

Recovering Platinum Group Metals from acidic and high chloride effluent streams using ion exchange resins

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Platinum group metals (PGM) include platinum, rhodium, iridium, osmium, palladium, and ruthenium. They are classified as high value precious metals. PGMs are grouped together due to their similar chemical and physical characteristics. Trace amounts of the metals can be found in wastewater. It is worthwhile exploring methods of recovering the metals from waste streams, due to their high value. Ion exchange was explored as a method of recovering PGMs from wastewater. Laboratory scale test work was conducted to determine the most suitable ion exchange resin to recover the PGMs. The criterion for a suitable resin includes selective recovery of PGMs from the wastewater containing base metals. The initial work consisted of isotherm testing in which different ion exchange resins were used to determine the most PGM selective resin. The resin types that were tested included chelating with a thiourea group, chelating weak basic anion, standard strong base anion and weak base anion. The four ion exchange resins were all able to recover the PGMs from the wastewater. Bench scale column test work was conducted on the three best performing resins which were strong base anion (Lewatit MonoPlus M 500), weak base anion (Lewatit A 365) and chelating with the thiourea functional group (Lewatit MonoPlus TP 214). These tests were done to determine the loading potential of the resins in a fixed bed configuration. Platinum was effectively recovered by the three tested resins. The recovery of iridium was improved by introducing an oxidant to the feed. Ion exchange was shown to be a viable technology to recover trace amounts of PGMs from wastewater. The Lewatit MonoPlus TP 214 and Lewatit A 365 were determined to be the best performing resins and should be applied in series for the best recovery

Keywords: Platinum group metals, ion exchange, base metals, wastewater

INTRODUCTION

Platinum Group Metals

Platinum group metals (PGMs) are elements that have similar structure and chemical properties. They are used in many applications, including industrial, medical and electrical fields. PGMs are usually found together in the same ores such as ultramafic and mafic igneous rocks. They are also a by-product of nickel mining and processing. The six PGMs are platinum, palladium, rhodium, ruthenium, iridium and osmium. ^{[1] [2] [3]}

