



Leaching and recovery of platinum group metals from UG-2 concentrates

by B.R. Green*, D.M.C. Smit†, H. Maumela†, and G. Coetzer†

Synopsis

Existing processes for the recovery of platinum group metals (PGM) from UG-2 ores place stringent requirements with regard to chromite content upon feed material to the plant. An alternative hydrometallurgical process for which this is not an issue is proposed that involves reductive roasting of the ore followed by leaching with HCl/chlorine, ion exchange, and recovery of PGM from the ion exchange eluate by reduction. Problems associated with leaching of PGM are discussed and results of laboratory testwork for each of the process steps are given.

Introduction

Existing processes for the recovery of platinum group metals (PGM) from UG-2 ores place stringent requirements with regard to chromite content (about 2.8 per cent) upon feed material to the plant. The conventional process sequence involves:

- ▶ smelting of a flotation concentrate to remove gangue material and to produce an iron-nickel-copper-PGM matte
- ▶ converting by blowing air through this matte to oxidize iron sulphide and to transfer the oxidized iron to the slag
- ▶ leaching the resulting copper-nickel-PGM matte to dissolve the copper and nickel and obtain a residue for feed to the refinery.

A drawback of this process is the build-up of chromium bearing spinels in the furnace when treating UG-2 materials that restricts the chromium content of the feed to the furnace.

When the present work was started about a decade ago, it was estimated that an extra 2–3 per cent of PGM might be recovered if 10 per cent chromite were allowed into the concentrate during flotation. Furthermore, waste dumps from chromite mining of LG-6 and MG-1 ores also containing PGM were estimated to represent a resource of 350 000 oz. Current arisings from these operations added another 50 000–75 000 oz per annum.

Alternative options including pyrometallurgical and hydrometallurgical processes were

considered, and this paper deals with the hydrometallurgical route.

Background to leaching

Leaching of PGM from ores is not trivial and was expected to be the most problematic step in a hydrometallurgical process. Some effort has been expended by different investigators on evaluating and testing possibilities for leaching of various types of ores.

In Mintek's most significant work, the mineralogy of a feed to a leach was shown to affect PGM recovery¹⁻³. In the case of a UG-2 feed tested², only 30 per cent of PGM grains were liberated, and 60 per cent of PGM grains were associated with base metal sulphides (BMS; mainly pentlandite and chalcopyrite) either on edges or locked into BMS. Eighty-five per cent occurred as PGM-sulphides and the remainder as compounds with arsenic, bismuth, tellurium, antimony, iron, lead or mercury. Hence, accessibility of lixiviant to non-liberated PGM and refractory species such as PGM-sulphides would be expected to cause poor direct leachability.

This had been found during preliminary testwork³ in which a variety of lixiviants were evaluated before and after a nitric acid pressure oxidative pre-leach. The lixiviants were hydrochloric acid (HCl)/chlorine, bromine, cyanide, thiocyanate, polysulphide, and sulphite. Generally, results were not good, but an oxidative nitric acid pressure pre-leach at 105°C improved PGM recoveries slightly, particularly with HCl/chlorine and cyanide lixiviants.

More comprehensive work² on UG-2 involving oxidative nitric acid pre-leach (150°C) followed by cyanide leaches indicated that BMS were almost totally decomposed during the pre-leach. PGM sulphides were unchanged and refractory, thus PGM leach

* Mintek, Randburg, South Africa.

† Formerly of Mintek.

© The South African Institute of Mining and Metallurgy, 2004. SA ISSN 0038-223X/3.00 + 0.00. Paper received Jan. 2004; revised paper received Apr. 2004.

Leaching and recovery of platinum group metals from UG-2 concentrates

yields were not good (less than 40 per cent). Platinum leaching was particularly poor with cyanide (ambient temperature). A HCl/chlorine leach on untreated material had the same effect as a cyanide leach with a nitric acid pre-leach, which led investigators to believe that dissolving base metals in both cases exposed some of the non-refractory PGM, which were then amenable to leaching.

In this regard, various attempts at oxidative leaching to remove or oxidize base metals to upgrade PGM in a substrate have been described by other workers. These included sulphur dioxide/sulphuric acid⁴; 10 per cent HCl followed by 17 per cent hydrogen peroxide in 2 per cent sulphuric acid⁵; oxygen/110°C⁶; pressure oxidation at 190°C (oxidant not specified) followed by cyanide leaching of the residue⁷. The latter method resulted in lower cyanide consumption and increased PGM recovery.

Pre-roasting of UG-2 in air (at temperatures greater than 800°C) converted PGM sulphides to oxide phases and native metals and alloys². HCl/chlorine leaching gave much improved recoveries of platinum (Pt), palladium (Pd), and rhodium (Rh): Pt (96 per cent), Pd (79 per cent), Rh (28 per cent). Cyanide (ambient temperature) still did not leach PGM well (recovery less than 25 per cent). The reason for this was considered to be passivation of the metal, but the low leaching temperature might also have contributed. Much improved leaching was observed with an excess of cyanide at 150°C after a dilute sulphuric acid treatment to remove the presumed oxide layer: Pt (76 per cent), Pd (79 per cent), Rh (43 per cent). Poor leaching of Rh was thought to be due to formation of Rh₂O₃ in the air roast. In a set of experiments employing similar conditions⁸, the effect of grinding in cyanide (75 micron down to 10 micron) after roasting was investigated. Pt leaching improved from 57 to 76 per cent, Pd from 74 to 86, and Rh from 23 to 40 per cent. Consumption of cyanide in these experiments was high, due probably to the high temperature and co-leaching of base metals.

