

SINGLE STEP SEPARATION AND RECOVERY OF PALLADIUM USING NITROGEN SPECIES CATALYZED PRESSURE LEACHING AND SILICA POLYAMINE COMPOSITES

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Abstract

The efficient separation of palladium from the transition metals copper, nickel and iron can be effected by passing a leach solution of these metals through a column of the silica polyamine composite material, WP-1, patented by Purity Systems Inc (PSI), Assignee, University of Montana with exclusive license to PSI. The separation can be done at the intrinsic pH of a nitrogen species catalyzed (NSC) oxidative pressure leach solution (~0) and stripping of the palladium from the composite can be effected with hydrochloric acid/ammonium chloride solutions at 50°C. Batch capacities of the composite for palladium are ~ 1.8 mmol/g resin. The possibilities for isolating the metal from the strip are discussed. Given the proven longevity and rapid capture kinetics of the polyamine composites, this new approach should prove to be an economically viable alternative to the multi-step concentration processes practiced in the PGM industry to date.

Introduction

The recovery of platinum group metals (PGM) from copper-nickel sulfide bearing ores is becoming increasingly important as the applications of platinum and palladium in the electronics and energy industries continue to grow. Depending on the composition of the ore, the separation of PGM from base metals (BM) involves a variety of multi-step processes that are usually a combination of leaching, flotation, solvent extraction, selective precipitation and/or volatilization in order to obtain a final PGM concentrate that can then be subjected to separation and refinement [1].

Recently, ion exchange (IX) technologies have received increased attention for applications in hydrometallurgy owing to greater process simplicity, efficiency and environmental compatibility [2]. In general, the IX resins are based on a polystyrene matrix but more rigid and hydrophilic matrices such as amorphous silica offer distinct advantages over polystyrene resins. Purity Systems Inc (PSI), in collaboration with the University of Montana (UM), has developed a patented series of silica polyamine composite materials that have shown to be extremely useful in a wide range of

hydrometallurgical applications [3-8]. The specific advantages of silica polyamines over polystyrene resins are presented in Table I. Related technologies such as the IBC-MRI technology offer similar advantages but have not been shown to have the demonstrated longevity of the PSI/UM materials [9].

Table I. Advantages of Composite Resins over Polystyrene Resins

- No shrink-swell in load-strip-regenerate cycles. Ideal for up or down flow fixed beds.
- Faster capture kinetics allows use of shallower beds.
- Available in four particle sizes: 200-165, 94-74, 74-38, and 38-22 mesh
- Faster operational flow rates at higher capacities than conventional resins.
- More porous structure gives lower pressure drops at comparable particle sizes.
- Much longer usable lifetimes due to more rigid structure.
- Shipped dry (<10% water) compared with 45-50% water for polystyrene
- Higher maximum operating temperature (110 °C) compared with 70 °C for polystyrene.
- More stable to radiolytic decomposition.
- Stable over a wide range of alkalinities and acidities.

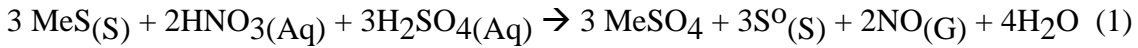
We report here the application of a poly(ethyleneimine) silica composite, WP-1, to the separation of palladium from nickel, copper and iron containing solution obtained from a nitrogen species catalyzed (NSC) oxidative pressure leach of copper – nickel sulfide ore.

Nitrogen Species Catalyzed Pressure Leaching

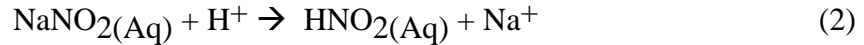
The use of nitric acid in metal sulfide oxidation is not new. Many derivations of the technology have been researched and piloted [10-15]. However, only NSC sulfuric acid pressure leach has ever been built and operated successfully on an industrial scale. Moreover, it has been thoroughly studied and has found successful application in oxidation of other feedstocks including PGM's [16-20]. It offers several definitive advantages. First of all, it is the only proven industrial process over the long term for pressure leaching of copper sulfides and direct precious metal recovery. Second, the rate of reaction is much faster and subsequent required reactor volume is thus smaller. Third, the process does not require excessively high temperatures or pressures. Fourth, the ORP can be adjusted and controlled to be extremely high so it oxidizes almost any sulfide at low oxygen overpressures. Fifth, the materials of construction are readily available stainless steels so there is no need for titanium cladding or brick with lead liners. Thus the capital and maintenance costs are less. Also, because of the simpler internal design, direct heat exchange can be utilized in-situ for optimal temperature control. Further, in a manner analogous to existing Ni/Co laterite HPAL systems, the energy from the in-situ heat exchanger can be readily utilized for optimizing the plant heat balance or co-generating electrical power resulting in significant process operating cost savings. Sixth, there is no need for a dip tube or special design radial agitators with cowlings and the like. Oxygen transfer is innate with the enhanced nitrogen species chemistry. So, with no titanium, and no titanium dip tube in particular, there is much less oxygen fire danger. Seventh, the design of the feed pump system is far less of a challenge as is the flash

