



Recovery of platinum from spent catalyst

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Abstract

During the manufacture of nitric acid from ammonia there is a slow loss of catalytic platinum gauze. This fine dust, which contains 13.7% Pt, 1.3% Rh and other impurities such as iron oxide and silica, is deposited on the internal reactor walls and cooling coils. The dust was refluxed with aqua regia at a liquid/solid ratio of 7.5 for 1.5 h to solubilise platinum for subsequent recovery. Platinum was separated from the leach liquor by direct precipitation and by solvent extraction using trioctylamine in kerosene. In both cases the platinum was recovered as diammonium hexachloroplatinate by precipitation using ammonium chloride. The precipitate was decomposed by ignition to produce platinum powder with purity of 97.9% and 99.9% for direct and SX routes, respectively. A platinum recovery of 97.5% was achieved by both routes.

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1. Introduction

Platinum gauze is used to catalyse the oxidation of ammonia in the manufacture of nitric acid. During this operation, part of the platinum is lost as fine dust due to operation at high temperature and pressure. The dust is deposited on the internal reactor walls and cooling coils. This dust can be recovered during a plant shutdown, the dust on the walls was collected manually while the dust on the coils was washed with dilute hydrochloric acid and the liquor was dried. In the Egyptian fertilizer industry, large amounts of such platinum enriched dust are accumulated. Recovery of the platinum metal from this dust has a vital economic impact on the process.

Different authors have investigated the recovery of platinum group metals from spent catalysts. Platinum

recovery from spent reforming and isomerization catalysts has been studied by selective dissolution of base metals in 50% H₂SO₄ 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 aluminium sulfate solution and platinum residue. The later was leached with concentrated hydrochloric acid and treated with chlorine gas at 95 °C to dissolve the platinum (Eugenia et al., 1983, 1984; Okuda, 1989; Ezawa, 1989). An aluminum chloride leach process was developed for recovery of both platinum and palladium from an alumina pellet catalyst (Letowski and Distin, 1985, 1987, 1989). The leachate was an aqua regia type solution in which part of the hydrochloric acid content was replaced by aluminium chloride to lower the acid consumption.

Narita (1998) investigated a method of platinum recovery from sludge and dust. Base metals were

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removed from chloroplatinic acid solution by alkaline precipitation. Ammonium chloride was then added to convert the dissolved platinum to ammonium chloroplatinate, which was subsequently heated to yield platinum sponge.

Secondary platinum scrap from the glass industry also containing iridium, rhodium and palladium was used to study the refining process. Dissolving this material in boiling aqua regia, diluting with water or hydrochloric acid and adding ammonium chloride gives a Pt precipitate, leaving the accompanying platinum group metals in solution (Schreier and Edmaier, 2003).

Solvent extraction has been practiced for the preparation of highly pure precious metals (Narita, 1998; Barnes and Edwards, 1982; Cleare and Charlesworth, 1979; Reavell and Charlesworth, 1980). Tributylphosphate (TBP) and trioctylamine (TOA) can extract platinum and have been commercially used for platinum refining. However, the drawback of using TBP is the coextraction of iron with platinum at a wide range of acid concentration. The stripping efficiency of platinum from the organic phase is known to be rather difficult. Precipitation stripping was recently investigated to overcome this difficulty. Pure diammonium hexachloroplatinate powder was efficiently prepared from platinum loaded alamine 336 and TBP using aqueous mixed solutions of ammonium chloride and ammonium hydroxide or ammonium chloride and perchloric acid (Sumiko, 1999).

The composition of the dust sample under investigation in this work is different from those cited in the literature as it is contaminated with several impurities such as excessive amounts of iron oxide from the surroundings and other base metal oxides. The aim of this study is investigation of the leaching and separation conditions for recovery of platinum from the dust of the spent catalyst arising from a nitric acid production plant. Acid leaching followed by either chemical precipitation or solvent extraction is examined. Parameters affecting leaching and separation processes such as time, temperature, acid concentration and liquid/solid ratio were studied. Rhodium was also found to be partially leached with aqua regia. The leaching residue and the filtrate after platinum separation are used for Rh recovery and the results will appear in a subsequent paper.

2. Experimental

A representative sample of 1-kg spent platinum dust was obtained from Kima Company for Fertilizers, Aswan, Egypt. The dust sample was homogenized by thorough mixing and the <106- μm fraction used. Preliminary investigations showed that grinding to finer sizes had negligible effect on the leaching of platinum. X-ray diffraction analysis (Cu radiation, Philips PW 1730) indicted the presence of Pt, quartz and haematite as the major phases present.

Chemical analysis of the dust and products was determined by using both of atomic absorption spectrometer type (Perkin Elmer Model 3100) and X-ray fluorescence (ARL 9400 Sequential XRF). The composition of the dust is shown in Table 1.