Reductive roasting followed by cooling under an inert atmosphere resulted in significantly higher recoveries than were obtained with the oxidative roast in the case of chloride leaching (6M HCl/chlorine, 90°C)¹: Pt (94–98 per cent), Pd (92–99 per cent), Rh (69–95 per cent). Improved leaching was attributed to formation of native metals and alloys such as Pt-Fe, Pd-Cu-Fe, Pt-Pd-Fe, Pt-Rh-Fe-Ni and Pd-Pb from PGM sulphides. Greater variation with different reductants was obtained for Rh with the lower Rh leaching results being attributed to alloys: Pt-Rh-Fe-Ni, Rh-As-Fe-Ni. No cyanide leaching was done on these materials but in subsequent work⁸, also on UG-2 materials, cyanide leaching of reductively roasted ore (excess cyanide, 150°C) gave relatively poor recoveries: Pt (16–38 per cent), Pd (26–42 per cent), Rh (13–27 per cent). This work employed carbon monoxide as the reducing atmosphere as opposed to Sasol gas and hydrogen that were used in the above work that gave the good results with HCl/chlorine.

A roast-leach procedure has been applied to Stillwater flotation concentrate⁹. The material was roasted at 1050°C to convert BMS to oxides and PGM sulphides to metals. After pre-leaching with sulphuric acid to remove soluble minerals, the PGM were leached at ambient temperature with 6M HCl in the presence of oxidant (hydrogen peroxide, chlorine, hypochlorite, or nitric acid). High recoveries (greater than 90 per cent) were obtained for Pt, Pd and Au.

A much quoted direct leaching method of late is the PLATSOL process developed by Lakefield Research. This method involves high temperature leaching in sulphuric acid/sodium chloride under oxygen. Comprehensive development work was carried out on a copper/nickel float concentrate from Northmet containing PGM¹⁰, with recoveries up to 98 per cent for Pt, 95 per cent for Pd and 96 per cent for Au being obtained. Results, when PLATSOL was performed on other feed materials, were not as good, but leaching had not been optimized¹⁰.

A PLATSOL-type leach was used at Mintek in an attempt to recover Pd (23 g/t) from a material derived from a sulphidic ore. The PGM (Pd:Pt = 4:1) included arsenide and bismuth tellurides. Leaching conditions included: high temperature (220°C), oxygen overpressure of 7 bar (total pressure at temperature, 30 bar), leach time of 3–6 hours, sulphuric acid concentrations between 50 and 100 g/l, and sodium chloride between 0 and 10 g/l. Recoveries of Pd varied between 40 and 50 per cent, with the higher percentage being obtained in the presence of chloride. In the absence of chloride the recovery after 6 hours was only 25 per cent compared with 40 per cent after 3 hours, suggesting re-precipitation of Pd. Limited work on UG-2 was also not promising.

Conclusions drawn from the foregoing information can be summarized as follows:

- ▶ HCl/chlorine leaching and cyanide leaching, when combined with the appropriate pretreatment of substrate, were the most effective methods.
- ▶ Successful leaching requires liberation of the PGM grains and conversion of refractory minerals (sulphides, arsenides, etc.) to native metals, alloys or amenable compounds.
- ▶ This is apparently achieved to varying extents by roasting under appropriate conditions, oxidation, and ultra-fine milling.
- ▶ On conventionally milled material, the more extreme solution oxidation methods are not effective on refractory PGM minerals. High-pressure nitric acid pre-leaching is ineffective—although destroying base metal sulphides, it does not decompose PGM sulphides. PLATSOL-type treatment in Mintek's work is presumed, because of poor results, not to have decomposed refractory PGM. In Lakefield's work, it is presumed that PGM minerals were less refractory because of good results obtained.
- ▶ One approach to a hydrometallurgical process is to remove interference from base metals by a pre-oxidative leach, of which the nitric acid method discussed above is an example, before extracting PGM.
- ▶ For conventionally milled material, roasting is necessary to convert PGM sulphides to metals and alloys. Reductive roasting is preferred with HCl/chlorine leaching, and for good leaching of Rh, cooling of calcine in an inert or reducing atmosphere is necessary. For a cyanide lixiviant, oxidative roasting produced better results.

Process options

Economics of leaching will be influenced by the inherent mineralogy of the feed, the complexity of pretreatment,

Leaching and recovery of platinum group metals from UG-2 concentrates

nature of the lixiviant, conditions that might require sophisticated equipment, and consumption of lixiviant caused by co-leaching of other constituents of the feed. The work discussed above suggested that the only acceptable option from a viewpoint of PGM recovery (target recoveries >95% Pt, >95% Pd, >85% Rh) involved roasting of the ore followed by HCl/chlorine leaching. Since the substrate intended for Mintek's process was a relatively high grade UG-2 concentrate, it was felt that the use of these harsh conditions, requiring special equipment, could be justified.

Recovery of PGM from the leach liquor by precipitation with sulphide was considered to be unsuitable because of the high acidity of the solution. Ion exchange seemed an attractive alternative. The selectivity of resin for PGM would determine whether base metals should be removed prior to the HCl/chlorine leach. Resin-in-pulp (RIP) would be an attractive option to avoid filtration and soluble loss of PGM.

Thus the conceptual process investigated further included:

- roasting
- leaching in HCl/chlorine
- ion exchange
- precipitation of PGM in a form suitable for feeding to a refinery.

Experimental

Roasting

Flotation concentrate was roasted in a Carbolite muffle furnace in the case of a static air roast, or in a Linn muffle furnace in the case of a reductive roast. In the latter procedure, the flow-rate of reductive Sasol gas was 1.5 liters/minute per 110 g of concentrate and the sample was allowed to cool under an argon atmosphere after 3 hours of roasting. Typical conditions are given in the discussion section.