system and the choke system. Eighth, like a smelter, precious metals recovery can be high and direct. Ninth, there is no sophisticated chloride chemistry or resultant corrosion issue to deal with. Tenth, by-product elemental sulfur formation, handling and treatment for contained gold recovery is proven and readily accomplished and value added by-products such as sodium sulfate can be produced from the waste streams. Finally, there is only a minor amount of nitrogen species utilized and it is readily removed and captured by commercially available equipment, so there are no major economic or environmental issues.

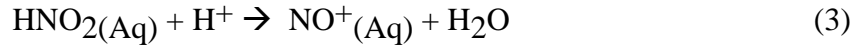
In order to understand the advantages of nitrogen species catalyzed leaching, it is important to review the principles behind it. The commonly reported leach reaction of a sulfide mineral with nitric acid in conjunction with sulfuric acid is shown below:



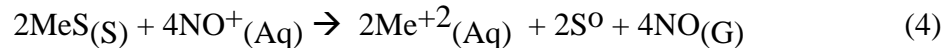
However, it is postulated that the actual reaction species is NO^+ and not NO_3^- [19]. The addition of, or presence of, NO_2^- instead of NO_3^- accelerates the formation of NO^+ . As shown in Table II, the NO^+/NO couple is capable of an extremely high redox potential [21]. So, NO^+ is readily formed from nitrous rather than nitric acid. For example, a convenient source of nitrous acid can be sodium nitrite [18]. When it is added to an acidic solution, nitrous acid is readily formed.



Nitrous acid further reacts to form NO^+ .



The NO^+ then reacts with the mineral and oxidizes the sulfide to sulfur.

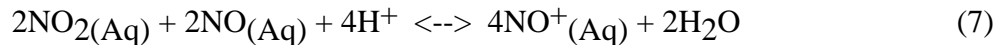


Of course, at higher temperatures and/or nitrogen species concentrations, the sulfide would be fully oxidized to sulfate.

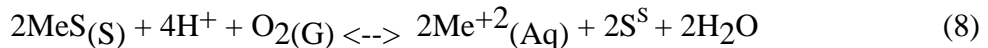
Table II. Relative Potentials of Hydrometallurgical Oxidizers [21]

Oxidant	Redox Equation	E^0_h (pH = 0, H ₂ ref.)
Fe ⁺³	Fe ⁺³ + e ⁻ → Fe ⁺²	0.770 V
HNO ₃	NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO(g) + 2H ₂ O	0.957 V
HNO ₂	NO ₂ ⁻ + 2H ⁺ + e ⁻ → NO(g) + H ₂ O	1.202 V
O ₂ (g)	O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.230 V
Cl ₂ (g)	Cl ₂ (g) + 2e ⁻ → 2 Cl ⁻	1.358 V
NO ⁺	NO ⁺ + e ⁻ → NO(g)	1.450 V

As can be seen, nitric oxide gas, NO, is produced from the oxidation of sulfides. As this gas has a limited solubility in aqueous solutions, it tends to transfer out of solution. In the pressure leach system, a closed vessel with an oxygen overpressure is used. The nitric oxide gas emanating from the leach slurry accumulates in the headspace of the reactor where it reacts with the supplied oxygen to form nitrogen dioxide gas. The NO is then regenerated to NO⁺. Overall, this can be viewed as:



Since the nitrosyl ion is continuously regenerated, its role in the overall reaction as the actual oxidizer is not obvious. The net overall reaction has the sulfide mineral reacting with the acid solution and oxygen to solubilize the metal value into the sulfate solution and form elemental sulfur (at low temperatures):



or sulfate (at high temperatures):



Overall, the nitrogen intermediates serve as an expedient means to transport oxygen to the surface of the solid particle and allow the resulting reaction to take place at a heightened redox potential. This inherent asset of the unique system precludes the use of high temperatures and high pressures, which lead to higher costs in other pressure leach processes. For example, commonly available stainless steel can be used for the reactor vessel. And, complete oxidation of sulfide to sulfate can be achieved without the excessive conditions found in other pressure leach systems. Finally, the rapid kinetics of the system leads to smaller reactor volumes and higher unit throughputs.

