

Leaching Platinum-Group Metals in a Sulfuric Acid/Chloride Solution

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A leaching process was established based on the ability of platinum-group metals to form stable chloro-complexes in acidic chloride solutions. Industrial catalyst losses were examined for the recovery of platinum, palladium, and rhodium by leaching with a mixture of sulfuric acid and sodium chloride to avoid using aqua regia or autoclave conditions. Extraction of platinum and rhodium in 60% H_2SO_4 at 135°C steadily increased with increasing NaCl concentrations reaching 95% and 85%, respectively, at 0.1 M NaCl after two hours. By comparison, palladium was dissolved more quickly but also reached 85% under the same conditions. Extraction of each metal increased with temperatures up to 125°C but plateaued at higher temperatures. Similar behavior was observed with increasing H_2SO_4 concentrations up to 60%. More than 99% extraction of each metal was obtained after ten hours using 0.1 M NaCl and 60% H_2SO_4 at 125°C.

INTRODUCTION

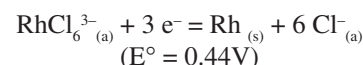
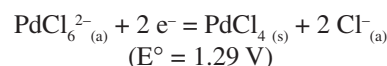
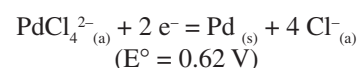
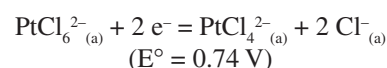
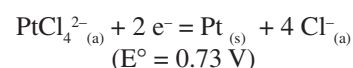
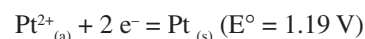
Platinum group metals (PGM) are barely soluble in mineral acids, and traditional aqua regia (mixture of concentrated hydrochloric and nitric acids) or hydrochloric acid/chlorine gas processes suffer from high reagent consumption, corrosion problems, and the need for scrubbing emitted hazardous gases.¹ Several attempts have been made to find alternative processes to overcome these drawbacks and increase PGM extraction efficiency.²⁻⁴ Complexation/oxidation leaching is a favorable approach regarding economical and environmental purposes. This technique is based on the ability of PGM to form stable aqueous complexes with ligands such as cyanide, halide, sulfite, and thiosulfate ions (Table I).⁵

Cyanide pressure leaching was examined for recycling PGM from spent catalysts where substantial care is needed to prevent evolution of the hazardous HCN gas and destruction of the remaining cyanide in waste solutions.⁶⁻⁸ On the other hand, halide processes were established after several modifications proved efficient and safe particularly with secondary recovery by pressure leaching with iodine/iodide solutions. However, pressure leaching is expensive and can render the process complicated with respect to materials and handling.^{9,10} F. Solomon has patented a process based on treating PGM residue with a polar organic solvent where bromine is dissolved to form a non-aqueous PGM complex.¹¹ The organic solvent is subjected to electrolysis to recover the PGM. A mixture of bromide salt and bromine was also used for leaching of PGM.¹²

HYPOTHESIS

For solubilization of platinum, palladium, and rhodium metals in aqueous chloride media, the standard electrode

potentials for the half reactions are:¹³



According to these potentials, dissolution reactions are rather difficult. However, the presence of chloride ions for the formation of stable complex ions and the resulting increase in the reduction strength of the metal is the reason it works.¹⁴