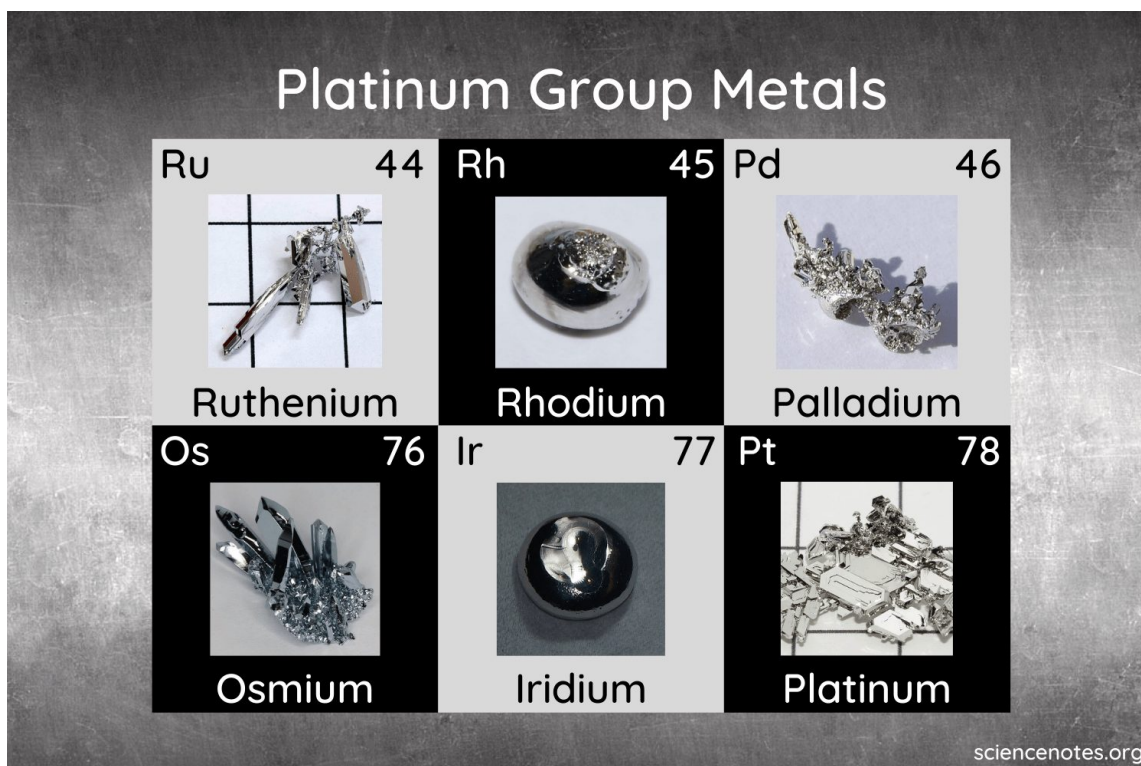


Figure 1. Platinum group metals (Helmentine, 2021).

The similarities of PGMs include high density, stability at high temperatures, excellent resistance, and good catalytic properties [3] PGMs are in high demand due to their suitability for many applications. Mining alone does not produce enough to meet demand. Recycling of PGMs is essential to establish a secondary source. (Helmentine, 2021). Rhodium is extremely rare, thus making it the most expensive PGM currently. It is used in the automotive industry to reduce harmful gases (such as carbon monoxide) in a vehicle's exhaust system into less hazardous products before they exit the exhaust pipe. In 2020 the rhodium prices went up (in US\$ terms) by 187.2% and 222.6%. Palladium is also valuable in the market of PGMs - its price has increased by 43.2% in US\$ terms. [5] The price increases were due to disruptions in production (Stats SA, 2022). The PGM sector is an essential contributor to mining in South Africa. In terms of value added, coal is the most important component of mining, accounting for 25%. PGM sales exceeded coal sales for the first time in the last decade to become the most significant contributor to total mining-industry sales, reaching R190 billion in 2020. This was greater than the total value of iron ore and gold sales (Stats SA, 2022).

Extraction of PGMs from wastewater

There are two advantages of recovering metals from dilute PGM process streams: pollution reduction of the aquatic environment, and recovery of metals with high commercial value (Oke *et al.*, 2017). Methods such as ion exchange resins, solvent extraction or reduction and precipitation can be used to recover precious metals such as PGMs. (Jing and Adreas, 2017). Ion exchange has an advantage for the recovery of low concentrations of PGMs. This paper focuses on the hydrometallurgical recovery of PGMs from wastewater obtained from a PGM refinery using ion exchange chromatography.

Ion exchange

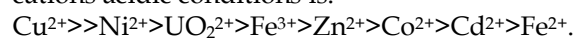
Investigated resins

Lewatit A 365

The Lewatit A 365 is a weak base anion resin which has a gel type structure and a polyamine functional group. The resin is supplied in the free base form. Lewatit A 365 is suitable for the treatment of aqueous solutions and high total dissolved solids waters.

Lewatit MonoPlus TP 220

Used for copper, nickel, and cobalt processing solutions, Lewatit MonoPlus TP 220 is a weakly basic resin that has chelating bis-picolylamine groups. The selectivity series for the removal of heavy metal cations acidic conditions is:



Lewatit MonoPlus M 500

Lewatit MonoPlus M 500 is a gel type 1 SBA resin, with beads of uniform size, which means it is monodispersed. Lewatit MonoPlus M 500 is chemically and osmotically highly stable. It has high organic fouling potential in high chemical oxygen demand waste waters. This resin is widely used in water purification and a metallurgical grade is also available.

Lewatit MonoPlus TP 214

Lewatit MonoPlus has structure and chelating thiourea functional group. The resin is designed to have high selectivity for precious metals such as PGMs. The expected extraction order of the metals onto this resin is shown below in order of decreasing affinity:

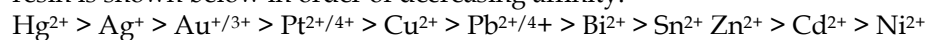


Table I. Properties of investigated resins

Resin name	Functional group	Operating pH range	Delivery form	matrix
Lewatit A 365	Polyamine	0-8	Free base	Acrylic
Lewatit MonoPlus TP 220	Bis-picolylamine	0-14	H ₂ SO ₄ salt	Styrenic
Lewatit MonoPlus M 500	Quaternary ammonium type 1	0-12	Cl ⁻	Styrenic
Lewatit MonoPlus TP 214	Thiourea	0-14	-	Styrenic

Experimental

Modified isotherm tests were conducted using different resins to determine the suitability of ion exchange technology to extract the PGMs from a wastewater sample with high zinc and iron background.

