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# TARGET RECOVERY OF PRECIOUS METALS FROM WASTE AND THE APPLICATION OF ION EXCHANGE IN THE LEACHING PROCESS

A thesis submitted in Partial Fulfilment of the Requirements for the Degree of

Doctor of Philosophy

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By

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# Abstract

The decrease in mineable precious metals (PMs) causes the increase in price and growing awareness of environmental sustainability has been a driving force into the advancement into recovery and recycling. A major point of interest is developing an environmentally sustainable system recovering PMs from waste or other competing metals. Development into more sustainable methods introduced the use of ion exchange resins with resins showing affinity towards PMs. In recent years, the research into deep eutectic solvents (DES), a more benign lixiviant, has grown immensely. Combining the resins with DES, this method has the potential to recover PMs more sustainably.

Five different ion exchange (IX) resins, Purolite® A200, Lewatit® MonoPlus TP 214, Puromet™ MTS9140, Dowex™ M-4195 and Lewatit® VPOC 1026, were screened for their affinity towards gold from a simulant pregnant leach solution. MTS9140 and M-4195 was found to have the highest affinity towards gold. These resins were then used in addition to DES to create the new recovery system for PMs recovery. The DES synthesised and investigated were ChCl (choline chloride): ethylene glycol (EG), ChCl: urea (Ur), ChCl: thiourea (TU) and Lactic Acid (lac). DES was used for leaching of rhodium (Rh) and platinum (Pt) from cobalt on a spent catalyst. It was determined that ChCl: Lac, ChCl: Ur and ChCl: TU had the highest affinity towards Rh and Pt. The addition of oxidants, sodium peroxide and Iodine, was investigated with a slight decrease of leaching. The combination of the resins and DES were investigated in resin-in-leach (RIL) and resin-in-pulp (RIP) systems and tested with a range of temperatures 30°C -80°C. It was determined to be successful *via* RIL at 60°C in combination of MTS9140 and ChCl:Lac, with RIP also showing high recovery of Rh and Pt from cobalt.

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TO BE YOUNG, GIFTED AND BLACK!!!

This thesis is dedicated to my family, Bernice, Radcliffe, Marcia, Charlotte and Raegan.

Thank you!!!

# CHAPTER 1: INTRODUCTION

## 1.1. Introduction To Precious Metals

Platinum group metals (PGMs) are rare, naturally occurring metallic chemical elements of high economic value. They are split into two groups that consist of gold (Au), silver (Ag), which are classified as noble metals and palladium (Pd), platinum (Pt), iridium(Ir), osmium (Os), rhodium (Rh) and ruthenium (Ru) which are the precious metals (PMs) (Figure 1).

| | 8 | 9 | 10 | 11 |
|---|---|---|---|---|
| 5 | 44<br>**Ru**<br>Ruthenium<br>101.07 | 45<br>**Rh**<br>Rhodium<br>102.96 | 46<br>**Pd**<br>Palladium<br>106.42 | 47<br>**Ag**<br>Silver<br>107.868 |
| 6 | 76<br>**Os**<br>Osmium<br>190.23 | 77<br>**Ir**<br>Iridium<br>192.22 | 78<br>**Pt**<br>Platinum<br>195.08 | 79<br>**Au**<br>Gold<br>196.967 |

**Figure 1 Periodic Table Placement of The Platinum Group Metals (PGMs)**

These metals have been historically known to be rare, highly unreactive and been used as currency, with Au being used as a monetary system where a fixed value of Au is set to a unit of a countries' currency, this is known as the "Gold Standard", this allowed paper a countries paper currency to have value tied to something real (1; 2). However, in 1931 Britain stopped using the gold standard, with the U.S.A. following suit in 1933 which led to the abandoned the system in 1973 (3). The high economic value of these metals is due to these metals having high melting points being highly chemically and heat resistant, corrosion-proof and they are in low abundance in the Earth's crust (4; 5).

Evidence of precious metals being used dates back to ~5,000 B.C. in Egypt, with Ag being used as form of money and Au dating back to ~3,000 B.C. being used in coin (6; 7). Evidence of PGMs state that they were first found in 700 BC; however, it was not until the 18th and 19th century that the PGMs were able to be separated from Au. PGMs were originally used for decorative purposes. Pt was discovered in 1741 by the British scientists Charles Wood and William Brownrigg (8). Pd, Os, Ir and Rh were all discovered between 1803 and 1804; William Hyde Wollaston discovered Pd and Rh, Smithson Tenant discovered Os and Ir and in 1844 Ru was discovered by

Karl Karlovich Klaus (9). Table 1 shows the meaning of name, the chemical and physical properties, health and environmental impacts of the PGM (10:33).

**Table 1. PGM Name Meaning, Chemical, Physical Properties, Health & Environmental Impacts.**

| Metal | Meaning behind name | Chemical and physical properties | Health and environmental impacts |
|---|---|---|---|
| Palladium | Comes the asteroid Pallas, in turn named after the Greek goddess of wisdom, Pallas. Also means “white gold” | Lowest density, melting point of all the PGMs. Easy to work with and ductile. Resistant to corrosion in air and acids. Dissolves in acids at raised temperatures. More reactive than other PMs. | Little environmental, or health effect. Palladium chloride, it has linked to causing bone marrow, liver and kidney damage in rats. |
| Platinum | Comes from the Spanish word platina, meaning "little silver". | Malleable, ductile and least reactive metal out of the PGM. Resistant to air and water. Can be dissolved in concentrated acids at raised temperatures. | Toxicity is dependent on the solubility; soluble Pt salts are much more toxic. Soluble Pt compounds showed mutagenic effects in bacterial systems as well as in mammalian cells. |
| Iridium | comes from the Latin word ‘iris’ means rainbow, due to many colours its compounds produce. | Second-highest density of precious metals, highly resistant to corrosion. High density and highly flammable. | Biggest health and environmental issue are from isotopes iridium-192, where it emits beta (β) and gamma (γ) rays. |
| Osmium | Derived from osme the Greek word for smell, because of the sharp odour of the volatile oxide. | Highest density of all PGM, brittle at high temperatures. Resistant to corrosion. Resistant to water and acids. Can be dissolved in the presence of molten alkalis. | Is not toxic or have a biological role. Osmium tetroxide is extremely toxic can be lethal to life, high risk of causing blindness. No information on Os effects on the environment. |
| Rhodium | Comes from the Greek word "rhodon" meaning rose, named for the rose-red colour of its salts. | Low electrical resistance and contact resistance. Rh is resistant to most acids, including nitric and acetic acid. | Generally considered non-toxic, some of its compounds are toxic and carcinogenic. Only one stable naturally Rh isotope, Rh-103. |
| Ruthenium | Named after the Latin word for Russia, in honour of where the scientists that discovered Ru are from. | Not tarnish at room temperatures but oxidizes at ~800°C. Readily attacked by halogens and hydroxides. Does not get attacked when in acids or aqua regia. When potassium chlorate is added it oxidises. Can readily be dissolved in molten alkalis. | Effects on healthy animals or human cells is low. If ingested, it can be deposited into bones. Compounds and isotopes of Ru leave impacts on people and animals. Oxide and tetroxide compounds are volatile, very toxic, unstable and poisonous with the isotope ruthenium-106 is a radionuclide, is harmful to human health increases the risk for cancer. |
| Silver | Derived from the Anglo-Saxon word "seolfor". | Very ductile and malleable, is excellent conductor of heat and electricity. Does not get attracted in the presence of water. Can easily tarnish when exposed to air with hydrogen sulphide present. | Soluble silver salts readily absorb into the body, accumulating in small amounts in the brain and muscles. Absorbed compounds can potentially damage a range of organs. Ag is extremely toxic to aquatic plants and animals. Silver nitrate is the most toxic towards aquatic life. |
| Gold | Originates from the Old English Anglo-Saxon word 'geolo' meaning yellow. | Low melting points, very malleable and easy to work with. Good conductor of heat and electricity. Will not tarnish, discolour, crumble, or be affected by most solvents or air. | Cause irritation to the respiratory system or skin if exposed for a prolonged period of time currently been no tests on golds ecotoxicity. |

# CHAPTER 2: LITERATURE REVIEW

## 2.1. Precious Metal Designation as Critical Elements

Precious metals (PMs) are finite metals; there are estimates that there is only 20 years left of mineable gold (Au) and silver (Ag) will run out between 2028-2033 (10; 11). Additionally, the current natural reserves of the platinum group metal (PGMs) are also limited, with estimations that there is only 69,000 Mt of PGMs left in the Earth's crust; however, palladium (Pd), iridium (Ir), rhodium (Rh) and osmium (Os) global reserves have yet to estimated (12). In 2017, the American Chemistry Society stated that the PMs were endangered elements with Ru, Rh, Os, Ir and Pt being 'rising threat from increased use', Ag and Pd classified as 'limited availability – future risk supply' and Au is categorised as 'serious threat in the next 100 years' this can be seen in Figure 2 (13).

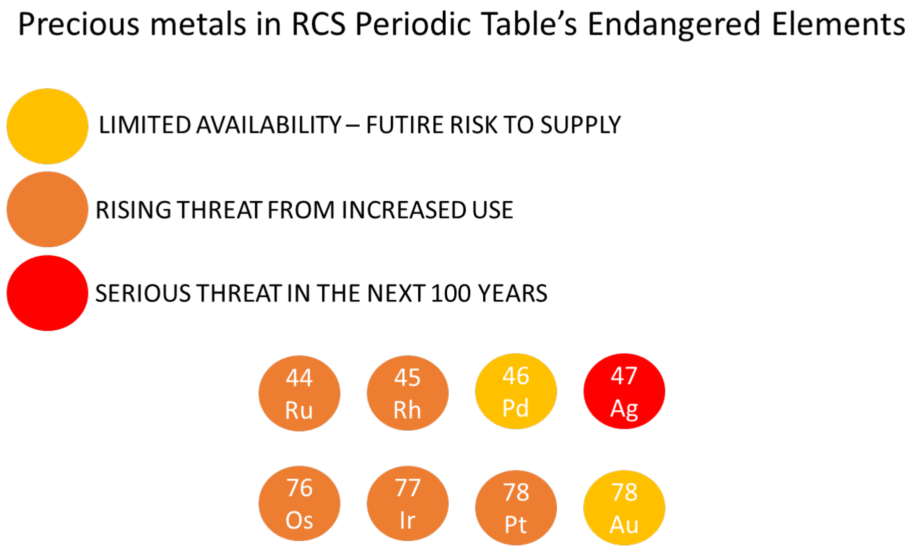


**Figure 2 Periodic Table of Endangered Elements Referenced From ACS.**

Finding a more environmentally sustainable and cost-effective method for recovering PMs, will extend the current timescales for how long left we have with these metals. Developing a new method for recovering metals from mining tailings will hopefully reduce the current threats placed on the PMs, as currently 25-30% of PMs that end up in mining tailings are left in storage (14).

The biggest concern with the depleting amounts of PMs left in natural reserves is due to the multiple products they are used for. With the main uses being for catalytic converters, chemical catalysts, electrical goods such as phones, laptops and computer chips, medications and so on, these can be seen in Table 2 (15; 16; 17).

**Table 2 Prices, Properties, Natural Abundance, & Main Industrial Uses of The Precious Metals.**

| PGM | Price per oz. (£) | Melting point (°C) | Density (g/cm$^3$) | Natural abundance | Main industrial use |
|---|---|---|---|---|---|
| Pd | 1,721.19 | 1,554 | 12.02 | Found uncombined in nature, but most is found in sulphide minerals such as braggite. It is extracted commercially as a by-product of nickel, copper and zinc refining. | Mainly used in, catalytic converters for cars, jewellery, electrical contacts, dental fillings and crowns. It is used in ceramic capacitors found in laptop computers and mobile phones. |
| Pt | 765.31 | 1,769 | 21.45 | Found uncombined in alluvial deposits. Commercially produced from the mineral cooperite. Some is prepared as a by-product of copper and nickel refining. | For jewellery, catalytic converters for cars, trucks and buses. Also, can be used in the chemical industry as a catalyst to produce nitric acid, silicone, and benzene. |
| Ir | 3071.31 | 2,443 | 22.56 | It is found uncombined in nature in sediments that were deposited by rivers. It is commercially recovered as a by-product of nickel refining. | Formation of alloys; with Osmium creating pen tips, electrical contacts and compass bearings, with platinum and iridium in making standard metre bar and spark plugs. |
| Os | 1,385.74 | 3,050 | 22.61 | Occurs uncombined in nature also in the mineral osmiridium. Most osmium is obtained commercially from the wastes of nickel refining. | Formation of alloys; fountain pen tips, instrument pivots, needles and electrical contacts. Also used in the chemical industry as a catalyst. |
| Rh | 13,652.54 | 1,960 | 12.41 | The rarest of all non-radioactive metals. It occurs uncombined in nature. It is also found in the copper-nickel sulphide ores. Obtained commercially as a by-product of copper and nickel refining. | The major use is for catalytic converters for cars. Also used as a catalyst in the chemical industry for making nitric acid and acetic acid and hydrogenation reactions. It used as a finish for jewellery, mirrors and searchlights. |
| Ru | 392.18 | 2,310 | 12.45 | It is found uncombined in nature. Obtained commercially from the wastes of nickel refining. | Mostly used in the electronic industry for chip resistors and electrical contacts. In catalyst for ammonia and acetic acid production. Also used in cancer treatment/diagnosing. It is one of the rarest metals on Earth. |
| Au | 1,371.48 | 1,064 | 19.32 | Gold is one of the few elements to occur in a natural state. It is found in veins and alluvial deposits. | Extensively used in jewellery, coinage. Often used in art, for decoration and architectural ornaments. In electrical industry, for protecting electrical copper, inside computer chips. |
| Ag | 17.42 | 961.8 | 10.5 | It is mostly extracted from lead-zinc, copper, gold and copper-nickel ores as a by-product of mining for these metals. The metal is recovered either from the ore, or during the electrolytic refining of copper. | Used in jewellery, dental alloys, solder and brazing alloys, electrical contacts and batteries. Also used in clothing for preventing bacteria from forming odours and it is woven into the fingertips of gloves so they can be used for touchscreen electrical goods. |

## 2.2. Precious Metal Mining, Supply & Demand and Waste Formation

### 2.2.1. Precious Metal Mining.

The method of PM production from ores to the pure metals primarily occurs through open-pit mining. This method creates enormous amounts of un-wanted gas by-products, additionally polluted water which is not currently being recycled or reused due to the hazardous chemicals in the water. Increased awareness of the amount of pollutants that are produced in metal production has caused metal organisations to start being more conscious of how they obtain precious metals.

Majority of the countries with the highest amount of the PM production were previously or still unstable politically, such as Russia, USA, Ghana, South Africa and China. To reduce the dependence on these countries for PMs, development into finding ways to retrieve products that contain PMs would greatly impact countries that rely on these metals. Additionally, being able to recycle used PMs would reduce each countries carbon footprint, as it would lower the amount of energy usage that is required for mining and the overall pollution that is released whilst transporting these metals around the world. Figure 3 shows a map of the world where the different PMs are mined (42-50).

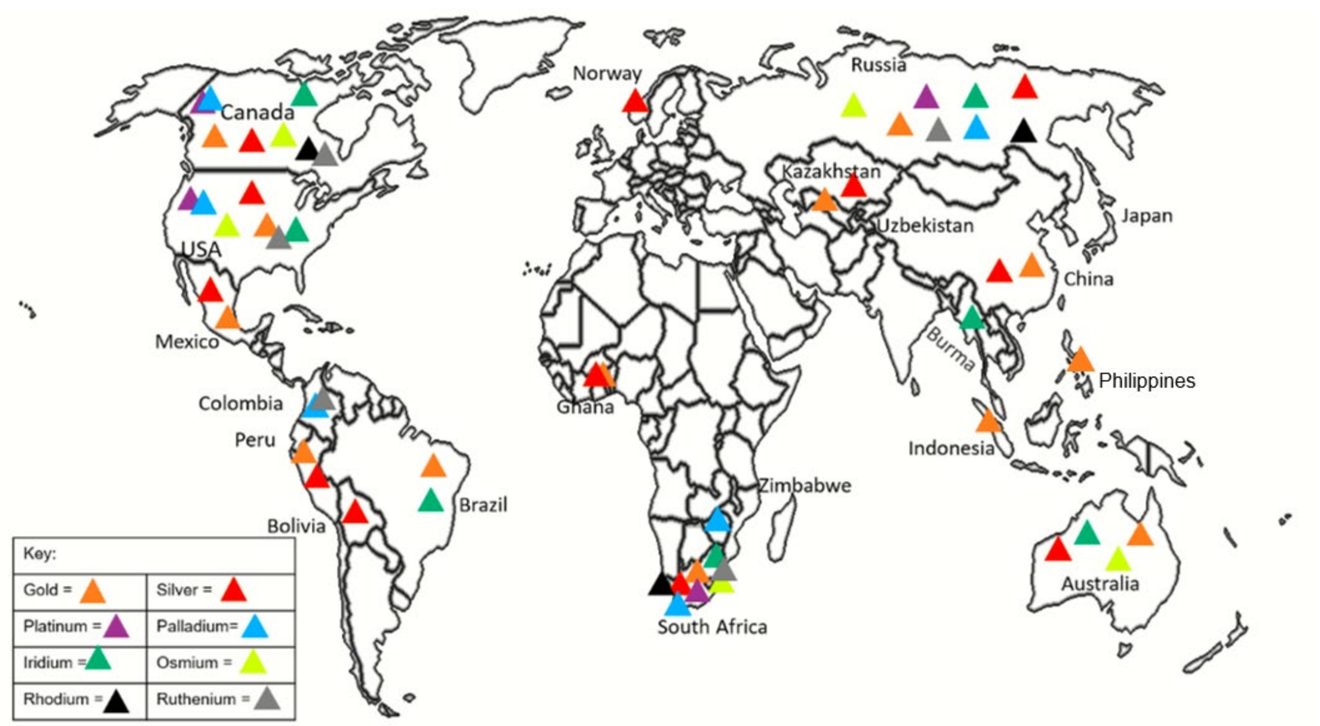


**Figure 3 Map of The World & Where the Different Precious Metals Are Mined.**

One of the most used reagents that are used for PGM production is cyanide. Cyanide is acutely toxic for humans, other mammals and aquatic species at relatively low dosages; and interferes with oxygen utilisation. This has caused a big push into the research of alternative compounds that are just as effective but less harmful to life.

The change in attitudes to mining, due to climate change, and the negative effects that metal production contributes to people and animals has caused a change in regulations, which has increased interest in the recovery of metals in waste, especially mining, electrical, chemical, spent nuclear fuel (SNF) and other industrial waste.

Additionally, with only a handful of countries having the natural reserves of PMs this can cause a high carbon footprint due to transportation of the PMs to get from one country to another. To be able to increase the current amount of precious metal waste that is recovered would reduce the greenhouse emissions that are being emitted from the transportation. A novel environmentally-friendly method of recovering PMs from waste is needed to improve supply and reduce the environmental impact and greenhouse gas emissions.

### 2.2.2. Precious Metal Supply & Demand.

The biggest cause for the increased for demand, supply and usage of PMs is the electrical industry. In particular, mobile phones, televisions, computers, electrical conductors and catalytic converters. Within the constant updating of software many of those products listed are constantly thrown out for new models leading to an increasing amount of E-waste. Research into recycling and recovering the precious metals from the environment and waste, such as jewellry, mining waste, (mining tailings); electronic waste, (e-waste), and spent catalysts would reduce the number of raw metals ores that would need to be mined annually.

Russia, Canada, South Africa, USA and Australia are the top five countries that contribute to the global mining with other noteworthy countries being Mexico, Ghana, China, Brazil, Zimbabwe and Colombia, shown in 2.2.1. As it was stated in section 2.2.1. a majority of these countries are or previously have been politically unstable. Being dependent on these countries for PM production could negatively affect the supply and price; developing a more efficient way to recover PMs from waste will hopefully reduce the current price and increase the supply. With the uses of PMs being mainly electrical goods, automobiles and in the medical industry there has been a rapid increase in demand which can be seen in Table 3, with many of the metals are either just about meeting the demands or are overwhelmingly under mining which can be seen with Ir, Ru and Rh (51-60).

**Table 3 Breakdown of how much precious metals are used in assorted products.**

| PGM | Amount mined per annum (Mt) | Estimated mineable amount left in reserves (Mt) | Demand of metals per annum (Mt) |
|---|---|---|---|
| Pd | ~290 | N/A | ~290 |
| Pt | ~190 | ~19,800 | ~160 |
| Ir | ~0.3 | N/A | ~7 |
| Os | ~0.01 | N/A | N/A |
| Rh | ~20 | N/A | ~30 |
| Ru | ~10 | ~5,000 | ~30 |
| Au | ~3,300 | ~57,000 | ~4,350 |
| Ag | ~30,000 | ~560,000 | ~30,000 |

The demand and use of precious metals have grown exponentially, due to the rapid population growth and technological growth; due to that, there has been a precipitous price increase. With the price of Au increasing by 450% and Ag increasing by 150% in the last decade (18; 19). Additionally, during the 2000s Pd prices increased by 500% and the price of Rh increasing by 55% in the Q3 of 2021 with Rh remaining the most expensive metals seen in Figure 4 (63-68).

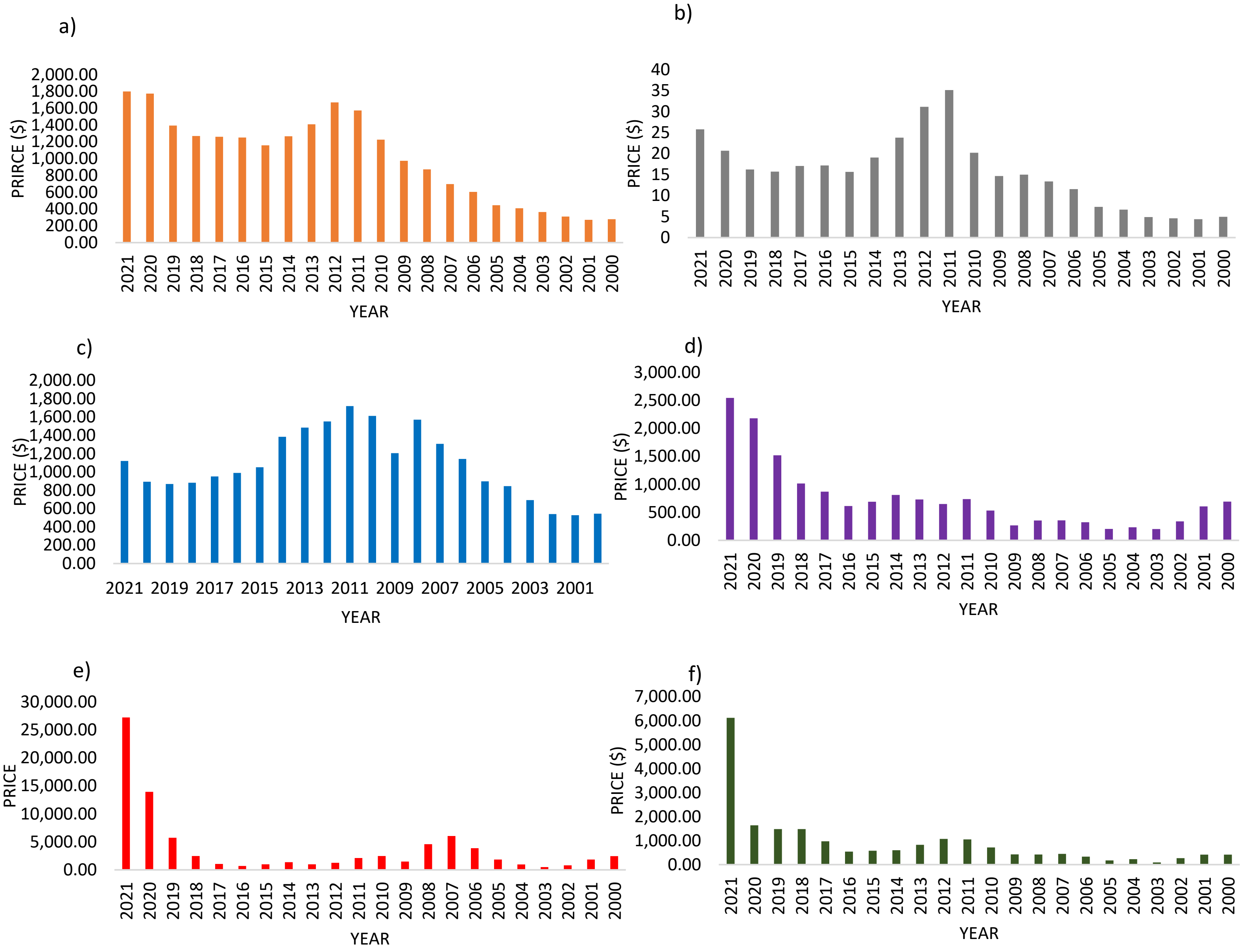


**Figure 4 Pricing Chart of the PGMs a) Gold, b) Silver, c) Platinum, d) Palladium, e) Rhodium and f) Iridium.**

Despite the worries of the supply and demand of PMs especially Rh, Pt and Pd which are the most expensive out of the PMs. Current growth of the development in Electrical Vehicles (EV), that could alter the demand of PMs, with 33-40% of all Pt and 75-80% of all Pd and Rh are currently used in emission control catalysts (20; 21). Chris Griffith, Chief Executive at Anglo American Platinum (JSE: AMS), has suggested that a car industry dominated by batteries will reduce Pt demand to only 2.5 million ounces in 2050 — that would be down from 3.4 million ounces in 2015 (22). However, the future of new technology is extremely difficult to predict due to the uncertainty of the longevity of EVs, so the overall demand of PMs may not decrease as drastically as many people are expecting.

An increase in recycling of products containing these metals and recovering metals from mining waste would decrease the overall demand of energy of producing new PMS from metals and the energy demand for separating PMs from each other, which tend to be found in the same deposits. A decrease in mining for precious metals would not only save on energy but also reduce the amount of money and resources spent on producing new metals.

An exploration into using more environmentally and economically sustainable methods of recovering PMs from ores and recycling them from waste would significantly improve the supply and demand discrepancy that is currently being seen especially with the metal's Ir, Os, Rh and Ru. Demand discrepancy in this instance is due to the major differences between the volume of PMs that are mined and supplied compared to the amount that is in demand by the various industries that use PMs. More environmentally benign and sustainable practices will be a greatly sort after methodology due to the increased use of precious metals in the electronics and automobile industries.

### 2.2.3. Waste Formed from Precious Metal Production and Use.

The traditional way of disposal of the spent catalyst, *via* landfills, is not environmentally friendly and that can lead to contamination of groundwater. This has caused an increase due to a change in the classification of hazardous waste by the environmental protection agency (EPA). The suggestions were i) minimising the amount of spent catalyst waste generated, ii) utilise the spent catalysts to produce a new catalyst, iii) recycle the spent catalyst through the recovery metals, iv) the treatment of spent catalyst for safe disposal (23).

Toxic waste, acid mine drainage and mercury pollution are major issues in the mining production sector. Mercury is a necessity in precious metal (PM) production; however, in Brazil there are estimates that more than 1,814Mt of mercury, have been released into the environment which is known as mercury amalgamation. This has caused the mercury concentration in fish in the lakes and rivers to increase to an unsafe level (24). Mercury is used in this metal production process as Ir, a noble element needs to be separated from nickel ores it is mined with. Au mining creates a huge volume of toxic wate, with mining companies generating ~20 tons of toxic waste for every 0.333-ounce gold ring, this toxic waste is laden with deadly cyanide and toxic heavy metals (25).

Waste from PMs is not just seen in the mining industry but also in the electronics industry and chemical industry, with Pt, Pd, Au and Ag mainly being used in electrical goods and catalysis. E-waste and spent catalysts account for over 90% of PM usage (26). E-waste typically includes discarded computer monitors, mobile phones, headphones, white goods such as Plasma televisions, air conditioners and refrigerators. Catalyst waste is known as spent catalyst which includes, metal-on-metal oxide (MoMO) catalysts and catalytic converters.

Currently 70-85% of PM supply comes from mining production with recycling material accounting for the remainder (27). This high amount of mining has caused the formation of large amounts of unwanted solid; liquid and gas by-products being released into the environment. With many of the PMs being mined with metals such as zinc, copper and nickel, production of those metals are the contributors to the impacts that are seen from PM production (28). PMs need separating from the by-products, which requires a large amount of energy and hazardous chemicals because PMs are noble elements therefore very unreactive to most acids.

In 2016, 44.7 million Mt of E-waste was produced globally (29). However, only 12.5% of E-waste was recycled (30). Every year, about 840,000 tons of spent catalyst are generated (31). Solid waste streams from mining are known as mining tailings. In total, 99.8 million Mt of tailings of economic interest, is produced annually (32). Au mine tailings will contain a significant volume of 385 Mt of Au (33). There are estimates that processing ~2Mt of automotive catalytic converter would reduce the production of ores by ~140Mt (34).

Table 4 shows the breakdown of each PGM in assorted products. From this table it shows that Pd, Rh and Pt are the most used and the metals that are most found in waste. Despite the low levels of PGMs in the waste products there is a large volume of the metals being thrown away and unrecycled; therefore, is a great demand for research into developing recovery of PGMs **(35; 36; 37; 38; 39; 40)**.

**Table 4 Breakdown of how much precious metals are used in assorted products (84-89).**

| PGM | Mobile phones (g/kg) | Automotive catalytic converter (g/kg) | Electrical contact (%) | Mine tailings of chromium mining (ppm) | Spent Nuclear fuel (Kg) |
|---|---|---|---|---|---|
| Au | ~0.034 | N/A | N/A | 0.10 | N/A |
| Ag | ~0.34 | N/A | 50-85 | N/A | N/A |
| Pt | ~1 X $10^{-4}$ | 3-7 | N/A | 0.25-3.20 | N/A |
| Pd | ~0.015 | 15-19 | 50 | 0.11-2.80 | ~1.50 |
| Rh | N/A | 3-7 | 3-5 | 0.05-0.45 | ~0.50 |
| Ru | N/A | N/A | 15 | 0.60-3.40 | N/A |
| Ir | N/A | N/A | 3-5 | >0.10 | N/A |
| Os | N/A | N/A | 3-5 | >0.10 | N/A |

With the growth of the demand for the electronic goods, nuclear energy production and overall mining increasing exponentially, the volume of PMs that will be in need of recovery, recycling or reuse will cause development in the current recovery of PMs from the different forms of waste. By researching new methods of recovering PGMs from waste that are more environmentally and economically sustainable, it could offset the current high demand for PGMs and hopefully in-return it can decrease the current amount of PGMs that are mined.

Specifically, with spent catalysts the method of regenerating spent metal on metal oxide catalysts creates a large amount of solid catalyse waste and consumes a great amount of energy. This has caused a great increase in the interest in the improvement and utilization of the waste catalyst materials. Additionally, the little research into the use of greener solvents in spent catalytic regeneration in terms of a wider range of catalytic systems. The current leaching method of using concentrated acids create a high amount of toxic and hazardous wastes with a low recovery rate. Being able to regenerate spent catalyst would reduce the amount of PMs needed for catalytic converters and allow less waste to be produced after the catalysts are no longer useable.

## 2.3. Social and Environmental Effects of Precious Metal Mining.

### 2.3.1. Social Impacts of Precious Metal Mining.

Mining of PMs often destroy the communities surrounding the mine. This has largely occurred by the displacement and loss of land, with this disproportionately effecting women and youth the most (41). This is mainly due to the loss of land-based livelihoods which the community relied on for money and with a loss of various water and food sources that these communities, used for a whole manner of uses from drinking and washing and cleaning of items; without that it will increase the workload which is mainly the women's responsibility. With more and more families and people going into poverty, due to loss of resources and livelihoods there is usually an increase in crime and violence in those communities this can lead to a family cohesion decreasing where women usually face the fall of violence, alcohol and substance abuse (41). Additionally, if communities are paid compensation and benefits from mining companies in the cities or villages it is paid to the men of the family, women are often denied access to the financial benefits and could increase their economic dependence on men (42).

Due to the losses in land-based livelihoods there will be an inevitable change in the areas economic structure, this mainly affects the younger population. With the loss of different livelihoods and guaranteed professions that their parents and grandparents would have had, this leads to loss of income and younger people from these communities can be drawn into drugs, brothels and crime (41). Additionally, when these mining companies start destroying the land, they often take the place of already established forms of livelihoods and replace them with underpaid, dangerous jobs.

The growing social concern for the way that metals are mined has created a growing number of activists that are demanding countries and companies no longer obtain their precious metals from countries where metals are produced *via* eco-unfriendly, immoral and socially damaging practices (43). The concerning lack of human rights with the mining of PGMs has come to public knowledge in the last couple of decades, with many non-profit organisations (NGOs) stating the lack of protection the miners have, the lack of personal protective clothing (PPE), child labour that is used, discrimination that female miners have faced and the growth of illegal mines that have started to appear.

Many of the areas that have PGM reserves are remote places and may have poor and or indigenous communities living there, this allows companies to exploit the community for land and work; this is especially true with the illegal mines that are occurring in Latin America (44). With many mines having polluted waterways and soil with toxic chemicals, this harms the health of the workers in the mines that have a lack of PPE and the livelihoods of the whole communities in those areas (45).

In Kyrgyzstan there are many foreign Au mining companies since the late 1990s, with Chinese companies taking over the Au mining industry (46). This influx of foreign Au mining companies has caused many social and environmental unrest between the workers and the villagers, which could be partly due to the failed promise of mining jobs for the Kyrgyz citizens which in-turn has caused many Kyrgyz citizens, specifically men, to move abroad for work causing xenophobia and anti-Chinese sentiments to manifest themselves (46). One of major reasons for this is prior to foreign mining companies took over the mining industry in Kyrgyzstan, the locals mined the Au which was a stable source of income in places were jobs are very limited (47; 48). However, now since foreign companies have started up or scaled up their operations the authorities will arrest and fine locals for ‘illegal mining’ (48).

There have been instances of civil unrest between the locals and mining workers in Kyrgyzstan since 2010. With some including Chinese Au miners being locked in a cargo container in 2018 and Chinese workers being injured during a conflict with the locals over an alleged theft in 2013 (47; 49). In 2019 locals near the Solton-Sary gold mine in Eastern Kyrgyzstan accused the Chinese mining company of releasing toxic chemicals into the soil of the surrounding are this escalated into a clash between the locals and workers, leading to 20 people being sent to hospital (50; 51).

Large-scale anti-China demonstrations become common since 2018 when evidence of corrupt contract between Chinese companies and local politicians was released to the public (52; 51). Between 2018 and 2020 42 anti-China protests were recorded, with more the half relating to environment or extractive industries, issues ranging from environmental degradation and corruption to Chinese immigration and Beijing’s repression of Muslims in neighbouring Xinjiang (52; 53).

In countries like Canada, Guatemala and Peru, there have been many peaceful protests in the aim to stop the exploratory of their sacred land. The growing demand of prime ministers and presidents to meet the demand of new mining projects that need to be created, causing a threat onto the lives of the population that currently reside in those areas and depend on the resources to survive and grow their community.

In July 2019, the Tŝilhqot'in Nation in Canada participated in another peaceful protest for the drilling construction at a sacred lake in their territory (54). This was one of many battles the Tŝilhqot'in Nation has partaken in attempts to protect the Teẑtan Biny (Fish Lake) from mining construction that would devastate land, waters, rights and ways of life for the nation from Taesko Mines. The protests and the in-and-out courts battles have resulted in the Taesko new mining project “New Prosperity Mine” being rejected in court and cannot legally be built (54).

This is repeatedly happening to Indigenous communities around the world. Most recently in Australia BHP have plans to expand one of the mines on that contains rock shelters that were 15,000 years old. BHP received approval to destroy the sites in May 2020 after it applied to expand an iron mine, which also mines Au, worth $3.2 billion (55). This was prior to another large company, Rio Tinto, had destroyed two sacred Indigenous sites, dating back 46,000 years, in the Pilbara in Western Australia (56). Mainly due to the prime minister of Australia having a more conservative and bigoted stance on issues surrounding race and the Indigenous community over the last 10 years; specifically, the lack of acknowledgment to the scientific and historical importance of the impacts of mining in those areas.

This standpoint is very different to New Zealand; within the 80s and 90s International Bodies had drafted instruments that gave Indigenous communities rights over their lands and in the 1970s legislation was implemented to engage in dialogue with Māori communities to assess the impacts of mining on certain lands on changes to land or water uses will impact on Māori community or cultural values (57; 58).

### 2.3.2. Environmental Impacts of Precious Metal Mining.

The biggest environmental issue with mining is the mining dam failings; there has been 9 in the last two decade (59). These incidents have caused injury and death. Furthermore, the dams release sludge into the surrounding rivers, contaminating water sources.

An example of the damage that can be caused by dam failings can be seen with Karamken (KGOK), located in the Fare Northeast of Russia, in 2009. This dam had a total mass weight of water-saturated tailing of ~340,000 tonnes; the dam failing released slurry mass flushed up to 20m downstream to the Khasyn River leading to deforestation of 300m x 1000m of the surrounding area (60). However, 9 years after operations closure due to failings, there was a significant amount of toxic substances which now has mostly not exceeded the Russian national values of the fishery industry (PDK) (60). This dam failing left 25 households and farm buildings severely damaged with two villagers dying (60). Other PM dam tailings accidents caused contamination of rivers, lakes and oceans with 3.74 million $m^3$ of tailings being released over the last two decades.

The impacts of dam failings are seen in the contamination of water, soil and sediments. This is mainly due to high volumes of cyanide and thiocyanates by-products that are produced during the processing of the metals; many of the PMs are produced as a by-product of nickel, copper and zinc refining the waste containing sulphate and chloride. The environmental impacts of the waste leaking into water sources and wildlife can be highly hazardous. This can be seen in 1998 in the Aznalcóllar dam at the Boliden Los Frailes Ag–Cu– Pb–Zn mine facility in Spain all of the fish and shellfish present in the polluted watercourses were killed (61).

