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Integrated Ion Exchange and Liquid-Liquid Extraction Process for the Separation of Platinum Group Metals (PGM)

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INTEGRATED ION EXCHANGE AND LIQUID-LIQUID EXTRACTION PROCESS FOR THE SEPARATION OF PLATINUM GROUP METALS (PGM)

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SUMMARY

A process for concentration and separation of platinum group metals (PGM) by a combination of ion exchange and liquid-liquid extraction is presented. First the PGM metals are dissolved by HCl/Cl_2 and then passed through an isothiouronium anion exchange resin, where specific absorption occurs. The thiourea eluate from the resin is converted to the chloride complexes. Further hydrolysis (conditioning) yields an aqueous feed to a liquid-liquid extraction step, with Alamine-336. Platinum and palladium are very well extracted, while most of the other PGM are rejected in the aqueous phase. The liquid-liquid extraction can be used by itself, if the level of the base metals does not exceed the concentration of the PGM ions.

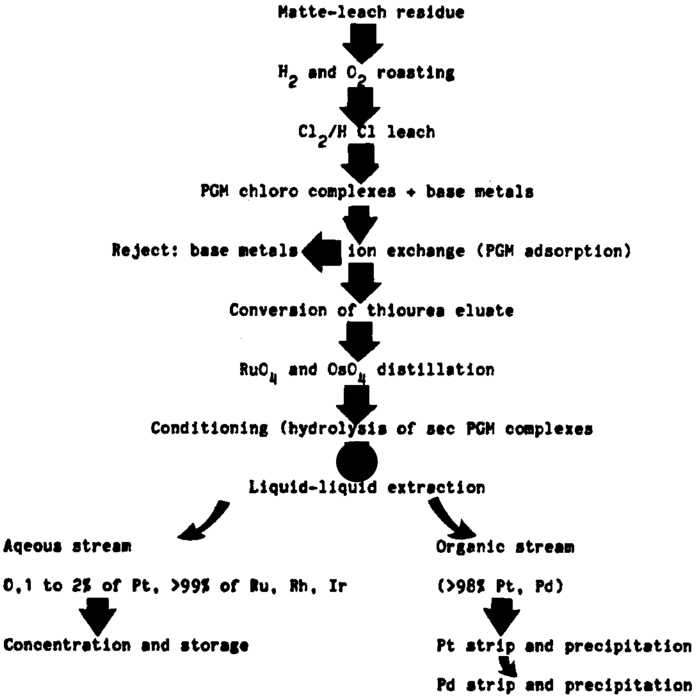
Platinum and palladium are now separated from each other by the selective stripping of palladium with thiourea, and platinum with thiocyanate.

The paper discusses the extraction chemistry of all the steps, and provides also experimental pilot-plant results.

1. INTRODUCTION

The classical process for the refining of platinum group metals (PGM) consists of a series of consecutive dissolution and recrystallization steps performed with great skill and care, yet suffer the disadvantages of batch type operations. Modern continuous refining of the PGM must be based on ion exchange and liquid-liquid extraction methods. Indeed, this statement is supported by the recent report on the new INCO[2a] PGM refinery, using liquid-liquid extraction with tributyl phosphate, and Matthey-Rustenberg, U.K. refinery, to be opened in 1983.[2b]

In earlier publications in this series[3a] the merits of processing the PGM in chloride media, were discussed and a selective anion exchange resin (MONIVEX) for the PGM ions was described. The present paper has the following objectives (see scheme no. 1).



Scheme 1: Process flowsheet for the refining of PGM.

(1) Maximal dissolution of PGM in refractory ores, slimes or concentrates in a pure chloride media (HCl and Cl_2).

(2) Quantitative absorption of the platinum group metal ions onto Monivex resin and separation from the less valuable transition metal ions, also called base metal ions.

(3) Quantitative elution of PGM ions by thiourea with the formation of PGM thiourea complexes.

(4) Conversion of the group of PGM thiourea complexes back into chloride complexes.

(5) Separation of the PGM ions into two groups:

  (a) Pd, Pt which form the major constituents in the PM group ("Primary PM").

  (b) Rh, Ir, Ru, Os which form the minor constituents in the group ("Secondary PM").

(6) Separation of primary PM metals.

(7) Separation of secondary PM metals.

2. SEPARATION PRINCIPLES

Any separation scheme must consider all chemical reactions taking place during the various process steps. In a separation system based on ion exchange and liquid-liquid extraction the following process steps must be well-defined.

(1) The aqueous chemistry of the noble metal ions in the chloride system.

(2) The phase-transfer chemistry.

(3) The chemistry in the organic (or polymeric) phase.

2.1 Chemistry in the Aqueous Phase

The chemistry of the PGM in aqueous media is dictated primarily by:

(a) The redox potential of the solution.

(b) The ligand or ligands present in solution.

(c) The coordination number of the metal ion.

All three factors are interrelated.

The oxidation potentials pertinent to reactions discussed in this paper are taken from the review by Goldberg and Helper[4] and presented in Table 1. Since $\Delta G° = -RT\ln K = -nFE°$, the negative signs of the oxidation potentials indicate thermodynamically unfavorable reactions. Thus, comparing the values for the same element in different oxidation states, the following conclusions regarding the prevalent oxidation state are derived: Rh(III) is much favored over Rh(IV), and so is Pd(II) over Pd(IV), whereas the

Table 1: Oxidation potentials for the PGM ions in chloride media*

Oxidation Reaction	Media	Half-cell potential (V)
$Ru(III) \longrightarrow Ru(IV)$	0.5 M HCl	-0.9
$OsCl_6^{3-} \longrightarrow OsCL_6^{2-}$		-0.85
$Rh \longrightarrow RhCl_6^{3-}$		-0.50
$RhCl_6^{3-} \longrightarrow RhCl_6^{2-}$		-1.20
$Ir \longrightarrow IrCl_6^{3-}$		-0.86
$IrCl_6^{3-} \longrightarrow IrCl_5^{2-}$		-0.87
$Pd \longrightarrow PdCl_4^{2-}$		-0.59
$PdCl_4^{2-} \longrightarrow PdCl_6^{2-}$		-1.26
$Pd \longrightarrow Pd(SCN)_4^{2-}$		-0.14
$Pd \longrightarrow Pd(Tu)_4^{2+}$		-0.07
$Pt \longrightarrow PtCl_4^{2-}$		-0.75
$PtCl_4^{2-} \longrightarrow PtCl_6^{2-}$		-0.77

*Taken from references cited in R.N. Goldberg and L.G. Hepler, [ref. 4].

Tu=Thiourea.

oxidation potentials of Ir(III) and Pt(II) are almost identical to those of Ir(IV) and Pt(IV) respectively. Thus, the higher oxidation states of Ir and Pt are readily maintained. Another conclusion is that soft ligands like thiourea or thiocyante form much more stable complexes than the chlorides (or the other halides) as indicated from the low negative values of the oxidation potentials.