The Eh-pH diagrams of Pt-Cl-H₂O and Pd-Cl-H₂O systems were con-

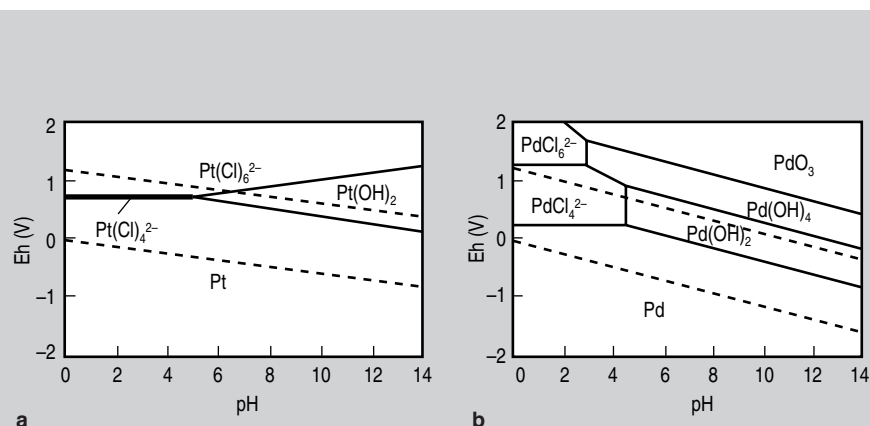


Figure 1. Eh-pH diagrams of (a) Pt-Cl-H₂O and (b) Pd-Cl-H₂O systems, metal concentration 10⁻⁵ M, Cl⁻ concentration 10⁻¹ M, 25 °C.

Table I. Stability Constants of Some Aqueous Complexes of Pt²⁺ and Pd²⁺ at 25 °C

Ligand	logβ ₄	
	Pt	Pd
CN ⁻	78.00	63.00
SCN ⁻	33.60	25.60
NH ₃	35.30	32.60
SO ₃ ²⁻	37.90	29.10
Cl ⁻	13.99	11.54
Br ⁻	15.40	14.90
I ⁻	29.60	24.90
NH ₃	35.30	32.60

Table II. Contents of Pt, Rh, and Pd in Different Fractions of the Catalyst Losses

Fraction	Metal Content (%)		
	Pt	Rh	Pd
+150 mesh	5.8	0.649	0.049
-150 + 200 mesh	8.1	0.904	0.068
-200 mesh	38.767	4.32	0.323
Whole sample	16.76	1.87	0.14

structured using *Stabcal* software developed by Hsin H. Huang, Department of Metallurgical and Materials Engineering, Montana Tech of the University of Montana, Butte, Montana. As shown in Figure 1a and b, most of the chloro-complexes of platinum and palladium ions lie within the water stability region. The PtCl₆²⁻ predominates at a wide area of acidic and high potential regions and the PdCl₄²⁻ in acidic and less potential regions. This confirms the possible dissolution of platinum and palladium as chloro-complexes in chloride media. In general, the dissolution of PGM is based on providing a high oxidation potential and effective complexing ions in solution. For instance, in case of PGM dissolution with aqua regia, the formed nascent chlorine (Cl₂) and nitrosyl chloride (NOCl) provide the high oxidation potential, and the high chloride-ion concentration acts as the complexing agent. A PGM dissolution system comparable to aqua regia can be created by using a mixture of a proper oxidizing agent, a chloride salt, and an acidic solution such as sulfuric acid. The sulfuric acid by itself cannot dissolve platinum, but partially dissolves palladium and hardly dissolves rhodium only at highly concentrated boiling acid. The addition of a chloride salt to a moderate H₂SO₄ concentration would stabilize the PGM ions in the

solution by forming corresponding chloro-complexes and hence improve their dissolution.

CASE STUDY

During the manufacture of nitric acid, Pt-Rh or Pt-Pd-Rh alloys are commercially used for catalytic oxidation of ammonia to nitrogen oxides by air. Losses of this catalyst are collected from the oxidation chamber for recycling. A representative sample of this catalyst loss was obtained from Kima Company for Fertilizers, Aswan, Egypt. Because it is desirable to develop a process that is unsophisticated, a simple dissolution system for PGM recovery is proposed. A mixture of sulfuric acid and sodium chloride was utilized to investigate dissolution of the PGM contents.