These accidents have caused many countries to start issuing or tightening up regulatory laws regarding the management of metal waste, especially waste disposal or the methods used in the recovery of the metals. This can be notably seen with the 2006 Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation in Europe (62). This caused an increase in research into the recovery of precious metals in a more environmentally and economically sustainable manner.

The continued use of aqueous solvents in the metal recovery process causes a large amount of waste that is currently created. Treatment of waste requires a large amount of energy and hazardous or toxic chemicals. The potential to limit the number of aqueous processes would greatly decrease the volume of waste and could reduce the severity if a dam tailing does leak.

It is not just dame failings that can cause the environment to process the mining waste produced is highly toxic containing arsenic, lead, mercury petroleum byproducts, acids and cyanide. Many companies globally ignoring the current waste disposal laws that are in place and continuous dump the toxic waste into rivers, lakes, streams and oceans, with estimations that 180 million tonnes of mining waste annually being released (63). Massive amount of toxic being released into various sources of water will impact the water quality, leading to aquatic, mammals and people living in the surrounding areas being poisoned due to the water being contaminated.

The size of the actual mining location can also cause environmental issues such for deforestation and disruption of soil and rock. One mining sight impartial has shown the effects of having large mining open-pit located in the Sudirman Mountains of the Irian Jaya province of Indonesia, the Grasberg complex (also known as the Freeport Mine) (64). The Freeport mine is one the largest Au and copper mining operation in the world and spans 4 Km, which can be seen from space, with extensive underground mining working as well (64). This mine is located to rare equatorial mountain glaciers and with the removal of vegetation, steepening of slops related to mining activities the earthquakes and heavy rainfall that now result in deadly landslides (64). The effects of removals of vegetations and the change of the natural terrain has caused habitats of the local animals and aquatic life to be affected by mining; one example being a gold and copper mine in Alaska Bristol Bay has been estimated that 24 miles of streams have been destroyed that support the largest sockeye salmon fishery (65).

### 2.3.3. Sustainability in Mining

The are many different ways sustainability can be defined in a range of industries; however, in mining the term it has been referred to by Beejays Canvas, a manufacturing and supply company based in Australia, as, “the minimisation of negative environmental, economic, and social impacts of mining activities and the limitation of extraction rates that will not compromise the potential needs of future generations” this way of mining can also be referred to as eco-friendly mining. With the goal of sustainability in mining all three aspects of it are linked (66).

To improve the environmental sustainability this would mainly be done by investing in modern technologies and techniques that should reduce the environmental impact such as water waste management, investment into less thermal intensive methods of mining processing and more integration of renewable energy solutions. Economically, by switching to less energy-intensive methods, pyro- to leaching would reduce the overall cost of the process and it would it cut down the amount of energy that would be required to process the mining ores and mining tailings. Socially, by maintaining and hopefully improve the livelihoods of the people that live and work near these mines including a more ethical approach to the way companies treat the tribes and land they want to or are already mining.

Globally, there are some countries that are currently working towards a more sustainable mining with the establishment of Towards Sustainable Mining (TSM) in 2004 (67). The TSM is an initiative with the Canadian mining industry towards more responsible mining which in 2015 was adopted by the Finnish Minning Association with currently 10 countries including Norway, Brazil, the Philippines and Australia (68). The objective of the TSM is to enable mining companies to meet the societal needs for minerals, metals and energy products in the most socially, economically and environmentally responsible way (68). The three main ways is via engaging with communities, driving world-lead environmental practices and committing to the safety and health of employees and surrounding communities (68).

This research aids towards a more sustainable mining process, with the aim to reduce the environmental impact at the tail end of the mining cycle with the develop of a less highly hazardous solvent that can be used to recover precious metals from waste without the need for high temperatures or the production of wastewater in the process.

## 2.4. Solid Phase and Solvent Extraction of Precious Metals

### 2.4.1. Solid Phase Extraction of Precious Metals

Solid phase extraction (SPE) is an extraction technique using solid adsorbent to adsorb selective species from a solution; there are three different types of SPE adsorption, ion exchange (IX) and mixed-modes (69). There are two different types of adsorption, normal and reversed phase. Reversed phase is a technique that is best for a analytes with moderate to low polarity and separate analytes based on hydrophobicity with most polar compounds eluting first; normal phase is a more commonly used technique of the polarity of low to high; this technique elutes the polar compounds (69). Ion exchange is a process that is reversible and is a stoichiometric process in which one species displaces one desired ionic species in with an exchanger (70). With mixed-mode is a technique that combines both the adsorption and IX (69). Out of the three different SPE techniques IX is the most commonly used technique.

IX became a viable option in metal processing in 1944 with synthetic IX resins starting to receive attention in the 1950s in the recovery of Au cyanide solutions (71). 1850 was the first noting of natural occurring IX resins, which were occurring in aluminosilicate minerals, such as clays, aerolites, and ultramarines (72).

IX has been proven to be an effective method of recovering precious metals. It can minimize waste generation, improve the overall economics of the process and show to be effective for low-grade metal recovery. It has high selectivity, cost-effective and has an affinity to recover PMs from either low-grade or waste streams or both without forming extra waste which occurs when precipitation or cementation is used. IX was initially used for deionization of water and removal of metal contaminants from wastewaters this are the most used application for IX. IX has been used industrially for 30 years to use in the recovery of precious metals but mainly for Au and Ag recovery.

IX resins has two different types of matrix, gel and macroporous (73). The gel matrix has a high capacity, chemical efficiency and a translucent pseudo crystalline structure. Resins having the macroporous matrix have high mechanical stability a high resistance to oxidation and high temperatures and have an opaque porous structure. The resins used in IX are categorised by their functional groups that are bonded to the polymer matrix. IX resins are put into five groups, strong acid cation (SAC), weak acid cation (WAC), strong base anion (SBA), weak base anion (WBA) and specialty resin (73).

SAC is the most widely used resin, this type of resin is made up of the polymer matrix with sulfonic acid (74). SAC is mainly used for softening applications specifically the removal of magnesium or calcium. However, the resin can be damaged by oxidants (75). WAC resins tend to use carboxylic acid as its functional group. WAC are generally used in demineralization and dealkalization and tend to have an affinity to magnesium and calcium (73).

SBA there are two main types of SBA, type 1 and type 2. Type 1 SBA has a trimethylammonium group, which is the most chemically stable (74). Type 2 SBA functional group is a dimethylethanol ammonium group. WBA functional group was a tertiary amine. WBA are generally used for acid adsorption involving the removal of chloride, sulphate, nitrate that are associated with strong acids (73).

Specialty resins cover a wide range of resins that are used in a specific application, with a wide range of functional groups that can be used these include thiol, iminodiacetic acid, aminophosphonic acid and many others. The most common type of specialty resin being chelating resins. Chelating resins are exclusively used for removal and concentration of metals such as cobalt and mercury in dilute solutions.

IX systems are already being used in the recovery of gold, silver, and precious metals from mine waste (76; 77; 78). However, this still in its developmental stage for the recovery of gold and precious metals. Commercial resins have a huge variety of functional groups, and the adsorbent material can be selected to create synergy between the resin functionality and that of the lixiviant matrix (79). Alternative lixiviants like thiourea, thiosulfate or a combination of both, can be used instead of highly concentrated hazardous reagents.

A review by Dong *et al* states the current use and predicted future developments using IX resins as an adsorption techniques for Au recovery (80). There are 6 additional techniques discussed, precipitation, activated carbon adsorption, solvent extraction, electrowinning and mesoporous silica adsorption as well as adsorption by

IX resins (80). The review states a range of limitations of the resin adsorption. The limitations discussed were competitive adsorption of undesirable anions and lack of suitable gold extraction resin and eluent (80). It is common for copper and ammonia to be added to accelerate gold dissolution; however, with the use of ammonia it accelerates the oxidation of thiosulfate to produce an unstable tetrathionate which easily degrades into trithionate and thiosulfate (81; 82; 83). Additionally, most of the resins used in current research for gold recovery are generally not highly selective for $[Au(S_2O_3)^2]^{3-}$ anion because they were designed to adsorb singly charged $[Au(CN)_2]^-$ anion (84). When the presence of competitive anions, sulfur-oxygen anions and other metal thiosulfate complexes in the solutions also places greater demands on the selectivity of the resin (85).

Additionally, currently no literature was found on the recovery of Ag from mine tailing lixiviant; there have been studies into recovery of silver (Ag) from silver nanoparticles (AgNPs) via ion exchange resins (86). The IX resin investigated was a strong acid cation resin containing 8% Divinylbenzene (DVB) (86). This recovery method was successful for river water that contained AgNPs: $Ag^+$ at different ratios of 3:1, 1:1 and 1:3; however, this method was proven unsuccessful for wastewater with the amount of aqueous Ag left being consistently higher (86).

There are two methods that use IX resins on an industrial level; they are resin-in-pulp (RIP) and resin-in-leach (RIL) this process became widely used in the 1970s. IX in PMs recovery is a relative new method; this method was developed as an alternative to carbon-in-pulp (CIP) and carbon-in-leach (CIL), where the desired metals was extracted get adsorbed onto a resin rather than activated carbon grains this alternative was created due to the resins being a stronger absorbent and higher selectivity towards Au compared to using activated carbon (87). RIP and RIL follow a similar methodology of processing, IX resins addition, elution, separation, purification and recovery. The flowchart for RIL can be seen in Figure 5 (88).

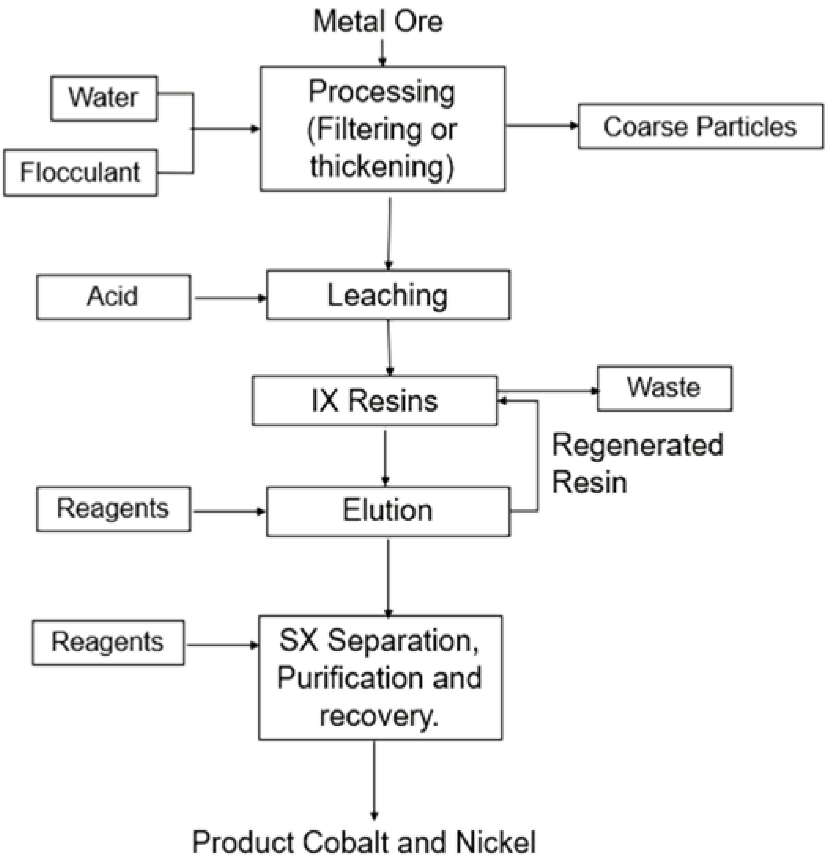


**Figure 5 RIL process for cobalt and nickel processing.**

The main difference between these two methods is the medium the sample is being reprocessed in. RIP eliminates the primary filtration or thickening stages; this process yields purified and enriched metal solutions (89). RIP is the preferred method for ores of exceptionally fine particle size which are extremely difficult to filter or thicken. Despite this, for both RIP and RIL the particle size of the resin should ideally be above 0.6nm to allow the resin to be separate from the pulp (90).

Previous literature shows that the initial stages of adsorption using carbon-in-pulp (CIP) having a low loading rate compared with IX, where equilibrium can be reached in under 24hrs (91; 92). RIP is thus a simple and potentially more environmentally sustainable method of recovering gold. An additional benefit is that the strong base anion (SBA) resins can be used which are more chemically and physically robust then activated carbon (93). It should be noted that despite this, RIP is considered unfeasible for some metal-recovery processes because of rapid attrition of the resin beads. The majority of separation and recovery processes involving IX resins are done hydrodynamically.

In recent years there has been an increase in the research into alternative methods of precious metal recovery (94). The huge capital cost per unit of product, cost of the process and various companies that have patented their resins; there would be a royalty fee if the resins were used on a large scale. Despite those drawbacks, the use of IX with PMs recovery is highly regarded as IX resins can recover the low-grade volumes of the PMs.

### 2.4.2. Solvent Extraction of Precious Metals

A wide range of different solvent extractants mechanisms can be used in the extraction of metals: anion, cation, chelation and solvation (95). Some of these have been used in the recovery of precious metals with different complications that occurred with each one. Shown in Figure 6 (96; 97).

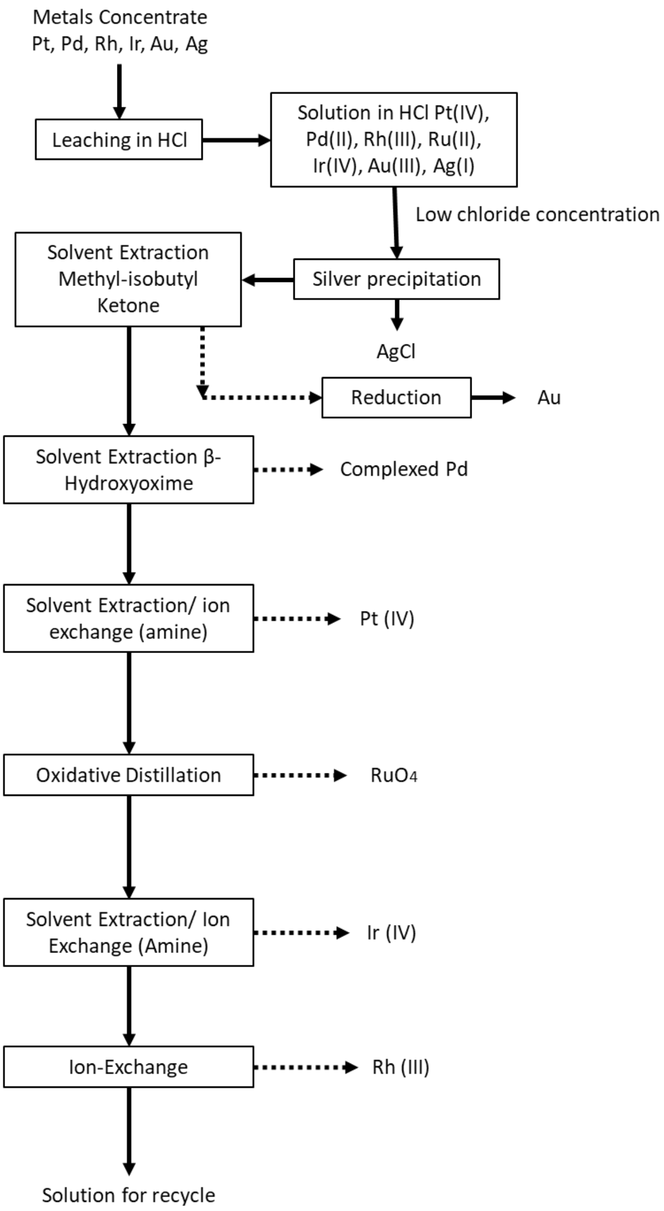


**Figure 6 Modern refining methods involving solvent extraction**

With many of the solvent extraction relying on a strong acid at some point in the methodology they cannot be seen as environmentally sustainable. This can be seen in Figure 6 with the initial step being leaching in HCl then followed with various different solvent extraction and leaching; two of them including methyl-isobutyl ketone (MIBK) and β-hydroxyoxime.

MIBK extraction is mainly seen in the extraction of Au from an acidic solution usually HCl. A low concentration of 3 M HCl is able to extract >99% with minimal extraction of the other competing compounds; however, the high recovery was possible due to the mixture that the Au was in prior to the MIBK solvent extraction, (5% KCN, 5%

$Na_2S_2O_3$ and hydrogen peroxide) (98). Even though in this research the reduced the concentration and volume of the hazardous chemicals there is still a requirement for the high extraction percentage of Au. The use of β-hydroxyoxime is mainly used for extraction of Pd from Pt (95). β-hydroxyoxime in the recovery of Pd and Pt of 97% and 86% respectively (99). A pH of 2-3 gave the highest recovery percentage; despite a high recovery being seen with more environmentally sustainable lixiviant of β-hydroxyoxime a strong acid of hydroiodic acid (HI) to obtain the required pH needed; similarly, with MIBK hazardous chemicals was needed to strip the Pt and Pd from the impurities (99).

Other reports of solvent extractions needing a strong acid to recover PGMs can also be seen with literature from Ohto et al. With their experimental using p-(1,1,3,3-Tetramethylbutyl)phenyl hydrogen [N,N-di(2-ethylhexyl)aminomethyl-phosphonate was shown to have high selectivity towards Pt and Pd ions in a low acidic region; however, the stripping of the metals was only possible *via* a mixture of thiourea and HCl (100).

Another similarity is seen in literature by Raiguel et al. with Au being extracted by diethyl carbonate (DEC) which has been evaluated to be a green, renewable alternative to current lixiviants used in the recovery of Au from copper-rich sources (101). Despite the method being relatively benign and showing high affinity towards Au for the extraction a chloride species was needed which was either HCl, NaCl or LiCl; specifically at high concentrations of the chloride species allowed for the Au to be extracted; however, when separating Au from copper (Cu) LiCl had a high affinity towards Au at 100% and Cu being underneath the detection limit (101).

## 2.5. Industrial & Research Development in Precious Metals Recovery

### 2.5.1. Pyro-Processing of Precious Metals

Pyrometallurgy is “the extraction and purification of metals by processes involving the application of heat;” the most important operations are roasting, smelting and refining (102). The first documented evidence of the use of pyrometallurgy was in ancient Egypt with wall paintings depicting workers using a blowpipe and bellows to melt Au in a crucible (103). This method of metal extraction grew globally until the 20th century when new techniques were discovered.

Between the 18th - 19th century pyrometallurgy went through the biggest development in its method. Previously, the belief was that during the smelting process the metal ore would take up the flame that was released from the burning coal, to form the metal; Antoine Laurent Lavoisier in 1777 was able to explain the combustion as an oxidation-reduction (104). Metals such as cobalt, nickel, manganese, vanadium, titanium and cerium were discovered using the blowpipe. This was done by the blowpipe blowing air into the flame, allowing the metal to melt, oxidise or reduce, and then mixing of fluxes with metal. The metals would oxidise and form colour; this then allowed conclusions to be drawn about the composition of each metal (105).

In the 19th century roasting and smelting was used for the treatment of oxides ores, primarily used for copper ore treatment. Furnaces were not widely used for processing metals until the mid-1800s, with one major improvement to using furnaces in metal recovery. Thomas Williams adapted the horizontal furnace in 1849, to benefit low-grade ores *via* crushing and grinding; this process was named the ‘Welsh Process’ because the metallurgists who were skilled in this process resided in Wales seen in Figure 7 (106; 107).

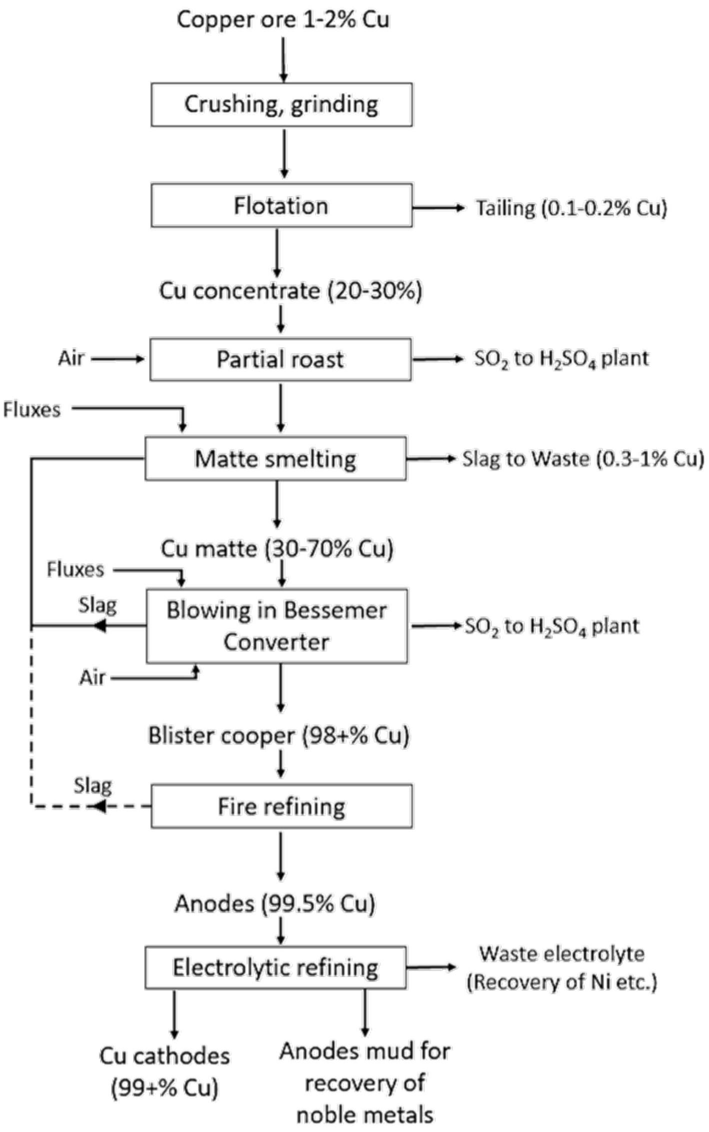


**Figure 7 Flowsheet for copper extraction process**

The extraction of copper from ores has been proven hard to control due to the high percentage of sulfur: 15-35%; this allowed the heat to oxidise sulfur into sulfur dioxide which is then emitted into the atmosphere (108). Another breakthrough was in 1856, by Sir Henry Bessemer, known as the ‘Puddling Process’. This process revolutionised steel marking. The ‘Puddling Process’ involved done by blowing air through the molten material instead of what was previously done where the molten material was exposed to air (103). This process allowed the processing time of steel production to go from days to minutes with the same amount of energy being consumed.

Pyrometallurgy is mainly used for high-grade metals, this leaves a lot of complex metals to become waste. Low-grade metals need grinding and flotation which causes high levels of dust formation. Moreover, the pyrometallurgy process is best suited to iron, chromite, lead, zinc, copper, tin and tungsten ores, with literature stating silver can be produced *via* the Merrill-Crowe process (109; 110). Additionally, after WWII there was a shortage of quality fuels: this resulted in a rapid increase in fuel costs (111). This leads to a growth in interest into new methods that could be used to reduce the energy-intensive, highly polluting method that is pyrometallurgy. Furthermore, with the introduction of hydrometallurgy into metal reprocessing, the use of pyrometallurgy has greatly decreased.

However, in the recent years there has been literature that has improved the pyrometallurgy method to have low energy consumptions and the reduce the amount of un-wanted hazardous by-products. Chen et al. (2020) found that using silica-saturated slags, pure $FeO_x$-$SiO_2$, $FeO_x$-$SiO_2$-$Al_2O_3$, and $FeO_x$-$SiO_2$-$Al_2O_3$-CaO slag, are effective in the recovery of Au, Ag Pt and Pd from a copper matte (112). Another literature stated that modifying the pyrometallurgy process in the recovery of Au and Ag from Cu from Waste Printed Circuit Boards (WPCBs). The modified method involved two-step process included oxidation of metallic granulate followed by pyrometallurgical refining in a DC arc-furnace; the yield obtained of Ag was only 60% but a high yield of Au with 94% was concentrated in metallic phase (113). With Despite these new methods is lower energy consumptions and reduction of unwanted by-products the method still requires a large amount of heat, ~1300 ℃, still demands a higher amount of energy compared to non-pyrometallurgy methods.

### 2.5.2. Selective Leaching of Precious Metals

#### 2.5.2.1. Aqueous Leaching

Aqueous leaching falls under hydrometallurgy. Hydrometallurgy is “the study of techniques for the separation of metals at low ℃” (114). These methods involve using aqueous chemicals for the recovery of metals from ores, waste or residual materials. Hydrometallurgy is divided into three different areas: leaching, solution concentration and purification of metal recovery (115). The modern-day use of hydrometallurgy can be traced back to the 19th century with the discovery of two major processes: cyanidation for Au and Ag, and the Bayer process for bauxite treatment (103). Hydrometallurgy is the preferred method for metal recovery, as it is often less energy-intensive and does not release as many highly toxic gases, volatiles and particulates (114).

One of the oldest methods of solvent leaching has been cyanide process which is also called the “Macarthur-forest Process” which is dated back to 1887 invented by chemists John S. MacArthur, Robert W Forrest and William Forrest (116). This method goes through these three steps: first being the finely grounded ore is dissolved in a sodium or potassium cyanide solution, continuing that the solids from the clear solution and finally recover the precious metals (PMs) from the cyanide solution *via* precipitation with zinc dust (116). This method is still used after 130 years because of cyanide being cheap, having a high selectivity towards Au and Ag, feasibility and it is the most effective method of recovering PMs (117; 118). This method is mainly used for extracting gold or silver from low-grade ores (116). However, cyanide is acutely toxic for humans, other mammals and aquatic species at relatively low dosages; and interferes with oxygen utilisation.

One way cyanide is used in the extraction of precious metals is with the use of activated carbon (AC). The use of AC in gold recovery can be traced back to the 1880s by Davis, who patented the process for adsorption of gold on activated carbon. Carbon has a high affinity for gold, in the chlorination process (119). This process was then developed by Gross and Scott by integrating cyanide in 1927 (120). The use of AC was not industrially used until 1952; when the United States Bureau of Mines undertook an investigation using boiling caustic without burning AC this changed the one use of AC from being burnt to ash and smelted, to being able to be re-used 15 times (121). As a result, the cost of this method decreased, and it allowed it to become industrially usable and environmentally sustainable.

Previous literature on recovery of gold from mine tailings that used cyanidation states a recovery rate of ~95% (122). However, alternative lixiviants such as thiourea and thiosulfate, also have high recovery rate percentages of 90-98% (123; 124; 125). The thiosulfate method of gold recovery has existed for the past century and is still being investigated as a more sustainable alternative (126). The use of an ammonium thiosulfate medium for extraction of gold from various forms of waste such as printed circuit boards (PCBs) and E-waste have been investigated (127; 128). A disadvantage of using thiosulfate is that leaching via thiosulfate is a less thermodynamically favourable method compared with cyanide, requiring thiosulfate to have a higher concentration (129). Approximately 40x more thiosulfate is needed in comparison with cyanide, which causes the price of the process to escalate (130; 131). Thiourea is also currently too expensive compared with cyanide to be commercially viable. However, the cost disadvantage could potentially be outweighed by escalating safety and waste disposal requirements for the cyanidation process (132).

In the recovery of precious metals (PMs), the starting materials that are used for making AC were coal, bone char, peat, petroleum coke, lignite, wood and other biomass sources such as nutshells and fruit shells (133). The different starting materials allows for different pore and surfaces to be used for the recovery of PMs. Palm nutshell AC gives the best recovery rate of ~95%, due to the pore volume of the palm nut being 0.54 cm$^3$/g (134).

There are mainly two methods that are used for precious metal recovery using AC in carbon-in-pulp (CIP) and carbon-in-leach (CIL). These methods are used to treat low-grade metal from their ores. CIP is a sequential leach then absorption of precious metals, specifically Au, from the ore (135). During the process, the pulp flows through a several agitated tanks where sodium cyanide and oxygen was used to dissolve the metal into a solution (136). This has caused a big push into the research of alternative compounds that are just as effective but less harmful to life. This solution then gets flowed through several agitated tanks again, with the tanks containing AC, where the Au gets absorbed by the AC which is then separated *via* electrodeposition. The process flowchart can be seen in Figure 8 (135).

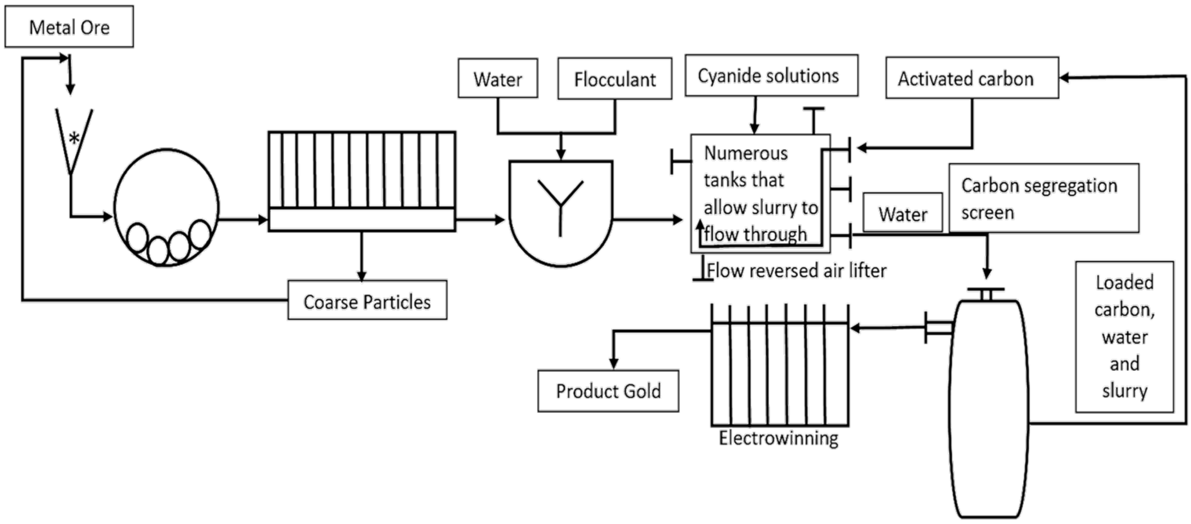


**Figure 8 Flowchart of the carbon-in-pulp process**

CIL is a simultaneous leach and absorption process (137). This was developed for processing PMs, specifically Au from ores that contain preg-robbing materials, for example, natural absorptive carbon. This method differs from CIP due to the leaching agent; sodium cyanide and activated carbon being added into the tanks simultaneously. Compared to CIL where they are added in separately; this method reduces the recovery yield (138). The flowchart for the CIL process can be seen in Figure 9 (137).

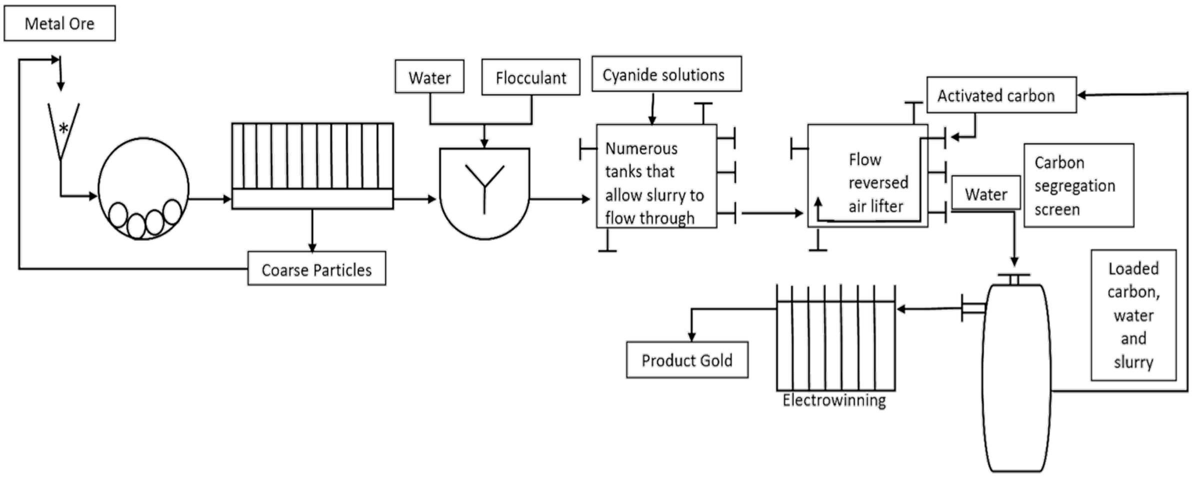


**Figure 9 Flowchart of the carbon-in-leach process.**

CIP and CIL processes still requires the use of cyanide and other hazardous chemicals; a high cyanide-to-copper ratio of ~2 is needed (139). Additionally, the recovery of gold from preg-robbing ores is low, filtration is needed for AC and the elution and regeneration are complex and highly energy-consuming (140).

Furthermore, CIP and CIL have slowed kinetic rates, weaker adsorption rates, adsorption speeds, adsorption capacities and loading rates. Another drawback in using AC in PM recovery is once the carbon loses its activity, this usually happens after a few weeks of use, the metal is no longer able to be adsorbed causing a significant increase of the metal being lost in the CIP and CIL adsorption circuit.

Heap leaching is a method used mainly for very low-quality ores or to reprocess waste material from other extraction methods (141). This process has more widely used technique for ores or waste that would not be processed using tank methodologies due to them not being economically viable, this method has been in use since 1969 (142). This method involves a mound of metals ores or waste on an impermeable pad that gets sprayed with a cyanide solution that would run over the rocks (143). When the rocks are being covered with the cyanide solution the desired metals will get dissolved the collected at the bottom of the mound then will get chemically processed (143). This method produces less extracted metals then processing from an ore in a mill but is a cheaper method which allows waste and low-quality metals to be extracted (141). Figure 10 shows the flowchart of the heap leaching methodology (142).

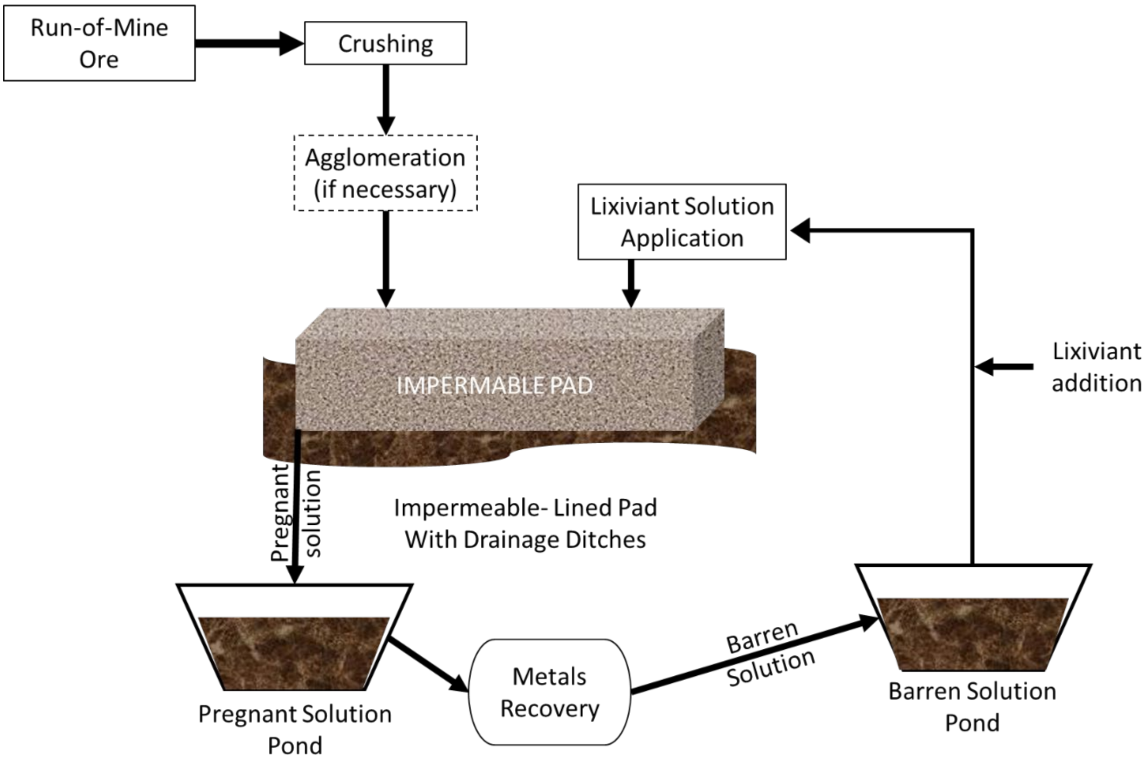


**Figure 10 Flowchart of heap methodology.**

Another aqueous leaching method that is used for solvent leaching is by using aqua regia; Latin for ‘royal water’ (144). Aqua regia is a mixture of two strong oxidising agents, usually nitric acid ($HNO_3$) and hydrochloric acid (HCl). The reaction of Au with aqua regia is shown in equation 1 and 2.

$$Au(s) + 3NO_3^-(aq) + 6H^+(aq) \rightleftharpoons Au^{3+}(aq) + 3NO_2(g) + 3H_2O(l) \qquad 1$$

$$Au^{3+}(aq) \ + \ 4Cl^-(aq) \rightleftharpoons AuCl_4^-(aq) \qquad 2$$

As stated in Table 1 and Table 2 the PGMs are extremely inert and only react with strong oxidizing agents which tend to be strong acids. However, the use of aqua regia has potential to be a dangerous solvent mixture and has many environmentally related issues with its use (145; 146). Aqua regia was originally used in the production of chloroauric acid; used in the Wohlwill process for refining Au (144).

The Wohlwill process invented in 1874 by Emil Wohlwill it is the chemical procedure used to refine Au that has the highest degree of purity at 99% (147). This process involves an electrochemical where an Au ingot is the anode, and the cathode is gold-plated in a chloroauric acid solution used for ion transfer (148). When the electric current is applied to the system the impure Au on the anode dissolves and travels through to the chloroauric acid then it sticks to the gold-plated cathode, which continues to the Au on the anode dissolves completely (148). Apart for the dangerous solutions that are used in the Wohlwill process it also is extremely time consuming and expensive; the Wohlwill process requires Au to refine the Au for the electrolysis components (149; 148). Due to the Wohlwill time scale, cost of the Wohlwill process is used for more specific applications, when the higher purity of Au is needed, the Miller Process is used instead.