Fig. 1 shows the procedures followed in this work for platinum separation from the dust.

Preliminary leaching of the dust sample with concentrated hydrochloric acid showed that although the haematite dissolved, so did some of the platinum. This can be attributed to the oxidative nature of the dust sample that was collected as fine particles from the highly oxidizing nitrogen oxide atmosphere. Thus, a preliminary stage to dissolve iron is not appropriate due to the losses of platinum.

Leaching experiments were performed in a 250-mL glass container immersed in a thermostatically controlled water bath equipped with magnetic stirrer. Aqua regia was freshly prepared by mixing concentrated hydrochloric acid (36%) and concentrated nitric acid (65%) by the volume ratio of 3 HCl:1 HNO₃ and used as leaching agent for the dust. A reflux system (glass condenser) was used to recover HCl and NO_x gases and any escaped gases were scrubbed in water. The reaction mixture was filtered and washed to

Table 1
Chemical analysis of the platinum dust

Element	Weight percent	Element	Weight percent
Pt	13.7	Cu	0.15
Rh	1.3	Zn	0.17
Fe	16.9	Pb	0.17
Ni	2.46	As	0.62
Ca	1.15	Re	0.84
Mg	1.35	Si	8.25

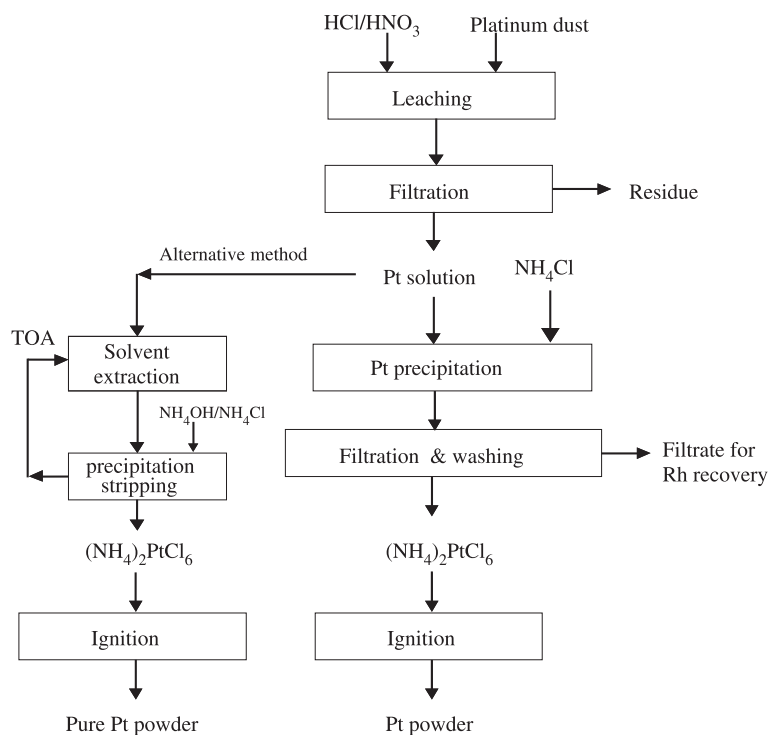


Fig. 1. Process flowsheet for platinum recovery from the dust.

separate the undissolved materials from the pregnant platinum solution.

Two alternative methods were investigated for separation of both commercial and pure grade platinum from the solution. In the first method, platinum was precipitated as diammonium hexachloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$, by adding ammonium chloride to the leach solution.

Solvent extraction experiments used 10% trioctylamine (TOA) in kerosine and were performed in 250-mL cylindrical glass vessels with equal volumes of the organic and aqueous phases. The vessels were shaken in a thermostatted shaker (GFL Model 1083) for the required time. After phase separation a sample from the aqueous phase was withdrawn for chemical analysis. An aqueous solution of ammonium hydroxide and ammonium chloride was used as the stripping agent with diammonium hexachloroplatinate immediately precipitated. Precipitation stripping was suggested (Sumiko, 1999) to enhance the stripping of platinum from Pt-loaded TOA.

In both cases, the precipitate was filtered washed with saturated ammonium chloride solution and dried. The dried precipitate was ignited to produce sponge platinum powder.

3. Results and discussion

The leaching results of platinum dust with aqua regia at different times, temperatures and liquid/solid (acid/dust) ratios are shown in Fig. 2. Fig. 2a shows the effect of leaching time on the recovery of platinum at a liquid/solid ratio of 25, and 109 °C. It can be seen that even after 15 min, the extent of platinum recovery was relatively high with a recovery of 72%. The recovery increases with increasing time, reaching a maximum and constant value of 98% after 1.5 h. The effect of liquid/solid ratios at 109 °C for 2 h is shown in Fig. 2b. At a liquid/solid ratio of 2.5, about 77% of the platinum was recovered; the maximum recovery of 98% was attained with a liquid/solid ratio of 10.