Nitrogen Species Catalyzed Pressure Leaching of PGM Materials

The application of NSC oxidative pressure leaching is illustrated by testing both a PGM smelting concentrate and a chalcopyrite, pentlandite palladium bearing ore on a lab scale. In this case, the partial oxidation of sulfide to sulfur was the goal. The test conditions and results are illustrated in Tables III, IV, V VI, VII and VIII.

Table III. Composition of PGM Smelting Concentrate Tested

<u>Pt g/T</u>	<u>Pd, g/T</u>	<u>Rh, g/T</u>	<u>Ni, %</u>	<u>Cu, %</u>	<u>Fe, %</u>	<u>Total S, %</u>
2004	5967	538	19.5	12.3	34.2	25.5

Table IV. Nitrogen Species Catalyzed Partial Sulfide Oxidation Leach Conditions

Initial Free Sulfuric Acid = 50 g/L
 Reactor Working Pressure = 620 kPag
 Slurry Solids Content = 100 g/L
 Solids Size = 80% -40 micron
 Maximum Temperature = 125° C
 Nitrogen Species Concentration = 2.0 g/L
 Reaction Time = 45 minutes

Table V. Mass Distribution of Nitrogen Species Catalyzed Partial Sulfide Oxidation Leach of PGM Smelting Concentrate Products

	<u>Pt %</u>	<u>Pd %</u>	<u>Rh, %</u>	<u>Ni %</u>	<u>Cu %</u>	<u>Fe %</u>	<u>Total S, %</u>
Solution	0.0	99.7	99.6	99.5	99.6	93.8	78.3
Residue	100.0	0.3	0.4	0.5	0.4	96.2	11.7

Table VI. Composition of Chalcopyrite, Pentlandite Palladium Bearing Ore Tested

<u>Cu, %</u>	<u>Co, %</u>	<u>Ni, %</u>	<u>Fe, %</u>	<u>Pd, g/T</u>	<u>Total S, %</u>
0.85	0.10	0.74	0.91	6.2	2.36

Table VII. Nitrogen Species Catalyzed Partial Sulfide Oxidation Leach Conditions

Initial Free Sulfuric Acid = 50 g/L
 Reactor Working Pressure = 620 kPag
 Slurry Solids Content = 100 g/L
 Solids Size = 80% -40 micron
 Maximum Temperature = 125° C
 Nitrogen Species Concentration = 2.0 g/L
 Reaction Time = 25 minutes

**Table VIII. Mass Distribution of Nitrogen Species
Catalyzed Partial Sulfide Oxidation Leach of Chalcopyrite,
Pentlandite Palladium Bearing Ore**

	Cu, %	Co, %	Ni, %	Pd, %	Fe, %	Total S, %
Solution	97.3	99.4	99.6	>99.0	95.3	1.5
Residue	2.7	0.6	0.4	ND	4.7	98.5

As can be seen in both cases, this industrially proven low temperature and low-pressure system was effective in leaching the palladium, rhodium, copper, cobalt, nickel and iron. Platinum is also successfully solubilized in the NSC system with the addition of chloride for complexation [22]. The applicability has also been confirmed on testing of other PGM bearing materials such as tailings, pyrometallurgical mattes, secondary recycled materials and concentrates.

Ion Exchange Experimental Methods

General

The silica poly(ethyleneimine) composite, WP-1, was synthesized according to patented [8] and published [7] literature procedures. Palladium chloride and nickel sulfate were from Fischer Scientific and were used as received. NSC oxidative pressure leach solutions were obtained by the procedures noted by treating samples obtained from Stillwater Mining. Metal concentrations were measured on a Thermo Electron Atomic Absorption Spectrometer or colorimetrically on a Perkin Elmer Lambda 2. Flow tests were done using an FMI piston driven pump. pH was measured with a VWR Symphony pH meter using a glass pH electrode. Metal concentrations are reported with a precision of $\pm 10\%$ throughout.