The Miller process invented by Dr. Francis Bowyer Miller patented in 1867, this process involves a blowing stream of pure chloride gas through a crucible with molten unprocessed metal ores that contain Au; the impurities and unwanted metals, usually zinc (Zn), copper (Cu), iron (Fe) and Ag, readily bind with the chloride gas compared to Au and rise to the top of the crucible as these metals form slats with the chloride that are now insoluble in molten metal (150; 151). This process is cheap, easy and produces a purity of ~99.95% (150).

Industrially it has been Au and Ag that have been able to be extracted *via* the use of aqua regia; however, the other PGM metals have also shown to be able to be extracted using the lixiviant. With both Rh and Pd can be leached from spent automotive catalytic converters using HCl: $HNO_3$ with a ratio of 3:1 and Pt extraction from Platinum black using a ratio of 3:1 HCl: $HNO_3$ produced a <95% digestion (152; 153). Rh can be leached out of metal ores or alloys with HCl: $HNO_3$ ratios of 9:1 and 39:1 respectively, due to the chloride gas from the reaction between the HCl and the $HNO_3$ attacks the Rh alloys (154). Pd has been able to be extracted using the “dry aqua-regia” method, which consists of iron(III) chloride-potassium chloride mixture (145). The “dry aqua-regia” is considered the more environmentally friendly leaching lixiviant, due to the lower environmental impact compared to aqua-regia and cyanidation (155).

Current methods of leaching used in the recovery of precious metals rhodium (Rh) and platinum (Pt) from spent catalysts have been aqua regia (3:1 HCl: $HNO_3$), cyanide and mineral acids in the presence of $H_2O_2$, $O_2$ or $Cl_2$ (271). Aqua regia is needed to dissolve gold as neither $HNO_3$ nor HCl cannot dissolve them separately. The $HNO_3$ is the oxidiser in this method that forms the gold ion $Au^{3+}$; which then forms tetrachloroaurate(III) anions from the HCl (279). Using cyanide is highly toxic towards human and aquatic life, with by-products of highly polluting gases such as NOx and HCN (272; 273; 274). The most common leaching reagent is concentrated aqua regia producing Pt and Rh extraction rates of 90-93% and PGMs dissolution in under 5 minutes (275). Due to the health and environmental issues associated with most reagents in hydrometallurgical leaching of PGMs, there is research interest in a solvometallurgical approach, where the leaching liquid phase is not water-based. Because of the need for the liquid phase to be polar, to solubilise the metal ions.

#### 2.5.2.2. Non-aqueous Leaching

Despite aqueous leaching being the most popular selective solvent method for PGM extraction, in the last 20 years, there has been a considerable amount of interest in the recovery of metals from ores using solvometallurgy. Solvometallurgy is “the extraction of metals from ores, tailings and other urban waste using non-aqueous solutions;” solvometallurgy differs from hydrometallurgy by the absence of a discrete water phase (156). Recovery from ores and waste non-aqueous leaching such as using bacteria or carbon dioxide ($CO_2$) have been shown to have affinity towards the platinum group metals (PGMs).

Using liquid carbon dioxide is a relatively new option for Au extraction first reported in 2000. However, Au nanoparticles are currently being used to covert $CO_2$ into liquid fuel; with the aim to make liquid fuel a more viable option then using gas for cars as it is safer, easier to produce and more economically sustainable to transport (157; 158). The Au nanoparticles are used as a substitute for chlorophyll; this can only occur due to the Au nanoparticles being able to absorb the green light and transfer photo-excited electrons that chlorophyll deposits (157; 159). Further studies have shown that $CO_2$ can be converted into hydrocarbon fuel molecules when synthesised with Au nanoparticles in iconic liquids (157).

Additionally, there is literature that shows that carbon monoxide can be used to synthesis Au particles (160; 161). This method is a simple method of using a microfluid reactor with a reaction time of <4 minutes using carbon monoxide as a gaseous reductant (160). The carbon monoxide (CO) is easily removed by venting the reaction mixture: this method is flexible and can be easily become a continuous production system for a variety of gold nanoparticles (160). As shown the carbon oxides and gold have shown to have affinity towards each other so it isn't surprising that $CO_2$ is now being research into its ability to recover Au particles from a slurry of minerals; however, the recovery of the Au was poor when this method was used to recover the Au using an Australian gold-mining gravity concentrate; however, this can be attributed to the size of the particles (162). Another example of the $CO_2$ being used for PGM extraction, is the recovery of Pt, Pd and Rh from spent catalytic converters; with this method a supercritical carbon dioxide containing a chelating liquid was used (163). This experimental showed Pd had the highest recovery rate at 96% with the conditions of 60°C, 20 MPa, and 60 min of static extraction time (163).

Another new method of Au extraction that is still being researched is the use of iodide-oxidising bacteria (164). Iodide ($I^-$) has shown to reach and dissolve Au to form a gold (I) diiodide or a gold (III) tetraiodide shown in equations 3 and 4.

$$2Au + I_3^- + I^- \rightarrow 2[AuI_2]^- \qquad 3$$

$$2Au + I_3^- \rightarrow 2[AuI_4]^- + I^- \qquad 4$$

$I^-$ dissolution of Au is not affected by changes in pH compared to cyanidation where the requirements are in the pH range of 10-11.5 (165). Microorganisms are already used in extraction of PMs from ores *via* biooxidation; with biooxidation being used as a pre-treatment to dissolve sulphide minerals from gold ores prior to cyanidation (166; 167). One particular bacterium, Roseovarius, completed the dissolution of Au within 5 days, with a further 3 being able to solubilise Au within 30; this shows that iodising bacteria can be used for gold recovery despite the method is currently very time consuming (168). However, in the literature it states that further research is needed to evaluate the techno-economic feasibility of this new approach.

#### 2.5.2.3. Ionic Media Leaching

Ionic media leaching involves solvents that are either organic solvents, inorganic solvents or ionic liquids (ILs). ILs are defined as compounds composed of ion with melting points below 100℃; first reported in 1914 by Paul Walden it has since gained wide attention (169). ILs are known for their unique properties which makes them useful for a wide range of industrial applications. Those properties include high polarity, negligible volatility, high thermal stability, high ionic conductivity, low melting points, and structural designability (170; 171).

There are various ILs that are used for PMs recovery. Au recovery rate when using ILs ranges from 73-99.7%, Pd extractions are all higher than 95%, Pt recovery was more varied compared to Au and Pd with the lowest extraction being 67% and the highest being 98% (172). Despite the high extraction rate of PGMs from metal ores using ILs the same cannot be said for extraction of PGMs from e-waste. When an imidazolium-based IL was used for extraction of Au, Ag and Pd from e-waste the recovery percentages were extremely low at 1%, 0.4% and 1% respectively (173). Regardless, of ILs for extractions is highly selective, rapid and reach equilibrium quickly; however, using this method requires pyrometallurgy and HCl and $HNO_3$ and seems to give low recoveries for waste compared to metal ores (172). Additionally, currently most of the research on ILs and PGM extraction is in the form of using metal ores which as we have seen shows vastly different results from when the metal is in a waste material.

Another ionic medium that is currently being researched in the recovery of PMs is the use of the molten salts. Molten salts is mainly used when the metals are being recovered from Waste Printed Circuit Board (WPCBs), with the molten salts NaCl-NaI, KOH-NaOH, LiCl-KCl being the most researched molten salts for metal recovery PGM and rare-earth metals (174; 175; 176). The process of using molten is efficient, environmentally friendly and produces waste that can be used a fuel gas and could be a favourable lixiviant alternative to the harsh lixiviants of cyanide and aqua-regia; however, the reagents used are hazardous with molten salts being typically being made up of sodium nitrate and potassium nitrate which can be harmful to humans and animals in excess (177).

However, one form of ILs that was been researched in PGM extraction from both waste and metal ores, with very benign reagents, are Deep Eutectic Solvents (DES). First reported in 2001, DES is the newest form of ILs and is considered a green solvent (178). They are mixtures of salts such as choline chloride with hydrogen-bond donors such as urea. DES is a non-aqueous solution. DES is obtained from a complexation between a hydrogen bond acceptor compound and a hydrogen bond donor compound (179). The most investigated DES that is used in metal recovery are choline chloride (ChCl): urea (U), ChCl: glycerol (Gyl) and ChCl: ethylene glycol (EG).

As DES is a new form of sustainable liquids there is little research into what they can or cannot do and the overall usage especially for PM recovery. They are currently being used in several chemical and biochemical processes use as separations and purifications, pre-treatments of biomass. They are being investigated as an alternative to using common organic solvents which will make many methods more environmentally sustainable.

There are four different types of DES, these are characterised based on the type of complexing agent being used, with most of DES being a mixture of quaternary ammonium salt with metal salts or a hydrogen bond donor (HBD) with a general formula of $[Cat^+ X^-][Y]$ (180). $Cat^+$ is the stand-in for any ammonium, phosphonium or sulfonium cation, $X^-$ representing a Lewis base, usually a halide anion and Y refers to a Lewis acid. These four types can be seen in Table 5 (180).

**Table 5 General Formula for the Classification of DESs.**

| Type | General formula (Y) | Terms |
|---|---|---|
| Type I | $MCl_x$, | M = Zn, Sn, Fe, Al, Ge, In |
| Type II | $MCl_x \cdot yH_2O$ | M = Cr, Co, Cu, Ni, Fe |
| Type III | RZ, | Z = $CONH_2$, COOH, OH |
| Type IV | $MCl_x + RZ = MCl_{x-1}^{+} \cdot RZ + MCl_{x+1}^{-}$ | M= Al, Zn and Z= $CONH_2$, OH |

Type 1 DESs are the analogues of the metal halide/imidazolium salt system. They have a wide range of eutectic mixtures with metal halides with a limited number of non-hydrated metal halides and low melting point (181). Type 2 DESs can incorporate metals or increase the number of metals into the ionic liquid *via* the hydrated metal halides and ChCl. Type 2 includes the presence of water which decreases the melting point, in turn, decreasing the lattice energy (181). The decrease in the lattice energy makes the hydrated salts in type 2 DES are more prone to form mixtures quaternary salts that remain liquid in ambient temperatures.

Type 3 DESs can solvate different metal species, those include chlorides and oxides. This type of DES is the easiest to adjust for specific applications because of the number of hydrogen bonds that this bond contains. Furthermore, type 3 DES is the easiest to prepare and handle (181). Type 4 DESs have can produce cationic metal complexes, which allows for a high metal ion concentration close to the electrode surface.

Currently, the research with using DES in precious metal recovery has been limited to the coinage metals Au, Ag and Cu. DES could be an alternative solvent to the current methods used due to it be low cost, easy preparation techniques, low volatility, biodegradable and non-toxic; however, the acids used in DES a high tendency to breakdown quickly. Additionally, DES has high conductivity, viscosity and high surface tension. This could potentially reduce the large amount of liquid toxic waste that is produced when organic solvents are used for precious metals.

Current research into the DES in metal recovery is with rare-earth metals. With one literature showing that DES can be used in the electrodeposition of copper using

DES based on ChCl, with recovery rates of 100% (182). EG with electrodeposition, in a solubilised deposit containing Au, Ag and other metals with a low recovery of 3-18% with gold and silver being the only metals that were in the deposit (182). Further development into using DES in PM recovery could increase the environmental sustainability of PM production.

The most commonly DES investigated for PGM recovery has been ChCl: ethylene glycol (EG) (183). The research by Jenkin et al (3-18% recovery) methodology was carried out with the use of electrolysis and has other competing minerals that was dissolved which may have affected the overall recovery (184). Precious metal recovery investigations were also done by Nguyen that shows a reasonable recovery rate of Rh and Pt at 35% and 30%, respectively. Additionally, this work had the addition of the oxidising iron chloride and copper chloride ($FeCl_3$ and $CuCl_2$) and was a two-step process of solvo-leaching and non-aqueous solvent extraction (185). With ChCl: urea (Ur), ChCl: thiourea (TU) they show promising signs of producing a high recovery rate of PGM leaching. The HBD for each DES have already been confirmed to have an affinity towards PGMs in different lixiviant systems as a solvated metal complex (186; 184; 187; 188; 189).

ChCl: lactic acid (Lac) has yet to be researched with any PGMs. The current knowledge of the complexation of metals by lactic acid is that the interactions between Cu(II) ions and Lac which occurs at low concentrations; out of the four metals investigated (cobalt [Co], Cu, manganese [Mn], cadmium [Cd]) (190). It was shown the micromolar levels decreased in this order Co(II)-Lac > Cu(II)-Lac > Mn(II)-Lac ~ Cd(II)-Lac (190). The interactions are dependent on the metal ions affinity for oxygen-donor atoms (190). There have been other investigations into ChCl: Lac for metal recovery of Co and nickel (Ni) (191). The recovery rates were 48-52% and 53-57% respectively with the addition of trichloroisocyanuric acid (TCCA) or glycine + $H_2O_2$ (191).

The most recent literature in regard to DES and PM recovery were investigated by Wang et al and Lanaridi et al (192; 193). Lanaridi investigated the PMS recovery; however, the waste medium was spent automotive catalysts (193). A range of different DES were investigated in this work; however, only one of the DES that was investigated in the literature by Lanaridi et al, was discussed in the results which was choline Cl/p-toluene sulfonic acid (pTsOH) 1:1.8 (193). Without the addition of any oxidising agent the recovery of Pt, Pd and Rh was fairly successful at 35%, 90% and 32% respectively with Pt and Rh being the only metals to see a major increase in recovery when oxidising agents were added (193).

Wang et al also investigated Iridium (Ir), Pt, ruthenium (Ru) and Rh recovery from wastewater using a DES of trioctylmethylammonium chloride (N263) and Oleic acid (OA) via a liquid-liquid extraction (192). The recovery rates of all the metals except Rh were above 90% at 97.57%, 94.26%, 99.55%, and 15.1%, respectively (192). The proposed mechanism of this reaction was the solubilised metal chloride complexes replacing the $Cl^-$ in the DES system (192).

## 2.6. Conclusion

There is a wide range of methods that are being used for PM recovery. The inertness of the PGMs cause current methods to be excessive in cost, use a large consumption of energy, require hazardous chemicals, or produce hazardous by-products. With the growing public knowledge of the way precious metals are mined the social and environmental unsustainability and concerns with the decreasing amount of precious metals that are left to mine, a change in the way precious metals are produced is needed.

Development into more environmentally and economically sustainable methods that will conform to the new regulations for how much waste is produced, the amount of hazardous chemicals that can be allowed into the environment is highly needed. The growing demand for PMs and the rarity of them makes the recovering of waste highly sort after. Current methods do have high recovery rates; however, the high cost and energy usage outweigh the benefits of the processes.

Cyanidation is the current industrially used method for PGM recovery; high rates of recovery but slow kinetic rate, short timeframe, which is also used in many different methods including IX which are still being researched into improving the recovery without using cyanide. The cost of resins has caused a high cost of the processes due to the nature of the companies owning and producing the IX resins. Using IX resins would increase the kinetic rate of the recovery processes compared to cyanidation. Current research into using IX resins with alternative non-acidic lixiviants shows promising new process of using IX without the need of cyanide or strong acids.

Overall, it can be seen that the metal recoveries achieved in DES systems are significantly lower then what has been seen in standard hydrometallurgy. Despite the DES system advantage in relation to health and environment compared to the current methods and potential ramifications. Research is needed to optimise the performance of solvometallurgical recovery of PGMs.

Furthermore, the development of DES has only recently been investigated for the potential use of PMs recovery from metal ores, spent catalysts, e-waste and other waste forms specifically Au and Ag. There is limited literature on how DES would work with recovery of PGMs. Moreover, the PGMs are mined with metals such as cobalt (Co) Cu, Zn and Ni, separating the PGMs from earth metals is currently extremely hard to do with acids.

The novel research is with regarding the combination of DES and IX resins in the recovery of PM from a spent catalyst. There is extremely limited research regarding using DES in metal recovery, especially that of waste containing PGMs. Currently there has been a large community discussing the recovery of heavy metals and earth metals, especially Ni and Cu. Additionally, being able to use the properties of IX, the selectivity and quick kinetic rate combined with DES that could potentially make a reprocessing method have a high recovery rate. IX having an affinity towards low-grade metals and DES potentially having affinity to separate PMs from earth-metals. It would create an economically and environmentally sustain that has a simple methodology.

# CHAPTER 3: HYPOTHESIS

## 3.1. Hypothesis and Aims

The main plan of this research is to find a new environmentally and economically sustainable method, using DES, in effectively recovering PMs from waste, specifically mining tailings, and spent catalysis. The biggest issue with finding a new method is finding a non-hazardous solvent or acid that can separate the PGMs from a complex metal solutions, even with current developments in different methods including pyrometallurgy and aqueous leaching still involve acids. Developing a new method of using DES, with pre-existing or completely new DES that has an affinity towards PGMs and that remain stable whilst dissolving the desired metals without dissolving either the catalyst support or other metals in the waste. The current gaps in PGM recovery are the lack of research using benign and environmentally sustainable lixiviants that could potentially replace the hazardous acids and chemicals that are currently being used.

A range of different IX resins will be tested to determine which resin has the highest affinity to Au and Ag through dynamic column testing; the resins that have been decided are Purolite® A200, Lewatit® MonoPlus TP 214, Dowex™ M-4195, Puromet MTS9140 and Lewatit® VPOC 1026. The prediction is that resins with thiourea functional groups, Lewatit® MonoPlus TP 214 and Puromet MTS9140, will have the highest leaching of Au as thiourea has a high affinity towards the PGM, especially Au. When determining what DES to use to combine with the IX resins; four different DES will be looked into, ChCl: EG, ChCl: Ur, ChCl: thiourea (TU) and ChCl: Lactic acid (Lac). The prediction for DES leaching that the urea and thiourea DES would have the highest affinity towards Rh and Pt as both HBA have an affinity towards PMs. Ethylene glycerol and lactic acid DES either have not been research as of yet or have shown a low recovery of metals with similar properties such as copper (Cu) or Au. A flowchart of this thesis is shown in Figure 11.

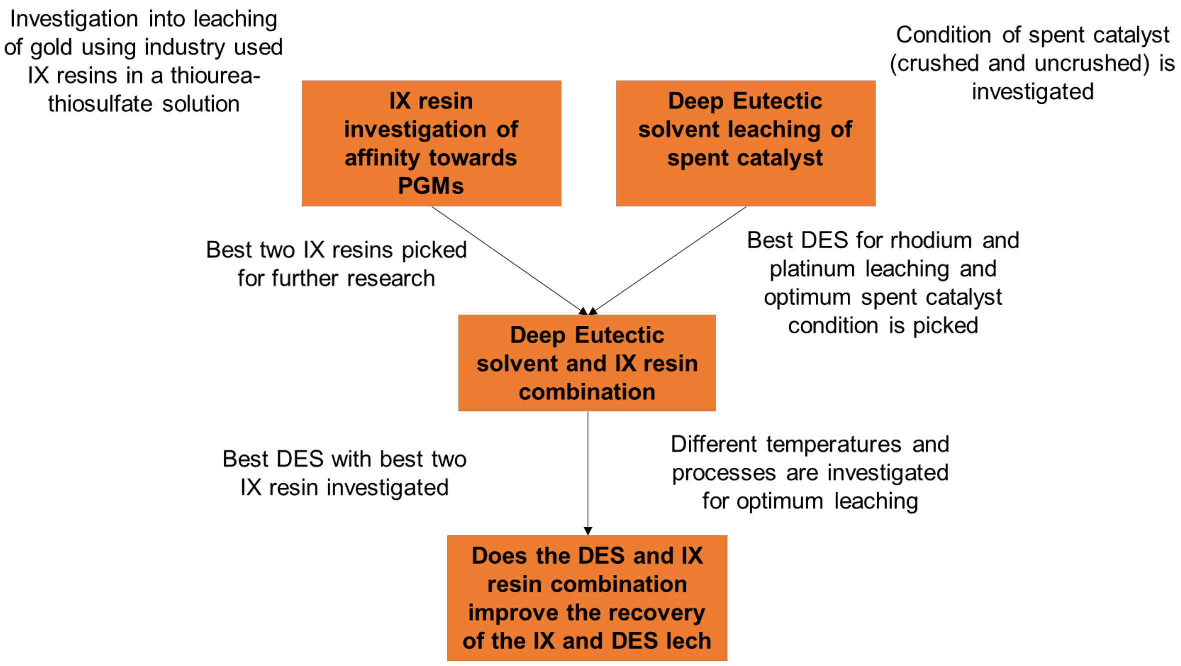


**Figure 11 Flowchart of PhD thesis work.**

Further investigation will occur into the mechanisms and complexes formed of the Rh and Pt with the DES by comparing to literature of Rh and Pt recovery with other chloride solutions. The final aim of this research is to combine the best IX resin from the Au leaching research project and the best DES for Rh and Pt leaching project. This research project will possibly make a new working method combining the dynamic column IX resin leaching and the DES kinetic leaching in either resin-in-pulp (RIP) or resin-in-leach (RIL). This will be the first example in the literature of combining the use of deep eutectic solvents and ion exchange resins that does not require strong acids or hazardous chemicals.

### 3.1.1. Hypothesis title

The current gaps in the question lead to a central research hypothesis of **“The combination of DES and IX for a more sustainable process for the recovery of precious metals from waste”**

Figure 12 shows a flowchart of the predicted methodologies of combining IX resins and DES into one system.

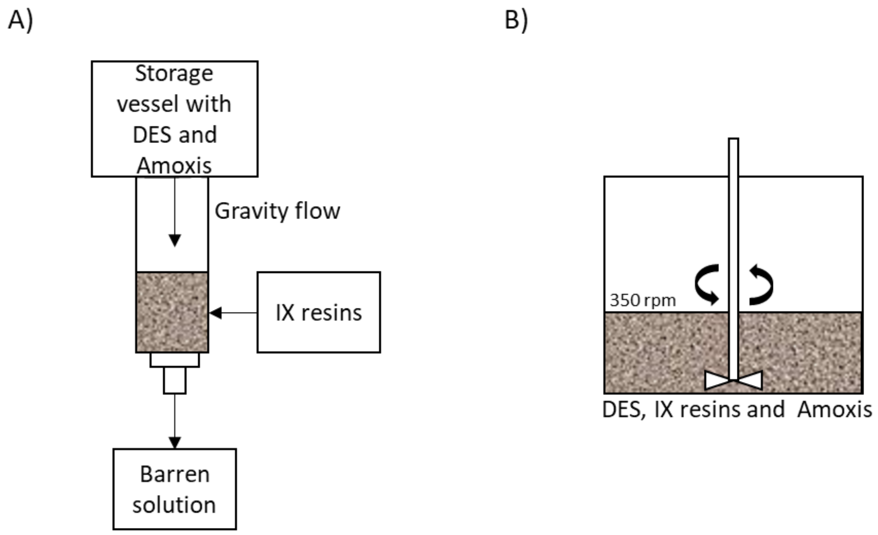


**Figure 12 Predicted Flowchart of final methodology (A: Resin-in-leach, B: Resin-in-pulp)**

The approach to ascertaining this central research hypothesis can be broken down into subhypotheses and steps in research as follows.

#### 3.1.1.1. IX utilisation of specifically target precious metals from a complex metal mixture representative of mining waste.

This work will include looking into more sustainable process of recovering PMs using IX resins. The use of IX resins are a more sustainable process due to them not being generating organic waste streams, present phase issues, or require excessive energy consumption. IX is a better compatible method to recovering PGM due to the affinity to the low concentration of metals that are present in the waste streams and mining tailings and can work at small scale compared to solvent extraction which is quite common method for metal recovery.

Resin screening will determine which resins have the best functionality and selectivity to effectively recover a high percentage of PMs. These screening testing would be done *via* dynamic testing using columns, and simulant leachate of metals typically found in Au mining tailings. By determining the uses and selectivity the different resins it would give a better pathway for future research involving metal on metal oxide catalysts and deep eutectic solvents. Two of the resins chosen, have yet to be investigated in its affinity towards Au or other PMs, Purolite® A200 and

Lewatit® VPOC 1026; this research will discover if those resins have any affinity towards the PGM.

Conventional IX material was chosen over silica material such as phosphonic and zeolites due to IX material being more robust, physically and chemically resistant. With silica material there is a risk of resin poisoning from cationic impurities in large quantities which is potential risk when PGM are often mined and used with the heavy metals that can cause the poisoning and will lead to a decreasing adsorption capacity (194). Zeolites also suffer with the same issue with sensitivity; zeolites can easily deactivate by adsorption or steric blockage by heavy products which again would cause a decrease in adsorption of the desired metals (195).

#### 3.1.1.2. Selective dissolving of precious metals on metal-on-metal oxide (MoMO) catalysts in DES.

Using, DES for the dissolution of PMs from MoMO would potentially open a new door in the spent catalyst regeneration sector. As the precious metals that are mainly used in catalyst have the highest price per Kg being, Rh, Pd and Pt. Being able to recover those metals from a spent catalyst without using large amount of waters, harmful chemicals and elevated temperatures could provide a more sustainable recovery process as well as greatly decrease the current demand for those metals.

The spent MoMO catalyst that will be used in this research project is an alumina substrate with ~20% cobalt, ~0.16% platinum and ~0.05% of rhodium from the metals recycling company RS Bruce in Sheffield. The desired metals on the MoMO spent catalyst would need to undergo a single-replacement reaction which would allow the Rh and Pt to get into solution; with predictions that the Rh and Pt would replace the choline in the ChCl to form rhodium and platinum chloride complexes. This experimental will investigate the change of temperature as a parameter. Additionally, by running leaching experiments of DES, aqua regia and HCl leaching will be run as a comparison of industrial used methods and DES to determine if acidity is a factor in the leaching of MoMO spent catalyst leaching.

Using the green solvent DES, would decrease the amount of potentially harmful waste formed from current MoMO regeneration methods but also it would make the method cheaper and easier to do on a large industrial scale. DES have previously been tentatively explored for gold, silver and copper recovery. There is limited literature that supports the development into expanding the use of DES in PGM recovery. This experimental will add to the literature and hopefully clarify the currently undetermined mechanism and reactions with relations to DES and PGMs.

#### 3.1.1.3. IX coupling with a DES system for the development of an effective recovery process.

Using previous findings on reductive IX mechanism and chemical behaviour of PMs in DES; the potential to combine the DES leaching and IX-unit operation processes will ultimately create a whole new environmentally and economically sustainable way of processing PMs. The prediction is that by combining the IX resins and DES; Rh and Pt would be dissolved into solution *via* DES and from that solution the IX resins would adsorb the Rh and Pt which would then be purified. However, the purification of Rh and Pt after the IX resin adsorption is not a part of this research project.

As stated in 3.0.2 question it is predicted that the $Cl^-$ in the ChCl plays a role in the dissolution of the PGMs; with that prediction the $Cl^-$ being the element that drives the reaction forward the metal species that would be expected to form would be $RhCl_6^{3-}$, $PtCl_4^{2-}$ and $PtCl_6^{2-}$. There is limited literature on how IX resins and chloride media work together except when IX resins are in need of flushing or regenerating, which uses $Cl^-$ or HCl (196). There is little literature about the applications of DES so the advancement has a wide scope; by doing this research, literature will be produced in DES applications with PMs which can potentially be used for other metals and other processes that have waste metals that could be recovered and can clarify the current suggestions on how DES work with PMs.

The aim of this work is to develop understanding of the process operational parameters which will allow effective coupling of these two-unit operations together. This methodology will create the basis of a previously unexplored methodology for the recovery of PMs which has the potential to minimize waste generation in comparison with current recovery methods that are used industrially. Despite there currently being no literature on how IX resins and ionic liquids work together in a system and the lack of literature on how PMs work with both DES or IX resins; the current research on Au, Ag and Cu shows potential in combining the systems into one new method. This PhD thesis will be the first example in literature of combining DES and IX resins in a column system.

## 3.2. Notes on thesis structure

This thesis is presented in an alternative format, information on each chapter is presented in the following table.

| Chapter | Description |
|---|---|
| 4. Methodology development | This section will show the development of certain methods that were used in this research specifically for chapters six and seven. The preparation of the crushed amoxis. The modification of the DES HBA: HBD ratio to take into account the lack of glove box for the synthesis of the DES in chapter 6. And the development of the RIL system of chapter 7 with regards to insulation of the IX packed column and the viscosity of the DES. |
| 5. Gold recovery from simulant mine tailings using chelating ion exchange resins with thiosulfate-thiourea lixiviant. | Paper was published to the Resources, Conservation & Recycling Advances Journal September 2023.<br>Determining which resin from SBA, WAC, chelating solvent-impregnated resins, from a simulated mine tailing from a thiosulfate-thiourea lixiviant.<br>Victoria R. Shields, Thomas J Robshaw, Christopher P. Porter, James T. M. Amphlett, Alan Hides, Richard Bruce, Joan Cordiner, Mark D. Ogden.<br>This paper presents fitted breakthrough models collected for gold recovery from simulate mining tailings *via* dynamic testing of five different IX resins. This data set was used to determine which IX resin has the highest selectivity towards gold and potentially the other PMs. |
| 6. Rhodium and platinum recovery from cobalt on an alumina substrate spent catalyst using DES. | Paper will be submitted to the Separation Journal.<br>Determining which lixiviant has the best affinity towards the PGMs *via* leaching using deep eutectic solvents (DES), rhodium and platinum from an alumina spent MoMO catalyst.<br>Victoria R. Shields, Thomas J Robshaw, Jordan Miller, Oliver Murray, Joan Cordiner, Mark D. Ogden.<br>This paper presents a set of data collect from aqua regia and different DES and aqua-regia. Specifically looking at the leaching of rhodium and platinum leaching. An assessment of the lixiviants and DES ability. |
| 7. Rhodium and platinum recovery from spent catalyst *via* ChCl: Lac DES leaching with IX resins. | Paper will be submitted to the Journal of Separation and Purification Technology.<br>This chapter aims to combine the IX resins that were determined to be the best for PMs in chapter 4 with the DES's that was determined to be the best for Rh and Pt from the amoxis determined in chapters 5.<br>Victoria R. Shields, Jordan Miller, Oliver Murray Joan |

| | |
|---|---|
| | Cordiner and Mark D. Ogden.<br>This chapter is to decide if DES and IX resins could be a new environmentally sustainable method of leaching PMs from spent catalysts. |
| 8. Conclusions and future work. | This chapter presents the overall conclusions from this body of work and the impact it has on the current literature. Discussions and questions are presented on what needs to be done in the future to develop the current methods of recovery of PMs from waste. |

# CHAPTER 4: METHODOLOGY DEVELOPMENT

## 4.1. Preparation of crushed amoxis

The amoxis was retrieved from RSBruce in Sheffield and were in solid pellet form. They were then crushed via a ball mill of the size of 30mm diameter alumina ($Al_2O_3$) ceramic balls for 30 minutes with the mass of 200g of the amoxis at one time.

## 4.2. Choice of resin for Precious metal recovery

All five resins that were investigated in chapter 5 were decided on two factors. A) IX resins have been previously investigated or are currently being used in industry of gold or silver absorption Lewatit® MonoPlus TP 214, Puromet® MTS9140 and Dowex™ M-4195. B) The functional group of the IX resins has been shown to have an affinity towards precious metals, specifically gold VPOC 1026 and A200. Additionally, the prices of the IX resins are relatively low in price with price ranges of £34.10 - £94.50 per 100g (197; 198). The IX resin investigation was repeated three times. The sources of error would be for each repeat and batch of simulant pregnant leaching solution despite the metals being added in the same order each time it is unknown if the metals in the solution react differently each time.

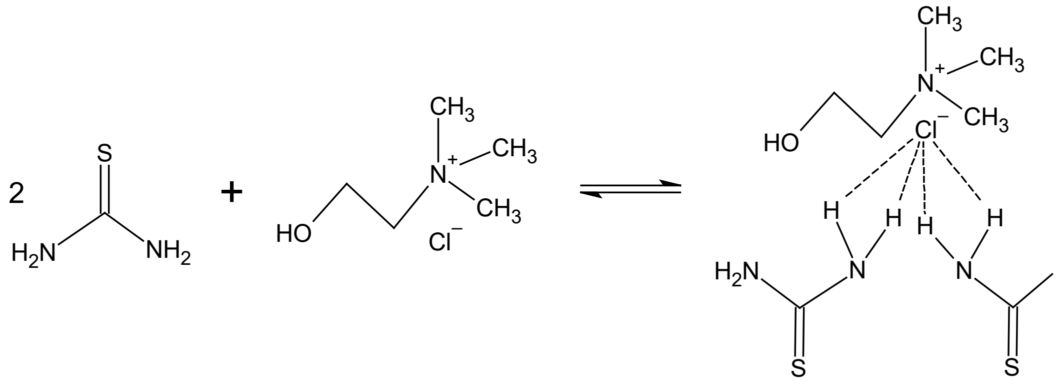
The overall choice for the resins progressed from chapter 5 to chapter 7 was decided on the amount of Au that was removed from solution during the screening study. Gold, platinum and rhodium are a part of the same reactivity of being very inert metals and are a part of the precious metal group.

## 4.3. Synthesis development of Deep Eutectic Solvents

Due to there being a lack of a glove box which is routinely used in the synthesis of Deep Eutectic solvents (DES) for some of the DES that was investigated (urea and thiourea) different ratios were needed to allow the eutectic point to be reached.

At first all DES used the same ratio of 1:2 Hydrogen Bond Acceptor: Hydrogen Bond Donor (HBA: HBD). When this ratio was used on urea (Ur) and thiourea (TU) the HBA and HBD would start to combine into an opaque white-yellowish thick liquid only at temperatures of 80℃ or higher then start to solidify when left to mix at ambient room temperature.

Below shows the expected reaction (equation 5, 6) between TU and Ur and chlorine chloride (ChCl) in the synthesis of the DES (199; 200).



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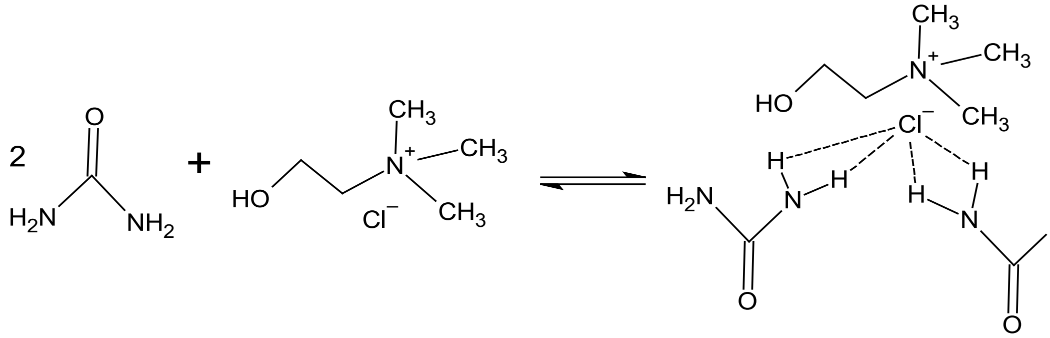

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There is currently no research into the production of TU or Ur DES with ChCl without the presence of a glovebox. However, as both the equations above show both HBD being investigated having a partial bond with the free chloride ion and both equation show that 2 Ur and 2TU are needed to create one DES; in comparison to the ChCl: Latic acid and ChCl: Ethylene Glycol where the equation ratio is one to one this could indicate why the amount of ChCl is needed in a greater quantity to allow enough free chloride ions to bond to each of the HBD in order for the DES get to and remain at the eutectic point with the presence of air. The air would introduce water vapour molecules to the DES mix, which would partake in the hydrogen bonding in a hydrophilic DES, which would affect the HBD/HBA ratio required.

Other ratios of ChCl: Ur and ChCl: TU were investigated to determine the ratio that would allow the DES to stay in liquid form, this is shown in Table 6 with the final ration for ChCl: TU being 15:6 ratio, and ChCl: Ur had a ratio of 13:6.

**Table 6 Attempts of the different ratios of ChCl, Tu and U to create DES.**

| Attempt | ChCl: TU ratio | ChCl: Ur ratio | Temperature(℃) | Appearance |
|---|---|---|---|---|
| 1 | 1:2 | 1:2 | Three different temperatures tested:<br>1. 80℃<br>2. 100℃<br>3. 120℃ | 1. Started liquid and opaque after ~1hr it started to solidify.<br>2. Started liquid and opaque after ~2hr it started to solidify.<br>3. Plastic beaker used to make DES started to melt. |
| 3 | 1:1 | 1:1 | 80℃. | Never turned liquid stayed solid and opaque. |
| 4 | 4:1 | 4:1 | 80℃. The decreased to 60℃ first hour. After two hours decreased to ambient temperature. | Both would start out as liquid would remain liquid but after both heat plates were turned off after the second hour, they would solidify again. Still opaque. |
| 5 | 7:3 | 7:5 | 80℃. The decreased to 60℃ first hour. After two hours decreased to ambient temperature. | Both would start out liquid would remain liquid but after both heat plates were turned off after the second hour, they would start solid again. Liquids were translucent. |
| 6 | 13.6 | 13.6 | TU: Two experiments run one at ambient temperature other at 60℃.<br>Ur: 60℃. After two hours decreased to ambient temperature. | TU: Both were liquid and clear but very viscous.<br>Ur: Become liquid and clear at 60℃ and after it had cooled down to ambient temperature. |
| 7 | 15:6 | 15:6 | 60℃. After two hours decreased to ambient temperature. | TU was clear and less viscous than the ratio of 13:6.<br>Urea was liquid but was a translucent white colour. |
| Final | 15:6 | 13:6 | 60℃ After two hours decreased to ambient temperature. | TU was clear and less viscous then the ratio of 13:6.<br>Ur: Become liquid and clear at 60℃ and after it had cooled down to ambient temperature. |

## 4.4. Process of setting up Resin-in-Leach

The process to set up a successful Resin-in leach (RIL) system for DES and IX resins required many alterations, this was due to many factors such as the viscosity of the DES, mass ratio of DES: amoxis: IX resin, temperature of the system. With Figure 13- Figure 15 showing the process of the systems that were tested to get the DES and IX resin process to work.

