

# Evaluation of different types of ion exchange resins for the recovery of Platinum Group Metals from an acidic chloride solution

V. Bazhko and J. Van Deventer

Mintek, South Africa

Ion exchange technology is of special interest in the separation and upgrading of precious metals. This paper focuses on the evaluation of a number of ion exchange resins with different functionalities and their efficiency in recovering noble metals from an acidic chloride solution that is typical of refining processes. The study consisted of a set of batch experiments to select the most suitable products. Breakthrough tests were conducted on the most promising candidates, along with preliminary elution tests to compare different eluants. During the scouting experiments, it was found that anion exchange resins with strong and weak base groups loaded all platinum group metals (PGMs) from the solution. The oxime type resins MTS9100 and MTS9701 showed selectivity to Pd while resins with S-containing groups were selective for Pt over other PGMs present in solution. Relatively high Ir extraction was achieved by the MTS9850 polyamine resin. Ru extraction was generally poor and the best results for Ru were obtained with the strong base resin MTA8000. Three different eluants were tested, i.e. 6 M HCl, a mixture of thiourea and HCl, as well as ammonium thiocyanate. Elution of PGMs were incomplete and in some cases very poor. It was found that 6M HCl showed promising results for removal of impurities, but it was less efficient for eluting the PGMs. Acidic thiourea was found to be more efficient for PGM elution but the formation of a precipitate was observed in the eluate. This would make operation of the elution circuit problematic.

**Keywords:** PGM, ion exchange resin, elution, selectivity

## INTRODUCTION

The recovery of platinum group metals (PGM) from ores typically involves the production of a base metals/PGM sulphide concentrate, followed by rejection of base metals via sulphuric acid leaching and PGM extraction via chlorination. The separation of PGMs, both from other elements in the aqueous stream and from each other is essential to produce products of high purity. Ion exchange (IX) has a number of advantages in the recovery of PGMs, such as the low operating cost, low energy consumption, the possibility of regenerating the resins, long life span of the resins, price, selectivity, high efficiency, and the simple process apparatus (Goc, 2021). Mintek evaluated the performance of various IX resins with different functional groups. Seven resins were evaluated for the recovery of PGMs from a solution containing high concentrations of base metals, amphoteric elements (As, Te, etc.) and free acid. Screening of the resins were done via batch contacts. The most promising candidates were subjected to column loading and elution tests. Successful implementation of an ion exchange system for the extraction and separation of PGMs would require not only good PGM extraction by the resin, but also the ability to effectively strip the valuable metals. The elution of PGMs from highly selective resins has been difficult to achieve because of the strong bond that forms between adsorbed metal ions and functional groups of the resins.

It often requires the use of eluents that form more stable complexes with the metals than what the metal ions form with the functional groups of the resins (Blokhin, 2007; Alam, 1997). In the current study, loaded resins were subjected to the elution test work with different eluents, namely hydrochloric acid, ammonium-thiocyanate and acidic thiourea.

## Experimental procedure

### *Solution composition*

The composition of the feed solutions used for the test work programme is shown in Table I.

Table I. Solutions for test work, mg/L

Pt	325	Fe	2143
Pd	1513	Pb	637
Au	1	Al	13
Rh	31	Zn	7
Ru	220	Se	39
Ir	91	As	2962
Ag	37	Te	1004
Na	2325	Bi	371
Cu	5089	Sb	31
Ni	3915	HCl	3.4 M
		ORP	500 mV (Ag/AgCl)

At a free acid concentration of 3.4 M HCl, it is expected that Pt and Pd present as  $[\text{PtCl}_6]^{2-}$  and  $[\text{PdCl}_4]^{2-}$ ; the secondary PGMs Rh and Ru, on the other hand, could have been present as a mixtures of anionic chloro- and chloro-aqua-complexes (Bernardis, 2005). Fe(III), Al, Co and Ni form positively charged or neutral species while Ag, Zn, Pb and to lesser extent Cu form anionic chloro-complexes. Te can present in the form of  $\text{Te}(\text{OH})_3^+$  and anionic chloride species (Nazarenko, 1971). Se forms anionic specie, As presents as  $\text{H}_3\text{AsO}_4$ .