Isotherm test

Initial testing consisted of three resins to solution ratios. Specific volumes of each resin and 250 mL of wastewater were added to glass bottles and agitated on a shaker for four hours at ambient temperature. The samples were then analysed by inductively coupled plasma (ICP).

Table II. Resin to solution ratios used for the isotherm tests

	Resin volume (mL)	Resin to solution ratio
Feed A	0	0
Point 1	2.5	0.01
Point 2	5	0.02
Point 3	10	0.04

A 365 was delivered in the free base form and had to be conditioned to the chloride form. Without conditioning, the pH of the solution increased when it was in contact with the resin, and this led to ferric iron precipitation. The precipitation clogged the column, and the feed could not pass through.

Conditioning was performed by stirring the resin with 100 mL of 1 M NaOH, which was decanted prior to rinsing with demineralised water. The resin form was converted to the chloride form by mixing 1 M HCl with the resin for 30 minutes. The acid was decanted, and the resin was rinsed with demineralised water until a stable pH was reached.

Column test

Column test work was conducted to determine the equilibrium and the kinetic conditions likely to be encountered in a full-scale plant.

Trial 1-Unoxidised feed

Column test work was conducted using Feed A as received. The columns were set up in series such that Feed A passed through M 500 then Lewatit A 365 and finally TP 214. The configuration is shown in Figure 2. The samples were then analysed using ICP. The test work conditions for this trial have been summarised in Table III.

Table 1

Table 1. Column test conditions for trial 1

Resins	Lewatit A 365, Lewatit MonoPlus TP 214 Lewatit MonoPlus M 500
Resin volume	50 mL (1 Bed volume, BV)
Feed B volume	2 200 mL (44 BV)
Flow rate	5 BV/h
Starting pH	-0.189

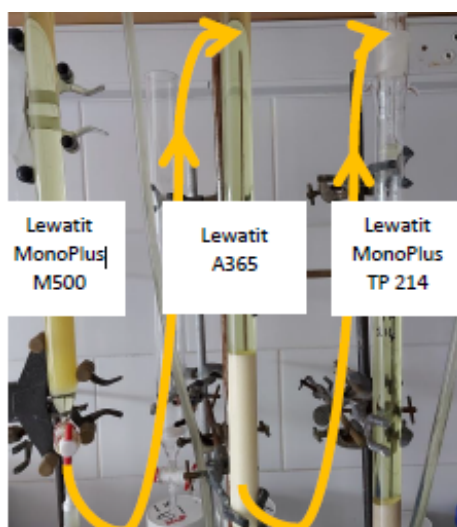


Figure 2. Configuration of the three resins for testing in series.

Trial 2 - Oxidised feed

Oxidation of the feed was explored to improve the loading of iridium. Calcium hypochlorite was the oxidant used.

The glass column tests were run in parallel as shown in Figure 3, such that they were independent of each other. Lewatit A 365 and Lewatit MonoPlus TP 214 were tested under the test conditions in Table IV.

Table IV. Column test conditions for trial 2

Resins	<ul style="list-style-type: none"> • Lewatit A 365 • Lewatit MonoPlus TP 214
Resin volume	50 mL
Oxidised feed volume	5000 mL
Flow rate	5 BV/h
Starting pH	1.9
Temperature	Ambient

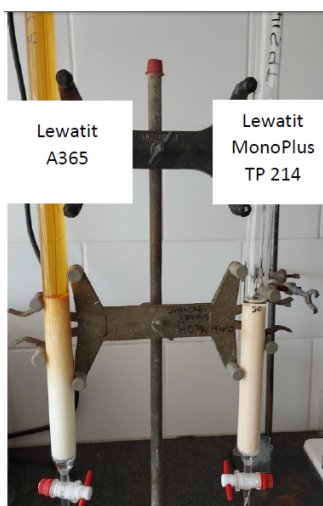


Figure 3. Parallel column setup of Lewatit A 365 and Lewatit MonoPlus TP 214.