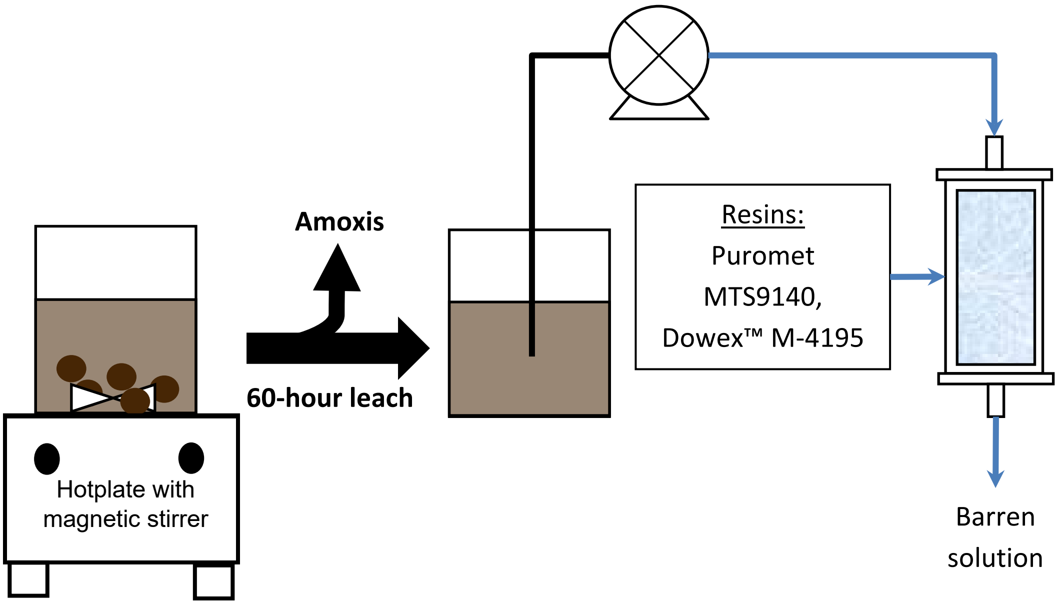

**Figure 13 First Set-up for RIL system.**

This system did not work due to the viscosity of DES being too thick and when pumped through the peristaltic pump it led to the tubing that was connecting the peristaltic to the leached amoxis and the IX resins would get clogged and eventually popped off. Also, during this system, it would not take into account the temperature that was required for the highest leach, as the current tubing was not insulated to keep the heat in. This thought process caused a gravity-flow columns to be considered. With a gravity-flow column the factor of the DES viscosity no longer a factor and a circulating heat baths can be connected to the gravity-flow column. This process can be shown in Figure 15.

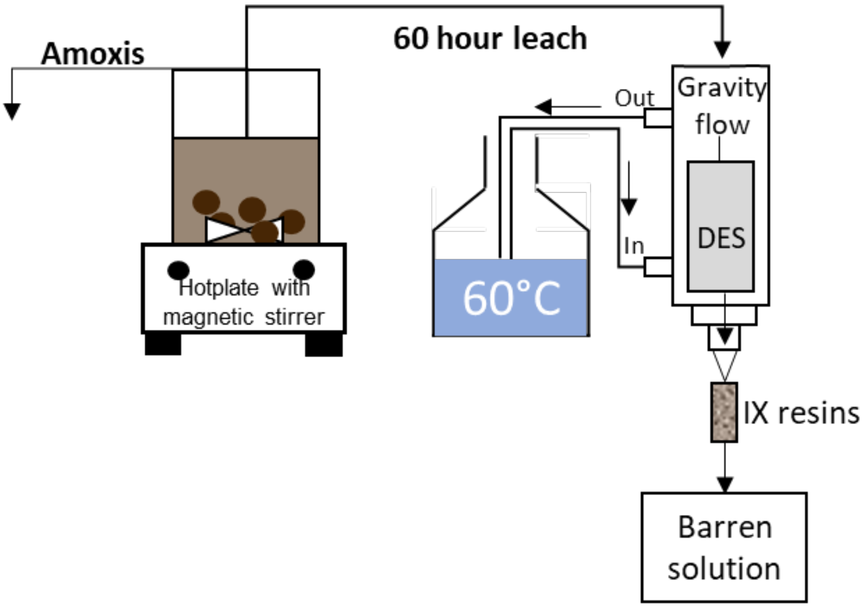

Figure 14 Second set up of RIL process.

Despite this setup allowing the DES to flow through the IX resin column, the IX resins are not connected to the water jacket. This hinders the experiment as there is a major temperature decrease from the water jacketed column to the IX resin packed column. That could greatly affect the leaching of the Rh and Pt from the amoxis. There was an attempt to eliminate the intersect between the IX resin and the gravity flow column. This was done by cutting the stopper of the packed IX resin to allow the IX column to fit in the bottom of the gravity flow column. Additionally, insulation with aluminium foil was used to cover the IX resin to keep the heat the IX resins to the desired temperature of 60°C. This improved set up can be seen in Figure 15.

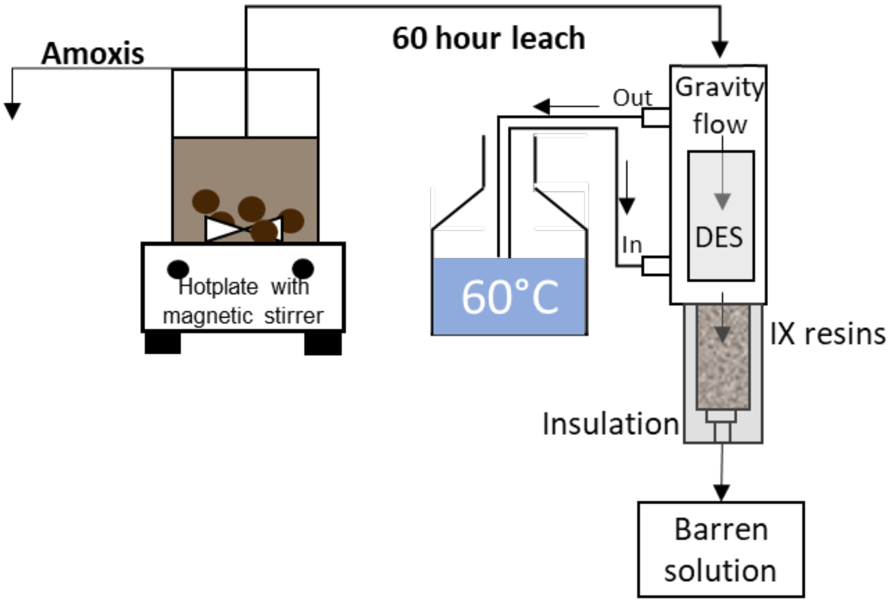

**Figure 15 Third set up of RIL process.**

The third set up for the RIL process has shown the current best method of getting the gravity flow column to work. However, as the water-jacket only surrounds the column where the DES-PM solution is contained where the IX resins are packed that is left at ambient temperature, so insulation (glass wool) and aluminium foil was used to wrap the IX resin packed column and the gravity flow column to keep and contain the temperature that is being used.

# CHAPTER 5: ION EXCHANGE RESIN SCREENING

## 5.1. Paper Overview

This paper investigates five different IX resins gold uptake in a thiosulfate-thiourea simulant mine tailings pregnant leach solution (PLS).

Purolite® A200 (quaternary ammonium), Lewatit® MonoPlus TP 214 (thiourea), Puromet MTS9140 (thiourea), Dowex™ M-4195 (bispicolylamine), and Lewatit® VPOC 1026 (solvent impregnated phosphonic acid) were characterised using X-Ray photoelectron spectroscopy (XPS). Each ion exchange resin chosen affinity and effectiveness to recover gold from the PLS is discussed.

Gold uptake investigation was performed in a sulfuric acid medium which a mixture of different metals that are usually seen in industrial mining waste of a final pH of 3. Dynamic column experiments were performed to obtain breakthrough points for each resin for comparison with other reins investigated in literature and to give insights into the mechanisms and interactions that occur between the resins, gold and other metals in the PLS.

Analysis of the dynamic column experiments were conducted at RS Bruce in Sheffield to determine the concentrations of all the metals in the barren solution after going through the resin packed column.

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Author contributions:

- V. R. Shields- Experimental work, data collection, data analysis and writing
- T. J. Robshaw- Manuscript review
- C. P. Porter- Hosting of V. R. Shields at RS Bruce and manuscript review
- J.M. Amphlett- Manuscript review
- A. Hide- Hosting of V. R. Shields at RS Bruce
- R. Bruce- Hosting of V. R. Shields at RS Bruce
- J. Cordiner- Manuscript review
- M. D. Ogden- Principal Investigator and Manuscript review

# 5.2. Gold recovery from simulant mine tailings using chelating ion exchange resins with thiosulfate-thiourea lixiviant.

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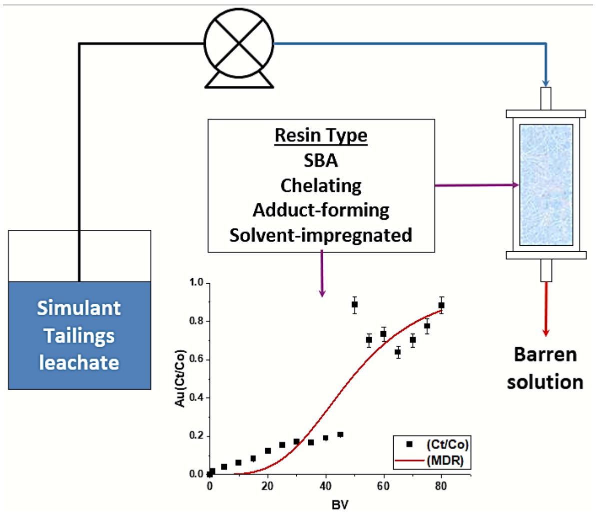
## Abstract

Recovery of gold from mining tailings is important economically and environmentally in the mining industry. With a limited amount of mineable gold remaining, the process of recovering gold from mine tailings needs development. This paper will specifically investigate the recovery of gold using ion-exchange resins in a thiosulfate-thiourea lixiviant solution. A range of resins of different functionalities: Purolite® A200 (Type II quaternary ammonium), Lewatit® MonoPlus TP 214 and Puromet® MTS9140 (thiourea), Dowex™ M-4195 (bis-picolylamine) and Lewatit® VPOC 1026 (di(2-ethylhexyl)phosphate- D2EHPA) were assessed for their gold uptake capabilities via dynamic column experiments. A mixed-metal solution was used to accurately simulate the spent lixiviant from thiosulfate/thiourea leaching of mine tailings. All resins showed selectivity towards gold over the numerous other metals in solution, which was believed to be due to the stability of aqueous gold thiourea complexes. Puromet® MTS9140 had the highest gold capacity, with a calculated uptake capacity of 41.6 mg/L. Modified-Dose Response (MDR), Bohart-Adams and Yoon-Nelson models were used to describe the data; the MDR model being the most successful.

### Graphic Abstract



**Keywords:** precious metals, resource recovery, mine tailings, ion exchange, surface assets.

# 1. Introduction

8.75 billion tonnes of waste are created from gold mining annually (201). Solid waste streams generated from gold mining and processing, better known as mine tailings, still contain a significant mass of gold, with a global estimate of around 425 tonnes (202). The U.S. Geological Survey estimates that there are only 58,000 tonnes of minable gold left in the world (203). Gold is used in a huge range of materials and products including electricals, such as integrated circuits (ICs) and printed circuit boards (PCBs), renewable energy technologies, catalysts, finance, jewellry, dental alloys, medicine and clothing (204). With increasing demand and diminishing supply levels, it will majorly affect a large variety of industries if mineable levels of gold run out. Many mining companies are becoming increasingly interested in mine tailings as a potential future source of gold (205; 206; 207). An average of 3,300 tonnes of gold was mined annually between 2015-2018, which has been steadily increasing by ~5% each year (208). Despite the increased amount of gold mining, only 40% of gold in mine tailings is recoverable using current techniques of cyanide leaching and adsorption *via* activated carbon (209; 210).

In cyanide leaching gold is extracted from ores or tailings, by the formation of the gold-cyano complexes $[Au(CN)]^{2-}$ (211). Because of the extreme toxicity of cyanide to many organisms, the method poses hazards to health and environment, in the case of industrial accident or environmental release. Commonly used industrial methods to recover gold from the cyanide pregnant leach solution (PLS) are carbon-in-pulp (CIP) and ion exchange (IX) (212; 213). They are both affected by preg-robbing, which is defined as the phenomenon whereby the gold cyanide complex $[Au(CN)_2]$ is reabsorbed from solution by the constituents of the ore (214). The CIP method has become popularised due to its ability to prevent the preg-robbing observed with ores containing high quantities of organic matter, such as gold ores (215; 216). It is a cost-effective method capable of recovering >99% of the recoverable gold in the mining tailings. However, the process involves the use of cyanide, which is severely detrimental to both human health and the environment (217; 218).

An alternative process to CIP is resin-in-pulp (RIP), which is almost identical in operation, except it utilises IX resins, rather than activated carbon to contact the leachate slurry (219). This process has many advantages, such as fast kinetics, adsorption capacity, and high customisability of the extraction process (220). Additionally, no filtration is needed with the resin being able to function in up to 60% solids in the pulp (78). IX has already been used in the recovery of gold, silver, and precious metals (76; 77; 78). However, the use of IX resins is still relatively novel in the recovery of gold. Commercial resins have a huge variety of functional groups, and the adsorbent material can be selected to create synergy between the resin functionality and that of the lixiviant matrix (79). Hence, alternative lixiviants like thiourea, thiosulfate or a combination of both, can be used instead of cyanide, negating the environmental and health threats previously mentioned. Previous literature shows that the initial stages of adsorption using CIP have a low loading rate compared with IX, where equilibrium can be reached in under 24hrs (91; 92). RIP is thus a simple and potentially more environmentally sustainable way of recovering gold. An additional benefit is that the strong base anion (SBA) resins used are more chemically and physically robust then activated carbon (93). It should be noted that despite this, RIP is considered unfeasible for some metal-recovery processes because of too-rapid attrition of the resin beads. The majority of separation and recovery processes involving IX resins are done hydrodynamically, with a column setup. Therefore, it is sensible to use such methodology in initial screening work.

Previous studies on recovery of gold from mine tailings have used cyanidation to achieve recovery rates of ~95% (122). However, alternative lixiviants to cyanide such as thiourea and thiosulfate, also have high recovery rate percentages of 90-98% (123; 124; 125). The thiosulfate method of gold recovery has existed for the past 100 years and is still being investigated as a more sustainable alternative to cyanide (126). The use of an ammonium thiosulfate medium for extraction of gold from various forms of waste such as printed circuit boards (PCBs) and E-waste has recently been demonstrated (127; 128). The main disadvantage of using thiosulfate is that leaching is less thermodynamically favourable compared with cyanide, requiring thiosulfate to have a higher concentration (129). Approximately 40 x more thiosulfate is used compared with cyanide, which causes the price of the process to escalate (130; 131). Thiourea is also currently too expensive compared with cyanide to be commercially viable. However, the reagent cost disadvantages may increasingly be outweighed by escalating safety and waste disposal requirements for the cyanidation process (132).

Thus far, reports of using thiosulfate in gold recovery have focused on using higher concentrations, which leads to higher consumption of thiosulfate through excessive oxidation. There has been extremely limited research into the use of a thiosulphate-thiourea dual- lixiviant in the recovery of gold from mining tailings. There is currently no literature regarding the use of a thiosulfate-thiourea lixiviant system in combination with IX resins in the recovery of gold or other precious metals. The potential to combine them together, in its novelty, could greatly improve the overall recovery due to the lixiviant synergy that has been previously seen for thiourea/iodine and thiourea/thiocyanate systems (221; 222).

In this paper, chelating, and solvent-impregnated resins, alongside SBA, are investigated for their efficiency in gold recovery from a thiosulfate-thiourea dual-lixiviant. An overview of the resins investigated, with the functional group, exchange capacity, and working pH range is seen in Table 7. Two of the resins have not yet been investigated for their affinity towards gold or precious metals which are Purolite® A200 and Lewatit® VPOC 1026. The other three IX resins shown in Table 7 have been investigated for their ability to recover gold, silver or other precious metals from solution; however, there are no reports of said resins being investigated in a thiosulfate-thiourea system. Screening of these resins will illustrate how functional groups affect the uptake of gold from the leachate and how the use of thiosulphate-thiourea dual lixiviant leachate affects the uptake behaviour of different resins, giving novel insight into using IX resins for precious metal recovery. The objective is to identify suitable candidate resins to progress to further experimentation, with a view to progression towards a new RIP or hydrodynamic system for gold recovery from mine tailings.

**Table 7 The resins used in this study and selected properties (223; 224; 225). PS-DVB= polystyrene- divinylbenzene.**

| Resins name | Functional group | Resin Matrix | Exchange capacity | pH range | Particle size | Appearance |
|---|---|---|---|---|---|---|
| Purolite® A200 | Type II Quaternary Ammonium | PS-DVB | 1.30 eq/L | 1-10. | 300-1200µm | Cream |
| Puromet® MTS9140 | Thiourea | Polystyrenic Macroporous | 1.0 eq/l | 0-14. | 300-1200µm | Cream |
| Lewatit® MonoPlus TP 214 | Thiourea | Crosslinked polystyrene | 1.0 eq/L | 0-14. | 0.55mm | Cream |
| Dowex™ M-4195 | Bis-Picolylamine | Styrene-DVB | ≥0.52 g/L (Cu) | 0-7. | 20/50 US Mesh | Green |
| Lewatit® VPOC 1026* | Di-2 ethylhexylphosphate (D2EHPA). | Macroporous styrene DVB copolymer | 1.8 meq/g | 1-4. | 0.31-1.65 mm | Cream |

*Solvent-impregnated resin

Being able to successfully combine thiosulfate and thiourea into one system where both thiosulfate and thiourea have been proven to have an affinity towards gold, this new lixiviant system could potentiality create a significant change in the current gold recovery methods and promote developments in moving away from cyanide use in industry.

# 2. Experimental

## 2.1 Equipment and Reagents

$CoCl_2$, $CuCl_2$, AuCl, $FeSO_4$, $MgCl_2$, $AgNO_3$, $Na_2S_2O_2$, $CH_4N_2S$ and $ZnSO_4$, were purchased from Sigma Aldrich and $K_2SO_4$ was purchased from Acros Organics these are the metal salts/lixiviants and the concentrations used are shown in Table 2. The metal salts were dissolved in 1 M $H_2SO_4$, dilute from (95%) $H_2SO_4$ from Fisher Scientific. All chemicals used were analytical grade or higher.

## 2.2 Mine tailing simulant composition

A simulant mine tailings pregnant leach solution (PLS) was produced based on literature values for average concentrations of acids, metals and lixiviants that would be present (226; 227; 228; 229; 230). This was intended to simulate the leachate produced from the treatment of gold mine tailings by thiourea and thiosulphate. The composition of this PLS is shown in Table 8.

**Table 8 Composition of the mine tailings leach stimulant used. Metals salts dissolved in 1 M $H_2SO_4$ solution.**

| Metal ion/lixiviant | Salt used | Mass (mg) ±0.05 | Concentration ($mg{\cdot}L^{-1}$) | Concentration ($mmol{\cdot}L^{-1}$) ±0.05 |
|---|---|---|---|---|
| Cobalt | $CoCl_2$ | 36 | 16 | 0.123 |
| Copper | $CuCl_2$ | 190 | 89 | 0.662 |
| Gold | AuCl | 200 | 129 | 0.425 |
| Iron | $FeSO_4$ | 635 | 233 | 1.533 |
| Magnesium | $MgCl_2$ | 334 | 85 | 0.893 |
| Potassium | $K_2SO_4$ | 81 | 18 | 0.103 |
| Silver | $AgNO_3$ | 153 | 97 | 0.571 |
| Thiosulfate | $Na_2S_2O_2$ | 27 | 27 | 0.171 |
| Thiourea | $CH_4N_2S$ | 10,000 | 10,000 | 13.372 |
| Zinc | $ZnSO_4$ | 73 | 30 | 0.185 |

## 2.3 Column experiments

Resins, ranging from 0.7 - 0.9 g, were packed in a 1.4 mL column and then pre-treated with 1 M $H_2SO_4$ overnight *via* being pumped through the column at a flow rate of 3.89 mL/min. Peristaltic pumps pumped the required flow rate of pre-treating $H_2SO_4$ or PLS through the columns. Each column experiment was run for 20 hours, with 80-bed volumes (BV) collected. BV is defined as the volume of the resin bed. BV was calculated by calibrating the flow rate of the peristaltic pump. A dry scint *via*l was weighted and the pump was set at 3rpm. The pump run DI water through the column for 10 minutes. The mass of the collected DI water was then measured and divided by 10 to calculate the flow in mL/min. This was then multiplied by 60 then divided by 1.4 to give the BV/h. This was repeated by with the flow rate was set at 5 rpm. 1 mL of each collected fraction was diluted with 9 mL of 1% $HNO_3$ (trace metal grade) for ICP-OES analysis, for all metals in the effluent solution.

## 2.4 Models used for fitting breakthrough curves

Breakthrough curves models are used to determine approximate breakthrough times and capacities for resins under dynamic operation. Comparing a calculated dynamic uptake value for a given metal to the manufacturer- quoted exchange capacity for the resin (Table 7) gives an insight into the selectivity for the given ion. Three models that can be applied to breakthrough data are the Modified Dose-Response (MDR) model, Bohart-Adams model and Yoon-Nelson model.

The MDR model, initially designed for pharmacology studies, has been used to describe metal-adsorption column kinetics (231). The MDR model is empirical in nature but has been used to reduce the margin of error between real and model data that is commonly found from the use of non-empirical models (232). The model equation is expressed as:

$$\boldsymbol{C_t/C_o = 1 - \frac{1}{1+\left(V_{eff}/b\right)^{a}}} \qquad 7$$

$$\boldsymbol{q_0 = \frac{bC_0}{m}} \qquad 8$$

Where a and b are both constants of the MDR model. $V_{eff}$ represents the volume pumped through the column (ml); this is calculated by multiplying the flow rate by the adsorption time. $C_t/C_o$ represents the concentration of the ion of interest at time ($C_t$), divided by the initial concentration in the inlet ($C_o$). The $q_o$ parameter is the dynamic uptake capacity of the resin on a dry mass basis (mg/g), and m is the dry mass of resin used in the experiment (g).

The Bohart- Adams model can be used to describe the initial part of the breakthrough curve by using the $\frac{C_t}{C_0}$ and time (*t*) with parameters like maximum adsorption capacity ($N_0$ mg/L) and kinetic constant ($K_{AB}$ L/min.mg) (233). This model equation 3 assumes that the adsorption rate is proportional to the residual capacity of the adsorbent and the concentration of the adsorbing species.

$$\mathbf{ln}\left(\frac{\mathbf{C_t}}{\mathbf{C_0}}\right) = \mathbf{K_{AB}C_0t - K_{AB}N_0}\left(\frac{\mathbf{Z}}{\mathbf{U_0}}\right) \tag{9}$$

$\frac{C_t}{C_0}$ represents the absorbate concentration ratio of the inlet and outlet solutions, $Z$ is the bed height of the column (cm), $U_0$ is the superficial velocity (cm/min$^{-1}$) $N_0$ is the saturated concentration (mg L$^{-1}$), and $K_{AB}$ is the kinetic constant (L/mg$_{\cdot}$ min). Results are shown in a plot of $In\left(\frac{C_t}{C_0}\right)$ versus time t.

The Yoon-Nelson model has been used to derive a rate constant for the dynamic adsorption, based on pseudo-second-order kinetics (234). First developed in 1984, this model assumes that as the rate of adsorption for each absorbate molecule decreases; it is proportional to the adsorption and the breakthrough point (235). Yoon-Nelson model is shown as:

$$\boldsymbol{ln\left(\frac{C_t}{C_0-C_t}\right) = K_{YN}t - TK_{YN}} \tag{10}$$

$K_{YN}$ is the rate constant with $t$ representing time (min), $T$ is the time required for 50% of the adsorbate to breakthrough (min). The parameters associated with these breakthrough curves for each of the models and error values were calculated by non-linear least-squares fitting, using the computer program OrginPro. The breakthrough models were calculated by using the function of each model for gold breakthrough and plotting the $C_t/C_0$ against.

The breakthrough volume is a calculation to determine how rapidly a given species in the inlet solution appears and increases in concentration in the effluent. It can give an indicator as to how quick breakthrough is for a certain species. It can also show to what extent a more weakly-bound adsorbate is pushed off the resin bed by a higher-affinity adsorbate:

$$\boldsymbol{Bv = \frac{(RT\times flow)-DV}{Wa}} \tag{11}$$

Bv represents the breakthrough volume (l/g), RT is the retention time of the analyte (in min), flow refers to the carrier liquid flow (ml/min), DV is dead volume (ml), Wa is the weight of the adsorbent resin (g).

## 2.5 X-Ray Photoelectron Spectroscopy

X-Ray photoelectron spectroscopy (XPS) was used to analyse prior to leaching and IX resins post-contact. Samples were prepared by first drying them in a 50°C oven for 48hrs prior and pressing the whole resins beads into a clean, high purity indium foil; this was placed on top of an adhesive carbon conductive tape. Analyses was carried out on a Kratos Axis Supra.

# 3. Results

The breakthrough data for gold and all other competing metal species are shown in Figure 16- Figure 20. The MDR model was found to be the most accurate in describing the data in all instances, and the derived parameters for gold breakthrough are shown in Table 9. The parameters for the Bohart- Adams and Yoon-Nelson model are found in SEI2 (Supporting Information). The mixed-metals breakthrough data for each resin is presented in the following sub-sections. In each case, the MDR model fit to the gold breakthrough data is also shown (black line), as this model produced a superior $R^2$ value compared to the other two breakthrough models used. The MDR model fitting for the gold breakthrough for each IX resin is shown in SEI1. SEI2 and SEI3 also show the MDR model fitting for silver and gold for each IX investigated.

## 3.1. Purolite A200 column data

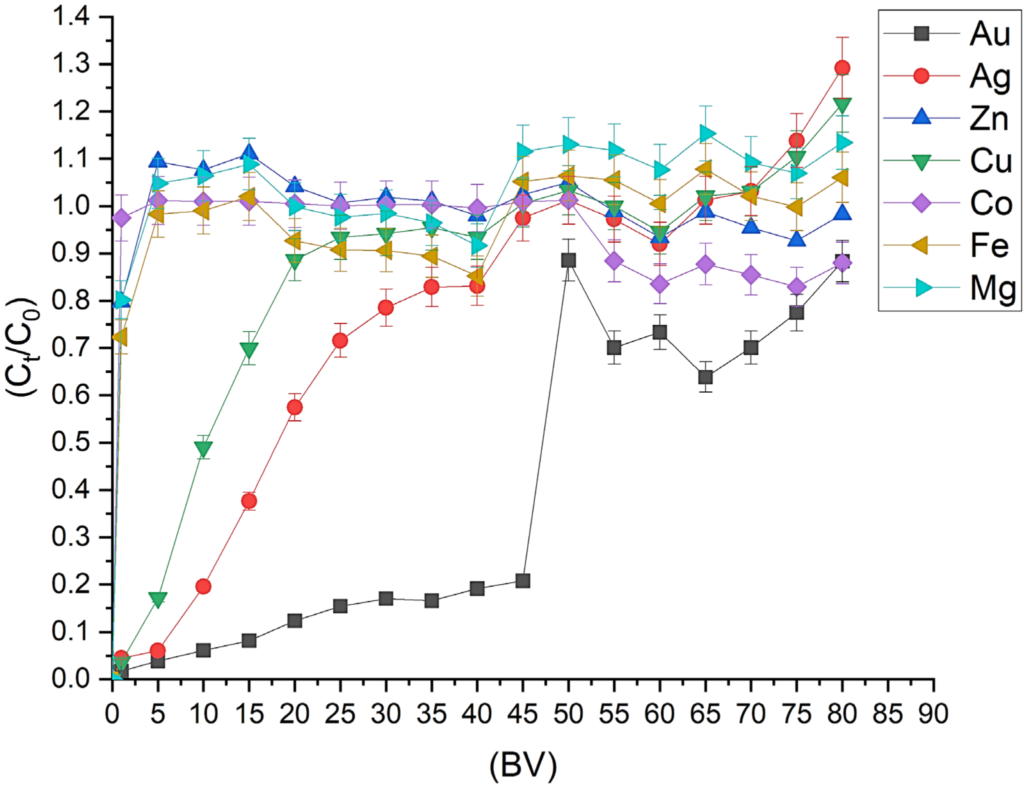


**Figure 16 Breakthrough of dynamic column system for resin Purolite® A200 (pH= 3, flowrate= 3.89 mL/min, 25 °C, $C_t/C_0$ = concentration at time/initial concentration, BV= bed volume).**

Gold breakthrough started immediately for the Purolite® A200 column shown in Figure 16. Gold concentration in the effluent increased gradually up to ~45 BV, after which $C_t/C_0$ jumped from 0.2 to 0.9. Purolite®. A200 exhibits a full breakthrough curve, something not seen for the other resins hence the adsorption of gold adsorption capacity was the lowest observed. Copper and silver show an affinity for the resin: however, they have a quicker breakthrough then gold. Cobalt, iron, magnesium, and zinc are not removed from the influent and show no affinity for the resin.

## 3.2. Lewatit® MonoPlus TP 214 column data

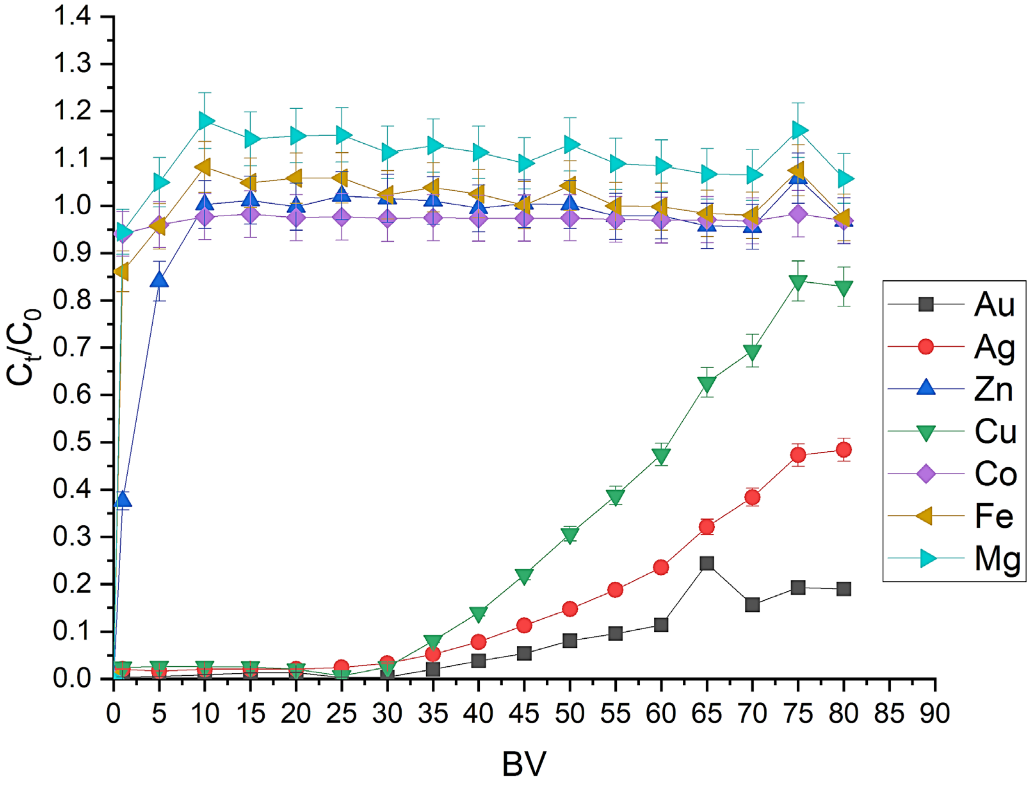


**Figure 17 Breakthrough of dynamic column system for resin Lewatit® MonoPlus TP 214 (pH =3, flowrate= 3.89 mL/min, 25 °C, $C_t/C_0$ = concentration at time/initial concentration, BV= bed volume).**

Lewatit® MonoPlus TP 214 adsorbed a large quantity of gold from the simulant leachate (Figure 17), with a full breakthrough ($C_t = C_0$) not being seen over the course of the experiment. Silver breakthrough occurs at 45 BV, with the final experimental Ct/C0 value being ~0.45 and the final effluent concentration 7.77 mg/L. Similarly, to A200, TP 214 appears to have a strong affinity of gold, silver and copper (in that order) compared with zinc, cobalt, iron and magnesium, for which there is no affinity, as evidenced by rapid complete breakthrough for these elements within the first 10 BV.

## 3.3. Puromet® MTS9140 column data

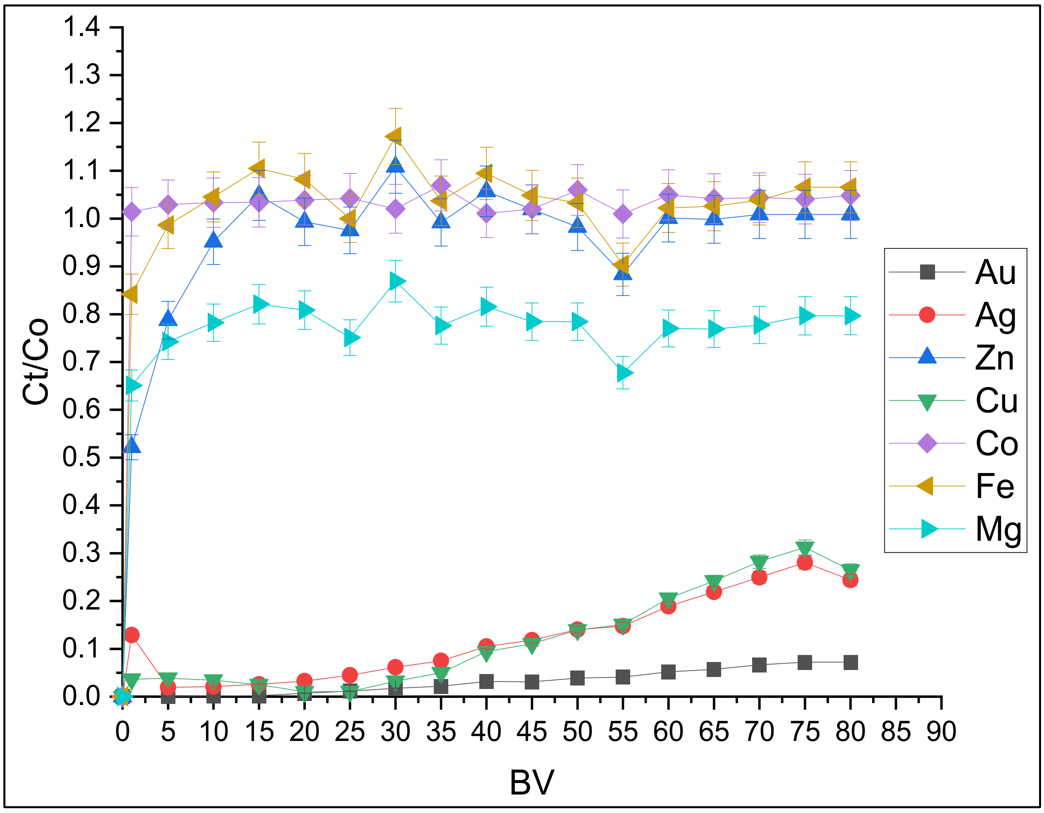


**Figure 18 Uptake of all metals *via* dynamic column system for resin Puromet® MTS9140 (pH= 3, flowrate= 3.89 mL/min, 25 °C, $C_t/C_0$ = concentration at time/initial concentration, BV= bed volume).**

Puromet® MTS9140 showed a similarly low level of affinity towards cobalt, zinc, iron and magnesium in the PLS compared to the other resins used in this experiment (Figure 18). Additionally, the silver and copper profiles are remarkably similar, and there does not seem to be the slight preference for silver that is seen with the other thiourea resin, with $C_t/C_0$ values not exceeding 0.3mg/L. The gold concentration in the effluent remained low to the end of the experimental run, with the final concentration of gold in the PLS after the 20 hours of column running being 0.644 mg/L. Again, this resulted in an incomplete breakthrough curve over the experimental period. Puromet® MTS9140 had considerably higher adsorption of gold than TP214, even though they have the same functional group and same quoted capacity (Table 7).