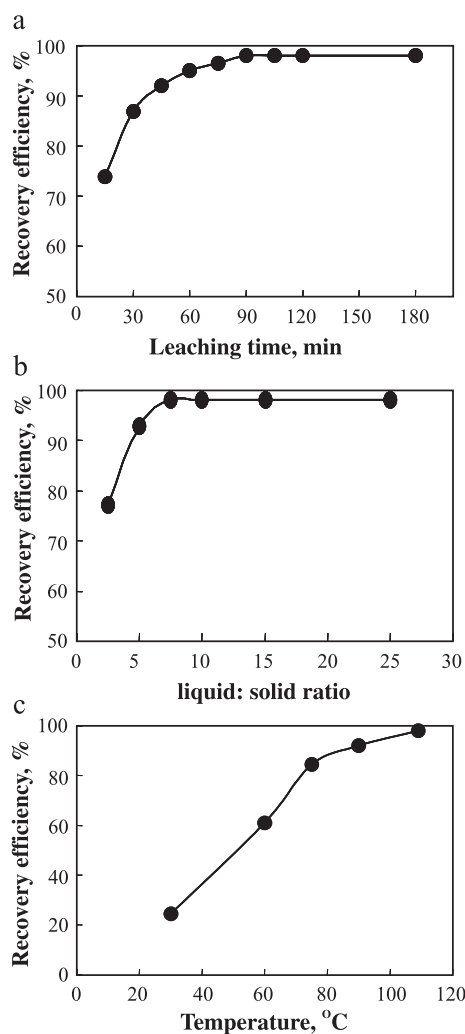
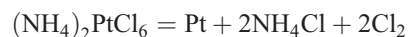


Fig. 2. Leaching tests. (a) Platinum recovery vs. leaching time, liquid/solid ratio = 25 at 109 °C. (b) Effect of liquid/solid ratio on platinum recovery, time = 2 h at 109 °C. (c) Effect of temperature on platinum recovery, liquid/solid ratio = 10, time = 2 h.

This required high value of the acid ratio is attributed to the refractory nature of the platinum content which needs vigorous reaction and excess acid to be dissolved and also to the reaction with the accompanied impurities. Fig. 2c shows the effect of temperature on the platinum recovery at a liquid/solid ratio of 10 for 2 h. It was obvious that leaching reactions are temperature-dependent; the recovery increased gradually with temperature reaching the maximum value (98%) at the boiling point (109 °C).

Saturated ammonium chloride solution was added to the leach liquor (as-prepared) that contains hexachloroplatinic acid to precipitate diammonium hexachloroplatinate complex (Loewen, 1995; Schreier and Edtmaier, 2003). The effect of temperature on the precipitation of this salt using ammonium chloride was investigated. The best results were obtained at 25 °C with 99.5% Pt precipitated, increasing the temperature resulted in lower recoveries—97.2% and 81.9% at 60 and 80 °C, respectively. This can be attributed to the higher solubility of the Pt-complex with increasing temperature. Fig. 3 shows the effect of ammonium chloride addition on the precipitation of platinum at 25 °C. It is obvious that the precipitation yield increases sharply with increasing amounts of ammonium chloride, reaching a value of 96% at the stoichiometric ratio of 2. For 99.5% Pt recovery a ratio of 4 is required. This excess of ammonium chloride is needed to overcome the negative effect of excess HCl from leaching.

The platinum precipitate was ignited to platinum powder according to:



The optimal decomposition temperature of the Pt salt (44% Pt) was detected by the weight loss percentage. Fig. 4 shows the relation between ignition temperature (from 200 to 450 °C) and weight loss. It was clear that the weight loss sharply increases with increasing temperature higher than 250 °C, reaching a maximum and constant value at 350 °C. Decomposition of the salt produces ammonium chloride. The latter is known to sublime at 340 °C (Weast, 1979). Table 2 shows the

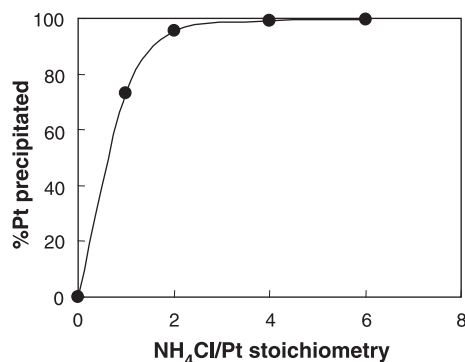


Fig. 3. Precipitation of platinum as a function of NH₄Cl/Pt.