Solutions and loaded resins were analysed using ICP-OES and XRF analysis. The XRF was calibrated for solutions assay using synthetic standards with known metals concentrations.

### *Resins chosen for evaluation*

The resins selected for the test work were provided by Porolite. They can be subdivided into three groups, according to their functionality:

- Anion exchange resins which could recover the PGMs as anionic complexes:
  - MTS9850: weak base polyamine resin.
  - MTA1701: weak base complex amine resin.
  - MTA8000: strong base quaternary ammonium resin.
- Resins with sulphur containing functional groups which can recover the PGMs due to the formation of strong bonds between sulphur and PGMs:
  - MTS9200: isothiuronium resin.
  - MTS9140: thiourea resin.
- Resins with oxime groups which potentially can be selective for Pd and Pt:
  - MTS9100: amidoxime resin.
  - MTS9701: amidoxime/carboxylic acid resin.

### *Scouting tests*

Initial scouting tests were done to determine the extent of loading of PGMs onto the different resins, as well as co-loading of other metals. These tests were done on:

- Feed solution, as is.
- Feed solution after 5x dilution with water. The dilution served to decrease the chloride concentration to a level where the majority of the base metals would be present as cations, rather than anionic chloride complexes.

The different resins were contacted with the feed solutions in batch at a solution-to-resin ratio of 100:1. Contacts interactions were done in glass rolling bottles at ambient temperature for a period of 24 hours. After 24 hours, the resin was separated from the barren liquor and washed with water. The feed and barren solutions were analysed for the elements of interest. Resin loadings were calculated, based on the difference in concentration.

#### **Column loading test: MTA8000 resin**

A resin sample (150 mL) was placed into a glass column and the feed was passed through the column at ambient temperature at a flowrate of 2 bedvolumes per hour (BV/h). A bedvolume is equal to the volume of resin in the test, in this case 150 ml. A flowrate of 2 BV/h thus equals 300 ml/hour. Portions of the barren liquors were collected and submitted for analysis. After completion of the test, the loaded resin was washed in the column with 1g/L HCl to displace entrained feed solution, followed by a water wash.

#### **Column loading test with MTS9140 and MTS9850 resins**

Feed solution for these column tests was prepared by blending selected barren samples collected after the column loading test with MTA8000 resin.

A resin sample (30 mL) was placed into a glass column and the feed was passed through the column at ambient temperature at a flowrate of 2 BV/h. Portions of the barren solution were collected and analysed for the elements of interest. Loaded resin was washed with water to displace entrained feed solution.

#### **Column elution test with MTS9140 and MTS9850 resins**

Loaded resins from the column loading tests were eluted with the following eluents:

- 6M HCl.
- 1M Thiourea+1M HCl.
- 2 M NH<sub>4</sub>SCN

The loaded resins were split into three equal portions of 10 ml each. These were placed into glass columns and the eluant was passed through the column at 60°C at a flowrate of 2 BV/h. Portions of the eluate were collected and analysed for the elements of interest.

## **Results and discussion**

### **PGM recovery: screening of the resins**

The extraction efficiency and loading of Pt, Pd, Ru and Ir were calculated for each of the resins. Base metals loading was negligible, except for Pb and Ag. It should be noted that Au and amphoteric were not assayed for this test.

Comparison of extraction of the elements achieved at a solution-to-resin ratio of 100 by different resins is shown in Figure 1. The cumulative loading of the major elements onto the different resins are presented in Figure 2.

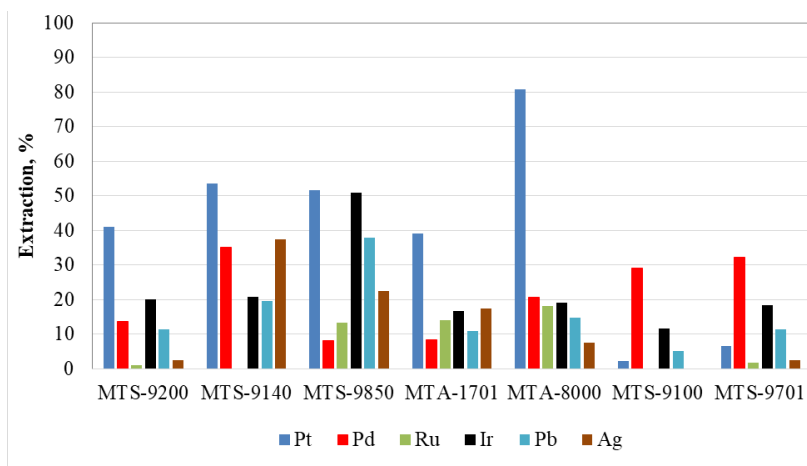


Figure 1. PGMs and impurities extraction.