Leaching

A mass of 100 g of roasted material was combined with 6M HCl in a 1:1.5 ratio. Chlorine gas was sparged through the stirred pulp. The leach was carried out at 90°C for 5 hours, whereafter the solids were filtered and washed with de-ionized water and then dried. Extraction efficiencies were

calculated from analyses of solids (fire assay) before and after leaching.

In one experiment a pre-leach was carried out in 6M HCl in the absence of chlorine to ascertain whether base metals could be removed selectively without dissolving PGM. Analysis of the solution was done by ICP-OES.

Ion exchange extraction

Ion exchange had to be conducted on synthetic solutions that resembled typical leach liquors because of an insufficient quantity of concentrate to produce enough leach liquor. Thus, the solution of composition given in Table I was prepared from chloride salts to contain residual 6M HCl. It was further subjected to conditions of leaching (95°C/3 hours with chlorine bubbling followed by 90°C/1 hour without bubbling to remove free chlorine). The potential of the final solution was 833 mV (Pt: Ag/AgCl), which was similar to that observed for leach liquors. Similar solutions were prepared at lower residual HCl concentrations so that the effect of this parameter could be evaluated.

Various strong- and weak-base resins were screened to obtain the one that best met the requirements for the process, i.e. relatively high capacity for all PGM. One of the more favourable resins and the one used in the present work was manufactured by Reilly and designated HP425.

Equilibrium loading curves

One-millilitre samples of resin were contacted with different volumes of synthetic PGM liquor and allowed to equilibrate at room temperature for 16 hours. Resin loadings were calculated from the changes in solution concentration. Isotherms were generated for different HCl concentrations (2.1M, 2.5M, 3.4M and 6.1M HCl). An isotherm was also generated at 6.1M HCl with a solution that contained no base metals.

Evaluation of different eluants

Six millilitres of resin was fully loaded in a column by passing synthetic pregnant solution through the resin at 4 bed-volumes (BV)/hour for 81 hours. The resin was washed with water to a final pH of 1.7. A dried sample of resin was analysed and metals loaded on the resin were calculated (Table II).

Table I

Metals and concentrations (mg/l) in synthetic PGM leach liquor

Pt	Pd	Rh	Ru	Ir	Au	Cu	Ni	Zn	Co	Cr	Fe	Pb
59.4	37.2	10.3	9.9	3.5	0.3	1180	994	7.7	23.0	104	5040	3.8

Table II

Metal concentrations on resin loaded for elution testwork

Metal analysis on dry resin, %						Calculated metal loading on resin, g/l					
Pt	Pd	Rh	Cu	Ni	Fe	Pt	Pd	Rh	Cu	Ni	Fe
3.5	0.7	0.25	0.02	<0.02	0.03	10.80	2.16	0.77	0.06	<0.06	0.09

Leaching and recovery of platinum group metals from UG-2 concentrates

One-millilitre samples of loaded resin were equilibrated with 5 millilitres of each of the different eluants for 16 hours. The solutions were analysed and percentage elution of PGM calculated. Results are given in Table IV.

Elution of resin with water and thiourea/HCl

Six millilitres of resin was loaded in batch with 2 litres of synthetic PGM solution containing 6M HCl. The loaded resin was introduced into a column and eluted (3.3 BV/hour) with about 4 BV of water followed by about 8 BV of thiourea (3 per cent) in 0.1M HCl. A sample of the eluate was taken every 10 minutes, analysed, and the elution profiles plotted.

Effect of elution conditions

A batch of loaded resin was prepared as described in the previous section. One-millilitre samples of the loaded resin were contacted with 5 millilitres of eluant for 20 hours. In the first set of experiments the concentration of thiourea (in 0.1M HCl) was varied. In the second set, HCl concentration was varied while thiourea concentration was maintained at 0.5M. In the third set temperature was varied for an eluant with composition 0.5M thiourea in 0.1M HCl. Solutions were analysed for metal content.

Precipitation of PGM

A synthetic solution was prepared containing Pt (2430 mg/l), Pd (499 mg/l) and Rh (252 mg/l) to resemble an eluate obtained by stripping the resin with thiourea. Metallic Pt was dissolved in aqua regia and the solution was boiled until the residue was almost dry. This product, PdCl₂ and RhCl₃.H₂O were dissolved in 0.1M HCl. All three solutions were combined and thiourea was added to be present at a concentration of 5 per cent.

The synthetic eluate (50 ml) was put into a Berghoff autoclave equipped with a thermostat heater and pressure gauge. The reactor was flushed five times with hydrogen and then pressurized with hydrogen while heating. Two reactions were carried out at 95°C/5.7 bar/ 3 hours and 140°C/5.8 bar/5 hours, respectively. At the end of the reaction period, the supernatant solution was analysed for PGM.

Results and discussion

Roasting and leaching

Extensive investigations of roasting and leaching have been

carried out at Mintek and elsewhere. As discussed, roasting is a necessary step to convert base metal sulphides to oxides, and PGM to their elemental states or alloys. In these forms they are amenable to oxidative leaching in strong hydrochloric acid solution. HCl/chlorine lixiviants gave consistently better results than the next best lixiviant, which was generally cyanide. Extraction efficiencies for HCl/chlorine leaches on reductively roasted ore were affected significantly by the composition of the reductant used during roasting but were quite reproducible when the same reductant was used.

