concentrated (at least 6 mol  $L^{-1}$ ) hydrochloric acid and nitric acid (0.20 vol.% HNO<sub>3</sub>, and 98.8 vol.% HCl) solution in a 5000 cm<sup>3</sup> round bottom glass balloon heated by a 1500 W heating element. The round bottom glass container used as a batch reactor was equipped with thermometer, thermostat, stirrer, and a glass condenser for performing the leaching experiments in a total reflux condition.

A cylindrical glass column with an internal diameter of 2.5 cm and a height of 30 cm was mounted on a metal base vertically, and was filled with fresh anionic resin for ion exchange. For hydroxylation of the strong base resin equal weights of resin and 4 wt.% sodium hydroxide solution were mixed and remained for 30 min. Then the solid was filtered out and washed thoroughly by fresh de-mineralized water, and used immediately. To obtain the capacity of the anion exchange resin and its breakthrough curve, a small cylindrical glass column with internal diameter of 8 mm, and a height of 14 cm was utilized. For breakthrough experiments, the inlet volumetric flow rate was fixed at 4 mL min<sup>-1</sup>. The initial concentration of platinum in the feeds of the ion exchange beds of intact and pretreated resin were 177 and 183 mg Pt L<sup>-1</sup>, respectively.

The yield of extraction was measured by drying the solid precipitates at 120 °C, and measuring the platinum content of the residual solids based on ASTM D 4642-92 standard wet chemistry test method. The absorbance of the solution containing stannous hydrochloride complex produced in this ASTM test method was measured by a UNICAM 8625 UV–vis spectrometer at 403 nm.

The yellowish clear solution containing platinum complexes was separated from solid residues by centrifugation using a Megafuge 1.1 centrifuge (Heraeus, Germany). Separation of platinum complexes from the supernatant of the leaching test by ion exchange was carried out in a cylindrical fixed-bed of AMBERTJET 4200 Cl resin. The saturation of the column was monitored by measuring the absorbance of the effluent practicing ASTM D 4642-92 test method. The ion exchange experiments were carried out after diluting the clear supernatant, volume for volume, with de-mineralized distilled water. The ion exchange experiments were finished when bed was saturated. Finally the platinum containing resin was rinsed with distilled water, dried, and calcined with a constant slope of  $20 \,^{\circ}\text{C}\,\text{min}^{-1}$ up to 750-800 °C. The remaining gray metallic/black look powder was cooled, weighed, and characterized. EDX experiments was performed by a Philips XL 30 model scanning electron microscope (SEM), and a Philips X'pert-MPD model X-ray powder diffraction (XRD) system was utilized for phase characterization of the calcination products. It is good to mention in measurements, experiments were conducted in duplicates, and the reported values is the arithmetic average of the duplicate results.

### 2.3. Chemistry of leaching of platinum group metals

Platinum and other platinum group metals contained in the spent catalyst are leached out from the catalyst matrix by concentrated hydrochloric acid and nitric acid as the sole oxidizing agent in the form of chlorocomplex, [MCl<sub>6</sub>]<sup>2–</sup>. For instance, platinum is converted to hexachloroplatinic acid according to the following equation [2]:

$$3Pt + 4HNO_3 + 18HCl = 3H_2PtCl_6 + 4NO + 8H_2O$$
 (1)

The actual formula for hexachloroplatinic acid is  $[H_3O]_2[PtCl_6]$ , and its crystal structure has been determined at room temperature by single crystal X-ray diffraction. The space group is cubic *Fm3m* with  $[PtCl_6]^{2-}$  ions on octahedral sites and  $[H_3O]^+$  ions on tetrahedral sites [34]. Thus, in ion exchange with strong base exchanger the anion of interest is in the form of  $[PtCl_6]^{2-}$ .

# 2.4. Ion exchange, chemistry of hydroxylation and selectivity of hydroxylated resin

Ion exchange process is a reversible chemical reaction wherein an ion from liquid phase is exchanged for a similarly charged ion attached to an immobile particle. The solid ion exchange agents are either inorganic or synthetic organic resins. Inorganic solid ion exchange agents are naturally occurring or synthetically produced zeolites. The synthetic organic resins are the most favorite ion exchange agents used in process industries in solid and liquid forms because of their capability to accommodate a wide variety of needs.