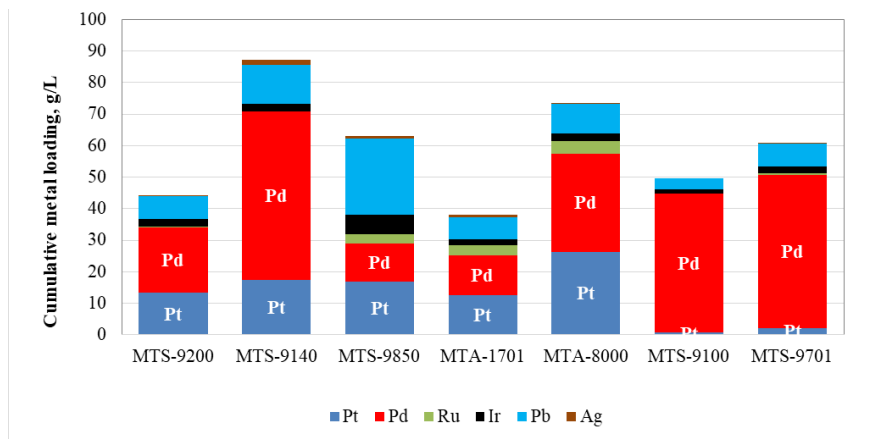


Figure 2. Resins loadings.

Analysis of information obtained reveals the following:

- PGM loadings obtained with the 'as is' solution was higher than from the diluted solution.
- Cu and Ni did not load, but Fe and Pb loaded from the 'as is' solution. After dilution of the feed liquor, Fe and Pb loading was negligible, indicating that the base metals were present as cations in the dilute solution that did not compete with the anionic PGM-chloride complexes.
- Anion exchange resins with strong (MTA8000) and weak base (MTS9850) groups loaded all PGMs from the solution.
- Oxime type resins MTS9100 and MTS9701 showed selectivity to Pd over other PGMs present in solution.
- The highest Pd extraction was achieved by oxime type resins and MTS9701 and MTS9140 resin with thiourea group.
- Resin with S-containing groups and strong and weak base anion exchangers were selective for Pt over other PGMs present in solution.
- Relatively high Ir extraction of 50% was achieved by weak base MTS9850 resin.
- Ru extraction was generally poor and the best results were obtained with MTA8000 (18% extraction).
- Highest Pb and Ag co-extractions were reported for MTS9850 and MTS9140 resins, respectively. An attempt to minimise Pb co-loading was done by targeting a change in metals speciation by diluting the feed with water 5 equivalents. At the lower chloride concentration, anionic species  $PbCl_4^{2-}$  and  $PbCl_3^-$  would transform to  $PbCl_2$  and  $PbCl^+$  with lower affinity to anion exchangers. Ag in the diluted feed was too low to be traced.

The diluted solution was contacted with the resin at a ratio of 100-to-1 and comparison of PGM and Pb distribution in the resin phase with diluted solution and the feed 'as is' is presented in Figure 3.