Thermodynamic considerations derived from E° or G° values are very important in understanding processes which reach equilibria, as in the classical PGM separation process which includes long-time crystallization steps. In fast, phase-transfer steps, kinetic factors must be considered and used to affect desired separations.

The complexes formed by the PGM ions fall into two major configurational groups:[5]

(i) Square-planar complexes, i.e., Pd(II), Pt(II), Au(III), Ir(I) and Rh(I).

(ii) Octahedral d^5 or d^6 complexes, i.e., Pd(IV), Pt(IV), Ir(III) and Ir(IV), Ru(II) and Ru(III) and Os(III).

The substitution mechanisms of both types are very different. Square-planar substitution[6] is a nucleophilic displacement reaction with complete retention of configuration, and the transition state is a trigonal-bipyramidal structure. The kinetic expression for square-planar substitution, in the presence of excess displacing ligand, is a pseudo first order term. The rate constants are, therefore, strongly dependent on the "nucleophilicity" of the ligand, which varies over four orders of magnitude for Pt(II) complexes (Table 2). In addition, the rate constants in square-planar substitution depend also on electronic effects of the metal ion, so called trans-directing and trans and cis labilizing effects, as well as on common steric and solvent effects.

In substitution reactions of octahedral complexes[7] two alternative mechanisms are known:

(i) Associative mechanism (also called interchange mechanism) involves a seven coordination state intermediate.

(ii) Dissociative mechanism involving a five coordination state (square-pyramid or trigonal-bipyramidal) intermediate.

Table 2: Nucleophilicity constants (N^{o}_{Pt}) for Pt(II) complexes. (ref. 5, table 7.4, in log term).

Nucleophile	Cl^-	NO_2^-	N_3^-	Br^-	I^-	SCN^-	Tu	CN^-
N^{o}_{Pt}	3.04	3.22	3.58	3.96	5.42	5.65	7.14	7.14

For the most commonly studied systems, Co(III), Cr(III) and Rh(III), it was established (ref. 7, sect. 6.3.2) that entering group effects are very small and insignificant, while leaving group effects, although small, are more significant (Table 6.3, ref. 7).

In conclusion, substitution reactions in square planar complexes are much faster and could be used to induce kinetically controlled separations. This, on condition, that proper control over the oxidation state (and hence over the configuration of the complex, is possible). Even so, in some cases, redox reactions can result in configurational changes. Notably the involvement of Pt(II) in catalyzing substitution reactions of Pt(IV) complexes (ref. 5). A qualitative guide to substitution rates for noble metal ions in predominant oxidation states is given in Table 3.

2.2 Dissolution of the PGM in HCl/Cl$_2$[8]

The platinum group metals are present in the earth crust in very minute concentration. Approximately 10 parts per million is the group concentration in the Merensky Reef deposits in the Transvall, South Africa. After various metallurgical concentration steps, a matte is obtained, which is further concentrated by leaching with non-oxidative mineral acids. The residue from this treatment is the feed material for the refining of the PGM. A typical composition of such a matte-leach-residue from the above source is given in Table 4.

The dissolution of this matte-leach-residue in 12 M HCl with 0.2 bar chlorine overpressure in a glass-lined reactor on 1-3 kg sample scale is given in Table 5.

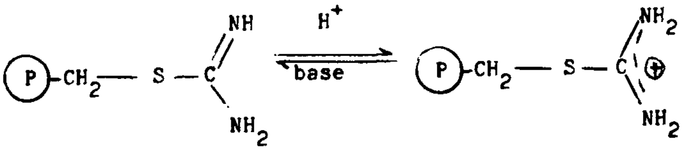
Table 3: Qualitative guide to substitution rates for noble metal ions, in predominant oxidation states.

Ru(III)	Rh(III)	Pd(II)	Ag(I)
slow	v. slow	fast	v. fast
		Pd(IV)	
		fast	
Os(III)	Ir(III)	Pt(II)	Au(I)
slow	v. slow	slow	v. fast
Os(IV)	Ir(IV)	Pt(IV)	Au(III)
v. slow	slow	v.v.slow	fast

If a sequence of oxidative and reductive treatments are initiated, prior to the ore dissolution step, the primary PM's and Au are liberated quantitatively. The solution contains a high HCl concentration which must be adjusted to the proper concentration for absorption on the ion exchange resin.

2.3 Adsorption of PGM by Monivex Resin[2,8]

This step in the process separates the PGM from the base metals. The functional isothiouronium group, as a weak-base is subject to the following acid-base equilibrium:



The adsorption mechanism depends strongly on the acid concentration. In concentrated acids an anion-exchange mechanism between the anionic chlorocomplexes and the chloride counterion takes place. In dilute acids, chelate compounds are formed, and the equivalent of

Table 4: Composition of the matte-leach residue

Group	Element	Concentration %	Group concentration %
1. Noble metals	Pt	18,18	
	Pd	8,06	
	Ru	1,73	
	Rh	0,81	
	Ir	0,19	
	Au	1,35	
	Ag	0,15	30,47
2. Volatile metals	S	8,40	
	Se	1,98	
	Te	0,36	
	As	0,36	
	Os	0,19	
	Sb	0,05	11,95
3. Base metals	Fe	1,80	
	Ni	5,00	
	Cu	5,00	
	Cr	2,90	
	Ca	0,50	
	Mg	1,02	
	Na	0,97	
	Al	1,80	
	Pb	0,11	
	Pi	0,05	
	Co	0,17	
	Si	9,95	35,27
4. Others	O	0,19	
	Cl	22,05	22,69
TOTAL		99,58	99,58

one hydrogen ion is liberated. Thus, to achieve quantitative elution the resin must be loaded from highly acidic solutions; loading from dilute acids makes the elution difficult and results in the gradual "poisoning" of the resin.

In theory, when the resin is converted into its free-base form, it should release the bound metals, which are held by simple electrostatic attraction forces, but this does not happen in prac-

Table 5: Effect of roasting on the dissolution of PGM

Treatment after	Total-dissolution of original PGM %					
	Pt	Pd	Au	Rh	Ru	Ir
1. no treatment	86	76,5	100	50	20,6	58
2. air roast	100	95	100	71	19,2	60,5
3. coal-gas roast	100	94	100	75	41	77
4. 2 then 3	99,6	98,5	98,5	78	45	99,6

(1) 12 N HCl/0.2 bar of Cl_2, at 80°C, 24 hrs.

(2) 700°C O_2 for 1 hr.

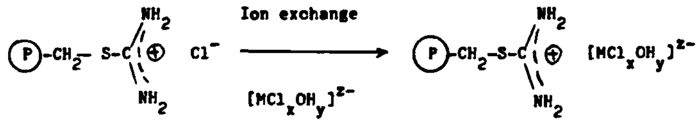
(3) 700°C H_2/CH_4 for 1 hr.

tice. In the neutralization step, the isothiourea group rapidly forms the chelate-type complex. Further complications are the hydrolysis of PGM inside the resin pores and base catalyzed hydrolysis of the isothiourea group itself.