## 3.4. Dowex™ M-4195 column data

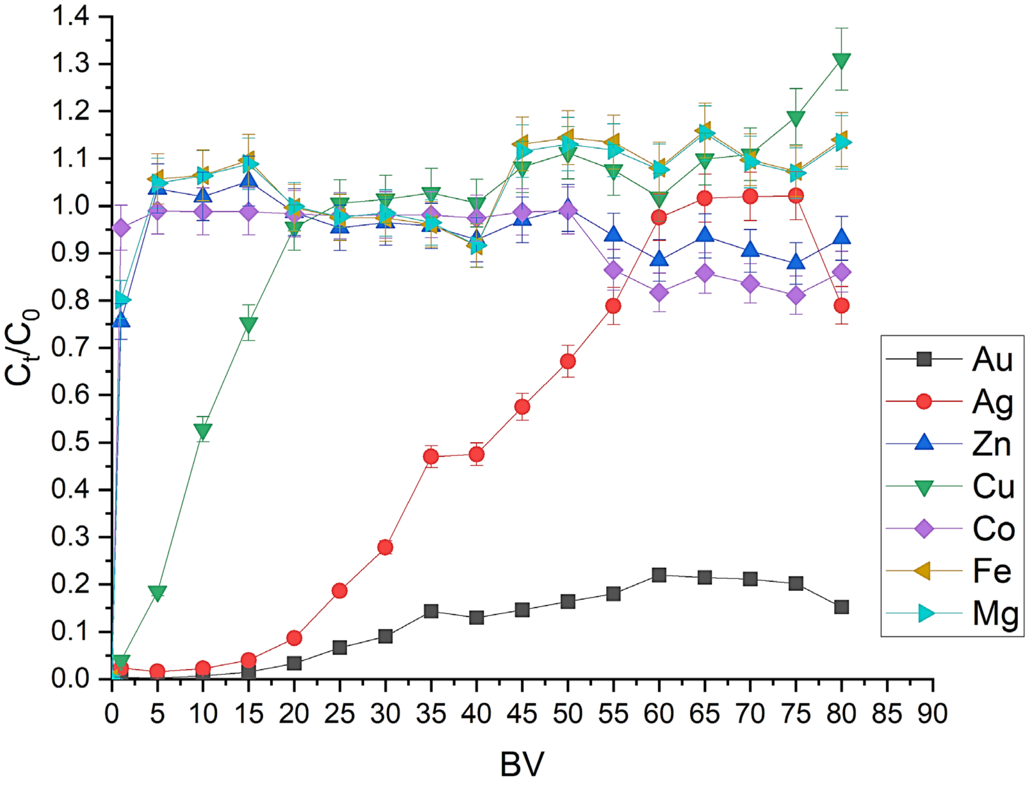


**Figure 19 Breakthrough of dynamic column system for resin Dowex™ M-4195 (pH=3, flowrate= 3.89 mL/min, 25 °C, $C_t/C_0$ = concentration at time/initial concentration, BV= bed volume).**

Dowex™ M-4195 exhibited a high uptake of gold shown in Figure 19. As with the other resins already discussed, uptake of zinc, cobalt, iron, and magnesium was minimal, and the concentrations of these metals quickly reached $C_t/C_0$ values of ~1. The $C_t/C_0$ value of gold did not exceed 0.2 with a gradual increase to 60 BV followed by a slight decrease at 80 BV which could be due to other adsorbed metals forming more weakly-bound species. This trend can also be seen with the uptake of silver, on a greater scale, with silver showing a gradual breakthrough with a sudden drop at 80 BV with $C_t/C_0$ being ~1 than at 75 BV $C_t/C_0$ being ~0.8. This could have due to the other metals reaching the saturation limit, which has allowed silver to be readsorbed onto the resin. Copper breakthrough was complete and quite rapid with the final $C_t/C_0$ being ~1.4. In common with the other resins, breakthrough for the harder metal cations was almost instantaneous.

## 3.5. Lewatit® VPOC 1026 column data

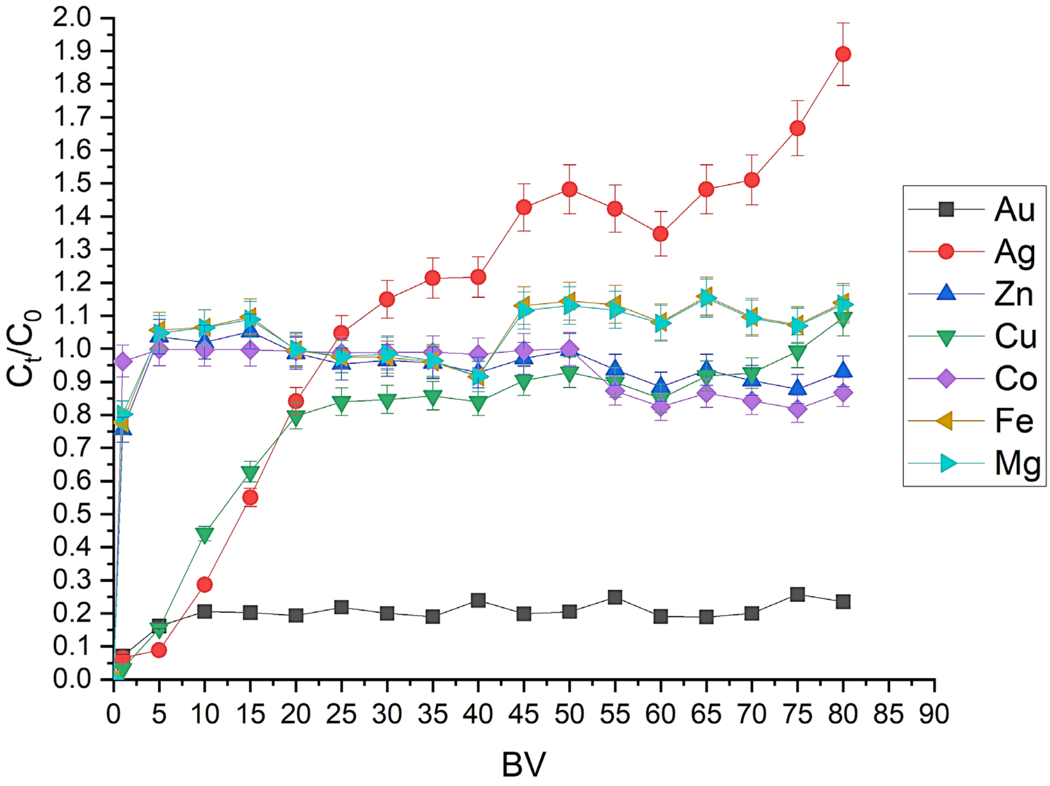


**Figure 20 Breakthrough of dynamic column system for resin Lewatit® VPOC 1026 (pH=3, flowrate= 3.89 mL/min, 25 °C, $C_t/C_o$ = concentration at time/initial concentration, BV= bed volume).**

The gold breakthrough behaviour for VPOC 1026 is unusual (Figure 20), as there is an almost immediate partial breakthrough of gold to a $C_t/C_0$ value of ~0.2, after which the gold effluent concentration remarkably remains at this level for the whole experimental duration. Similarly, to the other resins screened, adsorption towards of zinc, cobalt, iron, and magnesium was minimal, and the concentrations of these metals quickly reached a $C_t/C_0$ value of ~1. Copper and silver breakthrough curves were also interesting because both metals were taken up initially, but the silver $C_t/C_0$ value then begins to greatly exceed one. This infers that the initially adsorbed metal is then ejected from the resin bed by another more strongly-binding species, whereas the copper data do not suggest this behaviour. Due to this, the dynamic breakthrough equations were unable to model the VPOC 1026 experiment and returned unrealistic values for the dynamic uptake capacity (Table 8).

## 3.6. Breakthrough Modelling

The relevant parameters from the MDR model for all experiments are seen in Table 8. The other two dynamic models used produced inferior $R^2$ values, Figures SEI2. The calculated dynamic uptake capacities of the resins have a significant degree of uncertainty because, except for A200, the breakthrough curves are incomplete and are not fully modelled. A similar pattern is also seen with silver and copper. The MDR models with Ag only fit the two IX resins Lewatit® MonoPlus TP 214 Dowex™ M4195 with Puromet® MTS9140 partially fitting the model. The other two IX resins hit the equilibrium by the 50ml mark and do not. With Cu and the MDR model only Puromet® MTS9140 partially fits the MDR model with the other four hit the equilibrium by the 40ml mark. a and b shown in Table 9 are the calculated parameters of the MDR model equation shown in equation 1. The qo (mg/g) parameter is the theoretical dry mass capacity maximum adsorption of the IX resin, while the qo (eq/Lwsr) parameter is more commonly used in engineering applications and is essentially, equivalent to mol/L, but also takes into account the valance of the metal ion (1 in the case of $Au^+$). It represents the practical operating capacity. It was determined that VPOC 1026 and MTS9140 have the highest affinity towards gold. However, as previously stated, the breakthrough model for VPOC 1026 was considered unreliable.

**Table 9 Calculated parameters and rate of reaction of the total column running time of the experimental from the MDR model each resin screened. Lwsr = Litre wet settled resin.**

| Resin | Au ($q_o$) (mg/g) | Au ($q_o$) (eq/$L_{wsr}$)* (x $10^{-2}$) | a | b | $R^2$ | Rate of breakthrough (x $10^{-3}$) (mg/s) |
|---|---|---|---|---|---|---|
| A200 | 4.7 ± 0.3 | 1.03 ± 0.06 | 3.6 ± 0.7 | 50 ± 3 | 0.86 | 43 |
| TP214 | 13 ± 1 | 2.3 ± 0.3 | 2.5 ± 0.4 | 130 ± 20 | 0.89 | 9.4 |
| MTS9140 | 42 ± 7 | 9 ± 2 | 1.5 ± 0.1 | 430 ± 80 | 0.96 | 2.4 |
| M-4195 | 25 ± 6 | 5 ± 1 | 1.1 ± 0.2 | 250 ± 60 | 0.89 | 7.5 |
| VPOC 1026 | 5000 ± 8000 | 500 ± 900 | 0.19 ± 0.05 | 50600 ± 88000 | 0.84 | 8.2 |

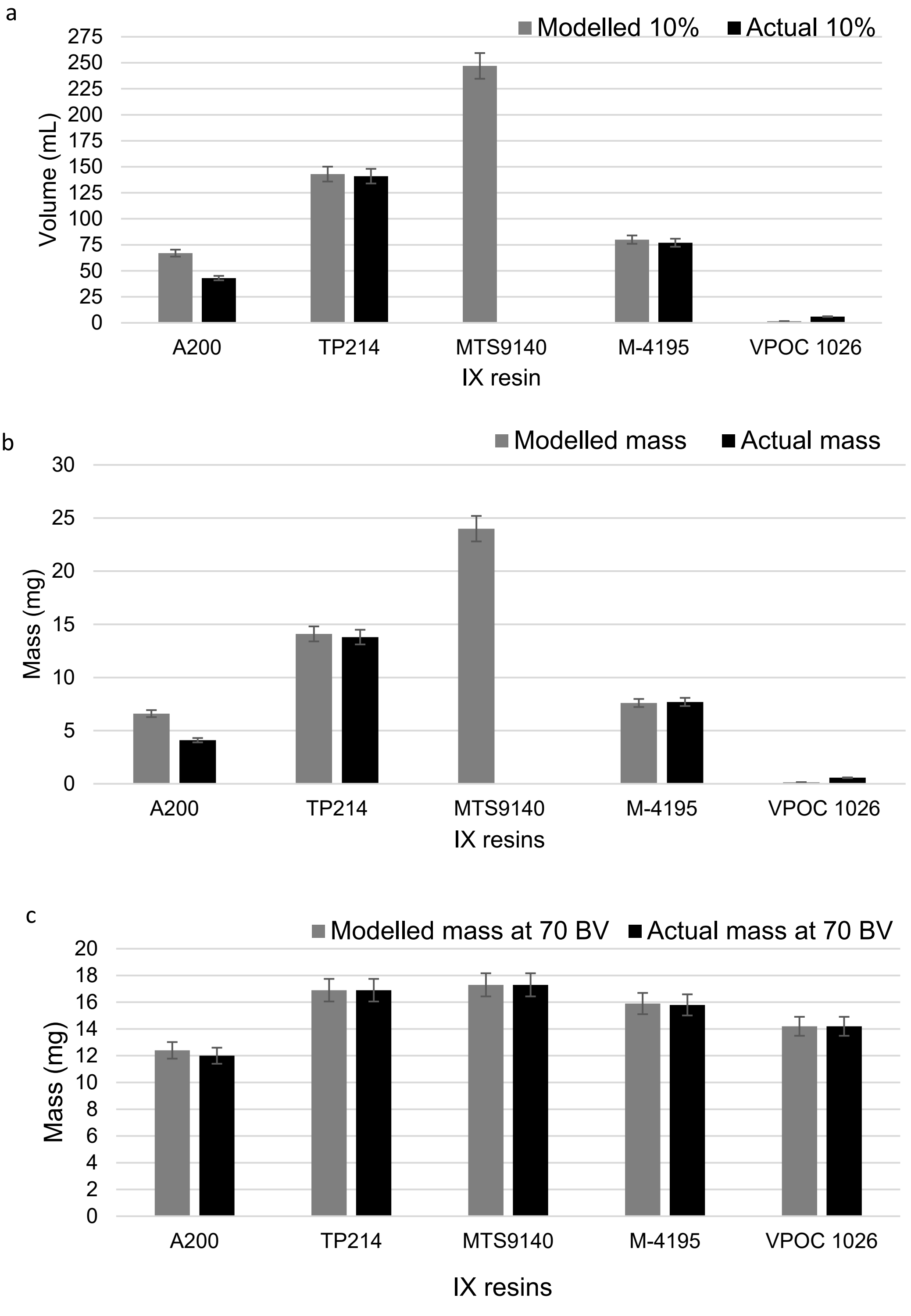


**Figure 21a Modelled Au breakthrough volumes at 10% and actual 10% breakthrough, b modelled mass of gold on resin at 10% and actual mass of the resin at 10% (Note: no actual values are given for MTS9140, as 10% breakthrough was not reached in the experiment). c Modelled mass of gold retention and actual mass of gold retention on the resins, with 70 BV collection considered to be the end of the experimental timeframe.**

For most 10% breakthrough volumes, the actual values generally agree with the predicted data (Figure 21a). The comparison of modelled and actual 10% breakthrough volumes shows that the TP214 values are the most similar, with the figures for A200 and M-4195 also being close. The MTS9140 actual 10% breakthrough is not achieved in the experimental timeframe but would be expected to be reached at 99 BV, according to the modelled data. As stated in section 3.5, VPOC 1026 breakthrough data is unusual and returned unrealistic dynamic uptake capacity values, also causing poor agreement between actual and modelled 10% breakthrough values; the modelled breakthrough being 1.5ml and the actual breakthrough volume being 6ml.

In Figure 21b, the data shown confirms the data shown in 18a. At 10% breakthrough, the actual amount of Au on the resin for TP 214 is most similar to the model value. Figure 21c confirms the data from section 3. A200 has the lowest amount of gold on the resin at 12 mg/g. A200 has the lowest amount of gold on the resin at 12 mg/g. MTS9140 has the highest mass at 17.3 mg/g and TP214 has the second highest at 16.9 mg/g. M-4195 and VPOC 1026 are similar, with 15.8 mg/g and 14.2 mg/g respectively at 70 BV. The concentration of gold present in the barren solution was calculated to be 6.8 mg/g for MTS9140 and 71 mg/g for A200.It can be seen that, considering R2 values in isolation, the MDR seems poor at modelling the uptake. However, Figure 6 illustrates that it is generally successful at predicting relevant engineering parameters. Values are least accurate for A200, where there was the highest degree of scatter in the gold uptake data. This is generally a feature of weaker adsorption interactions, due to the number of competing adsorption interactions taking place in the active zone of the column (236).

## 3.7. X-ray Photoelectron Spectra of Resin Samples

Data from the XPS studies of the resins post uptake, are shown in Table 10. Images of all the spectra can be seen in Figures SEI3. All the resin samples revealed high carbon concentrations, reflecting the styrene/divinylbenzene matrices of the resins. Nitrogen and sulfur were present in large quantities for all samples, apart from VPOC 1026, which instead exhibited a high phosphorus concentration, representing the impregnated D2HEPA. Gold was detected on all resin surfaces, which confirms the high uptake compared with the other metals seen in the breakthrough data, with

TP214 and MTS9140 having the highest amounts of gold which agrees with the experimental data. Most of the other metals in the PLS were below detectable levels or present at low concentrations (magnesium, zinc, and potassium were not detected for any resin sample and so are not included in Table 10).

**Table 10 Selected data from XPS survey scans of samples of the 5 resins, following completion of the dynamic breakthrough experiments.**

| Element | Resin | | | | |
|---|---|---|---|---|---|
| | A200 | TP214 | MTS9140 | M-4195 | VPOC 1026 |
| C | 68.59 | 69.39 | 67.22 | 78.05 | 74.85 |
| O | 20.78 | 11.75 | 16.62 | 10.26 | 18.11 |
| N | 5.14 | 11.65 | 10.42 | 9.03 | 0.72 |
| S | 3.18 | 4.89 | 3.06 | 1.3 | 0.32 |
| P | <0.01 | <0.01 | <0.01 | <0.01 | 4.09 |
| Au | 0.48 | 0.86 | 0.7 | 0.39 | 0.5 |
| Ag | 0.02 | 0.28 | 0.11 | 0.1 | <0.01 |
| Cu | <0.01 | 0.14 | 0.03 | 0.06 | 0.01 |
| Co | 0.06 | 0.02 | 0.02 | <0.01 | 0.01 |
| Fe | <0.01 | <0.01 | <0.01 | 0.01 | <0.01 |

# 4. Discussion

Lewatit® MonoPlus TP 214, Puromet® MTS9140 and Dowex™ M-4195 have all previously been used for or are described as showing selectivity towards either gold, silver or the platinum group metals (237; 238; 239). TP 214 and MTS9140 possess a thiourea functional group, which has proven selectivity towards gold, leading to a prediction of high affinities. The main differences between Lewatit® MonoPlus TP 214 and Puromet® MTS9140 is the moisture retention at 43-48% and 50-56%, respectively, and the average bead size at 0.55 mm and 0.75 mm, respectively (223; 240; 241). Previous work has shown that these parameters can result in different performances for resins of similar functionality (242).

Dowex™ M-4195 is more well known as an ideal resin for copper and nickel extraction (243). However, it has been studied for the extraction of many other metals, including gold, in which some affinity was shown in $H_2SO_4$ matrices (244). Other resins with the same functional group have been previously researched into the absorption of the platinum group metals; gold and platinum have remarkably similar chemical properties, so there is potential to show high affinity to gold (245).

Similarly, VPOC 1026 and A200 resins have not yet been investigated for extraction of gold with VPOC 1026 mainly being used for the removal of zinc, uranium, vanadium, aluminium, and many others from sulfuric and hydrochloric acid solutions. Despite this, the functional impregnated solvent molecule of VPOC 1026 is di-(2-ethylhexyl)phosphoric acid (D2EHPA), which is used in gold extraction from electronic waste, so it follows that VPOC 1026 should have gold selectivity (246). A200 is mainly used for deionising water; however, the A200 functional group (quaternary ammonium) has shown strong adsorption of gold over other precious metals, although the mechanism of uptake was not clear (247).

Ion-exchange can be considered in terms of Brønsted acid/base and Lewis acid/base theory. Conventional SAC resins functional groups are Brønsted acids in that they release protons int solution during an ion-exchange uptake. However, chelating and adduct-forming resins, like those used in this work function as Lewis bases, as they donate lone pairs of electrons to the Lewis acid (the Au and Ag) complexes in solution) (248). The lewis acid and bases theory helps explain how the lone pair of electrons from each resins functional group investigated was able to create coordinate bonds with the Ag and Au in the PLS; such as the nitrogen (N) lone pair (Purolite® A200, Puromet® MTS9140 and Lewatit® MonoPlus TP 214 and Dowex™ M-4195), sulphur (S) lone pairs (Puromet® MTS9140 and Lewatit® MonoPlus TP 214) and oxygen (O) (Lewatit® VPOC 1026) have the lone pairs that would make the Lewis acid and bases theory a viable explanation of how the resins and metals investigated interact.

Further explanation of the acids and bases interactions between the IX resins and the metals in the PLS can be explained by the hard-soft-acid-base theory (248). Which is describes as when soft acids prefer to form bonds with soft bases, whereas hard acids prefer to form bonds with hard bases resulting the bonding having more ionic characteristics (248). This investigation can be explained with the hard-soft-acid-base theory with the use the competing metals in the PLS; Fe, Mg, Co, Na and Zn are all considered hard cations (249; 250). All the hard cations in the PLS are shown to be completely pushed off all the IX resins compared to the Ag, Au and Cu. . The three metals that are absorbed strongly on to the each of the resins are soft acids, which interact favourably with the soft base of the thiourea functional group. It is less clear in the case of A200 and M4195 why there is a strong interaction for Ag and Au. The uptake mechanisms and selectivity are discussed in more detail in section 4.3.

## 4.1 Mathematical Models

For each resin tested, the MDR model provided the best description of the breakthrough behaviour. The MDR model returning an $R^2$ range of 0.836 - 0.955. No assumptions about the fundamental uptake behaviour can be drawn, because of the empirical nature of the model, but as seen in other studies, the MDR model tends to minimise deviations from the breakthrough curves seen in other models as seen in other studies (252; 253).

The other models used to describe the breakthrough generally returned lower, but similar $R^2$ values, with the Yoon-Nelson and Bohart-Adams models showing ranges of 0.363-0.914 and 0.363-0.908, respectively (SEI2). The Yoon-Nelson model, which had good agreement with three out of the five resins screened (A200, TP214 and MTS9140), which indicates that the breakthrough behaviour probability of gold adsorption is proportional to the probability of adsorption versus the ability to breakthrough. The strong exception was VPOC 1026, where none of the models was able to give an accurate fit of the breakthrough behaviour. As will be discussed in Section 4.3, the data for this resin is believed to be influenced by factors other than adsorption favourability.

The Bohart-Adams model also showed good agreement with three out of the five models screened (again A200, TP214 and MTS9140). Thus, it is probable that the dynamic adsorption of gold is dependent on the initial concentration, residual capacity and kinetic constant (254). Comparing the three models used the MDR model is the one which best produced the most accurate curve for each resin screened with the highest $R^2$.

## 4.2 Comparison of Resins Screened with Literature.

The resins TP214, MTS9140 and M-4195 have all previously been used for, or are described as showing selectivity towards either gold, silver or the platinum group metals (255; 244; 237). MTS9140 has been shown to have selectively towards platinum and rhodium, with the literature predicting a subsequent affinity towards gold, due to their many chemical similarities (256). Despite this, the methods used for the uptake of gold onto resins TP214, and M-4195 were differently buffered solutions and a range of concentrations of different acids, respectively (257). Aktas and Morcali compared the use of TP214 with activated rice husk. The uptake of Au(III) by TP214 was 109.6 mg per gram compared with 93.3 mg per gram for activated rice husks. The higher uptake in these results compared with the present work is likely due to the use of batch uptake, as opposed to column uptake, (hence a reduction in kinetic factors) (255). The extraction percentages of the gold recovered by TP214, and rice husks were determined to be 99.50% and 99.55% respectively (255).

M-4195 was originally developed for selective copper, and nickel extraction. Figure 16 demonstrates the clearly superior affinity towards gold. M-4195 has previously been used for solid-phase extraction of gold (244). The experimental used Au(III) solutions in different acids and bases, at varying molar concentrations. A rather lower maximum uptake capacity, relative to this work, of 8.1 mg/g was reported (244). From this, it can be inferred that gold shows a much higher affinity for M-4195 in $H_2SO_4$ media than HCl, which helps to explain the high uptake observed. The choice of anion present in contact solutions has been shown to be quite influential in the affinity of M-4195 to different cations (258). Other resins with the same functional group have been previously researched for the adsorption of the platinum group metals. The similar chemical properties of gold and platinum are concurrent with the high gold affinity observed (245).

Similarly, VPOC 1026 and A200 resins have not yet been investigated for extraction of gold with VPOC 1026 mainly being used for the removal of zinc, uranium, vanadium, aluminium, and many others from sulfuric and hydrochloric acid solutions. Despite this, the functional impregnated solvent molecule of VPOC 1026 is di-(2-ethylhexyl)phosphoric acid (D2EHPA), which is used in gold extraction from electronic waste, so it follows that VPOC 1026 should have gold selectivity (66). A200 is mainly used for deionising water; however, the A200 functional group (quaternary ammonium) has shown strong adsorption of gold over other precious metals, although the mechanism of uptake was not clear (247).

Overall, in this study, the fact that all resins displayed some uptake of gold despite the, given the incredibly challenging chemistry of the simulant PLS used. It should be noted that A200 and VPOC 1026 were operating at a proton concentration higher than their specified working ranges (Table 7), which may explain why small quantities of the lower affinity metals were adsorbed (the XPS data suggests a considerable degree of protonation of the resin surfaces). Every resin showed a preference for gold and silver extraction over the base metals also present in the solution.

Various other IX resins have been used for recovery for gold, some at industrial scale. A summary is shown in  Table 11.

**Table 11 Ion exchange resins used in industry and literature. Selectivity, extraction conditions, recovery rate and resin capacity.**

| IX resins | Functional group | Reported Selectivity | Au Extraction Conditions | Recovery rate (%) | Resin Capacity (eq/l) | Ref |
|---|---|---|---|---|---|---|
| Amberlite® IRA-400 | Quaternary Ammonium (Type 1 SBA) | Chromium (III) | Acetone containing 5% hydrochloric acid and 5% water. | 98 | 0.66 | (259) |
| Puromet® MTS9200 | Isothiouronium (chelate) | Mercury precious metals/gold | Ratios: 10% HCl, 2 mol/dm$^3$ ammonium thiocyanate, 2 mol/dm$^3$ ammonium thiocyanate in 10% HCl, and 1 mol/dm$^3$ thiourea in 2 mol/dm$^3$ HCl. | 93 | 1.70 | (260) |
| AmberSep™ 91419 | t-butylamine (WBA) | Gold | Penjom Process | 85 | 0.33 | (261; 262) |

Table 11 shows three different IX resins that have been researched or are being used in industry for the recovery of gold from waste. Amberlite IRA-400 is an IX resin that has selectivity towards other metals but when put into contact an elution with excess Cl$^-$ that have both showed high selectivity towards gold. When comparing to the other two resins shown in Table 11, which were made specifically for gold or precious metal recovery and are currently used in industry for gold recovery that lower recovery rates compared to IRA-400. However, all three IX resins in Table 10 show a higher affinity towards gold. Notably, MTS9200 has a similar functionality to TP214 and MTS9140 and had a high Au capacity.

IX resins, other sorbents, and biomass, which have been thiourea grafted, have been investigated into the recovery of gold. All of which showed a better sorption capacity to Au compared to the IX resins that have been investigated in this work. Some literature that has shown biomass and sorbents capacity to gold is from Wang et al and Gao et al. shown in Table 12.

**Table 12 Thiourea-grafted sorbents in literature. Selectivity, extraction conditions, recovery rate and resin capacity.**

| Sorbent type | Functional group | Extraction Conditions | Recovery rate (%) | Resin Capacity (eq/l) | Ref |
|---|---|---|---|---|---|
| microporous poly(vinylidene fluoride) (PVDF) | N-methyl-2pyrrolidone | 200ml of Au(II) conc. (Range 2-6 mg/L), sodium hydroxide and HCl. 0.1g of resin was stirred at different temperature (25-45 ℃) | N/A | 1.28 | (263) |
| alginate biosorbent | polysaccharide | Multi-metallic solution of 0.2 mmol $L^{-1}$ including Au, Pt and Pd with conc. HCl ranging from 0.05 to 5 mol $L^{-1}$ at 303K dry biosorbent was shaken for 24 hours. | <95 | 1.09 | (74) |

Their work was providing coverage of chitosan-based adsorbents, surface-functionalised systems and biomaterial composites, and their modified forms for solid-phase extraction of precious metal ions (264). Despite the literature (Kong et al review) showing that the biomass and sorbents are cheaper and have a high selectivity towards gold; all such sorbents required synthetic steps for the sorbents to be grafted with thiourea. The advantage of IX resins is that they are ‘off the shelf’ technology, optimised for hydrodynamic systems. Additionally, industrial IX resins are designed to withstand continuous reuse, which entails less disposal of degraded sorbent beds, more process efficiency, and less waste. Additionally, the research work shown in Table 12 is in idealised conditions, which can explain the high recovery rate, compared to the work done in this research paper.

Studies into the regeneration and reusability of the IX resins are in progress. However, current literature and industry practices demonstrate that IX resins can be reused up to 20 times with a slight decrease in its activity and selectivity (265). The most common method of regeneration of used IX resins is *via* a high percentage, 10%, of brine or salt to restore the resins capacity (266). In specifics of a thiourea lixiviant one regeneration method involves the washing of IX resins with DI water, followed by the removal of the un-adsorbed gold by flushing the bed column with thiourea and HCl solution at the flow rate of 1ml/min (263).

## 4.3 Comparison of Resins Uptake Behaviour and Possible Mechanisms.

Overall, the A200 uptake parameters were considered the most reliable because they were derived from a full breakthrough, rather than a partial breakthrough curve. Despite that, the loading capacity was only 4.72 mg/g, which is the lowest value out of all the resins screened. This can be attributed to gold being mainly present in the PLS as cationic complexes (Equation 12).

$$\text{Au} + \text{Thiourea} + \text{Fe}^{3+} \rightarrow [\text{Au}(\text{Thiourea})_2]^{+} + \text{Fe}^{2+} \qquad (12)$$

The small quantity of gold that was adsorbed could have been due to the small proportion of gold existing as thiosulfate complexes, which are anionic (Equation 13).

$$4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-} + 4\text{OH}^{-} \qquad (13)$$

Additionally, SBA resins may not be 100% functionalised and can degrade to WBA resins under acidities outside of their operating range. This could potentially lead to small numbers of protonated (rather than alkylated) ammonium groups in the resin, which could exchange protons for lone pair coordination to metal centres. Some literature does show that WBA resins can act as chelators to bind large cationic complexes (267).

The MTS9140 gold uptake was the highest at 9.49 mg/g. Although the breakthrough curve was incomplete, the MDR $R^2$ value is exceedingly high (Table 9), so the uptake value is given with some confidence. The superiority of MTS9140 over TP214 could be due to MTS9140 having higher moisture retention of 50-56% (versus 43-48%). Additionally, the bead size for MTS9140 is, on average larger than TP214 (0.75mm versus 0.55mm). Collectively, this suggests a larger pore volume for MTS9140, meaning that large gold thiourea complexes would not be sterically hindered in reaching the inner adsorption sites within the resin beads (242).

The high uptake observed with MTS9140 (and TP214 to a lesser extent) is proposed to be due to the thiourea functional group of these resins and thiourea also being the dominant lixiviant in the PLS; this is likely to have positively affected the uptake. The stability constants of gold thiourea complexes increase as more thiourea ligands are added. Gold in ~10 g/L thiourea solutions mainly forms two complexes, $[AuTU]^+$ and $[AuTU_2]^+$ where TU indicates a thiourea molecule (268). However, $[AuTU_3]^+$ formation is also possible at high [TU] (257). When the contact PLS encounters the resin thiourea functional groups, the effective thiourea concentration within the pore environment increases further, and adsorption would essentially occur *via* the chelation of an additional thiourea ligand from the resin.

This is probably the reason for increased selectivity for gold, silver and copper, because these metals form the most stable thiourea complexes. For example, for $[AuTU_2]^+$, $\beta_2 = 2.0 \times 10^{21}$. For $[AgTU_2]^+$, $\beta_2 = 4.07 \times 10^{10}$ and for $[CuTU_2]^+$, $\beta_2 = 1.26 \times 10^{11}$. However, for $[FeTU_2]^{3+}$, the $\beta_2$ value is rather smaller ($2.75 \times 10^8$). $\beta_2$ represents two aspects of the complex β being the stability constant of a complex, and $_2$ being the number of ligands in the complex (257). It, therefore, follows that the adsorption of gold thiourea complexes by the mechanism proposed will be by far the most thermodynamically-favoured process.

This behaviour is quite predictable for the thiourea resins. However, we did not expect the same favourable adsorption of gold by M-4195, particularly at the expense of copper, as the latter is known to be very strongly bound by the BPA group (258). The probable adsorbed gold species, with respect to M-4195, can be thought of as a mixed-ligand complex with both BPA and thiourea ligands. An example of this specific species could not be found in the literature. Its formation however, is predictable on the basis of simple mixed-ligand complexation theory, and that gold(I) is known to form mixed-ligand complexes with thiourea and other adducts

(257; 256).The nitrogen's in the BPA ligand will be positively charged and would interact with the sulfate ions to for neutralisation. In this case, the overwhelming thermodynamic stability of the reacting aqueous gold-thiourea complexes (verses copper-thiourea) would likely dominate the selectivity of the system. This makes M-4195 a strong candidate for gold recovery within this remit.

Despite the VPOC 1026 breakthrough for gold not being able to be modelled it is indisputable that some gold was extracted; this is supported by previous literature showing the use of D2HEPA to recover gold from printed circuit boards, leading to efficiencies of <88% (269). The unusual gold breakthrough for the VPOC 1026 column is likely explained by the relatively weak interactions between D2HEPA and the resin matrix, compared to the other resins with chemically bonded functional groups. Although D2HEPA is known to exhibit high stability in sulfate media, a small amount of acid hydrolysis would still be expected. It is also known that most commercial sources of D2HEPA contain a percentage of mono-2-ethylhexyl phosphoric acid, which is more susceptible to hydrolysis (270). Since it is clear from Figure 5a that gold is the most strongly adsorbed metal within the PLS, it is feasible that gold complexes, with D2HEPA hydrolysis products as adducts, could be bleeding from the column at a fairly constant rate, resulting in the flat curve shown in Figure 5.

The VPOC 1026 data is also unusual in that the continuing gold adsorption appears to displace silver from the resin. This indicates that silver adsorption is kinetically rapid, but not thermodynamically favourable; this is occasionally seen in studies where more than one ion has a high affinity for the adsorbent (258; 271). Strangely, copper is not also pushed off the resin in favour of gold, despite initially breaking through at almost the same time as silver, which indicates similar affinity. Copper(II) has a rather smaller ionic radius (0.57-0.73 Å, depending on coordination number) than gold(I) and silver(I) (up to 1.37 and 1.26 Å respectively). So, it is possible that copper occupies D2HEPA bonding sites that are inaccessible to the larger ions (for example, cavities between two D2HEPA moieties) and therefore gold does not directly compete with copper for adsorption sites, as it does with silver. This can be seen with the XPS data (Figures S2) as gold was more strongly adsorbed then silver; however, XPS is surface-sensitive, and the concentrations of both gold and silver are extremely low, so it is difficult to draw any solid conclusions. Because of the considerable value of silver, it would be desirable in a hydrometallurgical process to recover silver in addition to gold, despite that VPOC 1026 is a suitable choice for the intended purpose.

### 4.4. X-ray Photoelectron Spectra

The XPS survey scans gave further insight into the likely dominant adsorption mechanism. Sulfur was present in all samples but was found at higher concentrations in the two thiourea resins (due to the sulfur-containing functional group) and A200 presumably because of high uptake of sulfate anions from the 1M H2SO4 preconditioning and the PLS matrix. M-4195 also contained significant sulfur, which could be attributed to the protonation of the amines in the BPA functionality and adsorption of sulfate counter anions (272). VPOC 1026 also contained sulfur, presumably because of the protonation of the D2HEPA moieties and counteranion adsorption. It was not possible to accurately speciate the sulfur in these experiments, but this will be a target of subsequent work. It is, however, highly likely that the majority of metals adsorbing on to the resins do so as thiourea complexes, especially the most strongly adsorbed gold, silver and copper species (257). Indeed, the presence of thiourea on the resins is all but confirmed by the fact that nitrogen was detected in the VPOC 1026 sample.

## 5. Conclusion and Recommendation

The capabilities of a range of commercial IX resins for selective gold extraction from a simulant thiourea/thiosulfate PLS have been investigated. In dynamic column experiments, all resins tested exhibited an affinity for gold ions existing mainly as aqueous thiourea complexes, as the highest quantities of this species were consistently adsorbed across all experiments. The selectivity series for all resins studied (with the possible exception of VPOC 1026) was Au > Ag > Cu » Co > Fe > Mg > Zn, which is most advantageous for the recovery of valuable species from the leachate. The gold affinity was attributed to the thiourea-thiosulfate lixiviant, specifically the high stability of gold thiourea complexes in solution, leading to thermodynamically favourable adsorbed species, probably with both thiourea ligands and mixed ligands. Classical breakthrough models could describe all experimental data (apart from VPOC 1026), with the Modified Dose-Response (MDR) model providing the best fit to the data.

Out of all the resins investigated, MTS9140 (thiourea functional group) was found to be the most promising, due to its calculated uptake capacity of 41.6 mg/g. Although the relevant breakthrough curve was incomplete, it exhibited good agreement with the MDR model (R2 = 0.955), which means breakthrough time could easily be predicted industrially. TP214 (also thiourea functionality) exhibited similar behaviour to MTS9140, but had the lower capacity, due probably to its lower moisture retention. M-4195 had the second-highest calculated uptake of gold in the study (24.7 mg/g) and unusually, affinity for gold was higher than for copper, which demonstrates that the high thiourea concentration in the leachate greatly affected the usual order of selectivity for this material. A200 (strong base anion) showed the lowest capacity for gold with the quickest and clearest breakthrough. The slight uptake was probably due to resin degradation, creating weak base/chelating functionality and by the uptake of anionic gold thiosulfate complexes. VPOC 1026 data did not fit any of the models used. While the resin showed selectivity towards gold, there appeared to be bleeding of the impregnated solvent from the column (probably due to acid hydrolysis) and excessive rejection of silver from the column, which meant that the data could not be modelled successfully.

This screening research has identified at least two very promising resins (MTS9140 and M- 4195) to take forward for further RIP studies with the thiourea-thiosulphate lixiviant system. Attaining full breakthrough curves over a longer timeframe is necessary. Also, the responses of the adsorbents to different flowrates need to be investigated. The next major step will be to carry the chosen resins forward to a small-scale RIP study, in which ore or mine tailings is leached with in-situ adsorption onto the resin, followed by attempted elution and separation of the captured gold and silver. The results attained here would of course, also be relevant in the consideration of a 2-unit system, with an independent leaching stage followed by a hydrodynamic column separation.

## Declarations of interests

None.

## Acknowledgements

The authors thank all the members of the SNUCER group, University of Sheffield, for their support whilst completing this work. Thanks to Dr. Deborah B Hammond (Surface Analysis Centre, Dept. Chemistry, UoS) for XPS training. Thanks to RS Bruce for ICP-OES training.