Typical results obtained with two different UG-2 ores using HCl/chlorine leaching are given in Table III. It is evident from a comparison of results for Ore A that a reductive roast produces higher extraction efficiencies than does a static air roast, particularly in the case of Rh. It has been suggested¹ after mineralogical investigations that reductive roasting results in the formation of alloys rich in iron and nickel that enhance leachability of PGM. The relatively poor leaching of Rh from oxidatively roasted material has been ascribed to it being partially present as R₂O₃. Iridium (Ir), osmium (Os), and ruthenium (Ru) extractions from reductively roasted material were not quite as good as those for the targeted PGM, and varied between about 80 per cent and 50 per cent.

There appeared to be a slight dependence of leaching efficiency on liquid to solid ratio. This is evident from a comparison of the first and second results on Ore B, carried out at ratios of 1.5 and 3, respectively. The third test on Ore B illustrates the effect of pre-leaching the roasted ore with 6 M HCl in an attempt to remove base metals. This was not very successful, but the result did suggest that removal of some of these metals had a beneficial effect on PGM extraction.

In summary, it would appear that reductive roasting of sulphide ores followed by leaching with 6M HCl could result in PGM extractions in the region of 95 per cent.

Ion exchange

Liquor derived from leaching of roasted ore contains PGM and base metals in equilibrium with relatively high concentration hydrochloric acid. The objective of an ion exchange step is to upgrade PGM, as a mixture, in concentration and purity. Reactivities of the metals undergoing ion exchange reactions depend to a degree on the concentration of the

Table III
Extraction efficiencies of PGM and base metals under different conditions

Ore	Roast	a Extraction efficiency, %					
		Pt	Pd	Rh	Cu	Ni	Fe
Ore A	Sasol gas, 1000°C, 3 h, cool under Ar	95.7	96.5	94.2			
Ore A	Static air, 800°C, 3 h, cool under air	93.3	90.3	22.5			
Ore B	Sasol gas, 1000°C, 3 h, cool under Ar	91.6	96.6	92.6	98.6	99.6	32.8
Ore B	Sasol gas, 1000°C, 3 h, cool under Ar	^b 94.2	98.6	94.4	98.5	99.9	33.3
Ore B	Sasol gas, 1000°C, 3 h, cool under Ar	^c 0	0	0	41.8	104.1	25.5
		^d 92.9	99.3	94.4	100	95.1	36.6

a. Extraction efficiencies were calculated from analyses of solids (fire assay) before and after leaching. No solution analyses except where indicated.

b. Liquid/solid ratio, 3.

c. Pre-leach with 6M HCl: liquid/solid, 1.5; 96°C; 6 h; extraction efficiency based on analysis of leachate.

d. HCl/chlorine leach after HCl pre-leach.

Leaching and recovery of platinum group metals from UG-2 concentrates

acid¹¹. Pt and Pd, designated primary PGM, exist as the same complex, depending on solution potential, at all acid concentrations (PtCl_6^{2-} , PtCl_4^{2-} , PdCl_4^{2-}), secondary PGM (Rh, Ir, Ru, Os) are present as equilibrating mixtures of chlor- and aquochloro-complexes (e.g. $\text{RhCl}_6^{3-} \leftrightarrow \text{RhCl}_5(\text{H}_2\text{O})^{2-}$). Base metals such as copper and iron form chlorocomplexes at high acid concentrations in equilibrium with cations, which become the more prevalent species at lower acid concentrations. (e.g. $\text{FeCl}_4^- \leftrightarrow \text{FeCl}_3(\text{H}_2\text{O})_3 \leftrightarrow \text{FeCl}_2(\text{H}_2\text{O})_5^+$). Thus, the affinity of an anion exchange resin for these metals is expected to decrease in the order primary PGM > secondary PGM > base metal and the differential is expected to become greater as acid concentration is reduced. These predictions suggested that PGM might be separable from base metals by adjustment of acid concentration before loading or during elution of the loaded species. However, it is difficult to predict absolute selectivities.

Mintek's first objective was to screen different types of resins to identify the more promising ones. These included conventional strong- and weak-base anion exchangers, and resins with thiuronium-, thiourea-, guanidine- and pyridine-based groups. The screening tests involving batch extractions from a real leach liquor indicated overwhelmingly the superiority of the pyridine-based resins. Thus these were favoured over the next best resins containing thiourea groups because of the expectation that the latter would be difficult to elute. Thus, results of a more comprehensive characterization of loading and elution behaviour of the Reillex HP425 pyridine resin is discussed below.