If the regenerated resin is washed with neutral or alkaline solutions, both the isothiourea groups and the residual metals on the resin will hydrolyze. This hydrolysis can be avoided if the metals are dissolved in an oxidizing medium like chlorine water, but the isothiourea group is very sensitive to oxidation. It is, therefore, strongly recommended that the resin should never be in contact with alkaline or neutral media.

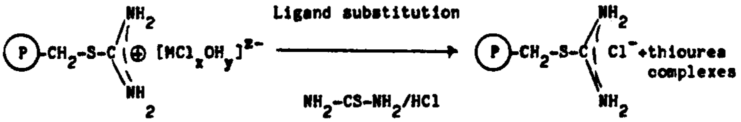
The basic reactions taking place on the resin can be summarized as follows:

(1) adsorption:



$$Ⓟ\text{-}CH_2\text{-}S\text{-}C\overset{NH_2}{\underset{NH_2}{\oplus}}\ Cl^- \xrightarrow[{[MCl_xOH_y]^{z-}}]{\text{Ion exchange}} Ⓟ\text{-}CH_2\text{-}S\text{-}C\overset{NH_2}{\underset{NH_2}{\oplus}}\ [MCl_xOH_y]^{z-}$$

(2) elution:



In the adsorption reaction the resin adsorbs any anionic complexes of the general type $[MCl_xOH_y]^{z-}$ by anion-exchange mechanism, with high adsorption rates.[2b] During elution, the metals are released from the resin only when the negatively charged chlorides in the PGM anionic complex have been replaced by neutral thiourea to the degree that the complex is positively charged or neutral. As expected from the variation in the rates of substitution of the PGM in solution (Table 3), the elution rates also vary considerably. Platinum, palladium, and gold are eluted quickly, and the remaining PGM much slower.[3]

2.4 Separation of PGM and Base Metals: Pilot-Plant Work[9]

The application of Monivex to the processing of PGM requires the use of a continuous ion-exchange process. High concentrations of PGM in solution can be expected, and early breakthroughs will occur in any fixed-bed process. For a reasonable service cycle period, the use of continuous ion-exchange reduces the resin inventory by a factor of approximately two.

A PGM pilot plant having a production capacity of between 120 and 220 g of platinum per day has been built and successfully operated. Solutions produced from matte-leach residue have been in use for a period of four months. In addition, many runs have been made on synthetic solutions, and considerable operating experience has been obtained with Monivex and its performance under practical conditions.

The prime requirements of the Monivex plant are as follows:

(1) It should produce a PGM-product stream substantially free of base metals.

(2) It should recover more than 99,95% of the platinum and palladium, and more than 95% of the secondary PM's from the leach liquor.

A three-column continuous countercurrent ion-exchange system was built as follows:

Column 1: Loading and washing of loaded resin.

Column 2: Elution.

Column 3: Washing of eluted resin.

	Solution flowrate $m^3/hr/m^2$	Ratio of resin to solution	Resin retention time hr	Number of stages	Height of stage m
Loading	1,275	1 to 1,45	4	6	0.7
Washing (loaded)	1,275	1 to 1,45	4	6	0.7
Elution	2,55	1 to 2,9	8	12	0.7
Washing (eluted)	2,55	1 to 2,9	8	12	0.7

Table 6 provides the composition of the feed solution (in 2 M HCl) to the Monivex resin, and typical results. The recovery of the primary PM's (Pt, Pd) from the feed is better than 99.9%, and the recovery of the secondary PM's which adsorb slower, is depen-

Table 6: Average test results from Monivex Pilot-Plant

Run	A				B			
	Pt	Pd	Sec. PGM	Ag	Pt	Pd	Sec. PGM	Ag
Feed p.p.m.	8480	3810	657	69	8334	3750	665	67
Barren p.p.m.	1,6	0,10	20,5	0,07	0,52	0,16	4,93	0,50
Recovery %	99,91	99,99	84,37	99,42	99,98	99,99	97,64	97,72
Grade of eluate (% of total recovered)		99,33				99,52		

Loading: 2 M HCl, 20°C Washing: 0,5 M HCl Elution: 5% Thiourea in 0,05 M HCl, 90°C.

dent on loading retention time, and in run B up to 97.6% are recovered. The metal recovery in the thiourea eluate is better than 99%, and the purity of the eluate is better than 99.9% (in PM versus base metals, see Table 7). The regeneration of the Monivex resin under the specified conditions is quantitative, as shown in Table 8.

2.5 Conversion of Thiourea Complexes to Chlorocomplexes[9]

In this step, the thiourea complexes are converted back into chlorocomplexes, which are suitable for liquid-liquid extraction. Since thiourea is a very strong ligand, it is almost impossible to break its complexes by hydrolysis or by simple ligand substitution. However, the sensitivity of thiourea to alkaline hydrolysis and oxidation makes it possible for its complexes to be converted to chlorocomplexes by either of these procedures.

Table 7: Spectrographic analysis of sulfide precipitate from Monivex eluate (Run B)

Parts per million		
Iron	Nickel	Copper
36	13	80

Table 8: Typical analysis of the pilot-plant resin

	Pt	Pd	sec. PGM
Feed resin, ppm	197	160	256
Loaded resin, ppm	71800	35600	4693
Eluted resin, ppm	196	150	283

Table 9: Conversion to chlorocomplexes (average of 10 precipitations)

Conc	Pt	Pd	Rh	Ru	Ir
Head, p.p.m.	1180	621	54	42	34
After precipitation, p.p.m.	0,02	0,02	0,03	0,02	0,015
In precipitate, %	99,998	99,997	99,95	99,95	99,95

Both procedures were tested. Direct oxidation by chlorine, which was used in the early stages of the pilot-plant work, was abandoned in favor of a procedure in which the thiourea was hydrolyzed by caustic soda, the PGM were precipitated (see Table 10) as a sulfide mixture of undefined composition, and the precipitate was oxidized with chlorine. The main difference between these two methods is that the solution from direct chlorination contains a large excess of oxidation products emanating from the excess thiourea in the eluant, whereas in the alkaline hydrolysis method they are removed in the filtrate.

Direct separation of the thiourea complexes would eliminate the conversion step. The literature indicates, however, that in the presence of excess of thiourea, the predominant ionic species are complex cations of platinum, palladium, rhodium, and osmium. But also some neutral species are present. The situation for iridium is even more complicated, and cationic, neutral, and anionic complexes coexist in equilibria. Thus, oxidative conversion must be used for further processing.

2.6 Conditioning (Hydrolysis) of Secondary-PGM Complexes[8]

The purpose of this step is the preparation of a feed suitable for the liquid-liquid extraction process using a tertiary amine solvent. In other words, this step ensures that the platinum, palladium, and gold are present as extractable anionic complexes, and the rhodium, ruthenium, and iridium as cationic or neutral non-extractable complexes.