Leaching Procedures

Leaching experiments were performed in a 250 ml Pyrex round-bottomed flask placed in a thermostatically controlled water bath. The flask was fitted with a Pyrex condenser and a thermometer. Sodium chloride was dissolved in sulfuric acid and the mixture was poured into the flask. Once the specified temperature was reached, a 1 g sample of the catalyst losses was added and the slurry was heated and stirred. After reacting for a set period of time, the leaching residue was filtered and washed with bi-distilled water acidified with 5% aqua regia. Contents of platinum, palladium, and rhodium in filtrate solutions were measured using an inductively coupled plasma-atomic emission spectrometer (ICP-AES). Standard solutions [1,000 ppm from SPEX (Metuchen, New Jersey)] of each metal were diluted with bi-distilled water and used for calibration of the ICP-AES. The PGM dissolution efficiency was estimated from the weight of the dissolved metal and the initial weight of the same metal in the sample. All reagents were chemical grade and obtained from Fisher Scientific.

Sample Evaluation and Preliminary Investigation

The precious metals contents in the catalyst losses were detected using fire-assay technique facilities of the StillWater Mining Company, Montana; results are presented in Table II.

The sample is very rich in platinum (16.76%), contains an appreciable amount of rhodium (1.87%), and only 0.14% of palladium. The ratio of Pt:Rh in the catalyst losses is 8.96:1; that approaches the ratio 9:1 in the new catalyst gauze. This indicates that the two PGM (platinum and rhodium) are not selectively lost in the nitric-acid manufacturing process. The silver and gold contents are as little as 0.01% and 0.0012%, respectively. The main components of the sample, other than precious metals, are iron oxides and silica, which were brought from the surroundings during the collection stage. The PGM are concentrated in

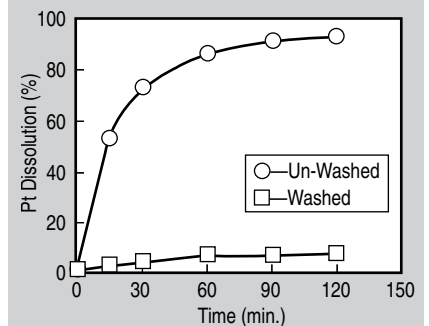


Figure 2. The leaching of platinum from washed and un-washed catalyst losses. 0.1 M NaCl, 125 °C, 60% H₂SO₄, S/L = 1:100 g/ml.

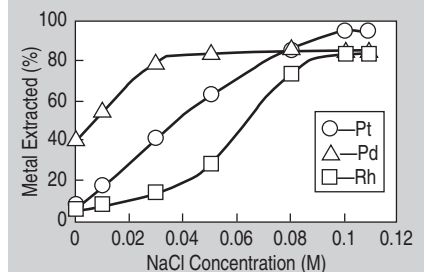


Figure 3. The effect of NaCl concentration on the extraction of platinum, palladium, and rhodium. 60% H₂SO₄, 2 h, 135 °C, S/L = 1:100 g/ml.

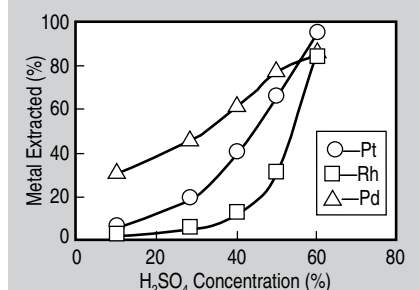


Figure 4. The effect of H₂SO₄ concentration on the extraction of platinum, palladium, and rhodium. 0.1 M NaCl, 2 h, boiling temperature, S/L = 1:100 g/ml.

the fine fraction (–200 mesh). Physical techniques were performed to isolate PGM concentrate from the sample contents using magnetic and/or size separation, but PGM losses in tails were high. Although results showed it was not necessary, catalyst losses were ground to prepare a homogeneous sample so that leaching experiments would be more reproducible.