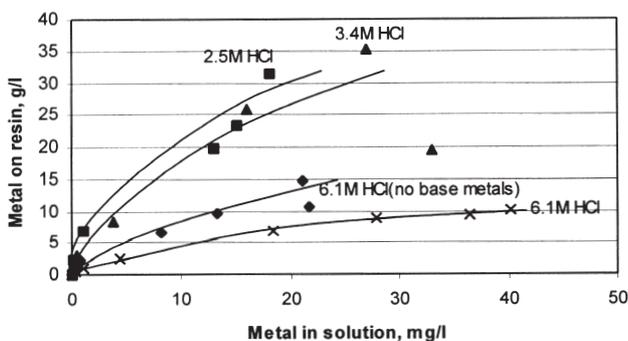


Figure 1—Loading of platinum at different HCl concentrations

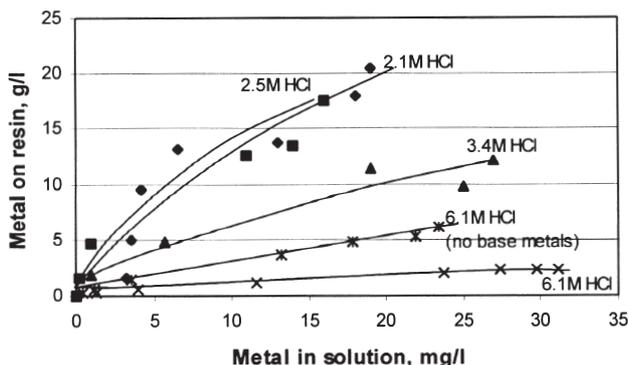


Figure 2.—Loading of palladium at different HCl concentrations

Loading curves

Loading curves (Figures 1 to 3) were generated for a typical synthetic solution at different HCl concentrations that contained PGM and base metals. Each point on a curve was obtained from a batch equilibration of resin with solution. For a solution of particular HCl concentration the ratio of resin to solution was varied to obtain an appropriate spread of points, particularly for the PGM. Base metal concentrations, being relatively higher than the PGM, did not reduce significantly, resulting in bunching of points on the graphs (Figures 4 to 6). Metal loaded on resin was calculated from the difference between metal concentrations in solution, before and after equilibration. This method is susceptible to accumulation of errors, especially where differences in

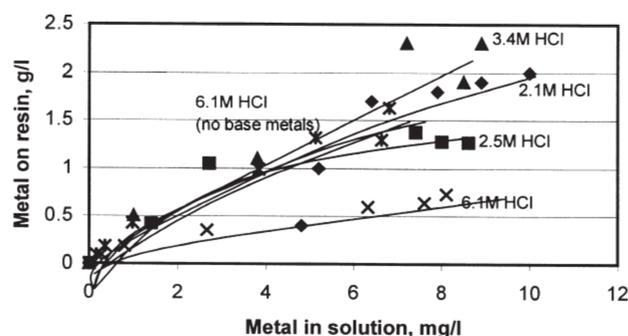


Figure 3—Loading of rhodium at different HCl concentrations

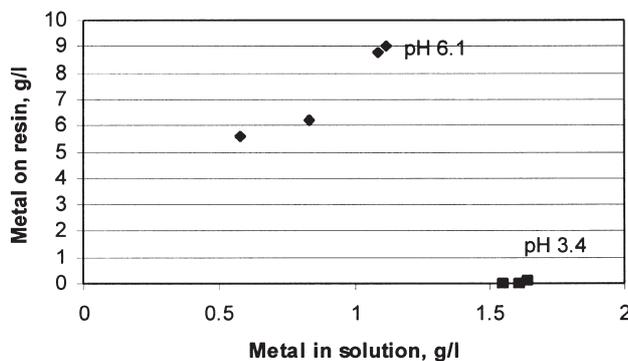


Figure 4—Loading of copper at different HCl concentrations

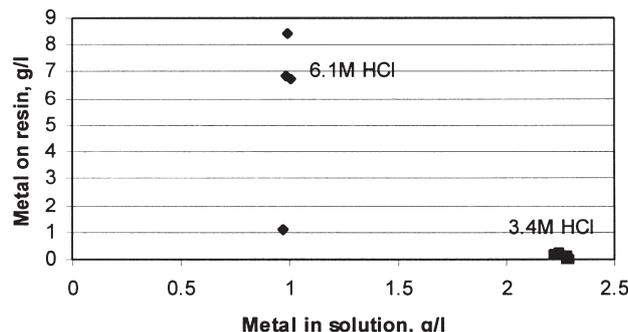


Figure 5—Loading of nickel at different HCl concentrations

Leaching and recovery of platinum group metals from UG-2 concentrates

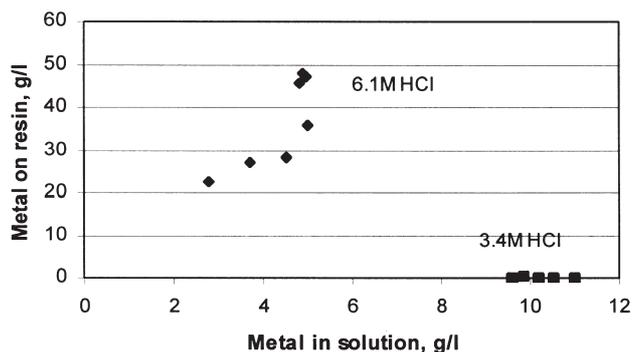


Figure 6—Loading of iron at different HCl concentrations

solution concentrations are not great, and results in a degree of scatter of point. Notwithstanding this problem, trends are quite clear and the series of experiments served their purpose as discussed below.

Equilibrium loading data for Pt, Pd, and Rh at different HCl concentrations are given in Figures 1 to 3. Good loading was obtained at relatively low solution concentrations resulting in upgrading ratios of about 300 to 1000 under the most favourable conditions with order of selectivity, Pt>Pd>Rh. The general trend appeared to be an increase in PGM loading as the concentration of HCl was decreased. As discussed above, at lower HCl concentrations the aquochloro-complexes of the base metals become more important. Thus, positively charged species that will not load onto an anion exchange resin are more prevalent. This clearly occurred in the present situation as evidenced by the loading of copper, nickel and iron, shown in Figures 4 to 6. Where significant loading occurred in the presence of 6.1M HCl, adsorption of these metals in 3.4M HCl was negligible. Therefore, it seemed that competition for resin sited from base metals at the higher HCl concentration was responsible for depression of PGM loading. Confirmation of this was sought by loading the PGM from a solution that contained 6.1M HCl but no base metals. The graphs of these experiments (Figures 1 to 3) indeed indicate that the absence of base metals results in higher PGM capacities. However, levels of loading were not elevated to those obtained by decreasing HCl concentration. It is thought that competition from chloride could also have been a contributing factor at the higher HCl concentration and that, together with base metal chlorides, it competed with PGM for resin sites.