Table 10: Hydrolysis of the PGM chlorocomplexes

Complex	Hydrolysis pH value	Cond. Temp.°C	Products	Rate	Ref.
$PtCl_4^{2-}$	5 to 7	25	Insoluble hydroxides	Slow	10
$PtCl_4^{2-}$	3	100	Insoluble hydroxides	Slow	10
$PtCl_6^{2-}$	2 to 7	25	Soluble mixed chlorohydroxides		
$PtCl_6^{2-}$	>12	25	$[Pt(OH)_6]^{2-}$		
$PtCl_6^{2-}$	3	25	Insoluble hydroxides	Slow	10
$RhCl_6^{2-}$	6,6 - 6,7	25	Insoluble hydroxides		
$RhCl_6^{2-}$	3,3 - 3,4	100	Insoluble hydroxides		
$RhCl_6^{2-}$	(H_2O) short time		$[RhCl_5H_2O]^{2-}$	Fast	11
$RhCl_6^{2-}$(red)	(H_2O) long time	25	$Rh(H_2O)_6^{3+}$ yellow	Slow	11
$RhCl_6^{2-}$	(H_2O)	100	$Rh(H_2O)_6^{3+}$	Fast	11
$IrCl_6^{2-}$	0,1 N to 3N HCl	25	Predominant species are $IrCl_6^{2-}$, $[IrCl_4(OH)_2]^{2-}$	Slow Slow	12 12
$IrCl_6^{2-}$	0,05 N HCl	25	Only $[IrCl_4(OH)_2]^{2-}$	Slow	13
$IrCl_6^{2-}$	0,1 N NaOH	25	$[IrCl_2(OH)_4]^{2-} \rightarrow IrO_2\ 2H_2O$	Slow	13
$IrCl_6^{2-}$	>0,1 N NaOH	25	Ir(IV)→Ir(III)		
$IrCl_6^{3-}$	5 (H_2O)	25	Insoluble products $[IrCl_5H_2O]^{2-}$; $[IrCl_4(H_2O)_2]^-$ and $IrCl_3(H_2O)_3$		
$RuCl_6^{3-}$	-	-	Mixture of $[RuCl_5(H_2O)]^{2-}$ up to $RuCl(H_2O)_5^{2+}$	Fast	14 14
$OsCl_6^{2-}$	4	25	Insoluble $OsO_2\ 2H_2o$	Slow	15
$OsCl_6^{2-}$	5	80	$[OsCl_5(H_2O)]^{2-}$		15

The conditioning may involve two separate procedures: prolonged hydrolysis in dilute acid (pH value 1 to 3), and rapid hydrolysis in alkaline solution followed by adjustment of the pH to a value of 2 to 3. Thus, both the hydrolysis of the chlorocomplexes and the properties of the alkaline species, oxides, hydroxides, and aqua complexes have to be considered.

The hydrolysis products of the chlorocomplexes under various conditions are listed in Table 10, which summarizes the relevant data from the literature. This permits the following conclusions:

(1) At pH values of less than 3, platinum and palladium exist as true chlorocomplexes.

(2) The true chlorocomplexes of rhodium, iridium, ruthenium, and osmium hydrolyze readily to the stable pseudo-chlorocomplexes $[MCl_5H_2O]^{2-}$.

(3) Rhodium can be hydrolyzed sufficiently quickly to form the hexaaqua cationic species.

(4) In the pH range 2 to 13, iridium exists as the complex $[IrCl_4(OH)_2]^{2-}$.

(5) Ruthenium chlorocomplexes hydrolyze rapidly to neutral or cationic species.

(6) Osmium chlorocomplexes hydrolyze very slowly and the main product is $[OsCl_5(H_2O)]^{2-}$.

The properties of the hydroxides and oxides of the PGM are listed in Table 11. Except for the oxide of osmium, all freshly precipitated oxides can be resolubilized in hydrochloric acid. It is worthy of note that iridium compounds are precipitated as iridium(III) oxides and that, when these are dissolved, iridium(III) complexes result.

The main merit of the precipitation of PGM as oxides is that redissolution of the precipitate in hydrochloric acid readily produces the mixed chlorohydroxy complexes. The diadvantage lies in handling a solid including the difficulty of redissolving in a slurry.

The above conclusions mean that platinum and palladium can easily be extracted as anionic complexes; iridium anionic complexes are poorly extracted; rhodium and ruthenium are cationic and therefore nonextractable; and osmium can be rendered nonextractable by long hydrolysis.

In handling a thiourea eluate the conditioning is part of the conversion step. In a process not employing anion exchange, it is a distinctly separate step.

Table 11: Common oxides of the PGM [16]

Reaction	Product	Properties
$PtCl_4^{2-}$ + NaOH	PtO x H_2O	Black, soluble in hydrochloric acid, Concentrated HNO_3, or H_2SO_4.
$PtCl_6^{2-}$ + NaOH	$[Pt(OH)_6]^{2-}$	Soluble in alkali precipitates as the acid $H_2[Pt(OH)_6]$ (PtO_2 $4H_2O$). This acid is soluble in mineral acids.
$PdCl_4^{2-}$ + NaOH	PdO x H_2O	Yellow to brown, insoluble in water, easy soluble in alkali or acids.
$RhCl_6^{3-}$+ NaOH + oxidant	RhO_2x2H_2O	Dark green, soluble in acids.
$IrCl_6^{3-}$ + NaOH	Ir_2O_3 x H_2O	Yellow-green, oxidized in the air, easily soluble in acids.
$IrCl_6^{2-}$ + NaOH	IrO_2 x H_2O	Bluish, Ir(IV) is first reduced to Ir(III), Ir_2O_3 x H_2O precipitates and oxidizes slowly in air to IrO_2 x H_2O.
$IrCl_6^{2-}$ + NaOH + oxidant	IrO_2 x H_2O	
$RuCl_6^{2-}$ + NaOH	RuO_2xH_2O	
$RuCl_6^{2-}$ + NaOH	$Ru_2O_3xH_2O$	Black-brown, insoluble in H_2SO_4 or HNO_3, soluble in hydrochloric acid.
$OsCl_6^{2-}$ + NaOH	OsO_2x2H_2O	Black, insoluble in hydrochloric acid or H_2SO_4.

2.7 Recovery of Ruthenium and Osmium[8,9]

At this stage, ruthenium and osmium can be distilled off as RuO_4 and OsO_4. This involves neutralization of the acid formed during the conversion with sodium hydroxide. Very accurate pH control is required for the removal of RuO_4. OsO_4 comes off over a wide pH range, and can even be formed during the conversion step. At pH value of 4 to 9, a large proportion of the PGM are present as insoluble hydroxides. Adjustment of the pH allows the OsO_4 and

RuO_4 to be distilled with vigorous chlorine sparging. They are recovered by absorption in concentrated hydrochloric acid.