RESULTS AND DISCUSSION

The wastewater received from the PGM producer was acidic and had a high chloride background. The compositions of the wastewater sample were different for each trial due to the varying operating conditions within the PGM plant. The samples have therefore been labelled as Feed A, Feed B, and Feed C to distinguish between them.

Modified isotherm test

The modified isotherm tests were conducted in a batch. This is a scoping test that verifies the suitability of ion exchange technology for recovering the PGMs from the acidic- and high chloride-containing wastewater feed. The batch tests also facilitated the selection of the most suitable ion exchange resins for this application.

The composition of Feed A is shown in Table V. Rhodium and palladium concentrations were below the detection limit. The feed had a pH of -0.286, ORP of 900 mV and low PGM concentrations in comparison to the iron and zinc. This introduced a challenge when conducting the loading tests due to the competition for the resins' capacity.

Table V. Composition of Feed A for the isotherm test

Fe	Zn	Pd	Pt	Rh	Ru	Ir	Os
mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1201	6446	<0.001	0.322	<0.001	0.98	1.46	0.045

Figures 4 to 7 show the fraction of the reported PGMs, iron and zinc, that were loaded onto the resins. The loading was determined by a mass balance of metals available in the feed and the barren solution. The initial scoping tests showed that all four of the resins tested were able to remove PGMs from the feed solution too. Zinc and iron were also co-loaded onto the tested resins. Lewatit A 365 seems to indicate the least amount of co-loading of iron and zinc.

Iridium was not loaded efficiently by the ion exchange resin. The fraction loaded was very close to zero. Oxidising the iridium might result in more iridium being loaded onto the resin. This could be due to iridium being unable to efficiently load onto the resin in the Ir (3+) state. The iridium might require oxidation to Ir (4+) to enable sufficient loading.

The low concentration of PGMs and high background base metals affected the margin of error. The modified isotherm testwork has indicated that ion exchange has the potential to recover the PGMs. The M 500, TP 214 and A 365 were selected for column test work due to the achieved recoveries and relative costs of the resins.

Trial 1 - Unoxidized feed

The PGM concentration in the Feed B to the column tests was higher than Feed A. This could have been due to changes in the PGM producer's operations

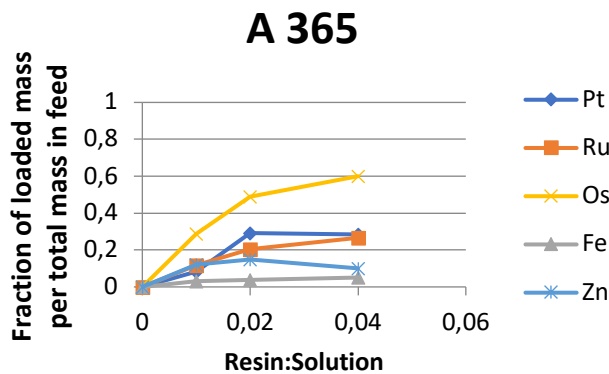


Figure 4. Loaded mass of PGMs, Fe and Zn on the Lewatit A 365 at varying resin to solution ratios.

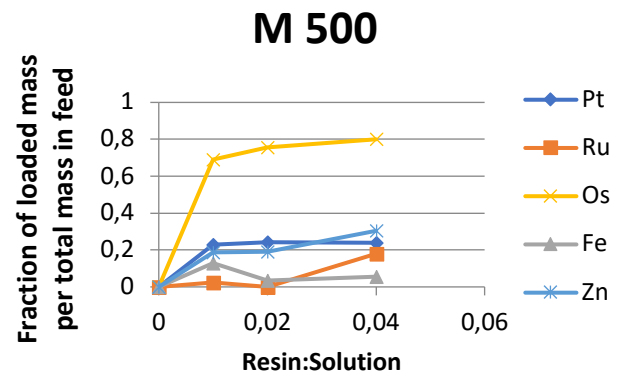


Figure 5. Loaded mass of PGMs, Fe and Zn on the Lewatit MonoPlus M 500 at varying resin to solution ratios.