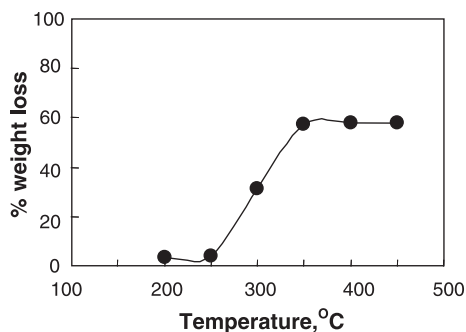
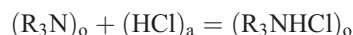


Fig. 4. Mass loss during ignition of ammonium hexachloroplatinate at different temperatures.

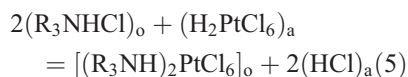
analysis of the produced powder after ignition at 350 °C. The product contains 97.9% platinum which is considered as a commercial grade product; the main impurity is Fe (0.7%).

Solvent extraction is a technique proposed for production of pure platinum with separation of Fe(III) from Pt(IV) an important factor in this process. A synthetic solution containing 0.1 g/L each Pt(IV) and Fe(III) was prepared and utilized for optimizing the separation conditions of the two metals. Trioctylamine (TOA) reacts with HCl to form the chloride species as follows:



where the subscripts (o) and (a) represent the organic and aqueous phases, respectively.

Platinum (IV) is extracted with TOA by an ion exchange mechanism according to following equations (Smith, 1971; Sumiko, 1999):



Solutions containing Pt(IV) and Fe(III) were prepared in presence of different concentrations of HCl (0.01 M–7 M) and contacted with an organic solution of

Table 2
Chemical analysis of the platinum powder produced by precipitation

Element	Weight percent	Element	Weight percent
Pt	97.9	Ca	0.10
Rh	0.70	As	0.13
Fe	0.70	Re	0.19
Si	0.27		

10% TOA in kerosine for 5 min. The relation between logarithm of HCl concentration and metal extraction is shown in Fig. 5. Nearly quantitative extraction of Pt(IV) was achieved using diluted or concentrated HCl, while the extraction of Fe(III) is negligible in dilute HCl. The extraction of Fe(III) is enhanced by increasing the HCl concentration, reaching >99% in the range 1–3 M, and gradually decreased at higher concentrations. Thus, excellent separation of Pt(IV) from Fe(III) would be obtained utilizing a very dilute HCl concentration (0.01 M). The separation factor ($\alpha_{Pt/Fe} = D_{Pt}/D_{Fe}$, where D is the distribution coefficient) reached a value of >4000 in 0.01 M HCl.

The effect of contact time (1–120 min) on extraction of Pt(IV) and Fe(III) from 0.01 M HCl was examined. However, almost all Pt(IV) was extracted to the organic phase within 1 min; even after 120 min there was little uptake of Fe(III). Thus, mixing for only 1 min is enough for effective separation of the two metals. It has been reported that Rh(III) extraction using TOA shows similar behaviour to that of iron(III) (Cleare and Charlesworth, 1979). Thus, TOA can be used as selective extractant for Pt(IV) from solution containing both iron and rhodium ions.

The leach liquor was shaken with 10% TOA in kerosine for 5 min to ensure the complete extraction of platinum. In this work, nearly complete precipitation stripping of Pt was achieved by precipitation stripping the Pt-loaded TOA with an ammonium hydroxide-ammonium chloride solution. The yellow precipitate was dried and ignited at 350 °C to produce sponge platinum with purity of 99.9%.

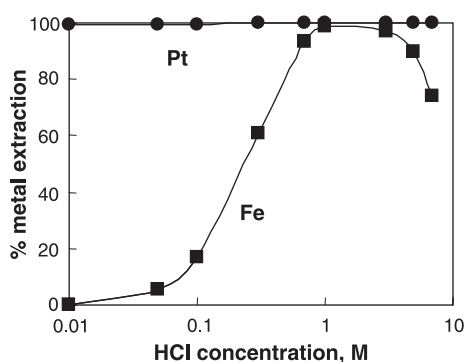


Fig. 5. Effect of HCl concentration on the extraction of Pt(IV) and Fe(III) with 10% TOA in kerosine.

4. Conclusion

Leaching and separation conditions for the recovery of platinum from spent catalyst dust arising from the fertilizer industry have been evaluated. Aqua regia leaching was used with a Pt recovery of 98% after leaching for 1.5 h at 109 °C with a liquid/solid ratio of 10. Platinum was separated from the leach liquor as ammonium hexachloroplatinate by two alternative methods, precipitation with ammonium chloride and solvent extraction with TOA. A separation factor for platinum over iron of >4000 was achieved by loading from 0.01 M HCl. Platinum was precipitation-stripped using an aqueous solution mixture of ammonia and ammonium chloride. The ammonium hexachloroplatinate was ignited at 350 °C to produce commercial and pure grade metals purities of 97.9% and 99.9% after direct precipitation and solvent extraction, respectively.

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