3. THE LIQUID-LIQUID EXTRACTION WITH TERTIARY AMINES[17-19]

The liquid-liquid extraction of PGM ions in chloride solution provides the following objects:

(1) Recovery of primary PM (Pt,Pd) and Au in the organic phase.

(2) Concentration of secondary pM (Rh,Ru) in the aqueous phase.

(3) Separation of Pt from Pd by selective stripping of either of them. Pt is stripped with thiocyanate and Pd with thiourea.

The chemical principles of these reactions are summarized briefly (full experimental details are given in ref. 20. Species in organic phase are denoted by bars.)

3.1 Extraction

$$\overline{[AmH^+]Cl^-} + PdCl_4^{2-} \rightarrow \overline{(Am)_2PdCl_2} \; / \; \overline{(AmH^+)_2(PdCl_4^{2-})}$$

$$\overline{[AmH^+]Cl^-} + AuCl_4^{-} \rightarrow \overline{(Am)_2AuCl_2} \; / \; \overline{(AmH^+)_2(AuCl_4^{2-})}$$

$$\overline{[AmH^+]Cl^-} + PtCl_6^{2-} \rightarrow \overline{(AmH^+)_2(PtCl_6^{2-})}$$

The formation of coordination complexes is favorable for Au and Pd, whereas Pt is favorably extracted as an ionic complex.

3.2 Stripping by Perchloric Acid (or Perchlorate)

With $HClO_4$ (acidic pH):

$$\left\{\begin{array}{l}\overline{(Am)_2PdCl_2}\\ \overline{(Am)_2AuCl_2}\\ \overline{(AmH^+)_2(PdCl_4^{2-})}\\ \overline{(AmH^+)_2(PtCl_6^{2-})}\end{array}\right\} \xrightarrow[pH<4]{HClO_4} \left\{\begin{array}{l}\overline{(AmH^+)ClO_4^-}\\ \overline{(Am)_2PdCl_2}\\ \overline{(Am)_2\,AuCl_2}\end{array}\right\} + PtCl_6^{2-} + (PdCl_4^-)$$

With $NaClO_4$ (basic pH):

$$\left\{\begin{array}{l}\overline{(Am)_2MCl_2}\\ \overline{(AmH^+)ClO_4^-}\\ \overline{(AmH^+)_2(MCl_6^{2-})}\end{array}\right\} \xrightarrow[\text{pH } 8]{NaClO_4} \overline{Am} + \text{mixed chloro-aqua complexes.}$$

The perchloric acid strip can be applied at pH = 2-4 to separate partially Pt from Pd, and at pH 8 to affect total regeneration of the amine.

3.3 Stripping with Thiourea

The labile d^8 square planar complexes of Au, Pd are transfered to the aqueous phase by ligand substitution of the chloride with thiourea. The cationic thiourea complexes are nonextractable by amines, and inert to further ligand substitution.

Since thiourea reduces gold, this step is not advisable for practical recovery of gold, and in fact, for that reason gold had to be seprated from Pt and Pd at earlier stage, prior to the adsorption on Monivex resin.

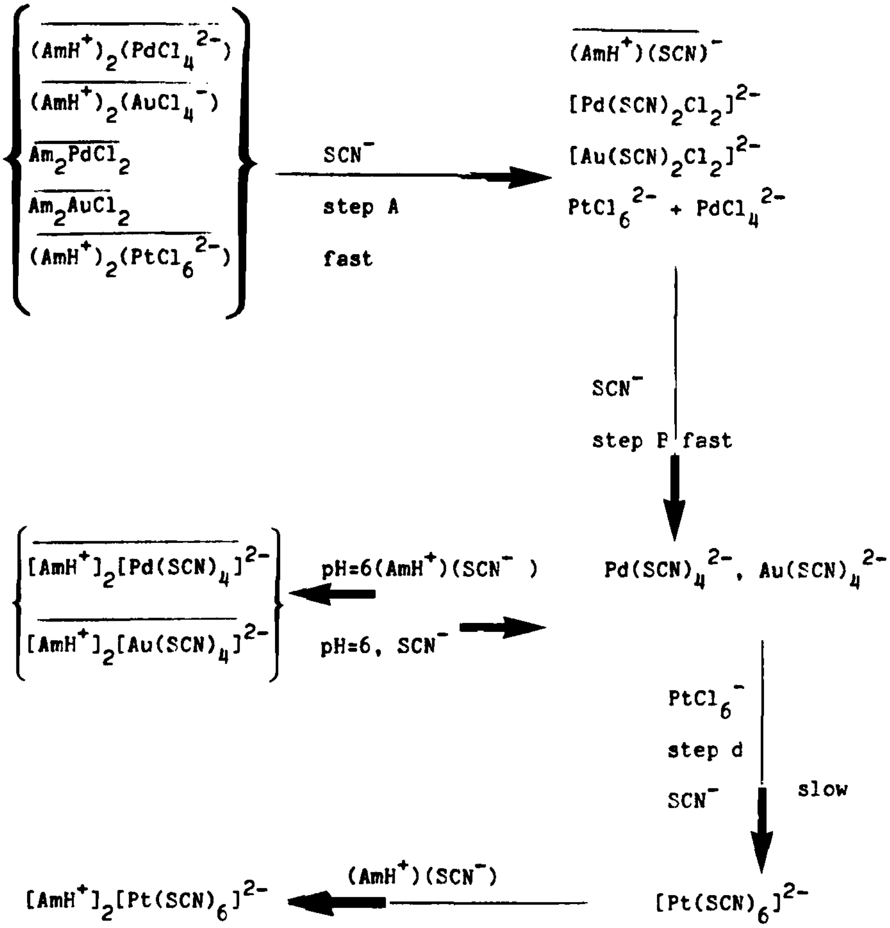
In this step, a small fraction of Pt is stripped. It is not yet conclusively established whether this is Pt(IV) or Pt(II). In other words, whether better control of the oxidation potential or of the stripping time, is required. The reactions of the thiourea stripping are outlined in the following:

$$\left\{\begin{array}{l}\overline{(AmH^+)_2(PdCl_4^{2-})}\\ \overline{(AmH^+)_2(AuCl_4^-)}\\ \overline{Am_2PdCl_2}\\ \overline{Am_2AuCl_2}\\ \overline{(AmH^+)_2(PtCl_6^{2-})}\end{array}\right\} \xrightarrow{\text{thiourea (Tu)}} \begin{array}{ll}\overline{(AmH^+)_2(PtCl_6^{2-})} & + \ Au(Tu)_4^+\\ \overline{AmHCl} & + \ Pd(Tu)_4^{2+}\end{array}$$

3.4 Stripping with Thiocyanate

Like thiourea, thiocyanate is a very strong nucleophilic ligand, and the ligand substitution of d^8 square-planar complexes is very rapid (Au,Pd).