Batch Capacity Tests

Batch capacities of WP-1 for palladium were evaluated by equilibrating 0.1 g of WP-1 with 20mL of a 1500mg/L solution of palladium chloride for 24 hours with occasional shaking of the capped 22mL vial. The pH of the palladium solution was adjusted by drop wise addition of 95% sulfuric acid. The solution was then carefully decanted from the composite and the concentration of residual palladium was measured by measuring the absorbance of the solution at 474nm and comparison with a standard Beer's law plot. Batch capacities were measured at pH = 0.0, 0.5, and 1.0.

Flow Separations Tests

Mock Nickel – Palladium Solution.

A solution containing 200mg/L of palladium and 900mg/L nickel was prepared from palladium chloride, nickel sulfate and deionized water. The solution was pumped through a 5cc column containing 3.5g of WP-1 at 0.5BV/min for 30 bed volumes. The column was then rinsed and then stripped using 25mL of a solution of 10 M hydrochloric acid containing 1% (weight/volume) ammonium chloride that had been preheated to

50°C. The flow-through and the strip were then analyzed for nickel and palladium by atomic absorption spectroscopy.

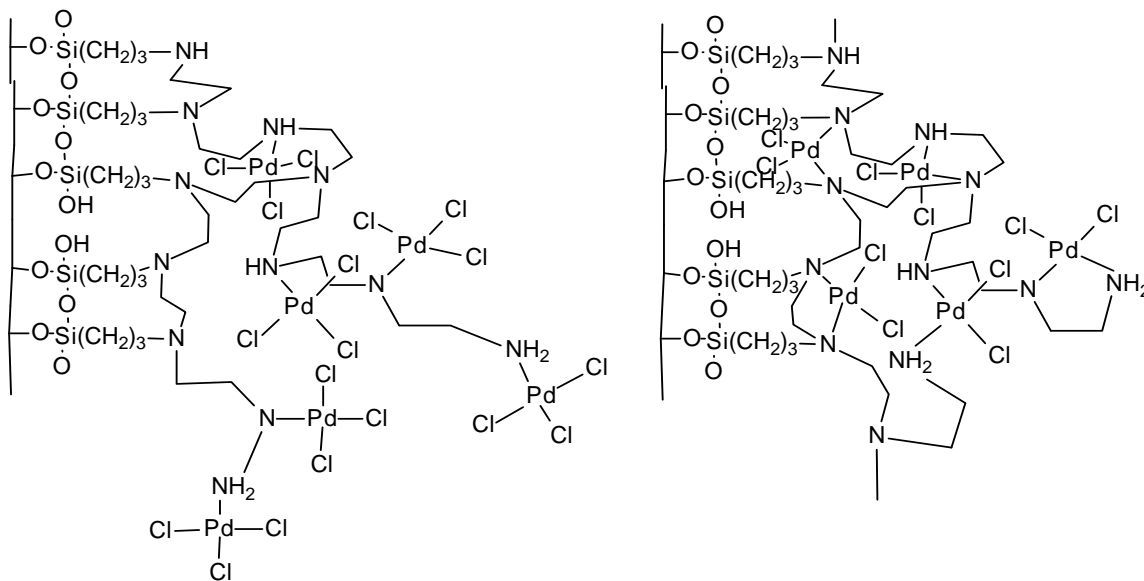
Nitrogen Catalyzed Oxidative Leach Solution.

A leach solution containing 6100mg/L iron, 17000mg/L nickel, 26000mg/L copper and 81mg/L palladium was adjusted to pH = 0 with 95 % sulfuric acid (original pH =0.4). 500mL of the solution was pumped through a 5cc column containing 3.5g of WP-1 at 0.5 BV/min. The flow-through was analyzed for metals every 100 mL by atomic absorption spectroscopy and after rinsing with 25mL water the column was stripped with 60mL 10 M hydrochloric acid containing 1% ammonium chloride at 50 °C. The strip was analyzed for all metals.