Table 2						
Properties of a commercial s	strong base	anion excl	hanger used	in	this	work
(AMBERJET 4200 Cl)						

Properties	
Matrix	Styrene divinylbenzene copolymer
Functional group	-N <sup>+</sup> (CH <sub>3</sub> )
Physical form	Insoluble, white translucent beads
Ion form	Cl <sup>-</sup>
Total exchange capacity	$1.3  \text{eq}  \text{L}^{-1}$ (Cl <sup>-</sup> form)
Specific gravity	1.06 to 1.08 (Cl <sup>-</sup> form)
Maximum reversible swelling	Cl <sup>-</sup> to OH <sup>-</sup> : about 30%
Harmonic mean size	600 to 800 μm

Types, preparation, classification, and properties of ion exchangers are treated in a large number of monographs (e.g. see [35–38]). Briefly, a solid organic ion exchange resin is mainly a high molecular weight polyelectrolyte that can exchange ions with ions of the same charge from its surrounding liquid phase. The mobile ions of the resins can be negatively or positively charged, the former ion exchange resins are called anion exchangers, and the later cation exchangers. Further, strong base anion resins are similar to strong bases, and are highly ionized and can be used over the entire pH range. Strong anion exchangers exhibit a preference for different anions. This preference is termed ion exchange selectivity, and the higher the preference/selectivity of a resin for a certain ion, the greater the efficiency of separation and capacity of that ion [35].

The properties of the strong base anion exchanger used in this study are given in Table 2. In this study the strong base exchanger was utilized in two ionic forms: first the supernatant obtained in leaching stage was passed through the resin as received. In this case the ionic form of the resin was in  $Cl^-$  form according to Table 2, then the resin was hydroxylated by equal weight of 4% sodium hydroxide to replace  $Cl^-$  by  $OH^-$  for 30 min according to the following equation:

Styrene divinylbenzene copolymer- $N^+(CH_3)_3Cl^- + NaOH$ 

= Styrene divinylbenzene copolymer-

$$N^{+}(CH_{3})_{3}OH^{-} + NaCl$$
<sup>(2)</sup>

and the ion exchange experiment was repeated. In this case the hydroxyl ion is replaced by  $[PtCl_6]^{2-}$ . Working capacity of ion exchanger can be expressed as either the weight of platinum ions (grams) per cm<sup>3</sup> of swollen exchanger resin, or as grams of platinum per grams of swollen exchanger resin. Here the capacity of the resin is defined and calculated as follows

$$C_{\rm R} = \frac{W_{\rm p}(\rm{mg, Pt})}{W_{\rm b}(\rm{g, resin})} \tag{3}$$

where,  $W_p$  is the weight of the platinum adsorbed (mg), and  $W_b$  is the weight of the resin bed (g). The amount of Pt ions loaded on the exchanger was calculated by mass balance. The mass balance calculations for computation of the exchanger capacity were closed by 99.9%.



Fig. 1. Effect of particle size on platinum recovery in leaching. (Temperature =  $100 \,^{\circ}$ C, time = 3 h, solid/liquid wt. ratio = 1/5.)

### 3. Results and discussion

### 3.1. Results of parametric studies

The main parameters of interest in leaching stage by hydrochloric acid and nitric acid in this study were particle size of de-coked and crushed spent catalyst, concentration of hydrochloric acid, digestion time, and leaching temperature. These parameters were varied in turn, and the recovery of platinum was measured experimentally following the procedure mentioned in Section 2.2, and compared with the platinum content of the spent catalyst reported in our previous work [33]. Results of these series of experiments are shown in Figs. 1-4. Fig. 1 shows that as the average particle size is varied from 2 mm up to a standard mesh size of 80 (equivalent to 0.177 mm) the platinum recovery is enhanced, and no improvement on platinum recovery is achieved upon further size reduction. The best average particle size is of order of a standard mesh size of 80 (equivalent to 0.177 mm), and further reduction of the particle size does not have any effect on the platinum removal. The intermediate particle sizes (40 mesh = 0.420 mm, and 60 mesh = 0.250) show poor results. This result shows that size reduction of spent catalyst for acid leaching has appreciable impact on platinum recov-



Fig. 2. Effect of hydrochloric acid concentration on platinum removal. (Temperature = 100 °C, time = 3 h, solid/liquid wt. ratio = 1/5.)



Fig. 3. Effect of digestion time on platinum removal.

ery. However, compared with platinum recovery by cyanide leaching from spent catalysts as an alternative route [33], acid leaching can handle larger particle sizes (80 mesh, equivalent to 0.177 mm) for a maximum recovery of 67 wt.%, as opposed to a maximum particle size of 140 mesh (equivalent to 0.105 mm) for cyanide leaching that gives a recovery of 85.5 wt.%. Therefore, any decision on selecting any of these two alternatives needs a careful comparison between the two, and consideration of cost of size reduction and profit of higher recoveries. Fig. 2 shows that increased hydrochloric acid concentration leads to increased platinum recovery and the best result is obtained when 9 mol L<sup>-1</sup> hydrochloric acid is used. This result indicates that better platinum removal occur when more concentrated hydrochloric acid is utilized, and hydrochloric acid concentration plays a measure



Fig. 4. Effect of temperature on platinum recovery in leaching.