The stripping mechanism is very complicated. First the displacement of chloride metal complexes by the thiocyanate anion (step A), then conversion of the chloride by thiocyanate in the aqueous phase, containing excess free NaSCN (step B) and finally reextraction of the metal thiocyanate complexes into the organic phase (step C). It is not yet clear whether the substitution of



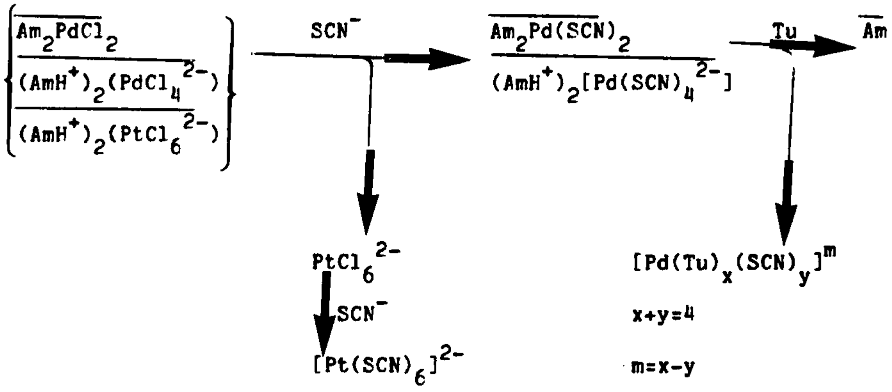
chloride by thiocyanate in gold and palladium complexes does not proceed directly in the organic phase.

It was noted that $PtCl_6^{2-}$ is slowly converted in the aqueous phase to $Pt(SCN)_6^{2-}$ and reextracted (step d). If the time of the stripping reaction is controlled good separation between Pt and Pd is obtained.

Another aspect of this system is the reversibility of step C, which is pH dependent. When the pH is controlled between 6-8, step C, can become a route for regeneration of the solvent from all metal ions including Pt. Failure to control this step will cause slow "poisoning" of the solvent by metal accumulation.

3.5 Combinations of Thiourea and Thiocyanate Strips

The sequence of performing both steps can be varied without changes in the separation results. It is more effective to strip Pt first with thiocyanate and then palladium by thiourea. The chemical transformations during this sequence are described hereby:



The exact chemical form of Pd and Pt in the end solution is not significant, since both are converted to other forms prior to their precipitation as metals.

4. PILOT-PLANT WORK[9,19]

The initial pilot-plant work was done on solutions containing base metals. It was found that iron showed a slight tendency to be extracted, probably as the chlorocomplex, $FeCl_4^-$. The addition of sufficient sulphuric acid to the hydrochloric acid scrubbing liquor minimizes the extraction or entrainment of both secondary PGM and base metals in the organic phase, breaks this complex and suppresses the extraction of iron. To avoid difficulties in the subsequent processing of the scrubbing liquor for the recovery of the secondary PGM caused by the present of base metals, it was decided that all further work on liquid-liquid extraction should be limited to feed solutions that passed Monivex resin and are substantially free of base metals.

The scrubbing efficiency for the secondary PGM was found to be somewhat erratic. Subsequently, it has been shown that both extractable and nonextractable species of ruthenium, rhodium, and iridium can exist in a chloride solution.

4.1 Selective Stripping of Palladium with Thiourea and Platinum with Perchloric Acid

Selective stripping of the solvent, firstly with thiourea for the removal of the palladium followed by platinum stripping with perchloric acid, proved troublesome because of the precipitation of a palladium-thiourea complex. Reasonable operation of the stripping procedure requires very careful control of the phase ratio and of the concentration of the thiourea relative to the concentration of palladium in the organic phase.

The structure of a continuous liquid-liquid extraction pilot plant, the chemical composition of the various streams and flow-rate data are given in Table 12 and typical separation results for the system 5% Alamine-336 Pd-thiourea strip, Pt-$HClO_4$ strip are given in Table 13.

The relatively low concentrations of secondary PGM in Alamine in the loaded solvent presented severe analytical problems. It

Table 12: Pilot plant characteristics

Stock solution	Flow ml/min	Cell no. in	out	Product stream	Flow ml/min
Fresh organic	50	1	25	Stripped organic	50
Aq. Feed	50	3	1	Secondary PGM + base metals	80
Scrub (0,1 N HCl, 0,2 N H_2SO_4)	30	10	1		
Strip (0,5% Tu, 0,1 N HCl)	20	11	11	Pd, Au/Tu	20
Strip (0,5% Tu, 0,1 N HCl)	30	18	12	Pd, Au/Tu	30
Wash (0,5 N HCl)	30	22	19	Wash/Tu	30
Strip (1,0 N $HClO_4$)	50	25	23	Pt/$HClO_4$	50

was, therefore, decided that the amount of Alamine in the Solvesso should be increased from 5 to 10%. Excessively slow phase disengagement was encountered when 10% Alamine-336 was used and consequently, a more concentrated form of a new extractant was used (Alamine-310). It had beer shown previously that Alamine-310 has similar extraction but superior phase-disengagement properties. The concentration of platinum in the scrub liquor remained low throughout and after seven hours was only 5 ppm. This represents a recovery of 99.9% for Pt and indicates that, when complete conversion of Monivex eluate is achieved, the extraction of platinum is satisfactory. The use of sodium chloride rather than hydrochloric acid in the scrubbing section affords a significant cost savings. The effect on phase disengagement and scrubbing efficiency is not marked.

The low concentrations of base metals and secondary PGM in the platinum strip liquor confirm that the scrubbing of the organic phase was satisfactory. Although the platinum-strip liquor contained only platinum, the palladium product contained excessive and unacceptable amounts of platinum. Therefore, in spite of the fact

Table 13: Typical pilot plant results on liquid-liquid extraction Thiourea/$HClO_4$ system.

	Concentration, p.p.m.								
	Pt	Pd	Au	Rh	Ru	Ir	Fe	Cu	Ni
Aq. feed	6250	2520	370	365	257	276	6150	1400	2870
Scrub liquor	3	2,3	1,1	190	132,2	110	2600	600	1800
Pd-strip liquor	35	1272	-	ND	ND	ND	0,3	ND	ND
Pt-strip liquor	4700	ND	0,25	ND	2,1	0,9	3,7	ND	ND
Stripped solvent	12,2	0,3	-	ND	ND	ND	-	-	-

ND means not detected

that very pure platinum could be produced by this route, it was decided to try another stripping system.

4.2 Selective Stripping of Platinum with Thiocyanate and Palladium with Thiourea (Table 14)

Table 14 gives a summary of the best pilot-plant results on PGM solutions derived from matte-leach residue. Whereas satisfactory recoveries of palladium are obtained, the stripping of platinum is incomplete and rather erratic. The best stripping results were obtained in run 4, namely, 96.1% of the platinum when 0.5 M sodium thiocyanate was used, and 99.7% of the palladium when thiourea at 2.5 g/l acidified in 0.1 M hydrochloric acid was used.