The results of loading tests suggest that solution chemistry can be exploited to differentiate between base

metals and PGM. Loading from 3M HCl results in selectivity for PGM, and obviates the need for removal of base metals by doing a pre-leach. A further advantage is that the resin inventory will be reduced because of the increased capacity for the PGM. A disadvantage is that the leach liquor containing 6M HCl would have to be diluted, and the barren solution concentrated up again. It is thought that this step could be combined with a METSEP-type process* to eliminate base metals from the circuit and recover pure HCl to be recycled.

Elution

Different eluants were evaluated for the stripping of resin loaded with Pt, Pd and Rh and results are given in Table IV. Thiourea was clearly the best eluant, although there seemed to be a general problem with stripping of Rh.

A more comprehensive column elution test was done with acidic thiourea, to ascertain the possibility of removing base metals with water prior to the PGM in the event that loading conditions are employed that will co-load base metals. Thus, the first four bed-volumes of eluant were water, which was followed by an eluant comprising 3 per cent thiourea in 0.1M HCl. The results for water elution, summarized in Figure 7, are consistent with the chemistry discussed for base metals. Dilution of the HCl phase that contains chloro-complexes causes them to revert to cationic species. Since cations cannot remain in micropores of the positively charged anion exchanger, they are eluted. Copper, nickel and iron are removed from the resin during the first two bed-volumes of the water elution. On changing to the thiourea eluant, PGM were eluted. Pt and Pd emerged from the column simultaneously almost immediately and were completely removed after four bed-volumes of eluant had passed through the column. The elution behaviour of Rh suggested that the loading mechanism of this metal is not analogous to that of Pt and Pd as the elution peak lagged and tailed somewhat. Furthermore, only 20–30 per cent of the Rh was removed. No attempt has been made so far to investigate this aspect of the ion exchange process, which will require a study of the chemistry of Rh in relation to the resin system employed. The observation that some Rh was eluted in this case compared to none in the previous experiment suggests that a solution to the poor elution of Rh is possible.

* METSEP is designed for treating pickle liquor, which involves pre-concentration of the liquor and then spray roasting. Dissolved solids in the HCl solution report to the base of the reactor.

Table IV

Evaluation of different eluants

	Eluant concentration, mg/l						Metal eluted, %					
	Pt	Pd	Rh	Cu	Ni	Fe	Pt	Pd	Rh	Cu	Ni	Fe
5% NH ₄ OH	524	385	0.58	2.2	<1	<1	24.3	89.1	0.4	18.3	8.3	5.6
5% Thiourea in 0.1M HCl	1920	427	0.14	3.4	2.1	3.1	88.9	98.8	0.1	28.3	17.5	17.2
5% NaOH	338	0.19	0.02	<1	<1	<1	15.6	0	0	8.3	8.3	5.6
1M NaCl in 0.1M HCl	0.28	0.07	0.01	1.1	2.7	<1	0	0	0	9.2	22.5	5.6
0.5M HCl	0.14	0.01	0.01	2.5	2.2	<1	0	0	0	20.8	18.3	5.6