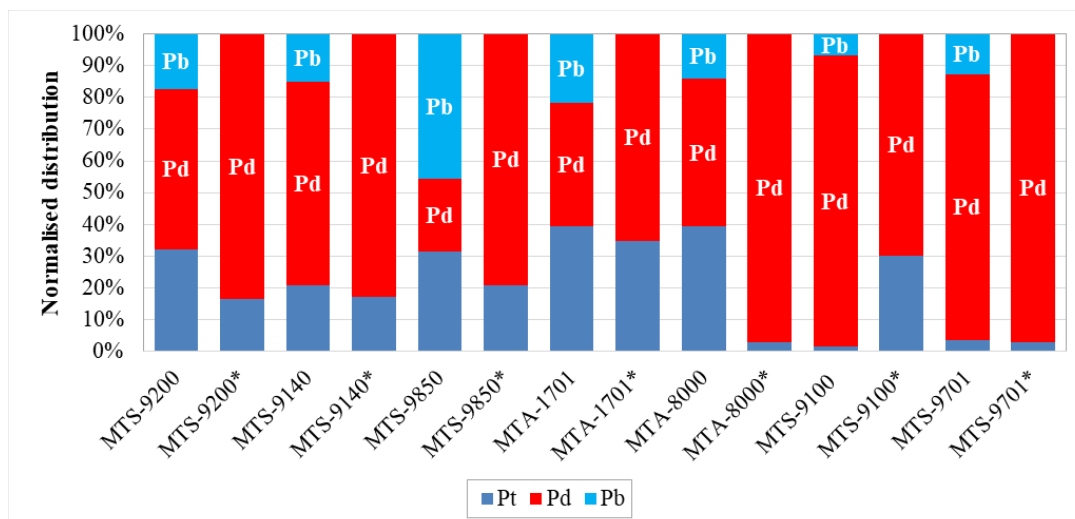


Figure 3. Normalised distribution of Pt, Pd and Pb before and after dilution (\*).

Dilution of the solution resulted in no loading of Pb by the resins tested, indicating that re-speciation had occurred.

Upgrades for each metal, as well as the sum of the PGMs onto the different resins, were calculated as follows:

$$\text{Upgrade} = \text{Metal on resin} \div \text{Metal in solution}$$

The order of total PGM loading, from highest to lowest, were as follows:

- Feed 'as is': MTS9140 > MTA8000 > MTS9701 > MTS9100 >> MTS9200 > MTS9850 > MTA1701
- Feed '5xdiluted': MTS9140 > MTS9200 > MTS9850 > MTS9100 > MTS9701 > MTA8000 > MTA1701

#### Column loading test with MTA8000 resin

The MTA8000 resin was selected for a column test targeting the removal of Pt from the original feed.

The following observations were done during the test:

- At the beginning of the test, the top layer of the resin in the column started to change colour from light brown to dark brown. The barren solution collected had a green colour, indicating that PGMs were probably adsorbed while base metals remained in the solution;
- During washing of the loaded resin with water, formation of a pink precipitate and its washing from the column was observed. The precipitate was dried and scanned. The scan indicated the presence of Rh, Ir, Pb, Bi and high Cl which was probably due to hydrolysis of chloride complexes with formation of insoluble oxychlorides, chlorides etc.

The results of the column test are presented in Figure 4. Rh analysis was problematic due to low Rh concentration in the solution. Pb and Rh breakthrough happened very quickly, within the first 10 BVs. Some Pd loading occurred initially, with breakthrough after approximately 40 BVs. The run was continued to allow complete Pd breakthrough. The selectivity order for the MTA8000 resin was as follows:

$$\text{Pt} > \text{Se} > \text{Pd} \sim \text{Bi} > \text{Ag} > \text{Rh} > \text{Pb}$$

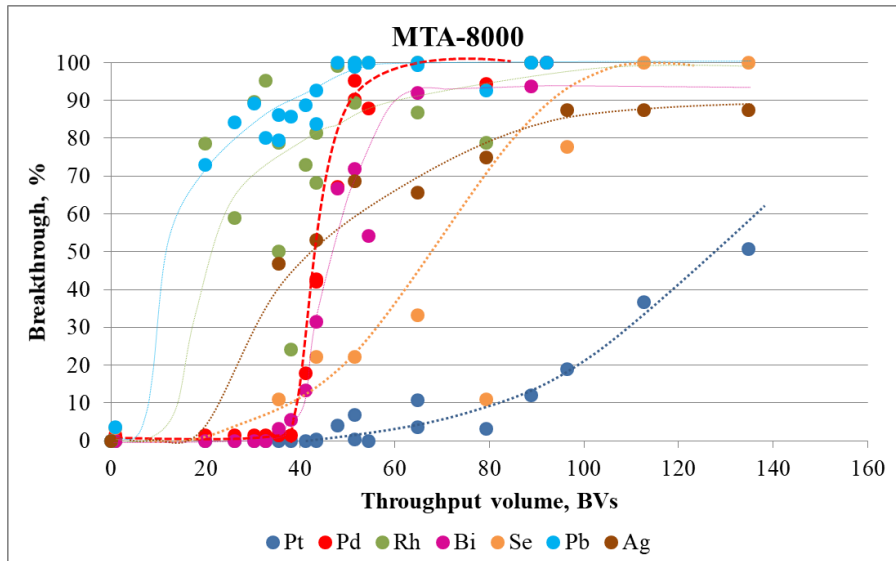


Figure 4. Breakthrough test for MTA8000 resin.