The subsequent processing steps required for the production of pure metals are more selective for platinum than for palladium. The allowable contamination of platinum in the thiourea strip liquor is, therefore, lower than that of palladium in the platinum product. It is felt, that if the platinum concentration in the palladium strip liquor is to be reduced, more platinum should be removed from the solvent during the thiocyanate strip. Since kinetic effects play an important role, more work is needed for optimization of the thiocyanate concentration and residence time.

The formation of some yellow precipitate (a palladium-thiourea chlorocomplex) in the cells was observed during the stripping of palladium. Further work should be done on the optimization of the concentrations of thiourea and hydrochloric acid so that the palladium values in the strip liquor can be raised without precipitation.

4.3 Extraction of Platinum and Palladium from a Converted Resin Eluate (Table 15)

Table 15 shows the results obtained for the extraction of platinum and palladium from a solution containing only PGM. The concentrations of product streams reported were taken at the end of each run. In spite of the relatively long runs, complete steady state had not been reached, as indicated by changes in the platinum concentration of the scrub-liquor stream.

Table 14: Stripping of platinum and palladium

	1		2		3		4		5		6	
Pt-strip	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
Loaded solvent*	669	567	2920	1295	3901	1470	2800	1190	3882	1410	6900	3533
Pt-strip liquor*	329	0,5	2480	3,4	4655	7,5	3660	1,9	3295	1,3	4652	9,2
Stripped solvent*	277	341	263	1280	436	1420	67	1090	1040	1420	898	3439
Stripping+	35	0,06	91,8	0,29	82,4	0,32	96,1	0,1	65,3	0,07	89,5	0,32
Sodium thiocyanate	0,25 N		0,3 N		0,4 N		0,5 N		0,4 N		1,0 N	
Pd-strip												
Loaded solvent*	246	305	233	1120	313	1190	46	1010	997	1490	746	3002
Pd-strip liquor*	14,5	104	13,5	514	13,3	517	9,2	214	11,2	767	12,1	688
Stripped solvent*	236	1,1	215	0,6	261	2,8	42	5,1	1007	1,7	611	12
Stripping#, %	14,7	99,86	13,3	99,98	9,7	99,86	33,2	99,7	2,3	99,94	4,9	99,87
Thiourea, g/l; HCl, N	1,5; 0		2,5; 0		2,5; 0,1		2,5; 0.1		2,5; 0,1		2,5; 0,05	

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[*] Concentrations of the product stream at the end of the run, p.p.m.

[+] Values for platinum are based on stripped solvent, those for palladium on strip liquor.

[#] Values for Pd based on stripped solvent, those for Pt on strip liquor.

Table 15: Concentrations of PGM in the product streams

	Run 1					Run 2				
	Pt	Pd	Rh	Ru	Ir	Pt	Pd	Rh	Ru	Ir
Aq. feed, p.p.m.	4640	2133	131	79,1	31,3	5176	2935	185	123	41
Loaded solvent[1]	4664	1530	0,8	1,2	<1	10895	2063	3,54	32	5,9
Scrub liquor[1]	88,8	191	69,4	40,8	15,2	86	23	137	99	31
Feed in scrub liquor %	4,5	21,2	>100	>100	>100	2,8	1,3	>100	>100	>100
Duration of run, h	-	-	13	-	-	-	-	4	-	-
Alamine in Solvesso, %	-	-	5	-	-	-	-	10	-	-

[1] Concentration of the product stream at the end of the run - p.p.m.

The best extraction of platinum achieved to date is about 99%, and the corresponding figure for palladium is 99.9%. It is noteworthy that excessively high concentrations of platinum and palladium in the scrub liquor were reached only after a period of 10 hours.

4.4 Separation of Secondary PGM[20]

The aqueous barren stream from the liquid-liquid extraction contains low concentrations (100 to 200 ppm) of rhodium, iridium, platinum, palladium, and possibly ruthenium. No pilot-plant work has yet been done on the recovery of the secondary PGM. However, a considerable number of laboratory tests have been performed, and a detailed account of this work is given elsewhere.[20] In view of the relatively small amounts of secondary PGM involved and their low concentrations in the aqueous barren stream, a concentration step is desirable before further treatment.

4.5 Regeneration of the Solvent

The regeneration involves three steps:

(1) Removal of entrained thiourea by passing the organic phase through a coalescing device or by washing with water.

(2) Regeneration of solvent with alkali solution to produce the free-base form of the solvent.

(3) Conversion of solvent to the chloride form by contacting with hydrochloric acid.

It was found that regeneration with a solution of sodium hydroxide or sodium carbonate with washed solvent resulted in very poor phase separation and the accumulation of some precipitate at the interface. Addition of sodium hydrochloride (6 g/l) to the sodium hydroxide solution considerably improved phase separation and permitted regeneration in mixer-settler units on a continuous basis. A slow build up of precipitate at the interface was prevented by the occasional addition of some hydrochloric acid to the settler. The results are shown in Table 16.

Table 16: Regeneration of solvent. (metal concentrations in ppm)

	5% Alamine				10% Alamine			
	A/O	Pt	Pd	OPM*	A/O	Pt	Pd	OPM
Solvent for regeneration	-	43	2.6	<1	-	448	9	2
Water wash	1,53	1,8	<0,1	-	2,2	-	-	-
NaOH(0,1 N) NaOCl	1,45	25	0,2	-	4	94	<3	<0,5
HCl(0,4 N)	0,96	1,4	0,3	-	1,3	<1	<3	<0,5
regenerated solvent	-	8	0,3	<1	-	76	6	1

Concentrations in p.p.m.

*OPM = other platinum metals.

A/O =aqueous-to-organic ratio

It can be seen that a large fraction of the PGM remaining in the solvent after the stripping of the palladium is removed during an alkali strip. Residual PGM values may be due to a short contact time in the mixer, the addition of hydrochloric acid to the settler, or impurities in the Alamine-336.

4.6 Parameters for Design for a Liquid-Liquid Process

The pilot-plant work has produced the following parameters for the liquid-liquid extraction process:

Section	Organic-to-aqueous ratio	Mixer retention time min	Settler area $m^2/(m^3/h)$	Number of stages
Loading	1 to 1	4	2	5
Scrubbing	1 to 1	4	2	5
Platinum strip	1 to 0,5	4	2	5
Palladium strip	1 to 3,0	4	2	5
Organic regeneration	1 to 1	4	4	2

5. PRECIPITATION OF PURE METALS

Investigations of the methods of precipitation were done on all the PGM. The main part of this work has been confined to platinum and palladium, derived from matte-leach residues. The aim has been to develop some selectivity against other elements present in the mother liquor in order to increase the purity.

5.1 Platinum

The work on liquid-liquid extraction with synthetic feed material produced two types of solutions from which platinum could be precipitated:

(1) Organic solvent from which palladium had previously been stripped selectively.

(2) The perchloric acid solution used for the stripping of the platinum from (1).

(3) Thiocyanate strip liquor.