Leaching and recovery of platinum group metals from UG-2 concentrates

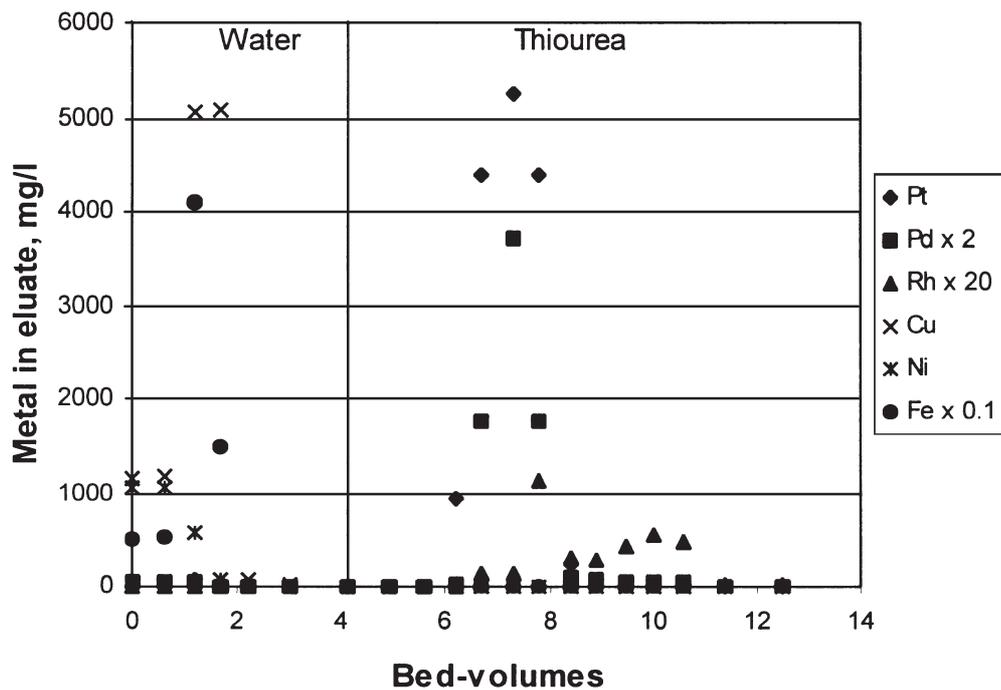


Figure 7—Elution of base metals with water and PGMs with thiourea/HCl

Table V
The effects of different conditions on elution

Thiourea, M	Effect of Thiourea concentration on PGM in eluate (HCl, 0.1 M; temperature, ambient)		
	Pt, mg/l	Pd, mg/l	Rh, mg/l
0.000	<1	<1	<2
0.008	<1	<1	<2
0.080	1800	430	<5
0.240	1740	684	21
0.480	2040	784	33
0.600	2590	1010	45
0.680	2410	933	45
HCl, M	Effect of HCl concentration on PGM in eluate (Thiourea, 0.5 M; temperature, ambient)		
	Pt, mg/l	Pd, mg/l	Rh, mg/l
0.000	1260	908	35
0.105	1240	937	38
0.225	1080	775	45
0.525	449	205	22
0.750	250	112	17
0.975	216	101	15
1.50	121	51	10
Temperature, °C	Effect of Temperature PGM in eluate (Thiourea, 0.5 M; HCl, 0.1M)		
	Pt, mg/l	Pd, mg/l	Rh, mg/l
20	2010	1560	4
35	2320	1780	12
45	2240	1690	6
60	1550	1180	19
70	1825	1345	46

Leaching and recovery of platinum group metals from UG-2 concentrates

Optimum conditions for a thiourea/HCl elution were sought by varying thiourea concentration, acid concentration and temperature during batch elution experiments, and results are summarized in Table V. The experiments established that an optimum eluant composition is 0.6M thiourea in 0.1M HCl. It was found that increasing temperature had little effect on Pt and Pd elution, but that the amount of Rh eluted increased ten-fold between 20°C and 70°C. More importantly, a further indication of elutability of Rh was obtained. The temperature dependence of elution confirmed the belief that the mechanism of loading of Rh is different to that of Pt and Pd.

Hydrogen reduction of PGM complexes

The ability of hydrogen to reduce precious metals has been discussed in some detail¹². Thermodynamically the process is favourable. For chloride complexes in 1M HCl a hydrogen pressure of 50 psig at a temperature of 80°C produces deposition in less than an hour. The solvent matrix has an important influence on the ability of hydrogen to reduce the metals. In solutions containing weakly binding ligands such as acetate, reduction is fairly rapid and independent of concentration of the ligand. When the ligand interacts more strongly with Pt, the rates are notably slower. Reduction in solutions containing chloride, iodide or ammonia is significantly slower when the ligand concentrations exceed 3M. No reaction occurs in a solution that contains the strong cyanide ligand.

Information on the reduction of PGM in a thiourea solution could not be found, but for the present work it was assumed that the reaction would be less favourable than in chloride because of the thiourea complex being stronger. Thus harsher conditions were employed. A synthetic eluate solution containing Pt, Pd and Rh, when subjected to hydrogen pressure of 5.7 kPa, and heated at 95°C for 3 hours, underwent no reaction. However, the reduction went almost to completion, as shown in Table VI, at 140°C during 5 hours. A black powder product was obtained, the mass of which confirmed stoichiometric reduction.

Proposed process

Various hydrometallurgical process options to obtain a mixed PGM refinery feed from a high chromium substrate could be suggested, based on the foregoing work and on other steps that have not been discussed because of lack of sufficient data. All of the options would involve a reductive roast, assuming the presence of refractory PGM, followed by leaching of the product in a HCl/chlorine solution. These roast/leach conditions are necessary to convert PGM to non-refractory forms and to leach Pt, Pd and Rh with efficiencies

of 95 per cent or more.

Subsequent treatment of the liquor might follow different routes. Conventionally, a liquor would be separated from the solids and subsequent steps would be carried out on a clear solution. PGM could be precipitated immediately, possibly by cementation on to a less noble metal such as copper (preliminary experiments suggest this might be possible). Otherwise, the PGM could be upgraded with resin to obtain a more concentrated and purer solution. If resin is the preferred route, a resin-in-pulp process could be employed to avoid solid/liquid separation and the inevitable soluble losses.

Separation of base metals might be accomplished by a pre-leach, but a more efficient option would be to dilute the pulp sufficiently to render the base metals non-extractable by the anion exchange resin. This operation would necessitate a METSEP-type process that involves evaporation followed by spray roasting to recover the HCl and isolate the base metals in a solid form. An advantage of doing this would be to ensure that the overall process is environmentally friendly.

PGM in the form of a mixture of the metals could be recovered from the eluate from ion exchange by reduction with hydrogen.

The preferred option at present includes RIP, to avoid solid/liquid separation, dilution of the pulp to allow for selective recovery of PGM, elution of the resin with acidic thiourea, and reduction of PGM in eluate with hydrogen. A block flow diagram of the process is given in Figure 8.

Economics

It was considered necessary to apply techno-economic evaluation techniques to the work which Mintek was carrying out on the development of new PGM recovery processes (hydrometallurgical and pyrometallurgical), in order to assess the relative competitiveness against the established process. The constraints of the most up-to-date version of the conventional process with respect to chromite in the feed, and a typical increased recovery that could be expected if this constraint could be lifted (a value of 2.5 per cent based on information received from an operating company), were used as the design basis.

Mintek's techno-economics group did a fairly comprehensive evaluation but stressed that the conceptual nature of the hydrometallurgical process and limited information derived from small-scale bench testwork allowed only an order of magnitude estimate. Advantages such as reduced PGM lock-up and fewer environmental concerns were not taken into account.

Although capital was costed as 26 per cent less than that of a smelting process, operating cost would have been about 82 per cent higher. The high level of operating cost was due mainly to chlorine, which contributed more than half the amount. It was considered that if chlorine could be generated on-site the operating cost would have been reduced significantly, to a level about 29 per cent higher than for smelting. This would have begun to swing economics in favour of the hydrometallurgical process as the net present value (NPV) would become marginally higher.