Resin loadings were also calculated, based on feed and barren solution assays and reported in Table II and Figure 5. The relative loadings were confirmed via XRF analysis. Pd and Pt loadings were high, followed by Bi, Pb and Rh.

Table II. Loaded MTA8000, mg/L

	Pt	Pd	Rh	Cu	Ni	Fe	Pb	As	Bi	Se
MTA8000	29619	49578	570	0	0	0	2050	0	15341	n/a

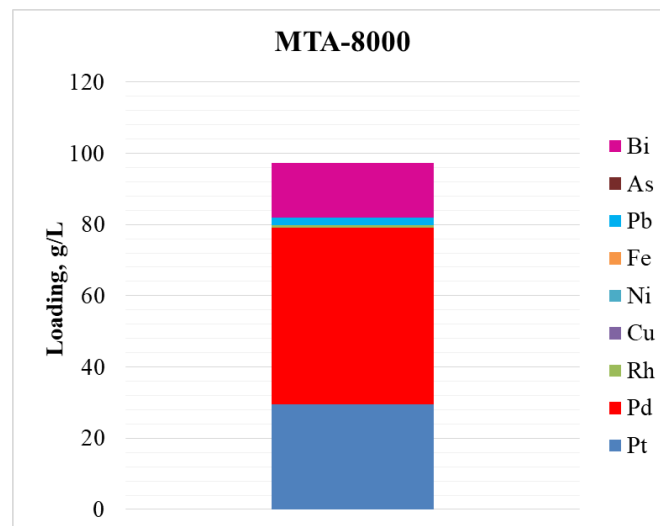


Figure 5. Loaded MTA8000 resin

### Column loading test with MTS9140 and MTS9850 resins

The aim of the test was to recover residual PGMs from the feed, after removal of platinum via the MTA8000 resin.

For these tests, Pt-free barren solution fractions from the column test conducted with the MTA8000 resin were combined. The resulting solution, feed#1, had a similar composition to the original feed of all the elements, albeit dilute, and with a low Pt concentration, as is shown in Table III.

Table III. Feed#1 analysis, mg/L

Pt	Pd	Rh	Ir	Ru	Ag	Cu	Ni	Fe	As	Te	Se	Bi	Pb
11	1102	27	62	135	21	2303	1734	1410	2384	558	1.5	193	201

The following observations were made during the two column tests:

- After the first few BVs of the feed were passed through MTS9850 resin, the resin colour changed to blue. This was most likely due to Cu adsorption.
- Over time, the blue zone disappeared as Cu was displaced by other metals with higher selectivity towards the MTS9850 resin functional groups.
- Loaded MTS9850 resin had a dark brown colour, while MTS9140 had a light brown colour.

The results of column loading tests are shown in Figure 6. Both resins loaded very little base metals (Fe, Cu, Ni) and As but a significant amount of Pd. MTS9140 had higher Pd loading.

- It was noticed that MTS9140 had a higher selectivity for Pd than Pb and Bi. Loaded Bi was displaced by Pd.
- Selectivity of MTS9850 resin was changing in the following order: Bi > Pb > Pd;
- MTS9850 resin had higher Rh loading.
- Te and Ru were not loaded significantly on either resins.
- MTS9850 resin adsorbed Ir while MTS9140 did not (based on ICP-MS analysis conducted on selected barren samples).