## Funding

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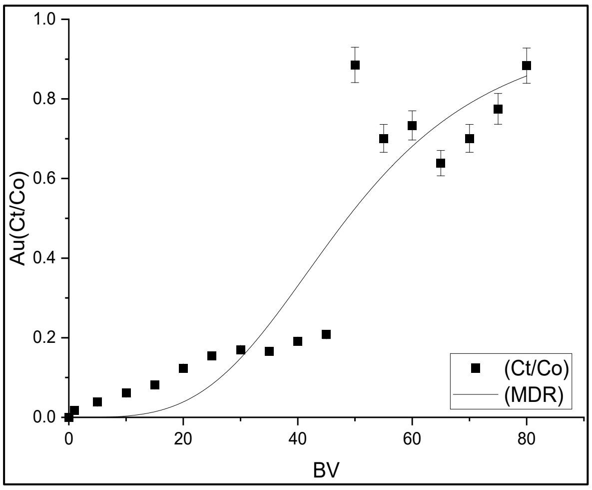
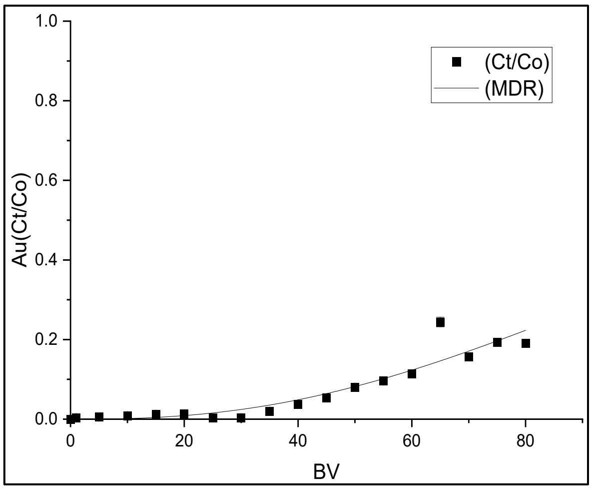
## 5.3. Supporting Electronic Information (SEI)

### SEI1. Gold breakthrough models

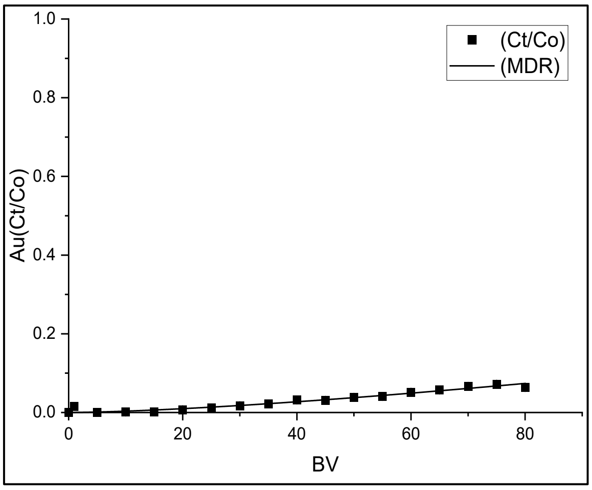
The modified dose-response (MDR) model fitting to gold breakthrough behaviour of each of the IX resins is given in Fig S1. Error bars of 5%. The experimental conditions of SEI1 1.4ml IX packed resin column, at ambient temperature at a flowrate of 3.89 mL/min; pH of 3.



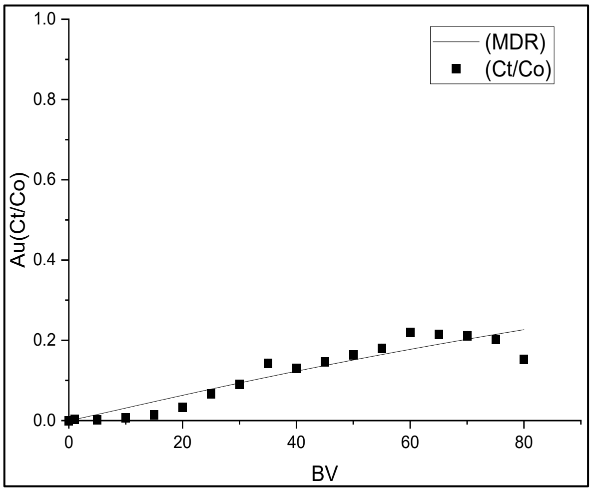
Purolite® A200



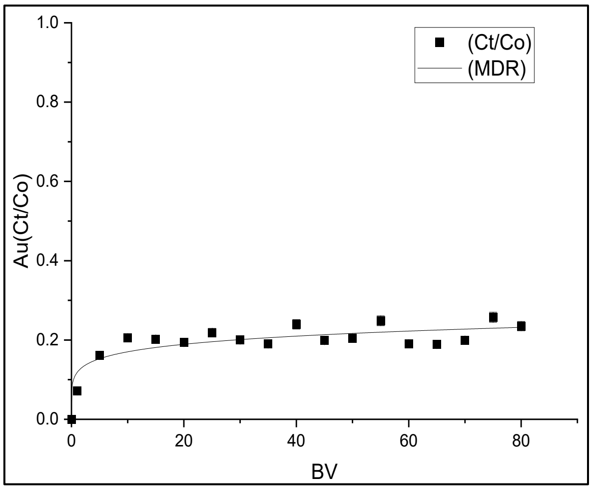
Lewatit® MonoPlus TP 214



Puromet® MTS9140



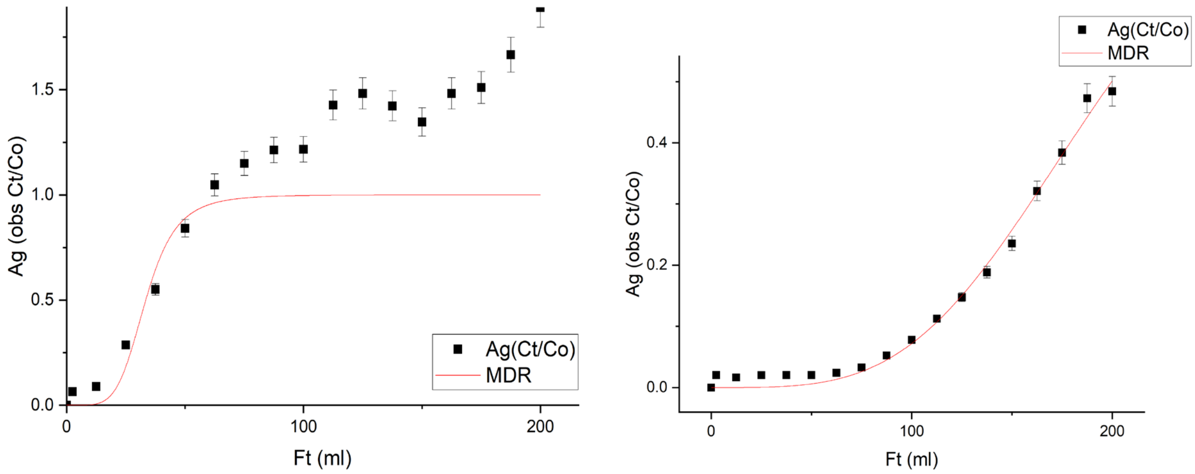
Dowex™ M4195



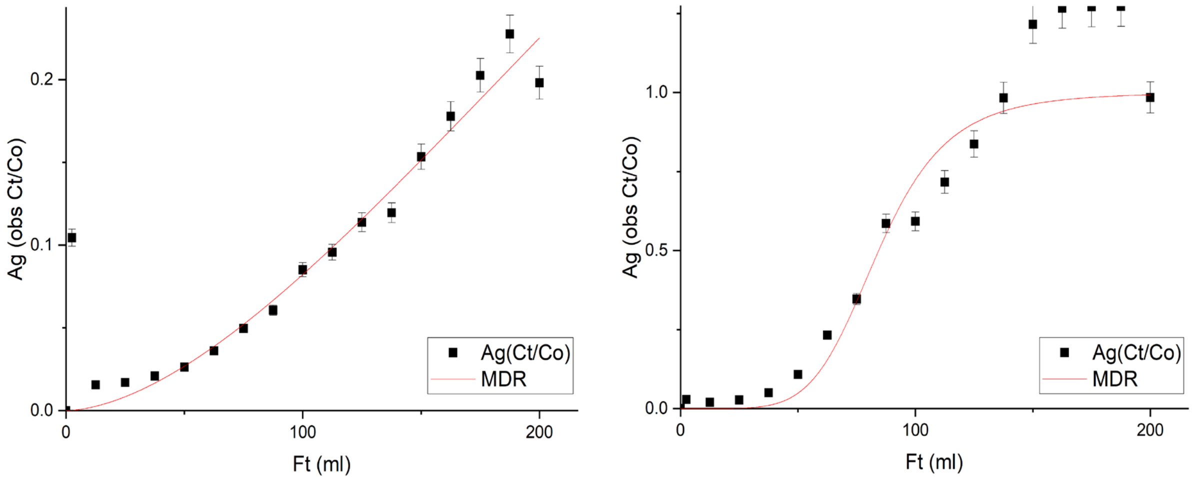
Lewatit® VPOC 1026

**Figure 22 (S1) Breakthrough curves for the uptake of gold onto various absorbents.**

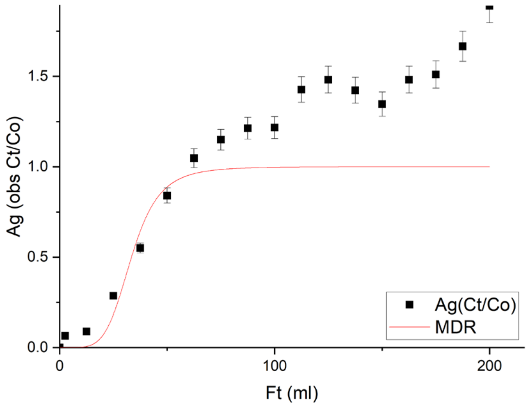
## SEI2. Silver breakthrough models



Purolite® A200 Lewatit® MonoPlus TP 214



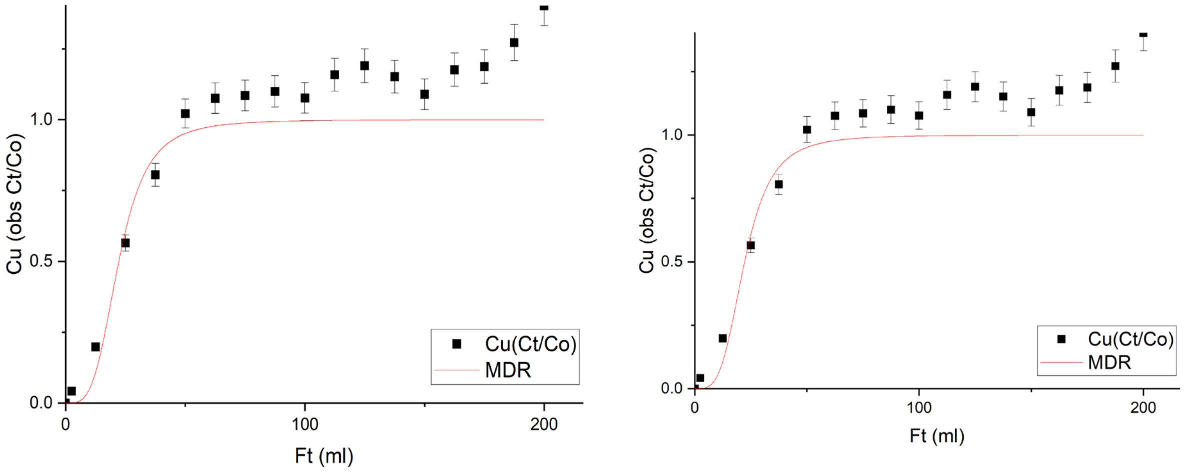
Puromet® MTS9140 Dowex™ M4195



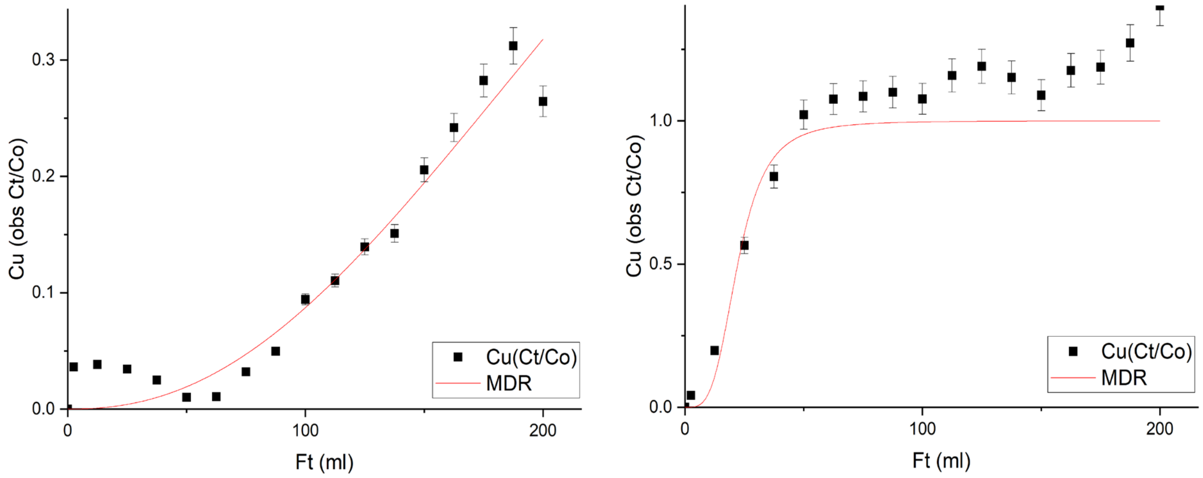
Lewatit® VPOC 1026

**Figure 23 (S2) Breakthrough curves for the uptake of silver onto various absorbents.**

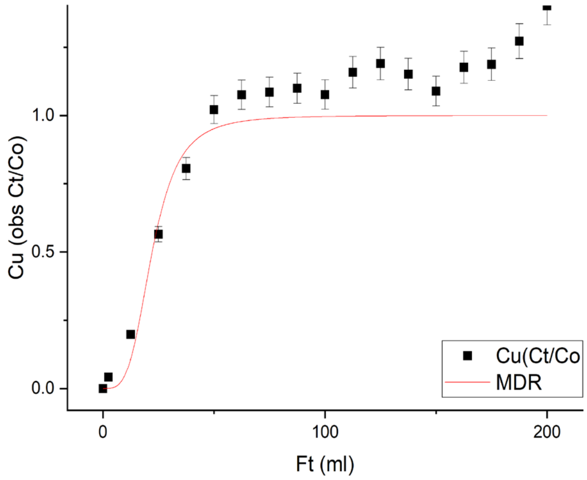
## SEI3. Copper breakthrough models



Purolite® A200 Lewatit® MonoPlus TP 214



Puromet® MTS9140 Dowex™ M4195



Lewatit® VPOC 1026

**Figure 24 (S3) Breakthrough curves for the uptake of copper onto various absorbents.**

## SEI4. Gold uptake dynamic model parameters

The parameters from the Yoon Nelson, Adams-Bohart, and Dose Response models are given in Table S1. The calculated parameters are based on the equations shown in section 2.4.

**Table 13 (S4) Calculated parameters Breakthrough curves for the uptake of gold onto various absorbents.**

**Adams-Bohart Model Parameters**

| Absorbent | $K_a$ | W | $R^2$ |
|---|---|---|---|
| A200 | 0.007 ± 0.01 | 33 ± 2 | 0.862 |
| TP214 | 0.0043 ± 0.0007 | 71 ± 4 | 0.851 |
| MTS9140 | 0.0030 ± 0.0003 | 106 ± 7 | 0.909 |
| M4195 | 0.0025 ± 0.0005 | 83 ± 9 | 0.747 |
| VPOC 1026 | 0.0009 ± 0.0003 | 140 ± 40 | 0.363 |

**Yoon-Nelson Model Parameters**

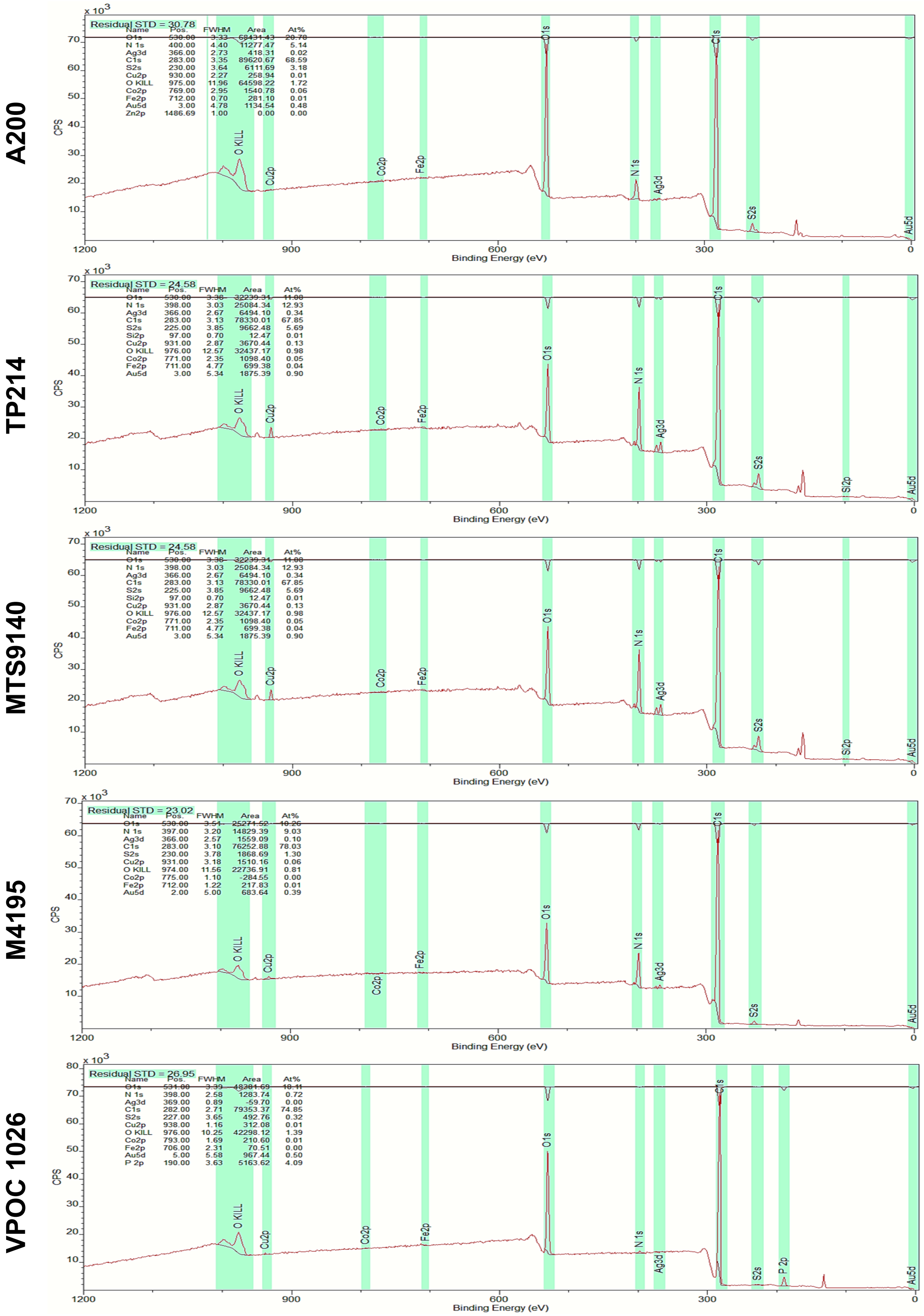
| Absorbent | $k_{yn}$ | $t_f$ | $R^2$ |
|---|---|---|---|
| A200 | 0.07 ± 0.01 | 50 ± 3 | 0.862 |
| TP214 | 0.044 ± 0.007 | 107 ± 7 | 0.851 |
| MTS9140 | 0.030 ± 0.003 | 160 ± 10 | 0.914 |
| M4195 | 0.025 ± 0.005 | 130 ± 10 | 0.747 |
| VPOC 1026 | 0.009 ± 0.003 | 200 ± 60 | 0.363 |

**Modified Dose-Response (MDR) Model Parameters**

| Absorbent | a | b | $R^2$ |
|---|---|---|---|
| A200 | 3.6 ± 0.7 | 50 ± 3 | 0.860 |
| TP214 | 2.5 ± 0.4 | 130 ± 20 | 0.886 |
| MTS9140 | 1.5 ± 0.1 | 430 ± 80 | 0.955 |
| M4195 | 1.1 ± 0.2 | 250 ± 60 | 0.891 |
| VPOC 1026 | 0.19 ± 0.05 | 50600 ± 88000 | 0.836 |

## SEI5. XPS survey spectra

Figure S2 the XPS spectra of the absorbent post uptake, given in Table 10. Was dried in the oven in 50°C oven for 48hrs prior and pressing the whole resins beads into a clean, high purity indium foil.



**A200**

Residual STD = 30.78

| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| O1s | 530.00 | 3.33 | 68431.43 | 20.78 |
| N 1s | 400.00 | 4.40 | 11277.47 | 5.14 |
| Ag3d | 366.00 | 2.73 | 418.31 | 0.02 |
| C1s | 283.00 | 3.35 | 89620.67 | 68.59 |
| S2s | 230.00 | 3.64 | 6111.69 | 3.18 |
| Cu2p | 930.00 | 2.27 | 258.94 | 0.01 |
| O KILL | 975.00 | 11.96 | 64598.22 | 1.72 |
| Co2p | 769.00 | 2.95 | 1540.78 | 0.06 |
| Fe2p | 712.00 | 0.70 | 281.10 | 0.01 |
| Au5d | 3.00 | 4.78 | 1134.54 | 0.48 |
| Zn2p | 1486.69 | 1.00 | 0.00 | 0.00 |

**TP214**

Residual STD = 24.58

| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| O1s | 530.00 | 3.38 | 32239.31 | 11.08 |
| N 1s | 398.00 | 3.03 | 25084.34 | 12.93 |
| Ag3d | 366.00 | 2.67 | 6494.10 | 0.34 |
| C1s | 283.00 | 3.13 | 78330.01 | 67.85 |
| S2s | 225.00 | 3.85 | 9662.48 | 5.69 |
| Si2p | 97.00 | 0.70 | 12.47 | 0.01 |
| Cu2p | 931.00 | 2.87 | 3670.44 | 0.13 |
| O KILL | 976.00 | 12.57 | 32437.17 | 0.98 |
| Co2p | 771.00 | 2.35 | 1098.40 | 0.05 |
| Fe2p | 711.00 | 4.77 | 699.38 | 0.04 |
| Au5d | 3.00 | 5.34 | 1875.39 | 0.90 |

**MTS9140**

Residual STD = 24.58

| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| O1s | 530.00 | 3.38 | 32239.31 | 11.08 |
| N 1s | 398.00 | 3.03 | 25084.34 | 12.93 |
| Ag3d | 366.00 | 2.67 | 6494.10 | 0.34 |
| C1s | 283.00 | 3.13 | 78330.01 | 67.85 |
| S2s | 225.00 | 3.85 | 9662.48 | 5.69 |
| Si2p | 97.00 | 0.70 | 12.47 | 0.01 |
| Cu2p | 931.00 | 2.87 | 3670.44 | 0.13 |
| O KILL | 976.00 | 12.57 | 32437.17 | 0.98 |
| Co2p | 771.00 | 2.35 | 1098.40 | 0.05 |
| Fe2p | 711.00 | 4.77 | 699.38 | 0.04 |
| Au5d | 3.00 | 5.34 | 1875.39 | 0.90 |

**M4195**

Residual STD = 23.02

| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| O1s | 530.00 | 3.51 | 25271.52 | 10.26 |
| N 1s | 397.00 | 3.20 | 14829.39 | 9.03 |
| Ag3d | 366.00 | 2.57 | 1559.09 | 0.10 |
| C1s | 283.00 | 3.10 | 76252.88 | 78.03 |
| S2s | 230.00 | 3.78 | 1868.69 | 1.30 |
| Cu2p | 931.00 | 3.18 | 1510.16 | 0.06 |
| O KILL | 974.00 | 11.56 | 22736.91 | 0.81 |
| Co2p | 775.00 | 1.10 | -284.55 | 0.00 |
| Fe2p | 712.00 | 1.22 | 217.83 | 0.01 |
| Au5d | 2.00 | 5.00 | 683.64 | 0.39 |

**VPOC 1026**

Residual STD = 26.95

| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| O1s | 531.00 | 3.39 | 48381.69 | 18.11 |
| N 1s | 398.00 | 2.58 | 1283.74 | 0.72 |
| Ag3d | 369.00 | 0.89 | -59.70 | 0.00 |
| C1s | 282.00 | 2.71 | 79353.37 | 74.85 |
| S2s | 227.00 | 3.65 | 492.76 | 0.32 |
| Cu2p | 938.00 | 1.16 | 312.08 | 0.01 |
| O KILL | 976.00 | 10.25 | 42298.12 | 1.39 |
| Co2p | 793.00 | 1.69 | 210.60 | 0.01 |
| Fe2p | 706.00 | 2.31 | 70.51 | 0.00 |
| Au5d | 5.00 | 5.58 | 967.44 | 0.50 |
| P 2p | 190.00 | 3.63 | 5163.62 | 4.09 |

**Figure 25 (S5) XPS spectra of absorbents post uptake from 80 BV of mine tailings leach stimulant**

# CHAPTER 6: PRECIOUS METALS ON METAL-ON-METAL OXIDE (MOMO) CATALYSTS RECOVERY *VIA* DEEP EUTECTIC SOLVENTS

## 6.1. Paper Overview

This paper describes the synthesis of four different deep eutectic solvents (DES), and the recovery of rhodium and platinum from cobalt on a spent metal-on-metal oxide catalyst (amoxis) using those DES.

ChCl (choline chloride): ethylene glycol (EG), ChCl: urea (Ur), ChCl: thiourea (TU) and ChCl: Lactic Acid (lac) were successfully synthesised. And the efficiency of each DES was compared to an already industrial used method of aqua regia (HCl: $HNO_3$).

Rhodium and platinum recovery was performed by a solid-to-liquid ratio of 1:5 in a dynamic experiment. The Amoxis was characterised using inductively coupled plasma optical emission spectrometry (ICP-OES), fourier-transform infrared spectroscopy (FT-IR), RAMAN, X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to obtain the initial amount of rhodium, platinum and cobalt on the amoxis. Two separate experiments were run with an uncrushed and crushed sample to obtain the most effective form the catalyst should be in for the highest recovery of rhodium and platinum. Additionally, was no improved impact in the addition of the oxidants in the recovery of the PMs.

Analysis of the dynamic experiments were conducted at RS Bruce in Sheffield to determine the concentrations of rhodium, platinum and cobalt that recovered from the amoxis.

This paper is expected to be submitted to the Separation Journal.

Author contributions:

- V. R. Shields- Experimental work, data collection, data analysis and writing
- T. J. Robshaw- Manuscript review
- Hides- Hosting of V. R. Shields at RS Bruce
- R. Bruce- Hosting of V. R. Shields at RS Bruce
- J. Cordiner- Manuscript review
- M. D. Ogden- Principal Investigator and manuscript review

# 6.2. Recovery of Critical Metals from Catalytic Waste Using Deep Eutectic Solvents

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## Abstract

Current prices of rhodium (Rh) and platinum (Pt) are in the top three most expensive metals in the platinum metal (PM) group. While the volume of Rh and Pt that are still mineable has currently not been documented, being able to recover Rh and Pt from spent metal on metal oxide (MoMO) catalysts could decrease the current high demand for Rh and Pt. Leaching of Pt and Rh has little development due to both metals being highly unreactive to many acids and leaching mediums. This paper will investigate different leaching media, 1M aqua regia of $HNO_3$: HCl and four deep eutectic solvents ChCl (choline chloride): ethylene glycol (EG), ChCl: urea (Ur), ChCl: thiourea (TU) and ChCl: Lactic Acid (lac) to determine which system has the best recovery of Rh and Pt from a spent MoMO catalyst. All the DES synthesised were found to have a higher affinity towards Rh and Pt compared to the aqua regia lixiviant. Lac and U DES showed the highest dissolution of Rh at 25% and 22% respectively, with TU showing the highest affinity towards Pt at 14%.

Keywords: platinum group metals, resource recovery, metal-on-metal catalysts, spent catalyst, deep eutectic solvents, ionic liquids.

# 1. Introduction

The European Union (EU) published a communication in 2011 on tackling the challenges in commodity markets and raw materials. This contained a list of 14 identified critical raw materials (CRM) (273). This list expanded to 20 materials in 2014 and 27 materials in 2017 (274; 275). The most up-to-date list from 2020 now contains 30 materials with bauxite, lithium, titanium, and strontium being added for the first time (276). The main parameters used to determine the criticality of a material are economic importance and supply risk (277). The economic importance aims at providing insight into a material in terms of end-use applications and the value added for manufacturing sectors. This economic importance is corrected by a substitution index related to technical and cost performance of any substitutes replacing the CRM for individual applications (273). Supply risk reflects the probability of disruption in supply of the material for the EU. It is based upon the concentration of primary supply, the global suppliers and the countries from which the raw materials are sourced. Supply risk is measured at the ‘bottleneck’ stage of extraction or processing (277). Substitution and recycling are considered risk-reducing measures.

Rhodium (Rh), platinum (Pt), and cobalt (Co) have been present on the EU critical materials list since 2011 due to their high import dependency rate (100% for platinum group metals (PGM) and Co), low recycle rates (35% and 16% respectively) and the fact that the bulk of their supply came from the DRC (Co), South Africa (PGM) and Russia (PGM) (273). The critical nature of these metals is usually reflected in their price volatility (278). The closing price for cobalt on the London Metal Exchange (LME) from 2017 to 2022 has been as high as $97,881 per ton (14/03/2018) and as low as $22,378 per ton (30/07/2019). Currently the price has climbed to $74,650 per ton (20/05/2022) (279). The value of Rh has grown exponentially with a 55% increase in the price of Rh in the first month of 2020 reaching a 11-year high (280). Pt price has steadily increased with an increase of 24% in 2019 and 4% in the first month of 2020 (281). Increased production in auto makers, specifically catalytic converters has caused a significant demand to increase for Rh and Pt. Reserves of PGMs estimate at 69,000 Mt, with mining production being estimated at ~490 tons annually with 37% of the global demand being catalytic converters (282; 283; 284). It was estimated in 2016 that between 150,100 and 170,200 tons of spent catalyst waste is generated annually. (285; 286).

In 2014, the Taiwan Environmental Protection Administration stated that approximately 21,572 tons of untreated spent catalyst was generated worldwide (287). This spent catalyst waste comes from a variety of applications in emission purification, oil-refining, chemical reactions engineering, pharmaceuticals and fine chemicals, in particular. The most common catalyst that uses PGMs is a catalytic converter. With the average catalyst converter having 3-7g of Pt, 15-19g of Pd and 3-7g of Rh, mined amount quantities of these precious metals used for catalytic converters 98 tonnes( 45%), 182.65 tonnes (65%), and 25.6 tonnes (84%) respectively per year (288; 289; 290).

With the growth in interest in electric cars that do not require catalytical converters (which accounts for 75% of Pt and Rh in circulation), there are still rising worries about the overall demand and pricing of PGMs (291; 292). Despite this, the projected pricing of Pt, Rh and the other PGMs will be buoyed by the jewellery and industrial demands (293). Electrical vehicles (EV) typically use gold and silver, which are also in high demand with a being identified as a serious risk in the next 100 years and gold as having limited availability. With the growth of EV and hybrid cars that still use PGMs there will still be a growing demand and the interest in recovering PGMs from waste (294; 295). Current research into recovery of Rh and Pt from spent catalysts has focused more on spent catalytic converters than spent metal-on-metal-oxide (MoMO catalysts). The main method that is being used for Rh and Pt recovery from catalytic converters uses pyrometallurgy, which is the traditional process mainly used for recovering non-ferrous and PGMs from waste (296). This process involves conflagrating, incineration, and smelting in a plasma arc furnace, drossing, sintering, and melting at high temperatures. The current industrial progress of recovering PGM *via* pyrometallurgy is shown in Figure 26 (297).

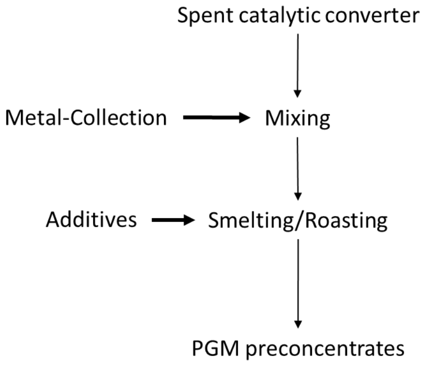


**Figure 26 Pyrometallurgy for PGMs recovery.**

Compared to typical spent catalytic converter waste there has been little research into metal-on-metal-oxide (MoMO) catalysts. MoMOs are a heterogenous catalysis with various uses such as petroleum refinement, energy conversion, and hydrogenation (298). Current method of regeneration of a multiple-step process which include chemical leaching *via* cyanide, volatilisation, cementation, using precipitation *via* solvent extraction (SX) and ion exchange (IX). With the leaching of spent metal-on-metal oxide catalysts using acids for recovery, it would just dissolve the catalyst without being able to remove the precious metal as they are extremely unreactive. Additionally, current industrial methods have long processing times and generate large volumes of toxic waste (289). Over the last couple of decades there has been a switch from a combination of mechanical and pyrometallurgical methods to hydrometallurgy.

Current methods of leaching used in the recovery of Rh and Pt from spent catalysts have been aqua regia (3:1 HCl: $HNO_3$), cyanide and mineral acids in the presence of $H_2O_2$, $O_2$ or $Cl_2$ (299). Aqua regia is needed to dissolve gold as neither $HNO_3$ nor HCl cannot dissolve them separately. The $HNO_3$ acts the oxidiser that forms the gold ion $Au^{3+}$; which then reacts with the HCl to form tetrachloroaurate(III) anions (300). The use of cyanide is highly toxic towards human and aquatic life, with by-products of highly polluting gases such as NOx and HCN (301; 302; 303). The most common leaching reagent is concentrated aqua regia (HCl : $HNO_3$) a molar ratio 3:1 which produces a Pt and Rh have extraction rates of 90-93% with concentration of the acids being a massive contributor to the extraction rates (304). The concentrated acids took the quickest to dissolve the PGMs from the cells investigated (304). Aqua regia at concentration (66%) PGMs dissolved in under 5 minutes (304).

However, concentrated acids are highly hazardous to humans and the environment. Being able to move away from using highly concentrated aqua regia to more sustainable lixiviants such as thiourea/thiosulphate will be extremely beneficial to the currently unsustainable methods used to produce and recover PGMs.

In the last two decades there has been a growth in research into using deep eutectic solvents (DES) in the recovery of precious group metals (PGMs) from spent catalysts. DES are a new class of ionic liquid (IL) first reported in 2003 (181). DES is unique to other solvents as the hydrogen bond acceptor (HBA) and bases, acting as the hydrogen bond donor (HBD) have a much higher melting point in comparison of the DES that can be formed at 12°C (305). This phenomenon can be contributed to the large, nonsymmetric ions that have low lattice energy due to the complexation of the two reagents via the hydrogen bonding (181). They are considered a green solvent, with the lack of research into DES, they cannot be claimed to be completely environmentally benign. More research is needed to confirm using DES would truly be environmentally benign. DES are formed by a eutectic mixture of Lewis or Brønsted acids, acting as the HBA and bases, acting as the HBD (178; 181). These have yet to be any properly investigations in literature how DES can be utilised in PGM production or used in the recovery from waste applications.

There are still debates on the definition of DES with one statement stating that despite the existence of a eutectic point in the mixtures does not mean they can be defined as a DES (306). This is partly because there has been no proven difference in the type of interactions that occur with the formation of DES; however, many studies have suggested multiple interactions including hydrogen bonding, π-covalent bonding, van der Waals interactions or intermediate bonding (307). Current literature on DES use for recovery of PGM is given in Table 14.

**Table 14 Recovery of PGMs and transition metals by dissolution in DES**

| DES system | Notes | Ref |
|---|---|---|
| ChCl:EG | Au, Ag and Cu recovery rate of 3-18%. $NH_4Cl$ in an EG system extraction percentage was 30% and 35% of Pt and Rh. Density: 1.08 g/cm$^3$ at 198.15 K and 1 bar atmospheric pressures. | (184; 185; 308) |
| ChCl: Ur | No previous literature of DES with PGM. Urea in different concentrations of HCl recovery Pt, Pd and Rh at 90-96%. Density: 1.194 g/cm$^3$ at 198.15 K and 1 bar atmospheric pressures. | (309; 310) |
| ChCl:TU | No previous literature of DES with PGM. TU showed recovery of Rh, ruthenium (Ru) and iridium (Ir), recovery at 98%. | (311) |
| ChCl:Lac | No previous literature of DES with PGM. Literature for lactic acid to be used for Cu recovery. With increased reagent concentration and temperature Cu leaching rate increased. Density: 1.159 gcm$^3$ at 198.15 K and 1 bar atmospheric pressures. | (186; 312) |

Additionally, leaching *via* DES would be categorised as a solvometallurgical method. Solvometallurgy is the extraction of metal from ores, tailings, industrial process residues, production scrap and urban waste using non-aqueous solutions. This method would greatly reduce the overall water waste of the mining cycle, this will be the first work to investigate a lower concentration of aqua regia and DES in the selective dissolution of PGMs separately from a Co metal on a spent MoMO catalyst. The DES systems explored in this research work are given in Figure 22. Research into new leaching methods for recovering PMs that are environmentally and economically sustainable could reduce the current high demand for PMs especially Pt and Rh using aqua regia and the four DES stated Table 14.

Currently the most common DES investigated for PGM recovery has been choline chloride (ChCl): ethylene glycol (EG) (183). The two investigations referenced in Table 14 experimental parameters are different. The research by Jenkin et al (3-18% recovery) methodology was carried out with the use of electrolysis and has other competing minerals that was dissolved which may have affected the overall recovery (184). Work done by Nguyen (30% and 35% Pt and Rh) involved a solvometallurgical approach, term used to describe the extraction of metals from ores, industrial process residues, production scrap, and urban waste using non-aqueous solutions (156; 185). Additionally, this work had the addition of the oxidising iron chloride and copper chloride ($FeCl_3$ and $CuCl_2$) and was a two-step process of salvo-leaching and non-aqueous solvent extraction (185). With ChCl: urea (Ur), ChCl: thiourea (TU) they show promising signs of producing a high recovery rate of PGM leaching. The HBD for each DES have already been confirmed to have an affinity towards PGMs in different lixiviant systems as a solvated metal complex (186; 184; 187; 188; 189).