The ground sample without further physical treatment was used for PGM dissolution. Preliminary tests showed that appreciable amounts of the PGM in the catalyst losses could be dissolved by boiling the sample in sulfuric acid in the presence of a chloride salt while no oxidizing agent was added. Due to brownish fumes that evolved when the 1 g catalyst sample was added to the leaching solution at the beginning of the experiments, it was assumed that the sample contained nitrogen oxides as a result of the nitric-acid manufacturing process. These nitrogen oxides were thought to act as self-oxidizing agents during dissolution. To confirm this postulation, a sample of the catalyst losses was washed by boiling with bi-distilled water for two hours and leaching tests were carried out using the washed and unwashed samples. Figure 2 shows the leaching behavior of platinum with 60% H₂SO₄ and 0.1 M NaCl at 125°C. The unwashed sample showed a continuous increase of dissolved platinum with time, while the washed sample showed very poor and slow dissolution of platinum. After two hours, <10% and >90% platinum were dissolved from the washed and unwashed samples, respectively. This indicates that the PGM sample has a self-oxidizing agent that was lost during washing in water. Thus, a leaching process in a mixture of H₂SO₄ and NaCl can be established depending on the self-oxidation of the sample.

Effect of Sodium-Chloride Concentration

Sodium chloride was used to study the effect of chloride-ion concentration on the extraction efficiency of platinum, palladium, and rhodium from the catalyst residue. Sodium chloride was preferred to prevent the precipitation of insoluble chloro-complexes that would be favored when KCl and NH₄Cl are

used, particularly in sulfate systems. Experiments were carried out using different sodium-chloride concentrations (from 0.01 M to 0.12 M) in 60% sulfuric acid at 135°C for two hours; results are shown in Figure 3. The addition of sodium chloride was found to be very essential for effective PGM dissolution. The extraction efficiencies of platinum and rhodium in the absence of sodium chloride were very low (about 7%) and steadily increased with higher NaCl concentrations. About 95% of platinum and 85% of rhodium were extracted using 0.1 M NaCl and the extraction leveled off at higher NaCl concentrations. By comparison, palladium was more easily extracted in the absence of NaCl, that is about 40%, and the extraction was enhanced by increasing NaCl concentration and plateaued at 85% with NaCl concentrations of 0.05 M or higher. The PGM are dissolved as their chloro-complexes, such as PtCl₆²⁻, PdCl₄²⁻, PdCl₆²⁻, and RhCl₆³⁻. The stability of these chloro-complexes increases at higher chloride-ion concentrations in solution, and this increases the

dissolution efficiency. The subsequent experiments were performed at 0.1 M NaCl in order to maintain extraction of platinum, palladium, and rhodium at a maximum.

Effect of Sulfuric-Acid Concentration

Different concentrations of sulfuric acid (from 10 to 60 weight percentage) were used for the extraction of platinum, palladium, and rhodium from the catalyst losses at ambient boiling temperature, and the extraction efficiencies of these metals are presented in Figure 4. It is worth mentioning that the boiling temperature of the reaction mixture sharply increased from 105°C for 10% H₂SO₄ to 135°C for 60% H₂SO₄. It is obvious from Figure 4 that extraction efficiencies of platinum, palladium, and rhodium continuously increased with increasing sulfuric-acid concentration but can also be attributed to increasing reaction temperatures. This double effect provides high dissolution temperatures at ambient pressure, which can be advantageous if it proves favorable to using more expensive pressure-leaching systems commonly employed for PGM processing. At 10% H₂SO₄, the extraction of platinum and rhodium was as low as 5% and 1%, respectively, while about 30% of palladium was simultaneously extracted.

Maximum extraction occurred for each metal at 60% H₂SO₄, with platinum at 95% and rhodium and palladium each at 85%. The extraction was on the order of Pd>Pt>Rh at low acid concentration (<50% H₂SO₄) but at higher acid concentrations was somewhat reversed and on the order of Pt>Rh>Pd. Subsequent experiments were therefore performed using 60% H₂SO₄ and 0.1 M NaCl in order to maintain extraction of platinum, palladium, and rhodium at a maximum.