Fig. 5. EDX spectrum of platinum containing powder obtained by clacination of untreated resin bed.

role in Pt removal. Fig. 3 shows that the increase digestion time would increase the platinum recovery and after 24 h the improvement of the platinum recovery is not remarkably appreciable. This large digestion time is for higher yields is not favorable and attractive compared with that of cyanide leaching that gives more than 80 wt.% of recovery in less than 90 min of the reaction time. Effect of temperature on recovery is depicted in Fig. 4. This figure shows that at atmospheric pressure the best recovery is achieved at 100 °C. Comparison of these results with the

results obtained for cyanide leaching  $(160 \,^{\circ}\text{C})$  reveals that the severity of acid leaching reaction is lower than that of cyanide leaching, however, the penalty of this low severity is paid by lower platinum recovery yields [33].

### 3.2. Results of ion exchange

EDX spectrum of the black looking powder produced by calcination of the platinum containing resin is shown in Fig. 5,



Fig. 6. XRD spectrum of platinum containing powder obtained by clacination of untreated resin bed.



Fig. 7. EDX spectrum of platinum powder produced by calcination of the hydoxylated (pretreated) resin bed.

and its XRD spectrum is depicted in Fig. 6. These two figures indicate that platinum recovery takes place in metallic form and the impurities are mainly small amounts of aluminates, iron, and thin bearing components that are adsorbed onto the bed and reappear in oxide forms in the ashes of the anion exchanger resin. This finding also indicates that other components are either carried out by the effluent of the ion exchange or are separated and left in the solids of leaching stage. At this juncture no further experiments were carried out to trace the fate of other species of interest, however, its treatment is subject of our on going research and the results will be reported in a later opportunity. As Fig. 5 shows, semi-quantitatively, the purity of the platinum is about 83% and no other platinum group metals are present.

EDX spectrum of the gray metallic powder produced by calcination of the platinum containing resin, produced by passing the supernatant of the leaching process through a column of hydroxylated form of strong base exchanger resin is given in Fig. 7, and its XRD spectrum is presented in Fig. 8. These two figures indicate that platinum recovery takes place in metallic form and the impurities are practically insignificant and/or negligible. Also, in this series of experiments, supernatant of hydrochloric acid leaching step was separated by sedimentation and centrifugation. These findings surely indicate that other components such as iron, aluminum, and thin-containing species has gone through the ion exchange bed. The comparison of the results shown in Figs. 5–8 shows that when Cl<sup>-</sup> is replaced by hydroxyl group and acts as the mobile ion of the strong base anion exchanger



Fig. 8. XRD spectrum of platinum powder produced by calcination of the hydoxylated (pretreated) resin bed.



Fig. 9. Breakthrough curves of strong base anion exchanger resin.

resin, the selectivity of the resin with respect to  $[PtCl_6]^{2-}$  is enhanced remarkably. As Fig. 7 shows semi-quantitatively, the purity of the platinum using hydroxylated resin is about 99.4%, and purity of platinum is increased by more than 16%. Finally the breakthrough curves of the hydroxylated strong base anion exchanger resin and intact anionic resin are demonstrated in Fig. 9. Based on this figure the capacity of the hydroxylated resin is about 116 mg Pt/(g resin), and that of the intact resin is about 135.8 mg Pt/(g resin). The comparison of these results indicates that the capacity of the hydroxilated strong base exchanger is decreased by about 14%. This decreased capacity is attributed to replacement of chlorine ion by hydroxyl group ion. Fig. 9 can quite easily be used for calculation of height of a practical exchange plate (HPEP) for design intentions (e.g. see [37]), and validation of mathematical models for the behavior of ion exchange beds.