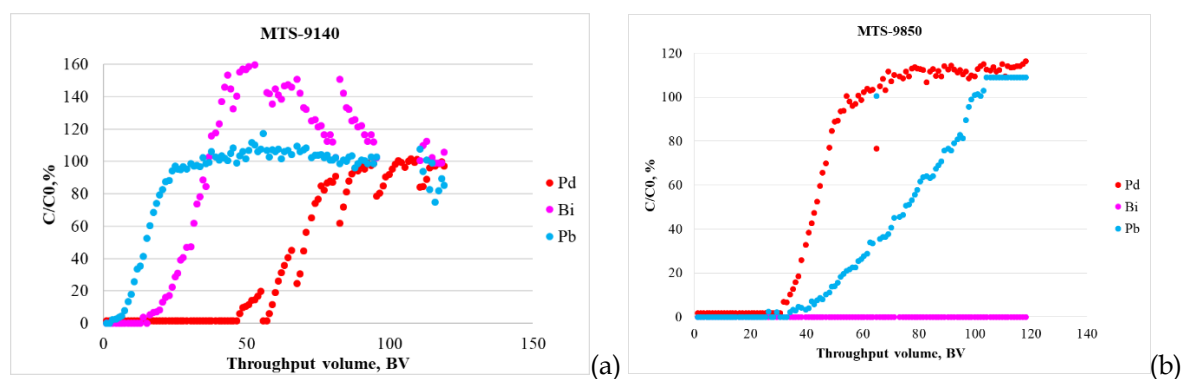


Figure 6. Breakthrough test for MTS9140 (a) and S9850 (b) resin.

Loaded resins after the test were scanned by XRF and loadings were also calculated based on feed and barren solution assays. The results are presented in Table IV.

Table 4. Loaded MTS9850 and MTS9140 resins, mg/L

	Pt	Pd	Rh	Cu	Ni	Fe	As	Bi	Pb	Ag
MTS9140	395	72338	27	0	0	0	0	5204	1940	1456
MTS9850	1305	47044	316	0	0	0	0	22827	14911	1040

Figure 7 shows the distribution of various elements on the loaded resins. It can be seen that MTS9850 and MTS9140 had similar resin capacity occupied by metals and metalloids. However, S9850 loaded much less Pd but significant amount of Bi and Pb. In the case of MTS9140 more than 90% of the resin capacity was occupied by Pd. The results indicated that this resin was more attractive for the selective removal of Pd from base metals and metalloids.

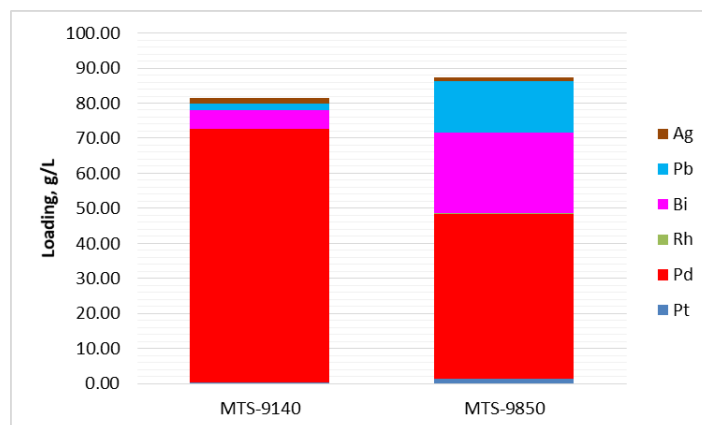


Figure 7. Distribution of elements in the loaded resins

#### **Column elution of MTS9140 and MTS9850**

Three column elution tests were conducted on each loaded resin to evaluate the efficiency of different reagents for the elution of PGMs and impurities from the resin. The eluates, wash waters and eluted resins were scanned with XRF. It was observed that in certain cases it was difficult to close the metal mass balances for the elution tests. This was attributed to the fact that for some eluate samples, such as thiourea and thiocyanate strip liquors, in-situ crystallisation and/or precipitation had occurred. This could be due to various reasons including reduction of PGM to lower oxidation state, low ligand/PGM ratio in some eluate fractions and/or oxidation of thiourea and thiocyanate with the formation of sulphur and/or PGM sulphides.

Elution profiles (Figure 8) are only reported for elements present in significant quantities.