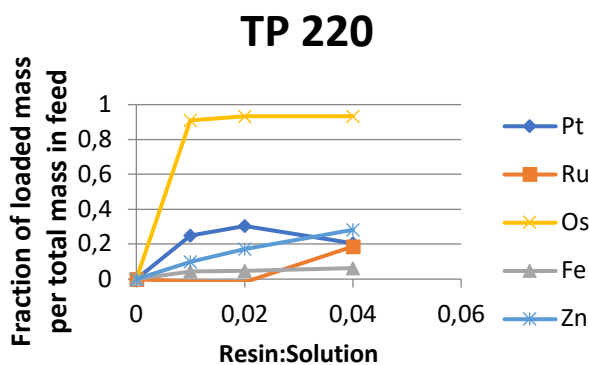


Figure 6. Loaded mass of PGMs, Fe and Zn on the Lewatit MonoPlus TP 220 at varying resin to solution ratios.

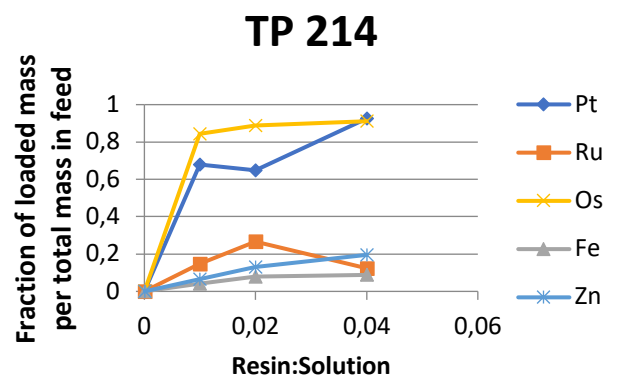


Figure 7. Loaded mass of PGMs, Fe and Zn on the Lewatit MonoPlus TP 214 at varying resin to solution ratios.

Table VI. Concentration of elements present in Feed B

Au mg/L	Ir mg/L	Pd mg/L	Pt mg/L	Rh mg/L	Ru mg/L	Fe mg/L	Zn mg/L
<0.01	2.87	0.07	1.21	1.4	0.75	1 075	5 986

All the resins were able to extract the PGMs from the wastewater. TP 214 (thiourea functional group) had the best PGM loading of the three tested resins. The M 500 had the least loading potential of the tested resins.

The palladium loading was most efficient on TP 214. Figure 8 shows that the concentration of palladium has remained close to zero until the 100 bed volumes. PGMs had not broken through at the end of the run. The loading of rhodium seemed to be impaired on all the resins which could have been due to the rhodium being stable in the Rh (III) form.

Iridium was best loaded on the Lewatit A 365 and Lewatit MonoPlus TP 214. Iridium loading was

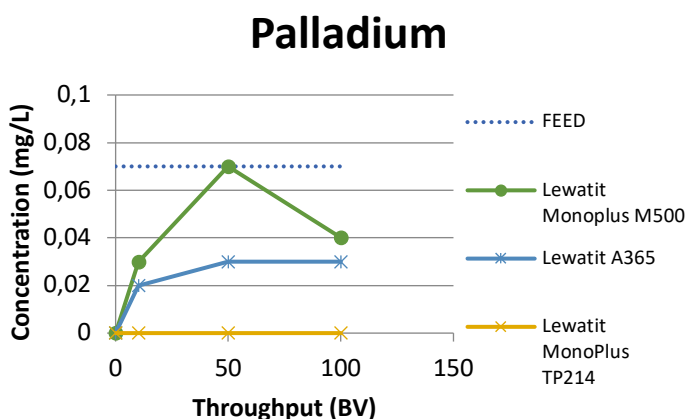


Figure 8. Palladium concentration in the barren solution after trial 1.

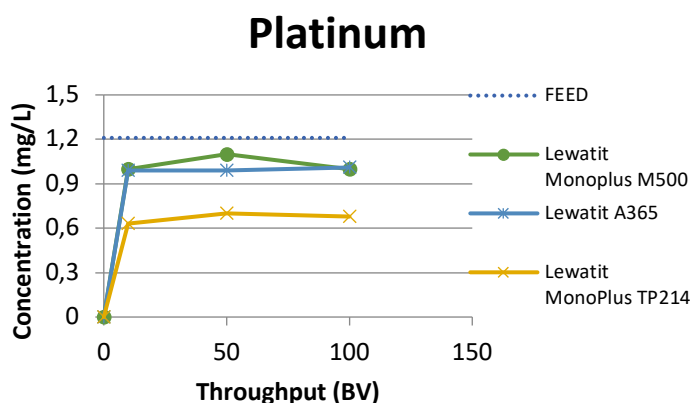


Figure 9. Platinum concentration in the barren solution after trial 1.

loaded best by the A 365 and TP 214. Iridium and ruthenium loading are loaded by the resins, but the loading efficiency is decreased by the resin reducing the iridium and ruthenium, which results in the ions being removed from the resin and reporting to the barren solution (Berman and McBryde, 1958).