# 4. Conclusions

The platinum recovery from a spent dehydrogenation supported catalyst (Pt/ $\alpha$ -alumina) is studied. In this investigation spent catalyst is leached by concentrated hydrochloric acid along with nitric acid (0.20 vol.%) as the oxidizing agent. Then the platinum recovery is followed by ion exchange of the platinum complexes using a strong base ion exchange resin (AMBERT-JET 4200 Cl, an industrial grade strong base anion exchanger, Rohmhaas, France). Platinum and other precious metal group (PMG) complexes are extracted by hydrochloric acid from decoked and crushed spent catalyst and heating. Effects of crushed catalyst particle size, hydrochloric acid concentration, leaching digestion time, and temperature in leaching stage is studied and the results are compared with those of extraction of Pt by cyanide leaching. The strong basic anionic resin is treated by sodium hydroxide solution to replace chloride anion by hydroxyl group ion. The supernatant of the leaching process is passed through a fixed column of intact and hydroxylated strong base anion exchanger resin. The intact and treated resin on which the platinum complex is adsorbed is dried and burned in an oxidizing atmosphere at 750–800 °C. The recovered gray metallic powder is mainly platinum. The breakthrough curves of the treated resin and intact ion exchanger are obtained and the capacity of the treated and untreated resins are computed and compared. Results show that:

- The particle size distribution profoundly affects the platinum recovery in leaching stage, and reduction of the particle size beyond 80 mesh does not have any effect on platinum removal. Recovery of platinum from spent catalysts using acid leaching compared with that of cyanide leaching requires about 60% less size reduction. This simply translates into a less energy intensive method. However, acid leaching gives less recovery yields compared with those obtained by cyanide leaching.
- Increased hydrochloric acid leads to increased platinum recovery, and the most effective results are obtained by using 9 mol L<sup>-1</sup> hydrochloric acid.
- Increased digestion time increases the platinum recovery and after 24 h the increase of platinum recovery is not appreciable. In case of platinum removal using cyanide leaching more than 95% of the maximum achievable recovery is reached in about an hour [33]. This indicates that acid leaching is a far less time-efficient (slower) process.
- Leaching is temperature sensitive, and the best extraction results at atmospheric pressure are achieved at 100 °C. This means that recovery of platinum from spent catalyst using acid requires lower leaching reactions severity than that of cyanide leaching (160 °C for cyanide leaching).
- Treating the strong base anion exchanger in Cl<sup>-</sup> form by sodium hydroxide and making the strong base anion exchanger resin in OH<sup>-</sup> form leads to a more selective anion exchanger resin with respect to [PtCl<sub>6</sub>]<sup>2-</sup> ion. Hydroxylation of the strong anion exchanger resin in Cl<sup>-</sup> form increases the selectivity by 16%, however, decreases the capacity of the resin in pretreated form by about 15%. This increased selectivity and decreased exchange capacity is attributed to the replacement of chloride anion by hydroxyl group anion in pretreatment.
- Study of the dynamics of ion exchange of the cyanoplatinate complex Pt[Cn]<sub>4</sub><sup>2-</sup> obtained in cyanide leaching using pretreated strong basic resin, comparison of the results with the results presented in this communication, and validation of the exact available models of the dynamics of sorption of fixed beds in literature [39] using breakthrough curves presented here is currently underway in our research group.

### Acknowledgment

We acknowledge financial support from Iran Chemical Industries Investment Company (ICIIC) under contract number: A-44192. K. Shams dedicates this paper to Prof. R.L. Miller for his mentoring, his pedagogical philosophy, and his dedication to excellence.

### References

- R.J. Allen, Two step method for recovering dispersed metals, US Patent 5,102,632 (1992).
- [2] J.S. Yoo, Metal recovery and rejuvenation of metal-loaded spent catalysts, Catal. Today 44 (1998) 27–46.
- [3] J.N. Armore, New catalytic technology commercialized in the USA during the 1990s, Appl. Catal. A: Gen. 222 (2001) 407–426.
- [4] D.L. Trimm, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysts, vol.3, VCH, 1997.
- [5] C.H. Bartholomew, P.K. Agrawal, J.R. Katzer, Adv. Catal. 31 (1982) 135.
- [6] M.V. Twig (Ed.), Catalyst Handbook, second ed., Wolfe, 1989.
- [7] B.C. Gates, J.R. Katzer, G.C.A. Schuit, Chemistry of Catalytic Processes, McGraw-Hill, New York, 1979.
- [8] D.C. Dowden, in: R.F. Leech (Ed.), Applied Industrial Catalysis, Academic Press, New York, 1983, pp. 103–110.
- [9] D.L. Trimm, Design of Industrial Catalysis, Elsevier, Amsterdam, 1980.
- [10] D.L. Trimm, The regeneration or disposal of deactivated heterogeneous catalysts, Appl. Catal. A: Gen. 212 (2001) 153–160.
- [11] U.S. Geological Survey, U.S. Dept. of The Interior, February 2003. http://www.amark.com.
- [12] Johnson and Matthey Inc., http://www.chemicals.matthey.com, February 2003.
- [13] Johnson and Matthey Inc., Platinum Met. Rev., 48 (3) 2004, 133.
- [14] Johnson and Matthey Inc., Platinum Met. Rev., 49 (3) 2005, 118.
- [15] K.D. Vesely, Recovery of platinum from deactivated catalysts, US Patent 3,856,912, UOP (1974).
- [16] J. Grosboi, L'Isle Adam, M. Thomas, Method for recovering the constituents of catalysts comprising an aluminuous carrier, Platinum and Iridium, US Patent 3,999,983 (1976).
- [17] M. Thomas, B. Billancourt, L Grosbois, Method for recovery of platinum from catalysts, US Patent 4,069,040, Rhone-Poulenc Industries, France (1978).
- [18] I. Peka, L. Vodicka, J. Ulrich, Method for recovery of platinum from spent catalysts, US Patent 4,077,800, Vysoka Skola, Prague, Czechoslovakia (1978).
- [19] P. Cichy, Recovery of precious metals from spent alumina-containing catalysts, US Patent 4,337,085, Kennecott Corporation, Stamford, Conn (1982).
- [20] S.C. Dhara, The recovery of platinum group metals by high pressure reaction method, in: M.C. Jha, S.D. Hill (Eds.), Precious Metals'89, The Minerals, Metals and Materials Society, 1988, pp. 503–519.
- [21] R.W. Bartlett, R.J. Wesley, R.J. McClincy, Platinum–palladium concentrate smelting and pressure leaching, in: M.C. Jha, S.D. Hill (Eds.), Precious Metals'89, The Minerals, Metals and Materials Society, 1988, pp. 477–482.