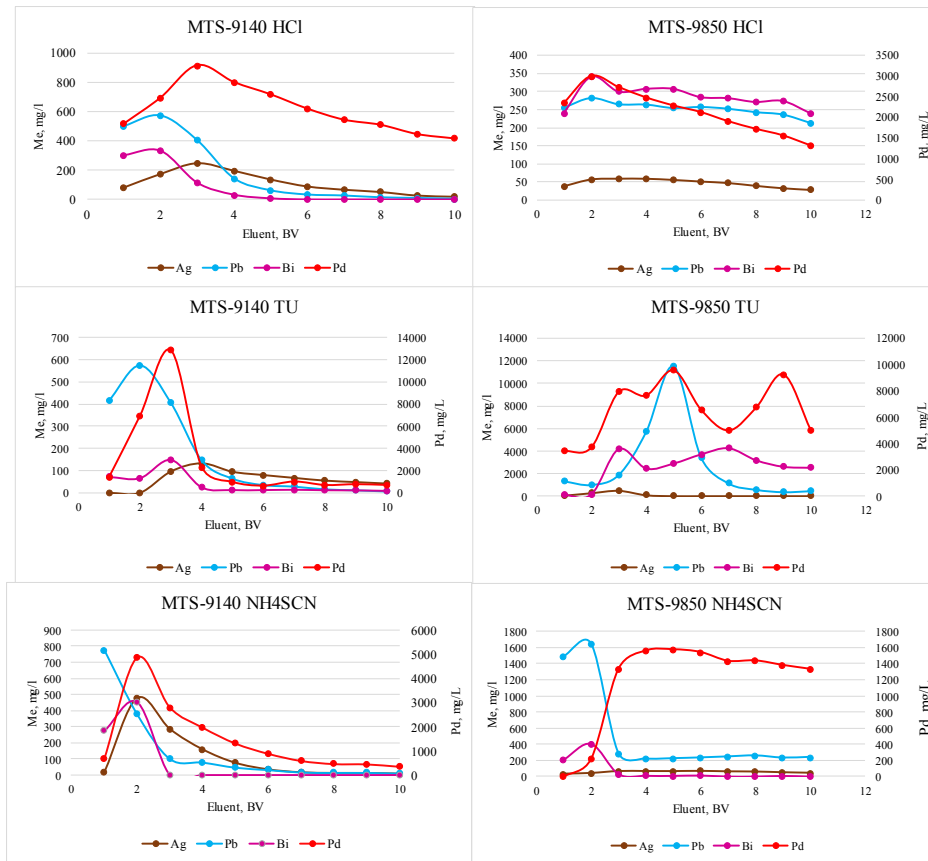


Figure 8. MTS9140 and MTS9850 elution profiles

MTS9140 resin had traces of base metals, As and Ag loaded. These elements were easily removed in the first few portions of HCl and NH<sub>4</sub>SCN. Thiourea showed low stripping efficiency for Cu, As and Ag. Bi was eluted with 6M HCl. Pd could be stripped with thiourea but not with any of the other reagents. The disadvantage of thiourea as eluant is the formation of precipitate in the eluate. A scan indicated the presence of high S, Cl and Pd in the precipitates. Low amounts of Pt and Rh were loaded onto the MTS9140 resin. Elution of these two elements was poor (Table V). The MTS9850 resin was first eluted with 2 BV of water at 60°C. This resulted in the removal of the majority of base metals from the loaded resin. The rest of the base metals and As could be eluted with HCl. Pb, Ag, Bi and Pd could be eluted with HCl but it would require a large volume of the eluent. Thiourea showed the highest elution efficiency for Pd, Bi and Pb. However, during elution (even in column) the formation of a precipitate was observed that would make operation of the elution circuit difficult. Eluted resin (after 10 BVs of each eluant) still contained significant amount of Pd, Bi, Pd (Table V).

Table V. Analysis of loaded and eluted resins

	Fe	Cu	Ni	As	Ag	Pb	Bi	Pt	Pd	Rh
MTS9140										
loaded resin	140	206	106	180	1405	544	3284	210	9761	60
eluted with HCl	44	2	15	18	0	20	538	193	9883	107
eluted with NH <sub>4</sub> SCN	38	23	16	39	0	61	2769	230	9227	71
eluted with TU	24	114	0	150	876	167	2214	138	2123	343
MTS9850										
loaded resin	181	134	52	1017	562	2788	41427	619	5803	423
eluted with HCl	57	45	18	798	0	1853	28852	593	2177	625
eluted with NH <sub>4</sub> SCN	105	86	26	1035	69	1973	39642	738	5224	417
eluted with TU	107	132	19	1170	0	1128	9597	658	715	394