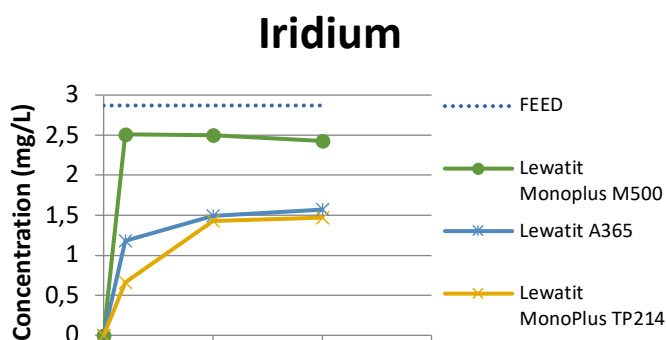


Figure 10. Iridium concentration in the barren solution after trial 1.

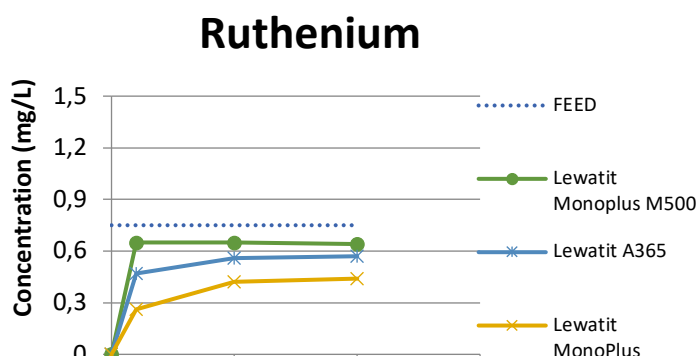


Figure 11. Ruthenium concentration in the barren solution after trial 1.

The rhodium loading was low on all three resins. The chloride complex that is likely to be present in the chloride containing wastewater is $[\text{RhCl}_6]^{3-}$ which can present a challenge during extraction by ion pair formation (Matsumoto *et al.*, 2019). Rhodium recovery by ion exchange can be improved by complexing with silver chloride (Susoyeva *et al.*, 2016).

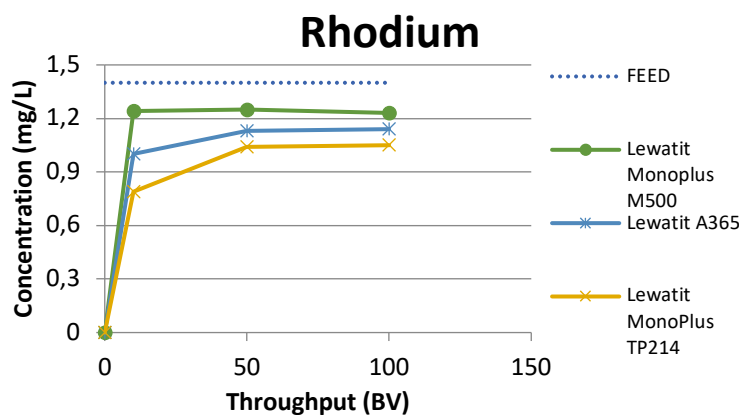


Figure 12. Rhodium concentration in the barren solution.

Trial 2 - Oxidised feed

Feed C was used for this test work. The composition of Feed C is shown in Table VII. The feed was pre-treated with calcium hypochlorite to improve the iridium loading. Iridium was oxidised from Ir (3+) to Ir (4+). Isotherm and column test work showed that Ir (3+) could not load efficiently onto the resin. Iridium loading improved due to the oxidation. Figure 13 shows the concentration of iridium remaining in the barren solution as a function of volume treated. The oxidation reduction potential (ORP) of the Feed C was 400 mV and was increased to 920 mV which indicated that oxidation had occurred.