ChCl: lactic acid (lac) has yet to be researched with any PGMs (Table 14). The current knowledge of the complexation of metals by lactic acid is that the interactions between Cu(II) ions and lactic acid which occurs at low concentrations; out of the four metals investigated (cobalt [Co], Cu, manganese [Mn], cadmium [Cd]) (190). It was shown the micromolar levels decreased in this order Co(II)-Lac > Cu(II)-Lac > Mn(II)-Lac ~ Cd(II)-Lac (190). The interactions are dependent on the metal ions affinity for oxygen-donor atoms (190).

An alumina spent MoMO catalyst that will be investigated has Rh, Pt and cobalt (Co) on its surface and the leaching process will be compared with the industry standard of aqua regia which is already used in precious metal extraction (Au and Pt) (144). This is possible because of the unique solvent of aqua regia; the $HNO_3$ part of aqua regia is a powerful oxidising agent, which is able to convert even small amounts of Au to its ionic form, $Au^{3+}$. After the formation of the $Au^{3+}$ ionic form is present in the solution, the HCl provides a source of $Cl^-$ anions which react with the Au cations to form tetrachloroaurate(III) anions (144).

The comparison of aqua regia and the DES solutions is the difference of redox activity (aqua regia) and non-redox activity (DES). In redox reactions the chemical species may change their oxidation state by gaining or losing electrons during the reaction; and non-redox the chemical species do not change their oxidation state during the reaction (313). There is currently no literature in the comparison of redox and non-redox activity with respect to leaching via DES. In the reaction process of aqua regia and gold the reaction of the $HNO_3$ and HCl occur one after another. The $HNO_3$ acts as the oxidiser that forms the $Au^{3+}$ ion, which then goes onto to react with the HCl to form the tetrachloroaurate$^{3+}$ anions. The redox reactions could potentially be faster with the ability to continuously change oxidation states leading to higher formation of the ionic forms that are needed before the tetrachloroaurate anions can be formed. However, literature do state that redox reaction tend to be slow, with the need of a catalyst for the reaction to become useful (313).

The expected oxidising leaching of Rh and Pt which will then be able to be leached out, which has been shown with the $E^0$ of Pt and Rh chloride complex formation is -0.758 and -0.44 V. The key reactions needed for the recovery process would be M+ $2e^- \rightleftharpoons M^{2+}$ and $MCln + e^- \rightleftharpoons M + NCl^-$. The reaction of each metal is:

$Co^{2+} + 2\ e- \rightleftharpoons Co\ (s) = -0.282V$ 14

$PtCl4^{2-} + 2\ e^- \rightleftharpoons Pt\ (s) + 4\ Cl^- = 0.758V$ 15

$RhCl6^{3-} + 3e^- \rightleftharpoons Rh\ (s) + 6\ Cl^- = 0.44V$ 16

It can be seen from the equations with an oxidising lixiviant, Co solubilisation would be expected to be more favourable. This would be a problem in terms of PM recovery. It is hoped that in the DES system, solubilisation will be governed more by complex stability. Therefore, there is a need, to determine which DES is able to dissolve the PGMs from the MoMO catalyst and is comparable to the one industrial method of aqua regia, without the addition of any harmful oxidants such as $I_2$ or $Na_2O_2$. Finding a lixiviant that could isolate the PGMs from other transition metals would economise the overall recovery method.

The possible mechanism of the DES and the separation of metals was discussed in a review by Yuan et al (314). With ChCl-based DES, it has been reported that the metal dissolution ability is dependent of the HBDs (314). This could be for two reasons; (1) high polarity with highly active dissociated protons of the HBDs could act as oxygen acceptors, leading to strong H-bonding interactions and formation of chloro- species (315). (2) the formation of extensive chains of dimers rather than single dimer units due to the functional groups, would result in the similar mobility of the HBD with the choline cation, and lead to the strong complexation ability (316). Additionally, it has been found that the metal complexation is a key factor in solubility with diol-based DES with $Cl^-$ anion dominating the metal speciation (314). It has also been reported that thiol-group DES can improve physical properties of ChCl based DESs and improve solubilities of late transition metals which could be attributed to the ligand structure and enhanced media acidity (317).

Current expected extraction behaviour between the metals investigated are predicted to be reliant on the HBDs ligands of Lac, TU, Ur and EG as ChCl is constant between all four DES investigated. It is known that the metal chloride complexes in equations 14-15 form larger complexes involving both the HBD and HBA DES molecules (192). As such the hardness and softness properties of both organic molecules of the DES that are being investigated, they are likely to be of relevance in establishing an order of affinity for the metals. It should be noted that it is not certain that the metal chloride complexes are the dominant species in the DES, and it is also possible that complexes could form with the HBD acting as inner-sphere complex ligands, which has certainly also been observed before in aqueous conditions (316).

The order in terms of the hardness of base is Lac ~ EG > Ur > TU. Based on this order and Pt being lower in the periodical table compared to Rh it is deemed a softer metal. With Pt being softer out of the two and following the hard-soft-acid-base theory with TU being a softest base out of the four HBD ligands investigated it can be predicted that TU would extract Pt at the highest rate. Comparatively with Rh being a harder acid, and Lac being the hardest base out of the four ligands investigated it can be expected that Lac and EG would extract the highest volume of Rh. Being able to bid as an anionic ligand from the carboxylate group compared to the EG which is diol and would not be expected to deprotonate readily.

The most interesting factor of this investigation is that Co will be competing with the Rh and Pt in dissolution. Co is a more reactive metal with literature stating the various HBD show affinity to Co. Santhosh and Nayaka investigated Co recovery from spent Li-ion batteries using Lac showed a 98% leaching efficiency (318). Xie et al investigated “Catalytic activity of nickel (Ni) and Co for amination of EG” and determined Co was more suitable than Ni for the animation of EG (319). Housecroft and Sharpe state that Co reactive more readily with more of the elements of the thiourea functional group sulfur (S) (320). Currently there is no literature regarding Co and urea.

Research into new leaching methods for recovering PMs that are environmentally and economically sustainable could mitigate the current high demand for PMs, especially Pt and Rh. DES picked for the research shown in Figure 27.

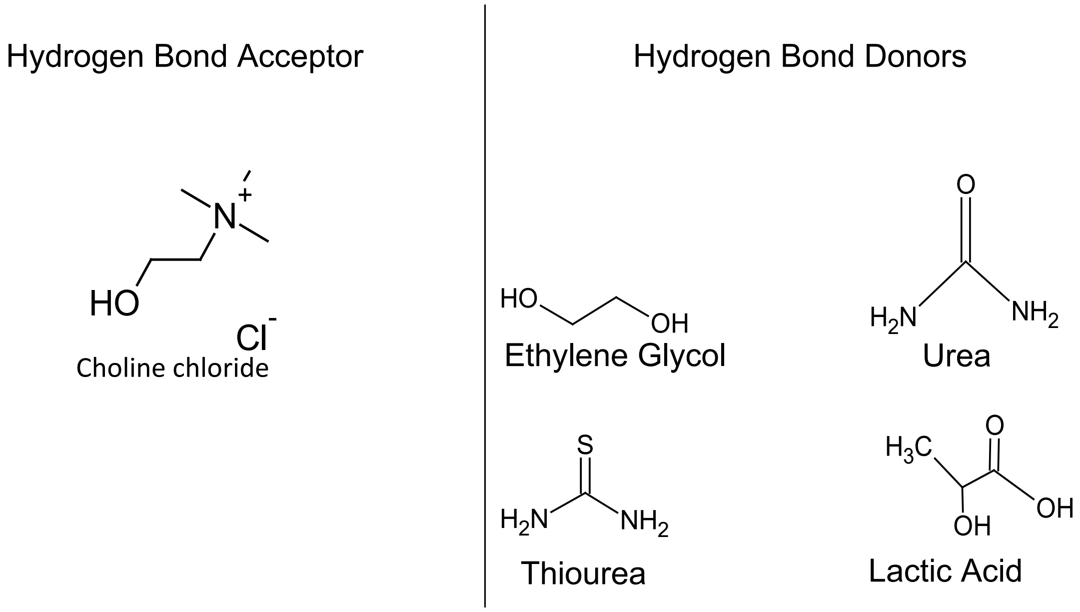


**Figure 27 Structural formula of the DES (HBA and HBD) components investigated.**

# 2. Experimental

## 2.1 Reagents and Materials

MoMO spent catalyst, also known as Amoxis (PNB 443), a $N_2O$ substrate, was sourced from RS Bruce. The results of chemical analysis of the material, provided by the supplier, are shown in Table 15.

**Table 15 Chemical analysis of the Amoxis (PNB 443).**

| Metal/ chemical compound | Percentage on Amoxis (mass%) |
|---|---|
| Co | 18.6± 0.9 |
| Pt | 0.16± 0.0008 |
| Rh | 0.05± 0.0025 |
| $Al_2O_3$ | 81.19± 4.1 |

All the chemicals were sourced as follows. Chemicals were used as received unless stated otherwise; choline chloride (Alfa Aesar, 98+%), ethylene glycol (Fluorochem, ≥99.8%), urea (Merck, ≥99.5%), lactic acid (lac) (Honeywell), thiourea (Sigma-

Aldrich, ≥99.0%), molecular sieves, 5A, 1-2mm (0.04-0.08in) dia. pellets (Alfa Aesar) nitric acid (Honeywell, 70%) and hydrochloric acid (Honeywell, 37%).

## 2.1. Amoxis Characterisation

ICP-OES, FT-IR,SEM, RAMAN, XRD and XPS were the characteristic techniques used for the solid-state analysis of the Amoxis. A crushed and uncrushed sample of the Amoxis was analysed. The amoxis was crushed using a ball mill, 150g of the uncrushed amoxis was used in the ball milled at 350 rpm for 30 minutes.

All ICP-OES analysis was performed in duplicate. 3 ml of conc. nitric acid and 1 ml of conc. perchloric acid was added to the 0.5g of the samples and heated to 200°C, they were then made up to 50 ml using 1% nitric acid before the sample could be run. Solid spent catalyst samples were run in a triplicate. FT-IR analysis was performed using <0.5g of both crushed and uncrushed samples with a PerkinElmer Frontier FTIR. RAMAN analysis was performed using <0.5g of both crushed and uncrushed samples, with a Horiba XploRA Plus (M06). Preparation for XPS analysis was performed by placing the crushed and non-crushed samples into a clean, high purity indium foil, separately. They were then placed on top of an adhesive carbon conductive tape. Analyses were carried out on a Kratos Axis Supra. XRD data were collected using a Bruker D2 PHASER instrument (Cu K-a radiation, 0.15418 nm). The tube voltage and current, step time, increment and scanning range were 30 kV and 10 mA, 0.4 s, 0.02°, 10°-90° respectively. The powder diffraction file (PDF) patterns database from the International Centre for Diffraction Dara (ICDD) was used for identification and semi-quantification.

## 2.2. Synthesis of DESs

Prior to synthesis ChCl (being highly hygroscopic) was dried in a vacuum oven at 50 °C for 72 hours. Lactic acid was dried in a vacuum oven at 50 °C for 48 hours before synthesis. Thiourea, urea ad ethylene glycol was kept dry prior to synthesis by being stored with molecular sieves in the fume cupboard. The DES ratio was 1:2 (HBA: HBD), except for ChCl: TU which was a 15:6 ratio, and ChCl: Ur had a ratio of 13:6. TU, Ur and EG, were handled in ambient conditions. The DES were left to mix at 80°C, except for ChCl: EG which was mixed at ambient temperature. Mixing was performed at 350rpm using a magnetic stirrer, till a homogenous clear liquid was formed. The mixtures were then kept at 80°C for another 4 hours. In between experiments they were stored in the vacuum oven.

## 2.3. Leaching Experiments

For each DES and aqua regia experimental there were two different parameters tested, the crushed and uncrushed amoxis. All experiments were run in triplets. 10g of Amoxis was used for each leaching experiment (45ml). The leaching experiments were left to mix at ambient temperatures for 7 days (168 hours); with 1ml of each sample taken every hour for the first fours then at the 12- and 24-hour interval. Samples were then after that every 24 hours and diluted to 10ml with 1M $HNO_3$ for ICP-OES analysis.

## 2.4. Addition of Oxidants to the DES system

Two different oxidants, $Na_2O_2$ and $I_2$, were chosen, as additions to the DES systems 0.5g of the oxidant was used with 4.5g of DES and 1g of amoxis. The redox equations of $Na_2O_2$ and $I_2$ are shown below.

$Na_2O_2(s) \rightleftharpoons 2Na^{+} + O_2^{-} + e^{-}$ $E_0 = +2.73V$ 17

$I_2(aq) + 2e^{-} \rightleftharpoons 2I^{-}$ $E_0 = +0.54V$ 18

The addition of the oxidants is to provide electrons, to allow the DES to potentially promote the bonding between the DES, Rh and Pt.

These oxidants were added to the DES and left to mix till a homogenous solution is formed that the MClx was added and was left to mix for 24 hours then 1ml of the DES-oxidant solution was taken and diluted to 10ml with 1% $HNO_3$ for ICP-OES analysis.

## 2.5. Calculating Parameters and Separation Factor calculations

Various calculations and models were used to determine the reaction mechanisms, percentage recovery and different parameters cause as distribution coefficient and separation factors and half-life. Equations 19-22 show each equation used.

Distribution coefficient : $\frac{[\text{metal conc.in the solid phase}]}{[\text{metal conc.in the DES phase}]}$ 19

Half-life: $\mathbf{t}_{1/2} = \frac{1}{\mathrm{K}[A_0]}$ 20

Percentage recovery : $\frac{[\textbf{mass of metal solubilised in the DES}]}{[\textbf{mass of metal in the sample of catalyst}]}$X100 21

Separation factors: $\frac{[\textbf{distr. coeff. of target species}]}{[\textbf{distr. Coeff. of co-contaminant}]}$ 22

The half-life refers to the amount of time it takes for half a particular sample to react. Where K is the rate constant and $[A_0]$ is the initial concentration (321).

The most common models used to monitor the kinetics of a leaching process are the shrinking core models. The shrinking core model is commonly-used to describe heterogeneous, hydrometallurgical leaching reactions (322; 323). This model assumes a reaction system of A+B → products, where A is the reactive species and B is leached species. The whole reactive outer layer of the particles present are exposed to a leaching solution and as the reaction proceeds the reaction portion shrinks forming a product layer (324). There are three variants that were used in this work shown in the following equations 23- 25, t is the time that the leaching experiment has progressed for at the point a given sample is taken (sec), τ is the total leaching time (sec) and $X_b$ is the reacted fraction of the leached species.

$$\frac{\mathbf{t}}{\boldsymbol{\tau}} = 1 - (1 - \boldsymbol{X_b})^{\frac{1}{3}} \qquad 23$$

$$\frac{\mathbf{t}}{\boldsymbol{\tau}} = 1 - 3(1 - \boldsymbol{X_b})^{\frac{1}{3}} + \mathbf{2}(\mathbf{1} - \boldsymbol{X_b}) \qquad 24$$

$$\frac{t}{\tau} = \left[(1 - X_b)^{\frac{1}{3}} - 1\right] + \frac{1}{3}\ln(1 - X_b) \qquad 25$$

If a dataset agrees with equation 23, the reaction is rate-controlled by the diffusion of A across the particle boundary layer (diffusion-controlled) (325). If equation 24 describes the data, the kinetics are dominated by the chemical REDOX reaction (reaction-controlled) (325). If equation 25 fits the data accurately, both stages are influential to the rate (mixed-controlled) (325).

# 3. Results

## 3.1. Amoxis Characterisation

### 3.1.1. ICP-OES

From 0.5g of both samples, 3 ml of nitric acid and 1 ml of perchloric acid was added to the samples and heated to 200°C, they were then made up to 50 ml using 1% nitric acid before the sample could be run as the spent catalyst samples were solid.

**Table 16 ICP-OES results of the Amoxis.**

| Sample | Co-59 (mg/l) | Rh-103 (mg/l) | Pt-195 (mg/l) |
|---|---|---|---|
| **Non-crushed Amoxis** | 0.13±0.006 | 0.013+0.007 | 0.059+0.003 |
| **Crushed Amoxis** | 0.33±0.02 | 0.010+0.001 | 0.036±0.002 |

This ICP data (Table 16) of the spent amoxis prior to leaching matches the estimations given from RS Bruce with the percentages of Co, Rh, and Pt in the spent catalyst 18.6%, 0.05% and 0.16% respectively 1 gram of the uncrushed amoxis 2.64x $10^{-4}$g Co, 2.72x $10^{-5}$g Rh and 1.12x $10^{-4}$g Pt.

### 3.1.2. XPS

**Table 17 XPS results of the Amoxis (mg/L)**

| Element | Uncrushed | Crushed |
|---|---|---|
| Pt | 3.9± 0.2 | 2.3±0.1 |
| Rh | 0.95± 0.05 | 1.00±0.05 |
| Co | 2.7±0.1 | 2.7±0.2 |
| O | 74.4±3 | 76.85±4 |
| Al | 8.10±0.4 | 8.2±0.4 |
| C | 9.3+0.5 | 9.5+0.5 |

The data shown from Table 17 agrees with the percentage estimations given from RSBruce$^{TM}$ shown in in Table 15 of the amoxis including O, Al and C that make up the alumina functional group. The full XPS spectra of the uncrushed and crushed amoxis analysis is shown in SEI1.

### 3.1.3. FT-IR

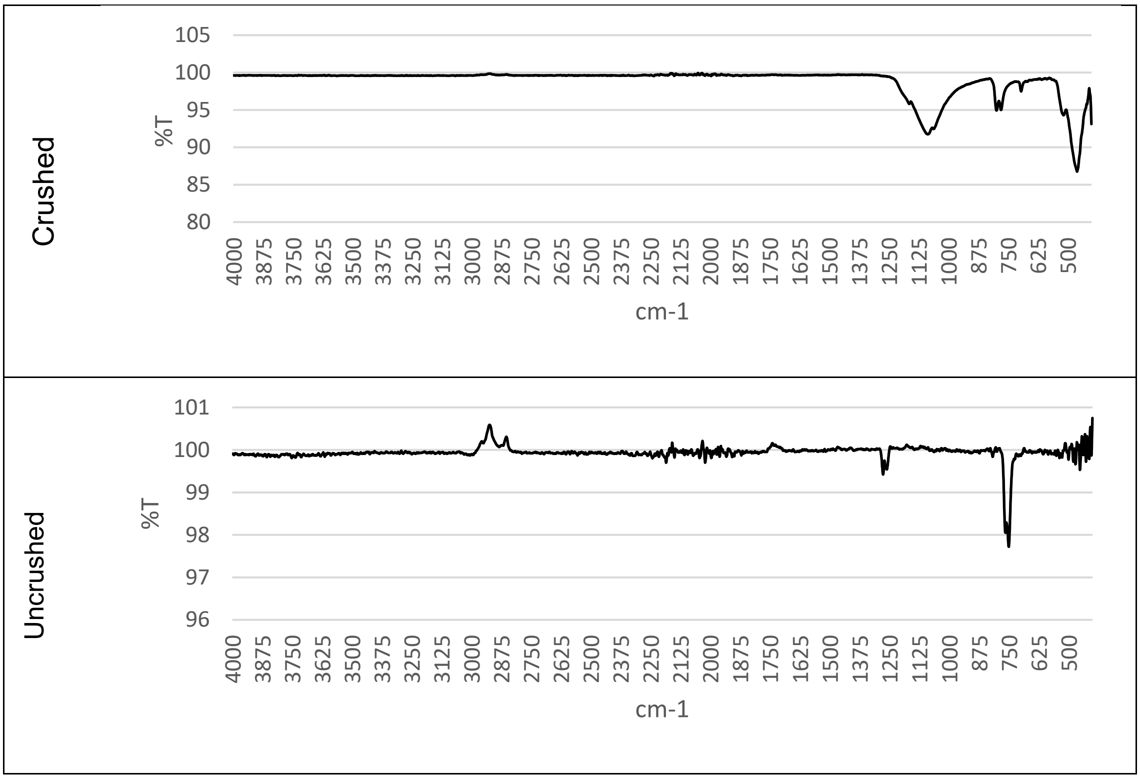


**Figure 28 Full FT-IR spectrum of crushed and uncrushed Amoxis**

**Table 18 FT-IR results of the Amoxis**

| Amoxis | Peaks (cm$^{-1}$) | |
|---|---|---|
| | Al-O | C-O |
| Crushed | 457,776-779 | 1027-1150 |
| Uncrushed | 748-754 | 1260-1275 |

The key bond vibrations identified in the FT-IR spectra are shown in Table 18, with the full spectra being shown in Figure 28 and SEI2, bong vibrations identified in the amoxis matches the information supplied by RSBruce$^{TM}$. With conformations of the metals seen in the XPS the carbon-oxygen bonds are seen in both crushed and uncrushed samples. Additionally, in Table 18 it shows how the $Al_2O_3$ compounds that are the main compound of the amoxis is only seen in the crushed amoxis sample as it would only be found inside the catalyst.

### 3.1.4. RAMAN

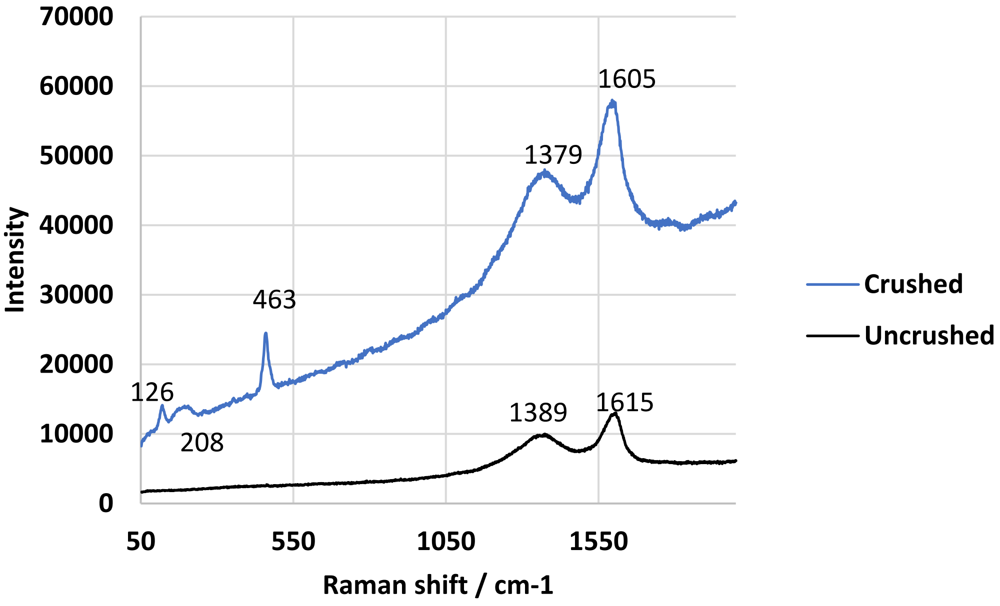


**Figure 29 RAMAN spectrum of crushed and uncrushed amoxis**

The spectrum (Figure 29) supports the elements that were identified by RS Bruce$^{TM}$ and the FT-IR. With possible peaks for the crushed and uncrushed at 1379 cm$^{-1}$ and 1605 cm$^{-1}$ being carbon and Pt-Co. With the crushed samples showing peaks at 105-249 cm$^{-1}$ which can be assigned as $Pt_4$, and a peak at 463 cm$^{-1}$ which can be assumed to be CoO (326; 327; 328).

### 3.1.5. XRD

Both the uncrushed and crushed sample amoxis sample show no peaks for Rh. With low levels of Pt and Co peaks <1% and 12% respectively for the crushed sample and <1% and 15% respectively for the uncrushed sample. This determines that the amount of Rh on the surface of the amoxis is extremely low, this matches with the other state-solid analysis with low values of Rh with the full spectra's (shown Figure 30). The XRD confirms the data shown in the ICP-OES and FT-IR data that show the functional groups that are on the catalyst surface.

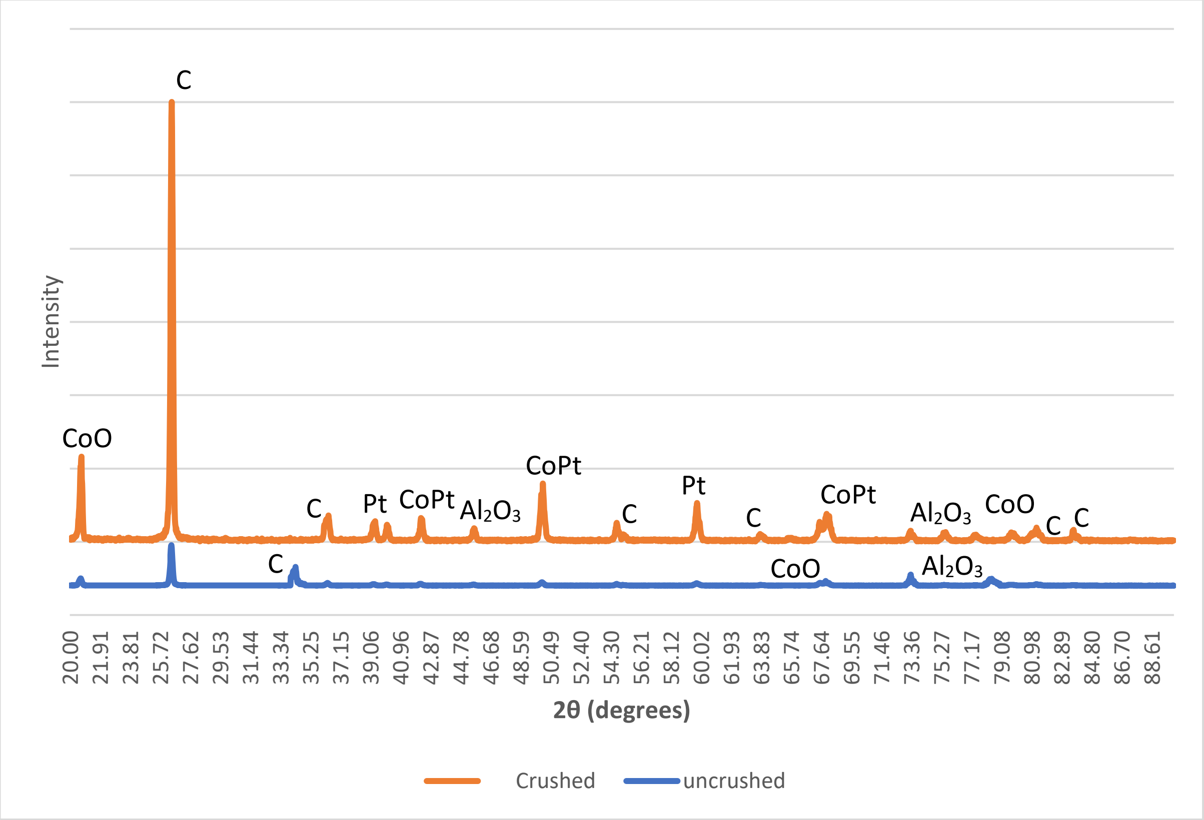


**Figure 30 Full XRD spectrums of crushed and uncrushed Amoxis.**

## 3.2. Leaching of MoMO (crushed and uncrushed)

The overall equilibrium data for the complete leach was reached at 24 hours. Shown in SEI3.

### 3.2.1. Aqua Regia

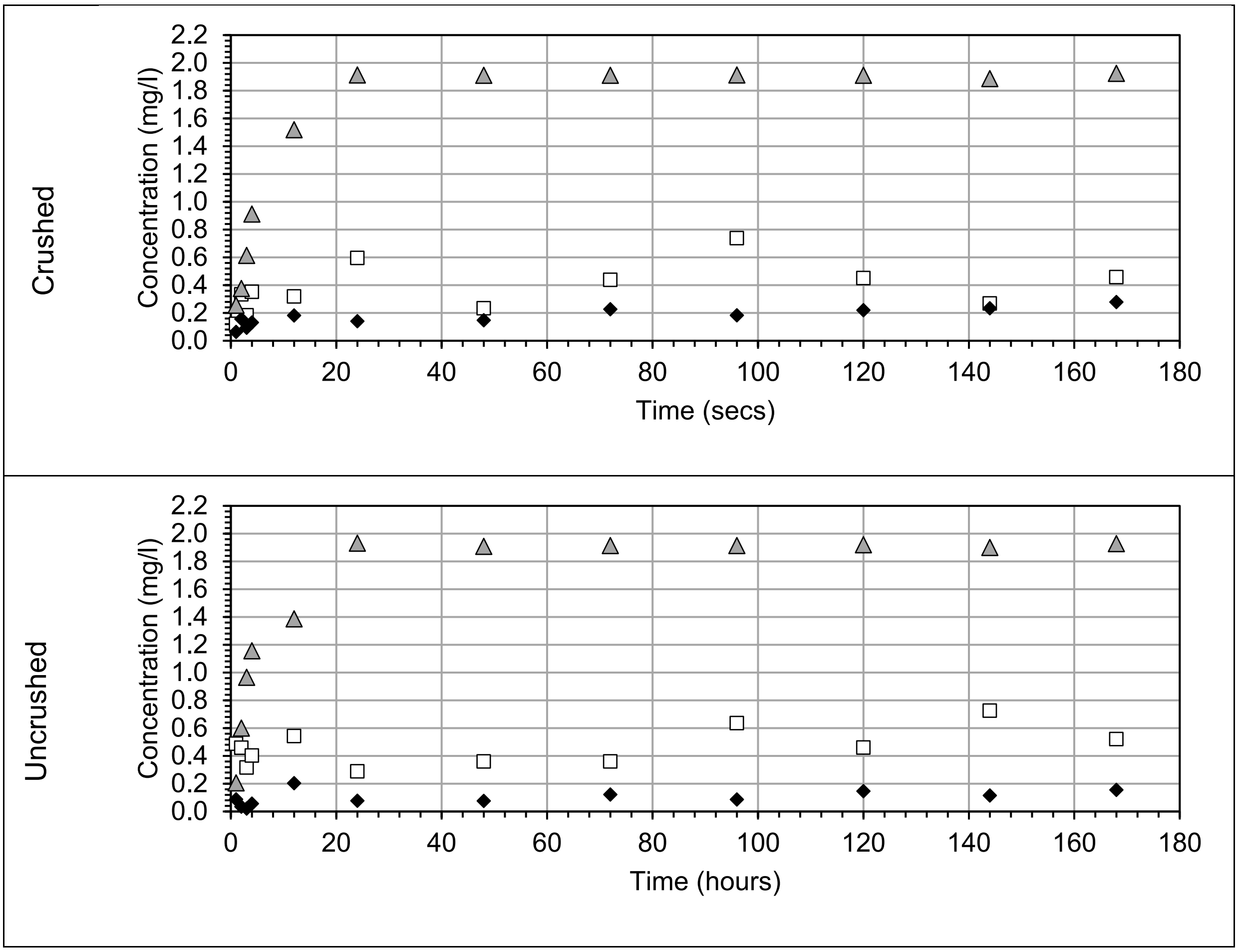


**Figure 31 Leaching of crushed and uncrushed Amoxis catalyst at ambient temperature with a solid to liquid ratio of 1:5 in aqua regia. □ = Pt, ◆ = Rh, △ = Co**

The aqua regia leaching of the crushed and uncrushed amoxis show the equilibrium occurs at the 24th hour (Figure 31). However, the Rh and Pt equilibrium does not seem to get reached with the crushed sample could show possible signs of preg-robbing, which can be seen with all the crushed amoxis runs. SEI4 shows what ratio of solid-to-liquid ratio gives the best leaches, after 24 hours, with ratios ranging from 1:1 to 1:5 (increasing the liquid amount in 0.5 increments) with Co only being shown in the solution that showed the lowest recovery. Similarly, to the uncrushed data shown in SEI4, the leaching of Co is at its highest of 0.401 mg/l with a 1:1 ratio and its lowest of 0.0301 mg/l at 1:5 ratio. As this work is trying to separate Rh and Pt from Co, the ratio chosen was that which one leached the lowest amount of Co.

### 3.2.2. ChCl: EG

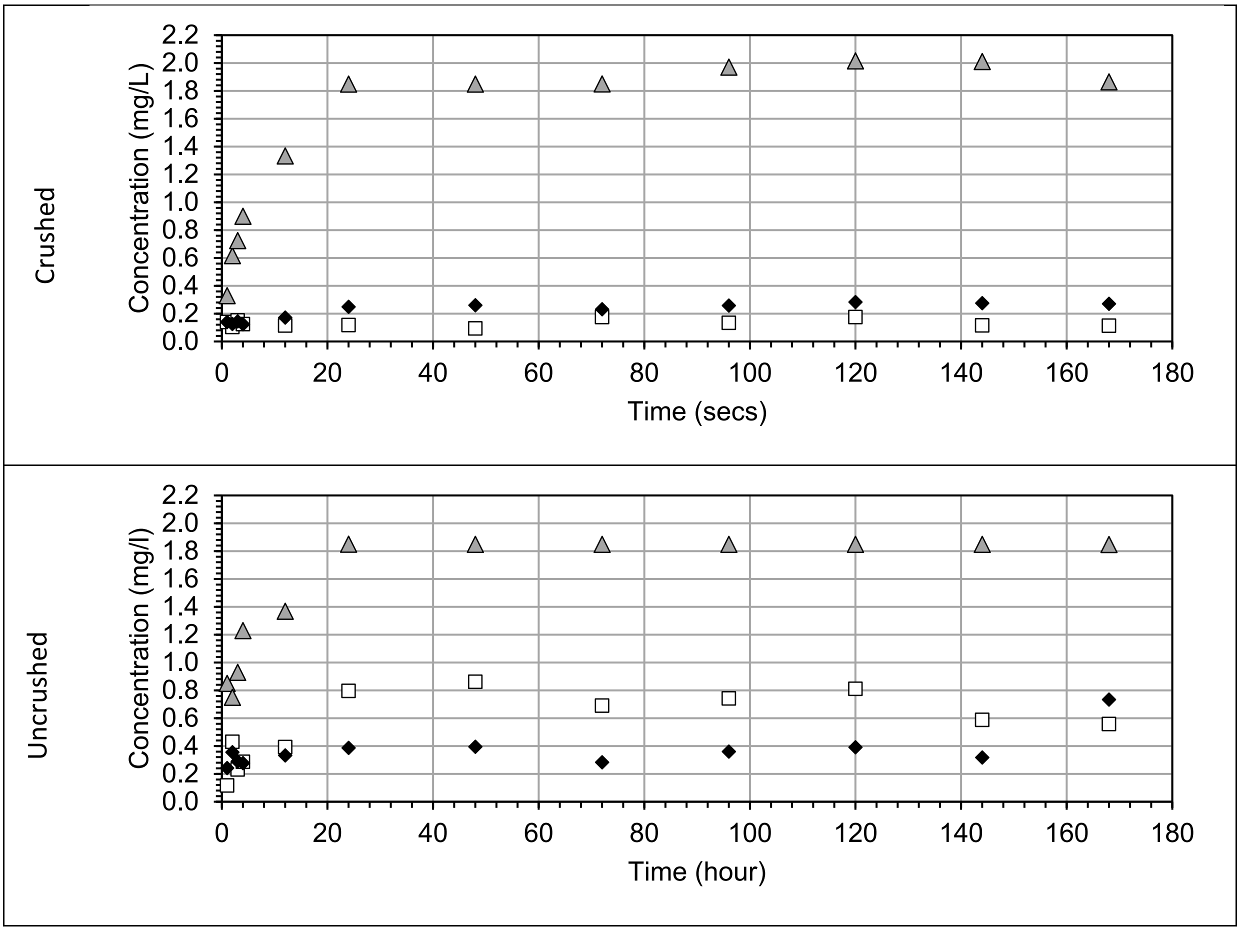


**Figure 32 Comparison of Amoxis leaching as a function of time at ambient temperature with solid to liquid ratio of 1:5 in ChCl: EG DES. ☐ = Pt, ◆ = Rh, △ = Co**

In the leaching of the Amoxis catalyst at ambient temperature in the EG DES (Figure 32) the cobalt leaching reaches a maximum value at 24 hrs. This can also be seen in the Pt and Rh data, except for the uncrushed sample, where the Rh solubilisation seems to increase at the end of the experiment timeframe. Interestingly, crushing has a more marked effect on the recovery of Pt than Rh with an overall reduction of leachability being observed for both metals. Crushing the Amoxis catalyst causes an approximate 50% reduction in Rh and a 75% reduction in Pt recovery at 48 hours.