Effect of Temperature

Due to these results, it became necessary to investigate the effect of temperature on the extraction of platinum, palladium, and rhodium at 60% H₂SO₄ and 0.1 M NaCl for two hours. Results are plotted in Figure 5 and indicate that metal extraction increases with increasing temperature but plateaus above 125°C. The extraction percentages

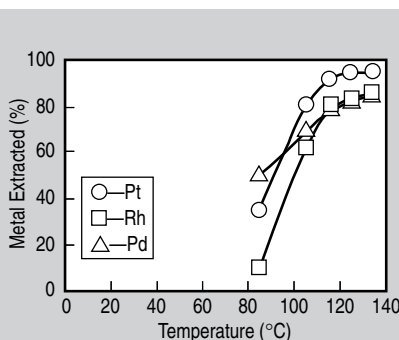


Figure 5. The effect of temperature on the extraction of platinum, palladium, and rhodium. 0.1M NaCl, 2 h, 60% H₂SO₄, S/L = 1:100 g/ml.

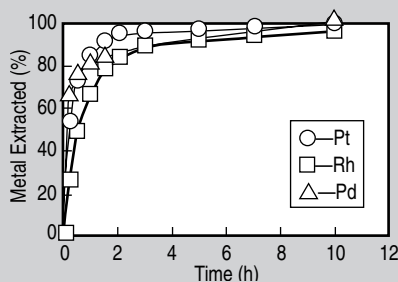


Figure 6. The effect of retention time on the extraction of platinum, palladium, and rhodium. 0.1 M NaCl, 125 °C, 60% H₂SO₄, S/L = 1:100 g/ml.

of palladium, platinum, and rhodium were 50.3%, 35.2%, and 9.7% at 82°C and increased to 85.5%, 94.93%, and 84.9% at 125°C, respectively.

In this regard, the extraction was on the order of Pd>Pt>Rh at low temperatures (<110°C) but at higher temperatures was somewhat reversed and on the order of Pt>Rh>Pd. It is interesting to note, but perhaps not surprising due to the double effect, that these orders were the same as observed for acid concentrations. Subsequent experiments to examine the effect of time were therefore performed using 125°C, 60% H₂SO₄, and 0.1 M NaCl in order to maintain extraction of platinum, palladium, and rhodium at a maximum.

Effect of Retention Time

Figure 6 shows the effect of retention time from 0.25 hour to ten hours on the dissolution of platinum, palladium, and rhodium with 60% H₂SO₄ at 125°C. For each metal, extraction increases with time and is dramatic at times less than approximately two hours then very slowly increased. After ten hours, extraction is practically complete for platinum and palladium and is 96.5% for rhodium. The slow increase in metal extraction after two hours may be due to

the depletion of nitrogen oxide from the system.

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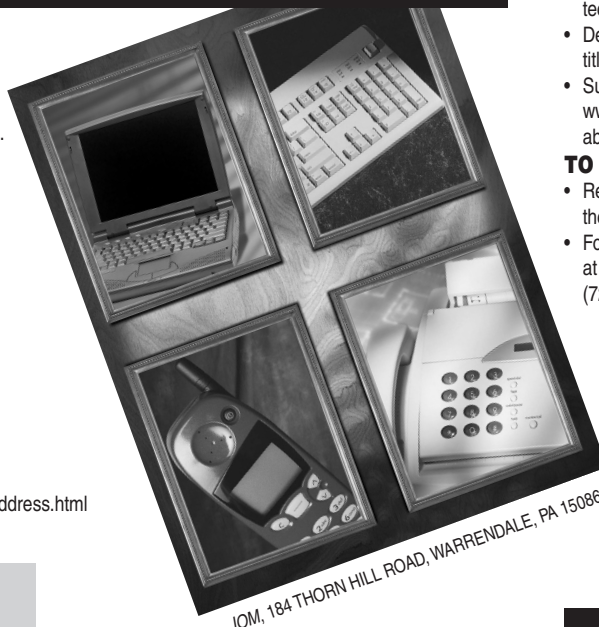
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