Results and Discussion

The batch capacity of WP-1 for palladium was evaluated at pH = 0.0, 0.5 and 1.0. The values obtained were 187, 196 and 205mg Pd/g WP-1 respectively, giving an average capacity of 1.84mmol/g (0.184mol/100g resin) over this pH range. The percent nitrogen in WP-1 is 4.9% on average, which translates to 0.35mol N/100g WP-1. The silanized silica gel prior to grafting of the polyamine had a chloropropyl content of 0.16mol Cl/100g silica composite. After grafting of the polymer the chloropropyl content was <0.10 %. This means that there are 0.19mol N /100g WP-1 available for binding metals if one assumes that the nitrogen atoms bound to the anchor propyl groups are not available for binding to the metal. This is consistent with one nitrogen atom/Pd atom and suggests that the bound species is a *cis*-(R₂NH)PdCl₃⁻. If all the nitrogen atoms are involved, then there are ~two nitrogen atoms per palladium and the bound species can be described as (R₂NH)₂PdCl₂. Based on the difficulty encountered in stripping the palladium from the gel (*vide infra*) the latter situation seems most likely. The poly(ethyleneimine) is a branched polymer (MW=1200) that consists of 35% primary amines, 35% secondary amines and 30% tertiary amines. It is reasonable to assume that the tertiary amines are not anchored to the propyl groups but, according to the above analysis, are involved in the coordination of the palladium. A schematic representation of these bonding framework possibilities is shown in Figure 1. Of course, the actual picture may be composite of the two possibilities. The important conclusion from these results is that every available nitrogen atom is involved in coordination to the metal.

The separation of nickel from palladium using WP-1 at pH=0 was demonstrated on the bench scale with a solution containing 200mg/L palladium and 1000 mg/L nickel. A 5cc column containing 3.5 g of WP-1 was loaded with 110mL of the test solution. After rinsing with 25mL of deionized water the column was stripped with 60mL of 10 M HCl containing 1% (mass per volume of 10 M HCl) ammonium chloride at 50°C. Recovery of palladium was 22.9 mg and 22.7 mg palladium were loaded making the recovery of palladium 100% within experimental error. More importantly, no palladium was detected in the nickel flow through and no nickel was detected in the palladium strip.



Anchored nitrogen atoms not involved

$$N/Pd = 1$$

Anchored nitrogen atoms involved

$$N/Pd = 2$$

Figure 1: Schematic representation of the binding of palladium chloride to the silica polyamine composite WP-1.

Furthermore, 19.8 mg of the 22.9 eluted from the column (86%) were contained in a 9.3 mL fraction of the strip at a concentration 2130 mg/L. This gives a concentration factor of 10.7 relative to the feed. The presence of ammonium chloride in the strip solution was critical to obtaining efficient stripping suggesting the formation of *cis*-(NH₃)₂PdCl₂ or (NH₄)₂PdCl₄ as a necessary condition for efficient stripping. The load strip cycle for this separation is illustrated in Figure 2.

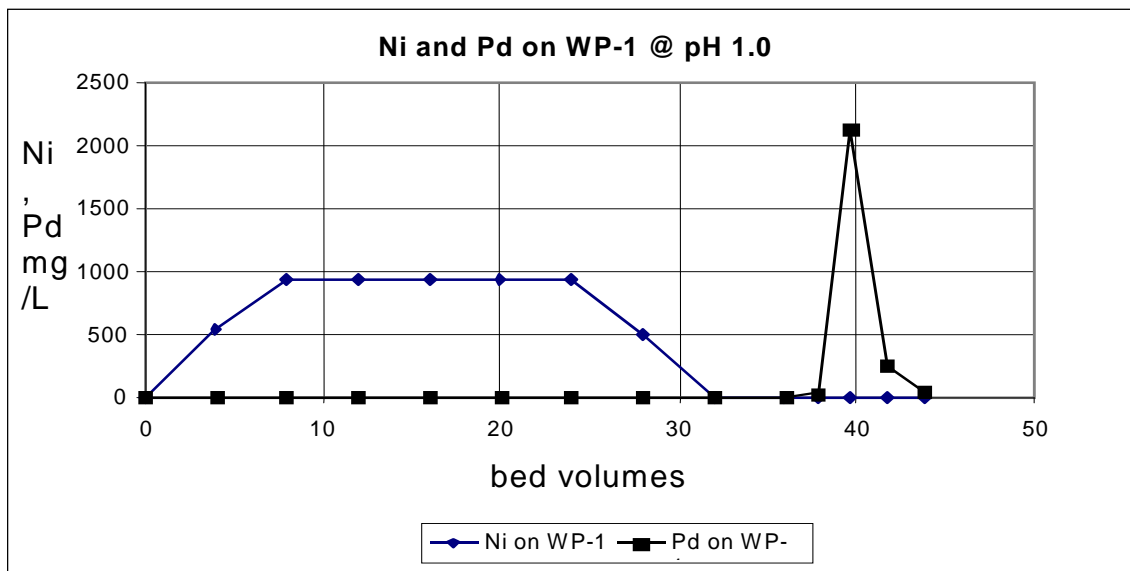


Figure 2: Load-strip cycle plot for the nickel palladium mock solution.