Other considerations were recovery of base metals, and increased recovery of PGM during leaching, which would have had significant effects on improving the NPV in relation to the smelting process.

Table VI

Metals before and after reduction with hydrogen (140°C/5h)

Metal	Pt	Pd	Rh
Concentration before reduction, mg/l	2430	499	252
Concentration after reduction, mg/l	42	0.3	0.5

Leaching and recovery of platinum group metals from UG-2 concentrates

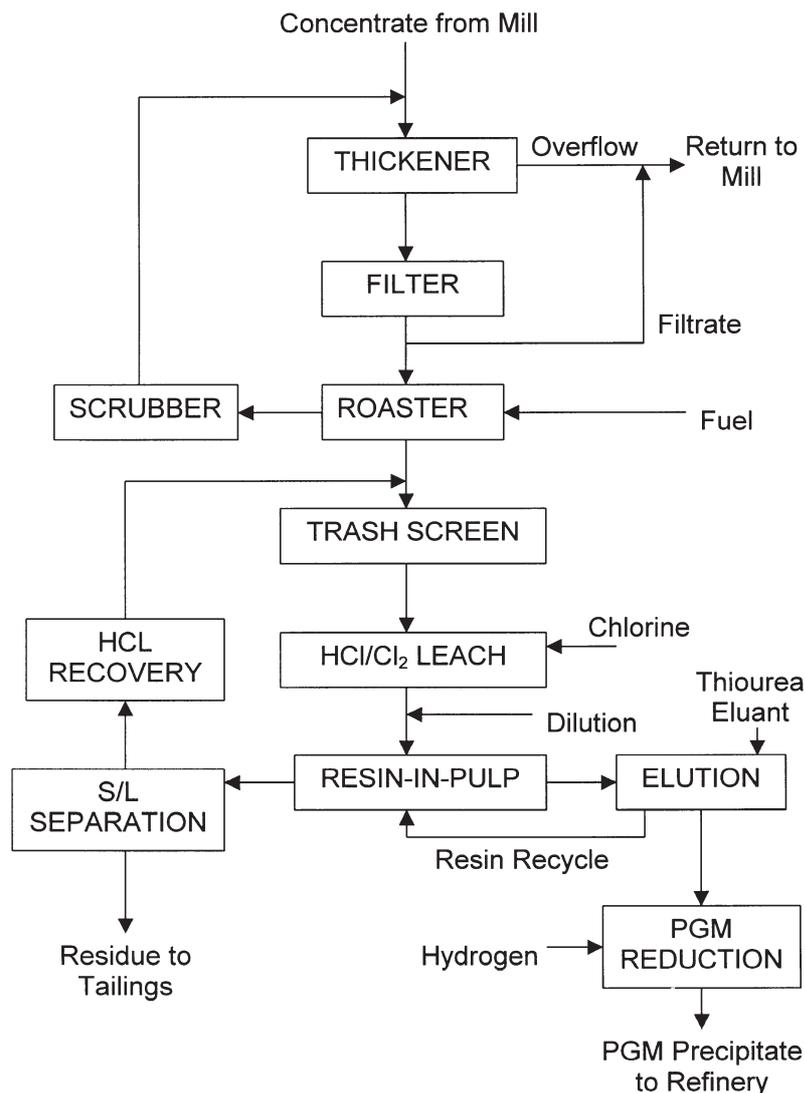


Figure 8—Block flow diagram of process to recover PGM precipitate

The techno-economic evaluation thus indicated possibilities for optimizing this process and making it more economical. However, it also indicated that an alternative smelting process that was being developed at Mintek (ConRoast), which had reached a more advanced stage of development, would be significantly more advantageous. Since the economics of ConRoast already appeared to be considerably more favourable than those of the established process, it was decided to suspend further development of a hydrometallurgical route until a need for one became apparent again.

Acknowledgement

This paper is published by permission of Mintek.

References

1. COETZER, G. and PENBERTHY, C.J. Mintek restricted report, 1996.
2. MARSH, J.H. Mintek restricted report, 1995.
3. MARSH, J.H., JOJA, B., and PENBERTHY, C.J. Mintek restricted report, 1994.
4. NAFTAL, M.N. and SHESTAKOVA, R.D. Chemical Abstracts 135:275656, 2001.
5. BUD'KO, I.A., KARAPETYAN, E.T., and MAZRUKHO, A.M. Chemical Abstracts 96:220926, 1980.
6. DISTLER, V.V. *et al.* Chemical Abstracts 98:57705, 1982.
7. CHMIELEWSKI, T. Chemical Abstracts 129:318956, 1998.
8. GREEN, B.R. Mintek restricted report, 2003.
9. BAGLIN, E.G., GOMES, J.M., CORNAHAN, T.G., and SNIDER, J.M. *Complex sulphides. Processing of ores, concentrates, and by-products*. Zunkel, A.D. *et al.* (eds). The Metallurgy Society, 1985. pp. 167–179.
10. DREISINGER, D.B., FLEMING, C.A., FERRON, C.J., and O'KANE, P.T. The hydrometallurgical treatment of base metal sulphide concentrates containing precious and platinum group metals. *Proceedings, Minprex 2000*, Melbourne, Victoria, 2000. p. 49.
11. WARSHAWSKY, A. Extraction of platinum group metals by ion exchange resins. *Ion Exchange and Sorption Processes in Hydrometallurgy*. Street, M. and Naden, D. (eds.). Society of Chemical Industry, 1987.
12. FINDLAY, M. The use of hydrogen to recover precious metals. *Proceedings, 6th IPMI Conference*. Newport Beach, California, 1982. ◆