- [22] CHEMENTATOR, A less-expensive way to recycle catalysts, Chemical Engineering, November 1990. p 21.
- [23] T. Okutani, Y. Nakata, M. Suzuki, Recovering method of catalytic component and carrier from waste catalyst, US Patent 4,960,573, Agency of Industrial Science and Technology, Japan (1990).
- [24] G.B. Atkinson, R.J. Kucczynski, D.P. Desmond, Cyanide leaching method for recovering platinum group metals from a catalytic converter catalyst, US Patent 5,160,711, USA (1992).
- [25] R.J. Allen, P.C. Foller, J. Giallombardo, Two-step method for recovering dispersed noble metals, US Patent 5,102,632, Metallgesellschaft Aktiengesell-schaft, Germany (1992).
- [26] G.B.J. De Bore, M. Hasselaar, Recovery of precious metals from catalyst residue, US Patent 5,302,183, Shell Oil Company (1994).
- [27] K. Toyabe, K. Kirishima, H. Hanawa, Process for recovering valuable metals from waste catalyst, US Patent 5,431,892, Sumitomo Metal Mining Co., Japan (1995).
- [28] W. Fogel, Y. Mottot, Process for the treatment by an electrochemical route of compositions containing precious metals with a view to their recovery, US Patent 5,783,062, Rhone-Poulenc Chimie, France, 1098.
- [29] T.N. Anjelidis, E. Skouraki, Preliminary studies of platinum dissolution from a spent industrial catalyst, Appl. Catal. A: Gen. (1996).
- [30] A.A. Mhaske, P.M. Dhadke, Extraction separation studies of Rh, Pt, and Pd using Cyanex 921 in toluene—a possible application to recovery from spent catalysts, Hydrometallurgy 61 (2001) 143–150.
- [31] C.W. Ammen, Recovery and refining of precious metals, Chapman and Hall, 1997.
- [32] R.K. Mishra, Recovery of platinum group metals from automobile catalytic converters—a review, Precious Metals'89, in: Proceeding of an international symposium sponsored by the copper, nickel, cobalt, and precious metals committee of the Minerals. Metals and Materials Society and the International Precious Metals Institute held at TMS Annual Meeting, Las Vegas.
- [33] K. Shams, M.R. Beiggui, A. Gholamipour Shirazi, Optimum conditions for platinum removal from dehydrogenation spent catalysts using cyanide leaching method followed by ion exchange, Appl. Catal. A: Gen. 258 (2) (2004) 227–234.
- [34] ISIS Experimental Report, Rutherford Appleton Laboratory, RB number:12092 (2001).
- [35] F. Helfferich, Ion Exchange, Dover, 1995.
- [36] M.J. Slater, The Principles of Ion Exchange Technology, Butterworth, 1991.
- [37] G.P. Simon, Ion Exchange Training Manual, Van Nostrand Reinhold, 1991.
- [38] R. Kunin, Ion Exchange Resins, Krieger Publishing Company, 1990.
- [39] K. Shams, Sorption dynamics of a fixed-bed system of thin-film-coated monodisperse spherical particles/hollow spheres, Chem. Eng. Sci. 56 (2001) 5383–5390.