Having successfully demonstrated the ability of WP-1 to separate palladium from a transition metal, we then turned our attention to an actual nitrogen species catalyzed oxidative pressure leach solution. The solution obtained had 86mg/L Pd, 6.4 g/L Fe, 18g/l Ni and 28g/L Cu. The intrinsic pH of the solution was 0.4 but and was adjusted to 0.0 for a direct comparison with the mock solution. After adjustment with 10M HCl the feed concentration was 81mg/L Pd, 6.1 g/L Fe, 16 g/L Ni and 26 g/L Cu. The feed, 500mL, was loaded onto the same 5 cc column of WP-1 and the concentration of metals in the flow-through was measured every 100mL by flame atomic absorption spectroscopy. No palladium was detectable in the flow-through and the concentration of the base metals remained unchanged. The column was then rinsed with 25mL of deionized water and no palladium was detected in the rinse. The column was then stripped with 65mL of 10 M HCl containing 1% weight per volume ammonium chloride. The concentration of base metals in the strip was below the detection limit by AA and of the 41 mg of palladium loaded onto the column 38mg (93%). The major portion of the strip, 30mg (81%), was contained 32ml of the strip. A profile of the load, rinse, and strip cycle is shown in Figure 3.

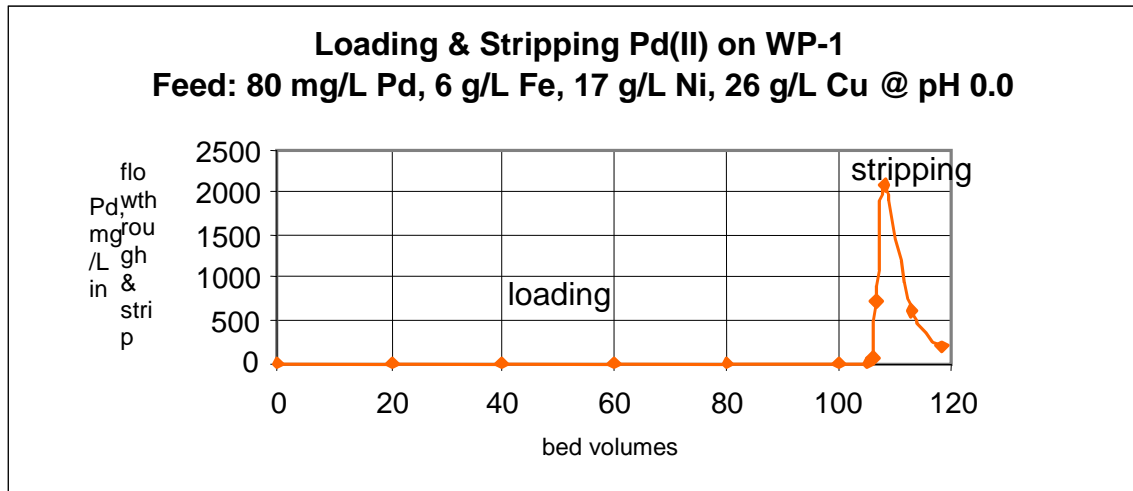


Figure 3: Load-strip cycle for the NSC oxidative pressure leach solution.

These results clearly show that WP-1 can recover palladium from leach solutions even when the concentration of base metals is very large compared with the PGM. The separation is 100% efficient and requires little or no pretreatment of the ore leach. However, most PGM producers would rather have the purified PGM as a solid metal rather than as a solution or as a salt. It should be pointed out that stripping of the HCl/NH₄Cl solution followed by firing of the residue should leave pure palladium metal as the residue since it is well known that salts such as (NH₃)₂PdCl₂ or (NH₄)₂PdCl₄ decompose to palladium metal and NH₃/Cl₂ or NH₃/HCl upon ignition [23]. Studies to evaluate the efficiency of this process and related resins to PGM separations such as rhodium are underway in our laboratories with the reported strip solutions and further studies on the application of WP-1.

Summary

This paper has illustrated a simple yet proven method of leaching palladium using NSC technology followed by the selective recovery of palladium from the acidic base metal metal solutions. The applications for this technology are numerous and joint efforts continue on the recovery of rhodium from acidic NSC base metal solutions utilizing similar techniques.

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