Table VII. Composition of Feed C

mg/L	Au	Ir	Pd	Pt	Rh	Ru	Ir	Pd	Pt	Rh	Ru
Raw/Feed	<0.01	0.94	0.10	0.54	1.59	2.16	0.95	0.49	0.60	1.52	2.03

The loading of iridium improved after oxidation. The loading of iridium was best achieved on the A 365. Ruthenium also had improved loading on TP 214 after oxidation.

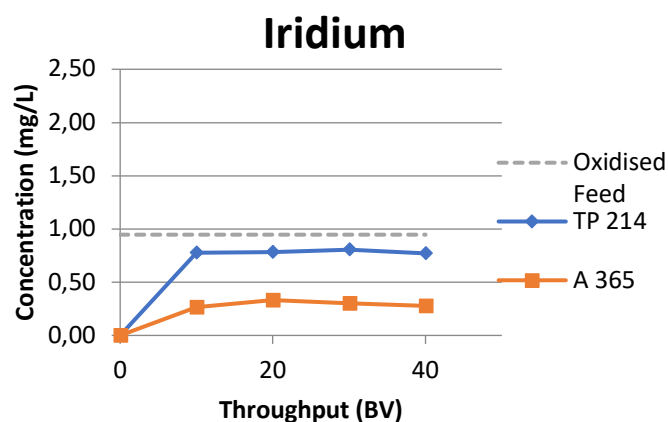


Figure 13. Iridium concentration in the barren solution.

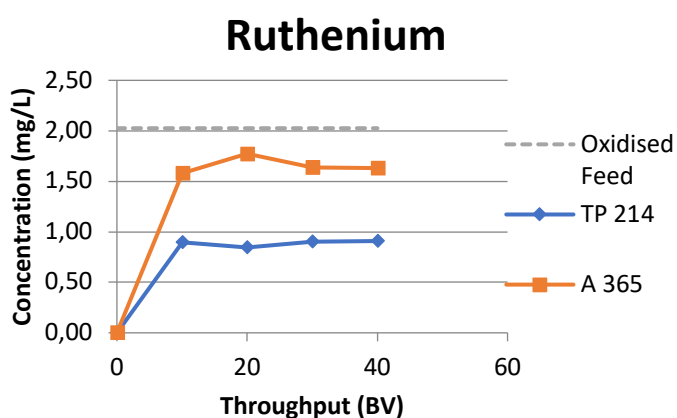


Figure 14. Ruthenium concentration in the barren solution.

Zinc and iron were also co-loaded onto the resin. This reduced the total available capacity for PGM loading. Oxidation also allowed for the removal of some iron by precipitation. The 'dumping effect' had also been observed for iron. This effect was characterised by the concentration of iron in the barren stream being higher than in the feed. This indicates that the iron is being pushed off the resin in favour of ions with higher affinity to the resin.

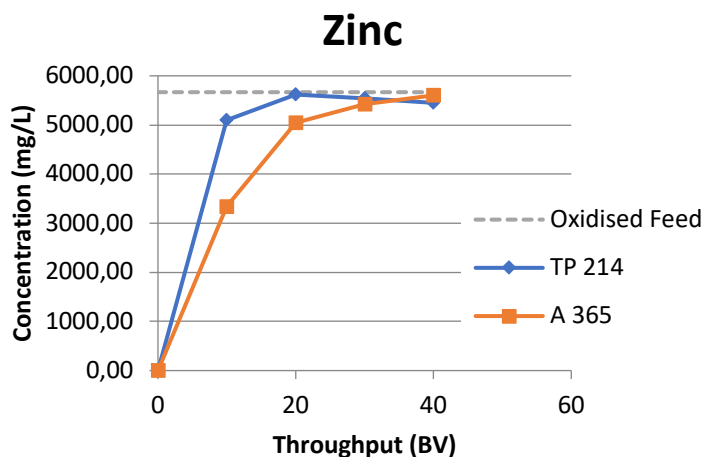


Figure 15. Zinc concentration in the barren solution.