## CONCLUSIONS

A range of chelating (S-containing and oxime) and anion exchange resins were evaluated for PGM recovery from an acidic chloride stream. Outcomes of the tests were:

- Anion exchange resins with strong and weak base groups loaded all PGMs from the solution, i.e. Pt, Pd, Ir, Ru, Rh.
- Oxime type resins MTS9100 and MTS9701 were selective for Pd over other PGMs present in solution.
- Resins with S-containing groups and strong and weak base anion exchangers were selective for Pt over other PGMs present in solution.
- Relatively high Ir extraction of 50% was achieved by the polyamine MTS9850 resin.
- Ru extraction was generally poor and the best results were obtained with MTA8000 (18% extraction).
- The resins co-loaded significant amounts of Pb which were in anionic form at high Cl concentration in the solution. However, dilution of the feed resulted in re-speciation of Pb, thereby minimising its co-loading.

This findings indicating a potential of development of an ion-exchange method for the recovery and separation of platinum and palladium (and other PGMs) from a highly acidic solution that contains a considerable amount of base metals and amphoteric. It was suggested to remove Pt first with MTA8000 resin followed by Pd adsorption with MTS9140 selective resin or bulk PGMs removal with MTS9850 resin.

Breakthrough tests were conducted, targeting loading of Pt and Pd onto the selected resins. First, the feed was passed through the column containing the MTA8000 resin with high affinity to Pt. Selectivity order for the resin was as follows:

Pt > Se > Pd ~ Bi > Ag > Rh > Pb

Barren solutions after MTA8000 test formed a feed for a second set of column tests. Results of column tests indicated that

- MTS9140 had higher selectivity for Pd than Pb and Bi. Loaded Bi was displaced by Pd.
- Selectivity of MTS9850 resin was as follows: Bi > Pb > Pd.

The efficiency of three different reagents were compared for eluting resins MTS9140 and MTS9850 which were obtained from the column loading tests. It was demonstrated that the elution of PGMs were incomplete and in some cases very poor.

The S-containing MTS9140 resin can be first eluted with 6M HCl to remove base metals and co-loaded amphoteric. Thereafter, Pd could be stripped with acidic thiourea. However, the elution was hampered by the formation of precipitates in the eluate.

The weak base anion exchanger MTS9850 can be washed/eluted with water to remove the majority of base metals loaded. Pd, Pb and Bi could also be eluted with HCl but it would require a large volume of acid. Alternatively, acidic thiourea can be applied to produce a smaller volume. Again, the formation of a precipitate was observed what would make operation of elution circuit difficult.

## REFERENCES

- Alam, M.S., Inoue, K. Extraction of rhodium from other platinum group metals with Kelex 100 from chloride media containing tin, *Hydrometallurgy*, 1997, 46 (3), 373-382.
- Bernardis, F.L., Grant, R.A. and Sherrington, D.C. A review of methods of separation of the platinum-group metals through their chloro-complexes, *Reactive and functional polymers*, 2005, 65, 205-217.
- Blokhin, A.A., Abovskii, N.D. Murashkin, Y.V. Ion-exchange recovery of palladium(II) from multicomponent chloride solutions, *Russian Journal of Applied Chemistry* 2007, 80 (7), 1058-1062.
- Goc, K.; Kluczka, J.; Benke, G.; Malarz, J.; Pianowska, K.; Leszczyńska-Sejda, K. Application of Ion Exchange for Recovery of Noble Metals. *Minerals* 2021, 11, 1188. <https://doi.org/10.3390/min11111188>
- Nazarenko, I.I. and Ermakov, A.N. *Analiticheskaya khimiya selena i tellura (Analytical Chemistry of Selenium and Tellurium)*, 1971. Moscow: Nauka.



## **Volha (Olga) Bazhko**

Chief scientist  
Mintek

Volha Bazhko has fifteen years experience in the field of gold, PGM, uranium, REE and base metals processing. Research and commercial projects involved flow sheet development and optimisation, evaluation of new products and technologies for metallurgical application, development of new technologies.