Hydrogen was sparged through both solutions. In the organic solution, the hydrogen overpressure was 1 bar, and a suitable temperature was found to be 110°C. Under these conditions, the concentration of platinum was reduced from 5000 ppm to less than 10 ppm in 2 hours, provided the solution was seeded. Without seeding, precipitation starts only after 3 hours.

In the perchloric acid solution (1 M), a similar result was achieved at 90°C. Without seeding, precipitation commenced after 4 hours.

The platinum metal from both precipitations was washed with acetone, dried, and analyzed for impurities by emission spectrography (Table 17).

It is evident that precipitation from the organic phase produces a considerably purer product than precipitation from a perchloric acid solution. A possible reason is that other metal ions catalyzed by precipitated platinum are reduced more easily in aqueous than in organic solution.

The precipitation of platinum from thiocyanate solution requires a conversion of the $Pt(SCN)_6^{2-}$ to $PtCl_4^-$. Direct conversion by chlorination proved unsatisfactory. Quantitative precipitation of the platinum was achieved by the addition of 200% excess sodium sulfide to the hot thiocyanate solution, followed by pH adjustment to a value of 1 (with hydrochloric acid). This procedure is to some extent selective against precipitation of base metals, results in a platinum sulfide precipitate that can be filtered easily, and releases into solution thiocyanate ions that can be concentrated and recycled by an ion-exchange or liquid-liquid extraction route. The platinum sulfide precipitate is readily converted to chlorocomplexes by chlorination.

Two techniques of platinum precipitation have been used:

(a) Reduction to metal by the use of hydrazine.

(b) Precipitation as the ammonium hexachloroplatinate, followed by calcination in a reducing atmosphere.

The rate of reduction to metal by use of hydrazine is very dependent on pH; in alkaline solution, the reduction is almost instantaneous. Seeding of the solution at 90°C and pH value of 3 gives a coarse precipitate and a recovery of platinum metal of over 99.9%.

Precipitation of the ammonium hexachloroplatinate is best accomplished in a concentrated acid solution (platinum ca. 60 g/l in 3 M hydrochloric acid). Rather low recoveries (ca. 95%) have

Table 17: Purity of the platinum produced by hydrogen precipitation.

Group	Impurity	Precipitation from $HClO_4$ solution p.p.m.	precipitation from Alamine -Solvesso* p.p.m.
Noble metals	Ag	>100	<3
	Au	>100	25
	Ir	>100	>100
	Pd	>100	60
	Rh	>100	100
	Ru	>100	100
Heavy metals	Bi	>100	>3
	Cd	>100	10
	Cr	7	5
	Cu	70	35
	Fe	100	100
	Mn	2	1
	MO	80	<30
	Ni	70	50
	Pb	<30	<30
	Sb	<10	<10
	Sn	>100	10
	Zn	40	20
Other inpurities	B	50	20
	Cu	40	40
	Mg	60	60
	Si	T	VW

Notes: 1. VW=Very weak

2. As, Be, Ta, Ti, Tl, V, Zr, Os and Te were not detected.

been achieved so far, possibly because the presence of platinum in species other than the hexachlorocomplex.

The results of three experiments are reported in Table 18.

Comparison of the results obtained in test 1 with those in tests 2 and 3 show that precipitation with ammonium chloride followed by calcining produces a considerably purer metal than direct reduction with hydrazine.

Table 18: Platinum precipitations by hydrazine or NH_4Cl.

Precipitating agent		NH_2NH_2	NH_4Cl	NH_4Cl
Temp., °C		90	60	60
Acidity		pH 3	3 N	3 N
Recovery, %		99,9	92	95
			Impurities p.p.m.	
Noble metals	Ag	15	<1	2
	Au	5	<3	<3
	Pd	>100	<5	100
	Rh	>100	21	20
	Ru	>100	<10	17
Heavy base metals	Bi	13	<10	<3
	Cr	1	<1	<3
	Cu	3	<1	<1
	Fe	<10	<10	10
	Mn	<1	<1	3
	Ni	<10	<10	<3
	Pb	<3	<3	<3
Others	Al	11	<10	15
	B	>100	<30	10
	Ca	<1	6	6
	Mg	<3	<3	<3
	Si	>100	100	<5
	Zn	10	<3	<3

Note: As, Cd, Cu, Ir, Mo, Os, Sb, and Te were not detected.

5.2 Palladium

The palladium strip liquor from the liquid-liquid-extraction section contains the metal complexed with thiourea. Conversion to the chlorocomplex is achieved in the same way as for Monivex eluate, i.e., quantitative and nonselective precipitation of the sulfide by hydrolysis at high pH, followed by conversion of the precipitate with chlorine water to a chlorocomplex.

Palladium metal is produced by reduction with ethylene. Some selectivity against other PGM is obtained as a result of the fact that palladium forms rapidly a strong π-complex with ethylene. The complex is hydrolyzed by water to form acetaldehyde and palladium metal. It was found that in mixed chloride-nitrate solutions, the precipitation is more selective than in pure nitric acid. Selectivity against iridium is excellent (see Table 19).

6. CONCLUSIONS

The integrated ion exchange and liquid-liquid extraction process presented in this paper is able to handle a platinum group solution, or nativce ore. The ion exchange step is capable of separating the PGM elements, and also their concentration into a suitable feed solution to a liquid-liquid extraction process.

The extraction system chosen, Alamine-336 in Solvesso 150, is able to handle both a converted pure PGM eluate from the resin or a feed solution containing appreciable amounts of base metals. The oxidative hydrolysis (conditioning) step, homogenizes the feed to the liquid-liquid extraction process and prepares both Pd and Pt in a form extractable into the amine solvent, whereas Rh, Ir, Ru, and Os are retained mainly in the aqueous stream.

The separation of platinum from palladium relies on kinetic stripping of Pd by ligand substitution with thiourea, or by platinum stripping with thiocyanate. In both cases, the higher activity of Pd(II) is responsible for the separation achieved.

The pilot-plant results that were presented, incorporated and proved most of the conclusions of the chemical principles outlined

Table 19: Effect of nitric and hydrochloric acid concentration on the selectivity of palladium precipitation

Concn of hydrochloric acid	Concn of nitric acid	Head concn, p.p.m.			Concn in soln after pptn, p.p.m.			Pd precipitated	Selectivity ratio
M	M	Pd	Pt	Ir	Pd	Pt	Ir	%	
-	1,0	563	93	30	7	40	30	98,8	1,7
-	0,5	806	173	6,5	12	153	6,5	98,5	8,6
0,5	0,5	938	196	6,5	110,0	184	6,5	88,3	14,4
0,5	-	768	155	6,5	6,0	134	6,5	99,2	1,4

and tested in the laboratory, and show that all the objectives of this work are obtainable.

An economical analysis of this process flow-sheet has shown that processes based on ion exchange and liquid-liquid extraction show economical advantages over the classical processes. Indeed, since the time this work was concluded new PGM separation processes, based solely on liquid-liquid extraction have become commercial.[2]

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