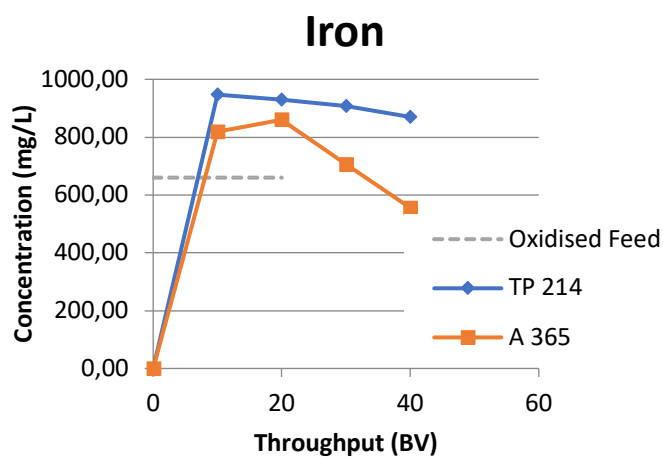


Figure 16. Iron concentration in the barren solution.

CONCLUSION

From the results and discussion, it can be concluded that no single resin will be able to load all the metals as a single step. TP 214 (thiourea functional group) and A 365 (polyamine) should be used in series to get the best recovery of all the PGMs. The platinum can be loaded by the TP 214 and iridium by the A 365.

Although ruthenium, platinum and iridium have higher affinity for the resin than zinc, the high zinc concentration had an effect on the loading of these PGMs.

Zinc is a competing metal, thus decreasing the loading capacity and the performance of the resins. To improve loading capacity of iridium, a zinc removal step should be done. Treating the feed with tin chloride might result in improved rhodium selectivity. The tin chloride forms a chloride complex with the rhodium, which is easily loaded, and thus improved rhodium recovery can be achieved. Resin recovery from the ion exchange resin is usually achieved by incineration. Further work using more data points and better monitoring of oxidation conditions is recommended. The selectivity of the resin may be improved by decreasing the acid concentration through dilution. Recovery tests on the resin are also recommended to investigate methods of recovering the loaded PGMs.

REFERENCES

- Aleksandar, N. N; Kwang-Loon, A; Li, D (2014) Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins
- Berman, S. S. and McBryde, W. A. E. (1958) "Separations of the platinum metals by ion exchange," Canadian journal of chemistry, 36(5), pp. 835–844. doi: 10.1139/v58-122.
- Helmentine, A. (2021) What Are Platinum Group Metals or PGMs? Available at: <https://sciencenotes.org/what-are-platinum-group-metals-or-pgms/>
- Hughes, A.E.; Haque, N.; Northey, S.A.; Giddey, S. Platinum Group Metals: A Review of Resources (2021), Production and Usage with a Focus on Catalysts. Resources
- Jing, H.; Adreas, K., (2017) Recovery of precious metals from waste streams

Oke, D.; Ndlovu, S.; Sibanda V (2017) 'Purification of a dilute platinum group metals process stream using waste yeast biomass immobilized on plaster of Paris', The Journal of South African Institute of Mining and Metallurgy (11).

Stats.SA, Department: Statistics South Africa Republic of South Africa (2022) PGM sales surge due to high process. Available at: <https://www.statssa.gov.za/?p=14225>



Ed Hardwick

Director
Cwenga Technologies

Ed has 40 years' experience in water treatment and 30 years specializing in ion exchange, applied all the way from initial laboratory tests to pilot and full-scale operating plants. These are applied in several industries, including sugar, chlor-alkali, and mining and mineral processing. Projects have successfully been completed in South Africa, Namibia, Zambia, the DRC, and Malawi. Ed has a working background in research and development, originally with De Beers Industrial Diamond Division, and later with De Beers Mining Division, Sappi R&D, and the NCP-ACIX division of SentraChem. He was a director of Chematron Products from 1993 until 2000, when the company was bought out by Veolia Water Systems. In 2001, Ed formed Cwenga Technologies, which specializes in adsorption technologies. Cwenga has been awarded the sole agencies and distributorships for the Lewatit ion exchange technology from Lanxess Germany (formerly Bayer AG), and for Chemviron Carbon activated carbon technology. Both products are extensively used in mining applications. Cwenga has also been associated with various engineering companies that specialize in the application of these technologies to specific industries. Ed holds various patents for the application of ion exchange in the metallurgical and environmental sectors. He has presented papers at various international conferences on specific applications of activated carbon and ion exchange in the treatment of mine waters and metallurgical processes.