### 3.2.3. ChCl: Lac

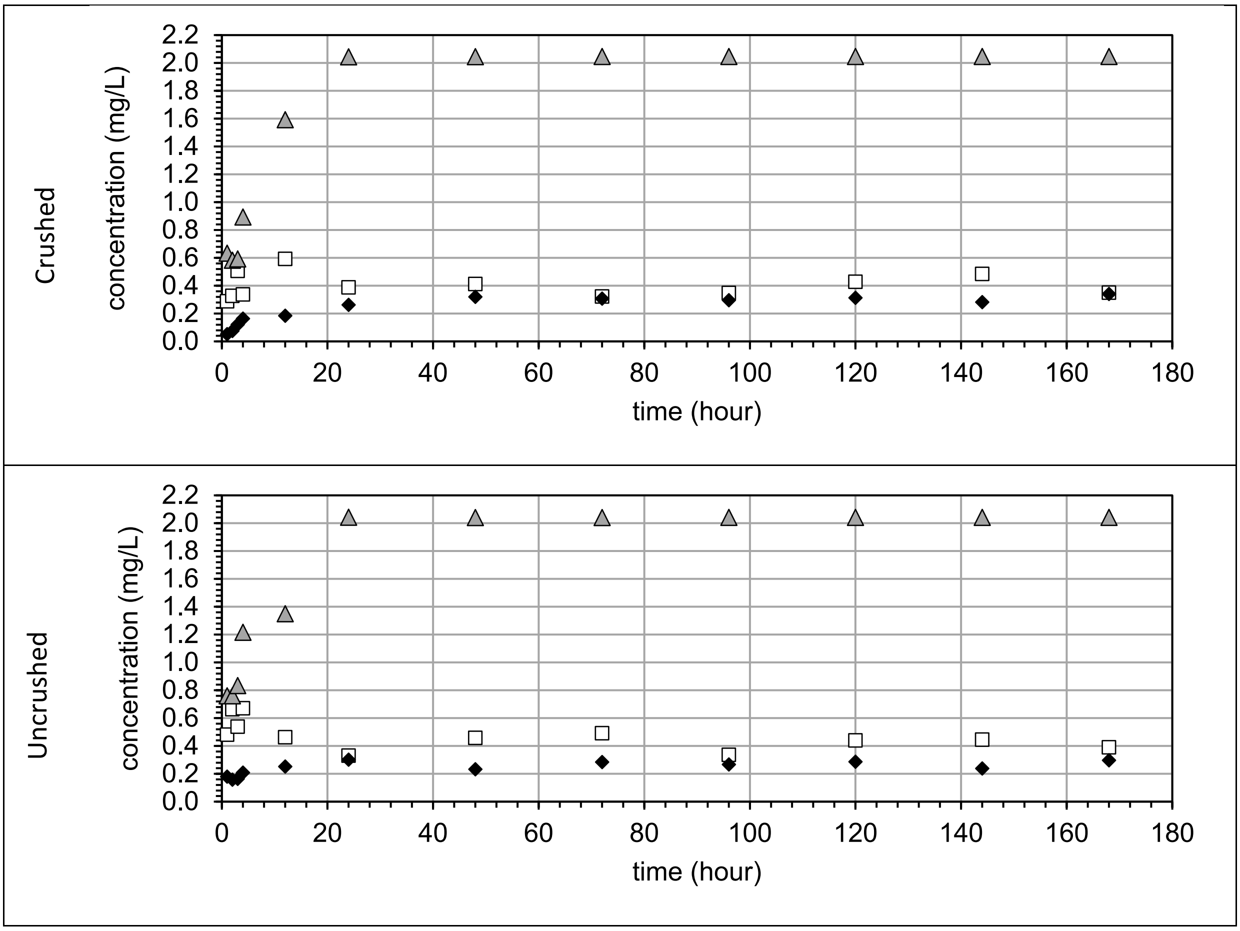


**Figure 33 Comparison of Amoxis leaching as a function of time at ambient temperature with solid to liquid ratio of 1:5 in ChCl: Lac DES. □ = Pt, ◆ = Rh, △ = Co**

The leaching of the amoxis spent catalyst is given in Figure 33. In these graphs we see lower recovery of Pt when compared with the other lixiviants investigated; interestingly, Pt data appear to reach a maximum of between 0.6 and 0.8 mg/L in the uncrushed system much more rapidly than ChCl: EG. As the leach continues on the Pt is reduced in solution which points to the surface of the catalyst reabsorbing Pt. The recovery of Rh using the uncrushed amoxis had the highest recovery out of all the lixiviants investigated in this work, at 25% shown in Table 19. Maximum recoveries of Rh for uncrushed and crushed samples in ChCl: Lac are 0.341 mg/l and 0.3 mg/l, respectively. Similar to the other lixiviants investigated Co reaches equilibrium at 24 hours with the recovery remaining at ~2 mg/L for both crushed and uncrushed data.

### 3.2.4. ChCl: Ur

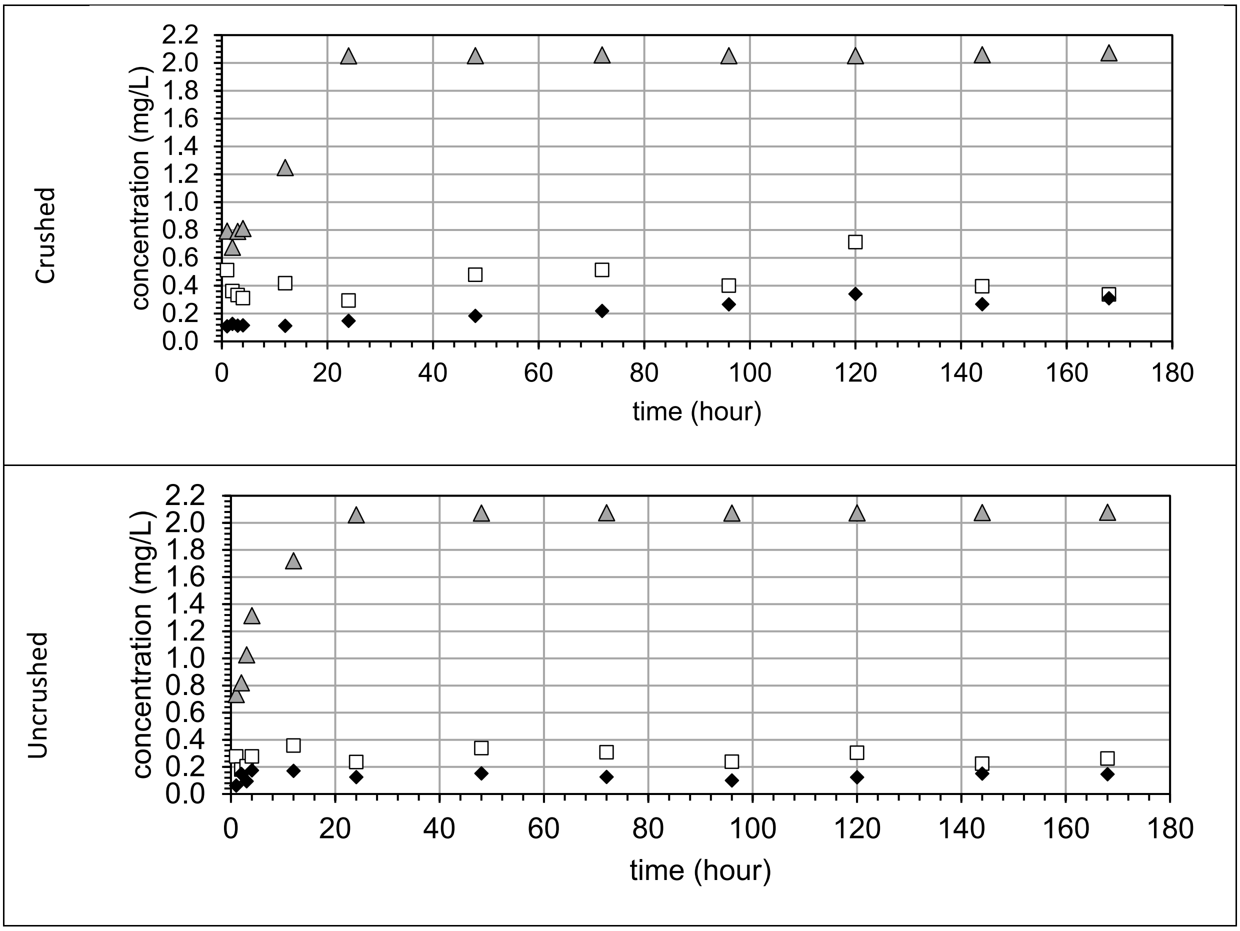


**Figure 34 Comparison of Amoxis leaching as a function of time at ambient temperatures with solid to liquid ratio of 1:5 in ChCl: Ur DES. □ = Pt, ◆ = Rh, △ = Co**

Leaching with the urea-based DES is shown in Figure 34 for both crushed and uncrushed spent Amoxis catalyst. Co leaching is comparable with the other DES systems with no apparent effect of crushing on the recovery. In this DES system crushing appears to increase the recovery of both Pt and Rh as would be expected. Similarly, to the other DES previously spoken about the reabsorption of the metals is shown again specifically with the crushed amoxis data. Despite this, it can be show that compared the other lixiviants ChCl: Ur the crushed amoxis data shows the second highest recovery of Rh. With the data also showing the second lowest recovery of Pt; with the Co showing the similar data to the other lixiviants previously discussed.

### 3.2.5. ChCl: TU

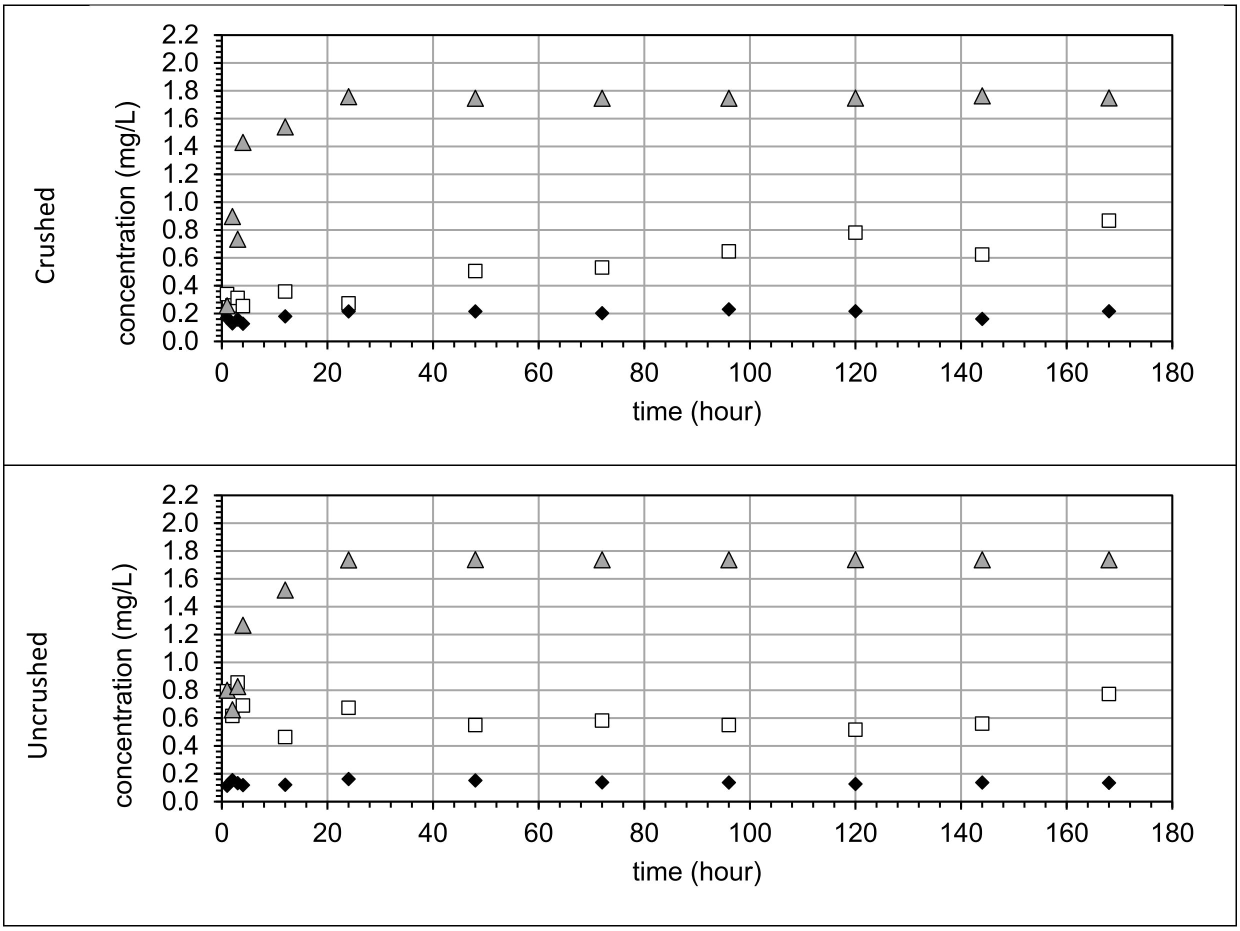


**Figure 35 Comparison of Amoxis leaching as a function of time at ambient temperature with solid to liquid ratio of 1:5 in ChCl: TU DES. ☐ = Pt, ◆ = Rh, △ = Co**

The DES using thiourea as the HBD in the leaching of the spent Amoxis catalyst is given in Figure 35. It can be seen that initial slope of the Co kinetic data is steeper than all the previous DES systems tested. Overall recovery of Co is lower than the other systems tested. It also appears that the Pt recovery is the highest of all the DES tested but the Rh recovery is comparable.

Both ChCl: TU and EG appear to have the highest affinity for leaching Pt compared the other lixiviants used with highest volume of Pt that was leached was at 48 hours at 0.86 and 0.862 mg/l, respectively. Compared to the uncrushed leach there is not as clear DES that leached the most Pt or Rh. With Pt both ChCl: Ur and ChCl: TU having similar values up to 120 hours, with ChCl: Ur highest leached concentration being 0.731 mg/l and ChCl: TU at 120 hours volume was 0.781 mg/l. Rh leach still shows that ChCl: Lac has a high affinity towards Rh but compared to the uncrushed Amoxis ChCl: Ur also shows affinity towards Rh with the highest leaching volume of

0.319 mg/l at 120 hours. Similarly, with the uncrushed Amoxis the Co leach they all have consistent leaching concentration with the highest being 2.05 mg/l with the ChCl: Ur DES the DES with the lowest affinity to Co is ChCl: TU with volumes of Co being ~1.75 mg/l. Figures 31- 35 show that leaching with the ChCl: lac and ChCl: Ur systems recovered the highest quantity of Rh and ChCl: TU recovered the highest quantity of Pt from the Amoxis. ICP-OES was run on the leached samples to determine the amount of Pt, Rh and Co in the leached solutions.

**Table 19 Percentage recovery of Rh, Pt and Co.**

| **Recovery %** | | Aqua Regia | ChCl: EG | ChCl: Lac | ChCl: Ur | ChCl: TU |
|---|---|---|---|---|---|---|
| Crushed | Co | 14.6±0.8 | 15.3±0.8 | 15.6±0.8 | 15.7+0.8 | 13.2+0.7 |
| | Pt | 12.4±0.6 | 14.5±0.7 | 8.14±0.4 | 9.13±0.5 | 14.4±0.8 |
| | Rh | 20.5±1.0 | 21.7±1.1 | 22.2±1.1 | 11.1±0.6 | 11.9±0.6 |
| Uncrushed | Co | 14.5±0.8 | 14.0±0.8 | 15.5±0.8 | 15.7±0.8 | 13.2±0.7 |
| | Pt | 12.2±0.6 | 11.4±0.6 | 8.27±0.4 | 12.0±0.6 | 14.6±0.8 |
| | Rh | 11.4±0.6 | 20.2±1.0 | 25.1±1.3 | 22.7±1.1 | 16.9±0.8 |

**Table 20 Half-life of Cobalt values uncrushed and crushed leaching experiments**

| **Lixiviant** | **Uncrushed (h)** | **Crushed (h)** |
|---|---|---|
| **Aqua-regia** | 14.9 | 16 |
| **ChCl: EG** | 42.8 | 19.3 |
| **ChCl: Lac** | 33.7 | 28.57 |
| **ChCl: TU** | 42.9 | 17.2 |
| **ChCl: Ur** | 32 | 34.9 |

The percentage recoveries of Rh, Pt and Co are shown in Table 19. All recoveries are low; however, ChCl: Lac, Ur and EG show the highest percentages for Rh solubilization, reaching 20%. The highest percentage recovery for Pt reaches 14.6% with ChCl: TU (uncrushed). The half-life of Co is shown in Table 20. Co was the only metal out of the three to be described as a half-life. Both crushed and uncrushed experiments, they show similar half-lives expect for the EG and TU DES unexpectantly. The half-lives show similar patterns between the lixiviants with the expectation of ChCl: Ur half-life. Aqua regia showing the half-lives out of all the lixiviants investigated at 14.9 and 16 hours for uncrushed and crushed.

The distribution coefficient calculated of Rh over Pt leach over time for all DES and aqua regia shows that crushed Rh and crushed Pt have higher distr. coeff. values which suggest that there are more bounds between the molecules and has a higher affinity to the DES shown in SEI5. SEI6 shows the separation factor of the highest volumes of Rh and Pt against Co, it shows that the separation factor of the uncrushed amoxis was able to separate the Rh and Pt successfully.

## 3.3. Addition of Oxidants to the DES System

Out of the two oxidants that were investigated $I_2$ showed the highest dissolution of Pt and Rh in the first 24 hours.

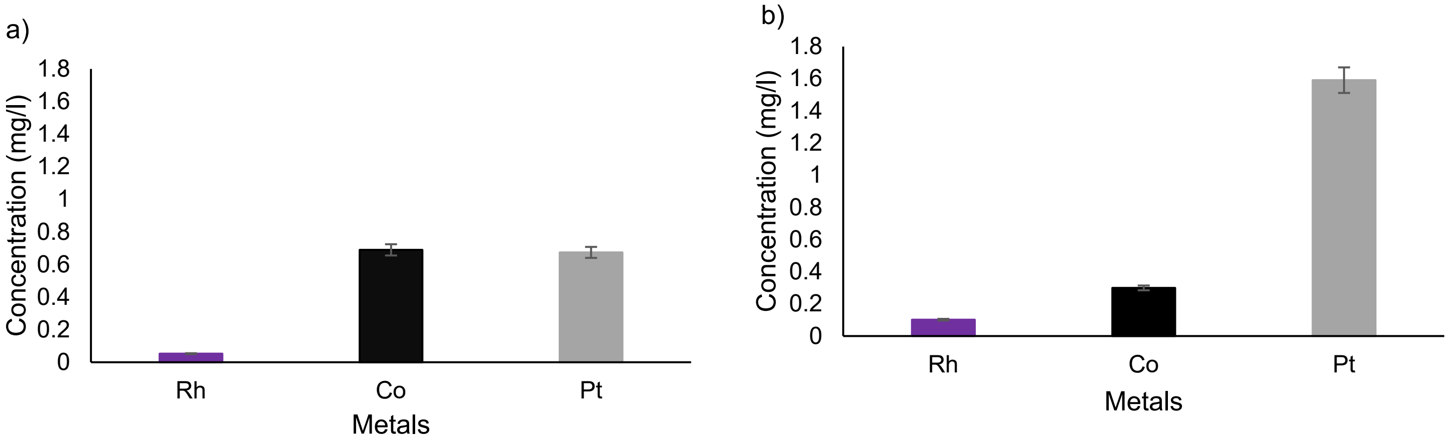


**Figure 36 24-hour leaching of Rh, Pt and Co *via* ChCl:Lac and oxidants a) $Na_2O_2$ b) $I_2$ Solid to liquid ratio of 1:5. Purple= Rh black= Co Grey= Pt**

Note: There was no leaching of ChCl:Lac and uncrushed amoxis for 24 hours at this moment; however, it was done at a later date stated in chapter 7.

The addition of $Na_2O_2$ and $I_2$ to the ChCl: Lac and uncrushed amoxis system is shown in Figure 36; with concentrations of 25% and 0.33%, respectively. When $Na_2O_2$ was added (Figure 36a), quantity of Pt and Co leached was similar, while Rh leaching was very low at 0.05mg/l. When $I_2$ was added (Figure 36b), Co and Pt no longer showed similar concentrations. Rather, Pt shows a significantly higher concentration after 24 hours of 1.59 mg/l as compared to Co and Rh with 0.29 mg/l and 0.10 mg/l, respectively. The performance of leaching Rh was remarkably similar in $I_2$ as $Na_2O_2$.

### 3.4. Kinetic Modelling of DES Systems in Comparison with Aqua Regia Leaching.

The shrinking-core models were used to describe the mechanism and interactions of the data sets. The parameters of each model are shown in Table 21 and the figures of the models are shown in SEI7-SE9.

**Table 21 Calculated Parameter for fitting models used for the leaching of Rh, Pt and Co using DES**

| Shrinking core Model Kinetic Model $R^2$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Lixiviant** | **Mixed-control** | | | **Reaction-controlled** | | | **Diffusion-controlled** | | |
| | **Co** | **Rh** | **Pt** | **Co** | **Rh** | **Pt** | **Co** | **Rh** | **Pt** |
| Aqua-Regia | 0.52 | 0.18 | 0.30 | 0.50 | 0.24 | 0.30 | 0.59 | 0.02 | 0.31 |
| ChCl: EG | 0.56 | 0.28 | 0.25 | 0.55 | 0.06 | 0.28 | 0.59 | 0.02 | 0.12 |
| ChCl: Lac | 0.58 | 0.26 | 0.29 | 0.57 | 0.27 | 0.28 | 0.60 | 0.13 | 0.29 |
| ChCl: TU | 0.49 | 0.00 | 0.05 | 0.47 | 0.00 | 0.05 | 0.54 | 0.00 | 0.06 |
| ChCl: Ur | 0.54 | 0.00 | 0.00 | 0.52 | 0.01 | 0.00 | 0.60 | 0.00 | 0.00 |

The shrinking core models shown in SEI7-9. When all three models were fit, the Mixed-control model were only able to fit Co the best, with many of the coefficient of determination ($R_2$) values being determined to be zero for Rh and Pt Table 21. Many of the $R_2$ values for Rh and Pt using the reaction-controlled and diffusion-controlled models were zero.

# 4. Discussion

### 4.1. Amoxis characterisation

From the different solid-state analysis run of the amoxis it confirms the percentages that RSBruce$^{TM}$ had estimated prior to the start of the experimental of 18.6% Co, 0.16% Pt and 0.05% Rh, with remainder being alumina. The XRD survey scans of the amoxis samples gave insight into the amount of Rh, Pt and Co for both crushed and uncrushed samples. The ICP-OES and XPS analysis (Figure 28 and Table 17 respectively) show the differences in amounts of Rh, Pt and Co from the crushed and uncrushed samples as a similar trend were seen between the two characterisation techniques. However, the XRD spectra shown in Figure 30 was unable to detect either metal on either the crushed or uncrushed amoxis; it can be assumed that the amounts of Rh was too low to pick up which matches the amounts detected in ICP-OES and XPS. Compared to Pt electrocatalyst supported on a multiwalled carbon nanotubes investigated by Zhi et al and Pt-based fuel cell catalyst material by Rees et al. There are various similarities to the amoxis characterisation; XRD data with the Pt and C that were analysed are the same peaks of 39-400 and 600 (329; 330). With the XPS of Pt shown in the literature showing similar peaks of 70-80 eV (329).

The RAMAN data (Figure 29) also confirms the low concentrations of Co, Pt and Rh that were given by RSBruce$^{TM}$. With literature showing similar peaks in $Pt_2$, $Pt_3$ and $Pt_4$ with all three being in the range of 200-250cm$^{-1}$, $Pt_3$ peaks being represented at ~150cm$^{-1}$ and ~225cm$^{-1}$ $Pt_4$ having peaks at ~50cm$^{-1}$ and 150-210cm$^{-1}$ (326). Literature by Ravindra support assumption of the peak at 463cm$^{-1}$ is that of CoO with CoO nanoparticles showing peaks at 447-687cm$^{-1}$ (327). The RAMAN spectra for crushed and uncrushed samples show that the carbon is present at 1378cm$^{-1}$, literature by Dychalska *et al* investigated amorphous carbon which showed that the D-band carbon is a single sharp line at 1332cm$^{-1}$ and G-band carbon was represent 1575cm$^{-1}$ (328). The peak for Pt-Co is supported by literature by Demirkan *et al*. investigations  bimetallic platinum-cobalt alloys nanoparticles (331). Characterisation of the platinum-cobalt alloys nanoparticles *via* RAMAN determined peaks between 1349 – 1577cm$^{-1}$ (331). From literature that both the carbon and Pt-Co peaks are in a similar range which makes it hard to determine which peaks are which. With currently no literature of a C-Pt-Co the cluster of peaks cannot be determined. Additionally, there is limited information on which band of carbon is used for the amoxis. Additionally, the peaks in both spectra are both fairly board, this can be explained by the amoxis being an amorphous material which is often unable to give accurate characterisation of heterogenous catalysts in which the active phase is a properly prepared surface (332). However, it can be seen that the crushed spectra has a higher intensity compared to the uncrushed sample, this could be because the particles are smaller therefore better packed, so the instrument can detect more of the sample (333).

However, the spectra was unable to determine any new information that was not already shown by the FT-IR or XPS. Both FT-IR spectras (Figure 28) only show the

$Al_2O_3$ and the C-O bonds. $Al_2O_3$ both γ and α and γ-AlOOH were investigated in literature for dechlorinating of propachlor through substitution by dithionite on an Alumina surface (334). In the literature by Liu et al it showed that all three Al complexes showed peaks between 465 – 760 $cm^{-1}$ (334). The C-O bonds were determined to be at the peaks 1027-1150$cm^{-1}$ for the crushed and 1260-1275$cm^{-1}$ for the uncrushed amoxis due to literature by Kristianto *et al* that investigated the effect of activated carbon support surface modification on carbon nanospheres (335). The activated carbon investigated showed peaks at 1100-1300$cm^{-1}$ that represent the C-O stretching (335). However, it can be seen that between the crushed and uncrushed amoxis the stretches vary; there are many potential reasonings for this. The chemical structure change on a molecular or unit cell level, polarisation of matter by light, influence of the refractive index on spectra, wave nature of light and interference effects and anisotropy and the continuity relations of the electric field at interfaces (336).

The RAMAN and XRD spectra confirm the other compounds and elements that are present in or on the catalyst that was not identified by the FT-IR, XPS or ICP-OES. With the presence of cobalt-platinum being seen in spectras. Additionally, XRD was the only analytical technique that was able to identify very low levels (<1%) of the substrate which is $N_2O$ in the crushed sample.

## 4.2. Comparison of DES Used with Literature.

All four of the DES and aqua regia investigated have relatively low recovery rates of both Rh and Pt. This could be due to the lack of an oxidant that has been used in the experiment. An oxidant was initially not added during this research to determine how well the DES itself was good at dissolving the metals with the addition of an chemicals that would reduce the environmental sustainability of this method if used on an industrial scale.

ChCl: EG is the most researched and used DES currently; however, there is limited research into its affinity towards PMs. The data collected in section 3, and the from Table 14 confirms that ChCl: EG a low affinity towards Pt and Rh (Table 14) uncrushed and crushed amoxis with the recovery rates being 12.3%, 20.2% and 14.5% and 21.65% respectively. When compared to literature shown in Table 13 Rh and Pt leached *via* an ammonium chloride ($NH_4Cl$) in a EG system a low extraction percentage (185). It can be shown for the recovery of Rh and Pt with EG DES the MoMO catalyst being crushed or uncrushed has minimal effect with the uncrushed sample doing slightly better.

ChCl: Ur has not previously been used for precious metal recovery; urea has been used researched into palladium electrochemistry the possible complex formation being shown in Equations 26 and 27 (187).
$Pt + NH_2CONH_2 \rightarrow Pt\text{-}NH\text{-}CONH_2 + H^+$ 28
$Rh + NH_2CONH_2 \rightarrow Rh\text{-}NH\text{-}CONH_2 + H^+$ 29

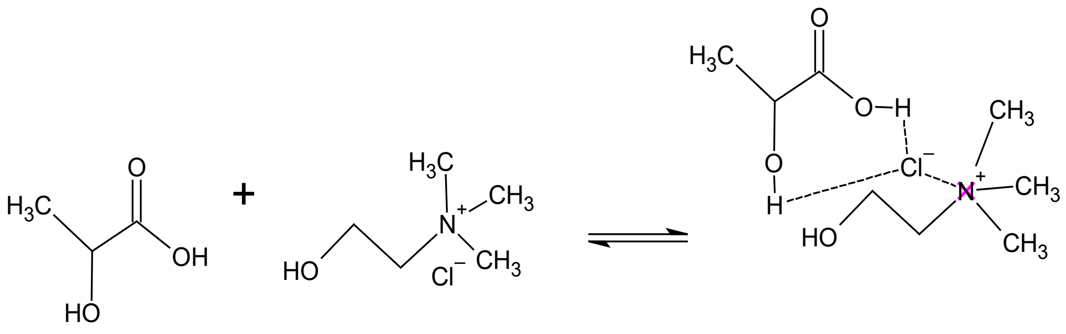
Urea is a well-known chemical that is used for leaching due to high affinity to PMs, gold and silver. However, this DES system has extremely limited research into its affinity towards PMs. Despite that literature of urea in a chloride system has shown affinity to PMs, specifically Pt, with the very high yield of Pt recovered from urea in different concentrations of HCl, shown in Table 14 (309). This higher recovery rate of Rh and Pt is shown in the crushed sample with a recovery rate of 22.7% and 12%, respectively. Equations 29 and 30 both metals form stable complexes with urea; however, with the limited literature it cannot be assumed it is the urea is the driving force of the of the leaching.

Additionally, ChCl: TU DES has yet been investigated in the leaching of precious metals from waste or metal ores, but it is widely known that thiourea has affinity towards the PMs group with the possible complexes of Rh and Pt with TU being shown in Equations 28 and 29 where the Fe in both equations are about of the other half of the REDOX couple (188; 189).

$2Pt + 2Cs(NH_2)_2 + Fe^{3+} \rightarrow 2[PtCS(NH_2)_2]^+ + Fe^{2+}$ 30
$2Rh + 2Cs(NH_2)_2 + Fe^{3+} \rightarrow 2[RhCS(NH_2)_2]^+ + Fe^{2+}$ 29

Similarly, with the ChCl: Ur DES there has proven affinity of the HBD, thiourea, affinity towards the PMs but limited research into the DES complex containing thiourea. However, it has been shown that thiourea has affinity to three of the metals in the PMs group, Rh, ruthenium (Ru) and iridium (Ir), and Rh had recovery rates of >85% shown in Table 14 (311). Overall, it has shown that thiourea has a high affinity towards all PMs with literature stating that in a study with thiourea solutions and platinum group metals (PGMs) that approximately 95% of PGMs were recovered (337). Which when compared to the percentage recovered of Rh and Pt leached from ChCl: TU with recovery rates of 16.9% and 14.6% respectively for the crushed amoxis and 11.9% and 14.4% for the uncrushed amoxis, respectively. The differences in results could a number of factors from temperature to pressure to thiourea not being the component that is chemical the PMs would react and bind with.

ChCl: Lac DES has yet to be investigated in the recovery or leaching of PGMs. Lactic acid has previously been investigated for copper leaching, literature stating with increased concentration there is promising data for lactic acid to be used for copper leaching from malachite (338). Unlike urea and thiourea there is currently no research into lactic acid leaching of Rh and Pt. Despite that DES ChCl: Lac produced the highest amount Rh leach of the leach from all the DES in both the uncrushed and crushed Amoxis with recovery rates of 22% and 25%, respectively. This could be due to Lactic acid is prone to degradation in 24 hours and can deprotonate quickly, which could aid in the binding of the PMs as the DES compound would already deprotonate (339). However, with the current assumptions that the main bonding between HBA and HBD for DES is H-bonding (340). The H-bonding could potentially stop the deprotonation. The relative weakness of the interactions could allow the HBD to be deprotonated easily and form complexes with the solubilised metal. That could be due to the predicted equation of ChCl + lactic acid bonding together, shown in (equation 30). This could explain the high recovery rates that is shown with Rh with ChCl: Lac ad ChCl: EG. The -OH groups on these molecules would not be as good H-bonds as the $NH_2$ groups on U and TU, so dissociation of the H-bonds would be favourable.



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The Pt solubilisation seems to be more dependent of affinity with the softer base ligands (TU).

## 4.3. Comparison of Lixiviants and Metal Recovery.

The lixiviants that showed the highest affinity towards Rh were ChCl: Lac, followed by ChCl: EG and ChCl: Ur. The lixiviants that were determined to have the highest affinity towards Pt were ChCl: TU, followed by ChCl: EG, with error values of 1-2% when a triplet was run from ICP-OES analysis and volume error of the 1ml being ±0.05ml. However, there is no clear findings that crushing the amoxis improved or negatively affected the dissolution of Co, Pt or Rh, despite the data of the crushed amoxis possibly showing signs of the preg-robbing effect compared to the uncrushed amoxis.

Comparing the data from the DES to the aqua-regia leach it be seen that all the DES shown for this experimental have a higher recovery with the concentration of aqua regia being ~70% and the concentration of ChCl being 70 – 75 % the two systems share a similar level of concentration the major difference between the aqua regia and DES are the pH with aqua regia being 1 and the DES being between 6 and 7. Despite using concentrated aqua-regia lower recovery rates are shown compared to thiourea and urea, which are also already being used in industry, with one study Pt, palladium (Pd) and Rh having percentage recoveries of 66.9%, 63.9% and 41% at 80°C after 180 minutes (309). This shows that the leaching of Pt and Rh does not rely on acidity which suggests it is the formation of stable complex ion that is important to the leaching process. This could be due the chloride species and the complexes formed with Rh and Pt; however, it cannot be a definitive answer on the complex that is formed with the metals.

The results determined what all four DES perform better then AQ shows that metal complexation is a key factor in solubility with diol-based DES with $Cl^-$ anion dominates the metal speciation and the thiol-group DES can improve physical properties of ChCl based DESs and improve solubilities of late transition metals which could be attributed to the ligand structure and enhanced media acidity (314; 317).

Furthermore, what can be seen in both the crushed and uncrushed amoxis is the steady leach of Co from the amoxis which seems to reach equilibrium after 24 hours with all the DES and aqua-regia being 1.7-2 mg for Co between 24-186 hours with a recovery rate of between 13-16% for both the crushed and uncrushed amoxis. The consistent lower recovery of Co can lead to a recovery noble earth metals from ferromagnetic metals can be mostly left in on the MoMO spent catalyst. This can be concluded that DES has a low affinity towards Co where the maximum absorption is reached quickly. As of yet, out of the four DES used in the experimental only, ChCl: Ur DES has been used in researching Co recovery, where 90% of the cobalt was leached out from Lithium-ion batteries which was reached between 18 and 24 hours (341; 342). However, there is currently no research into how Co could affect Rh and Pt leaching and vice versa; however, as Co has a higher reactivity compared to Rh and Pt it can be assumed that in any recovery system Co will have a higher recovery rate then Pt and Rh as Co would more likely bond with any reagent in the system.

What is interesting is the differences between the leaching efficiencies of Rh and Pt can be compared to literature where Pt has a higher leaching efficiency then Rh (343). Literature states that in a Rh was extracted less efficiency compared to Pt and Pd, with assumptions that Rh co-extraction efficiency of Rh(III) reduced by working at non-equilibrium conditions (344). Despite that, the recovery rate determined that Rh has a higher recovery rate then Pt it can be assumed that the reaction between the DES and the MoMO works in an equilibrium condition. However, there is currently no literature on Rh and Pt separation from Co but there is literature based on palladium (Pd) and gold (Au) from iron (Fe) in $Cl^-$ and bromide ($Br^-$) systems (344). Literature has found that when separating Au and Pd from Fe there was an efficiency in the both a $Cl^-$ and $Br^-$ system with $Br^-$ being the preferred system (344).

Literature supports the data seen in section 3 taking into account the differences in amounts of Co to Pt to Rh on the amoxis, also increasingly confirms the current assumption that the halide is the driving force of the leaching in the DES. Additionally, the interaction between the PMs and the DES is that due to PMs needing to be oxidised in order to be able form a complex with the DES which will mostly likely a binding of the $Cl^-$. The oxidisation of Rh and Pt which will then be able to be leached out, which has been shown with the $E^0$ of Pt and Rh chloride complex formation is -0.73, -0.68 and -0.44 V respectively which supports the equations shown in section 4.2. However, it should be noted that it is not clear from this work whether leaching relies on an oxidation mechanism. In fact, the leaching is superior in non-oxidising conditions (DES) vs the oxidising conditions of aqua regia.

$$\mathbf{Pt_{(s)} + 4Cl^- \rightleftharpoons PtCl_4^{2-} + 2e^-} \tag{31}$$

$$\mathbf{PtCl_4^{2-} + 2Cl^- \rightleftharpoons \boldsymbol{PtCl_6^{2-}} + 2e^-} \tag{32}$$

$$\mathbf{Rh_{(s)} + 6Cl^- \rightleftharpoons RhCl_6^{3-} + 3e^-} \tag{33}$$

The complexes that are expected to be formed are chloride complexes. Due to the high stability of the Rh and Pt chloride complexes formed are stable. $PtCl_6^{2-}$ is the most stable out of the two chloride complexes that are most likely to be formed during this reaction with $\beta_6$ being calculated at 33.9 (345; 346). Literature has stated that out of the Rh chloride complexes $RhCl_6^{3-}$ is most likely to dominate in chloride complexes compared to other chloride complexes such as $RhCl^{4-}$ and $RhCl_5(H_2O)^{2-}$ with the $\beta_1$, $\beta_2$, $\beta_3$, $\beta_4$ and $\beta_5$ being calculated as 2.62, 4.38, 5.94, 7.42 and 8.79 respectively with $RhCl_6^{3-}$ having the stability constant of $\beta_5$ with $RhCl^{4-}$ and $RhCl_5(H_2O)^{2-}$ not being determined alone (347).

Despite currently being able to determine the complexes that are formed is not available, previous literature has given evidence into which complexes are formed in the DES system. DES, ChCl: EG, redox behaviour was investigated by Lloyd *et al* using $Cu^{2+}/Cu^+$ (348). They investigated the reversible behaviour of the $Cu^{2+}/Cu^+$ couple (348). It was shown somewhat true with limiting measurements, however, it was determined that DES worked comparably to chloroaluminates and modern ionic liquids, with Cu often being researched along-side gold, silver and platinum, insight into how Cu interact with DES can give us insight into the REDOX behaviour that could occur between DES, Rh and Pt (348). The excess amount of $Cl^-$ implied that a high degree of dissociation of the ChCl (348).

Additionally, another assumption into why the ChCl: TU has an affinity towards to Pt and the ChCl: Lac as an affinity towards Rh could be due to the mixed-ligand complex that is formed. This may occur due to both the Rh and Pt complexes that could possibly be formed in the DES systems. Pt is a softer metal compared to Rh which can explain why TU and U, softer bases, are preferred over the Lac system.

As the ratio for TU and U DES system are significantly different of that of EG and Lac DES system, TU and U HBA: HBD ratio have excess ChCl. This could possibly lead to the Pt more readily bonded with the softer bases of TU and U in comparison to the Lac and EG systems. However, there is currently no literature that can explained why the EG system also has high affinity towards Pt. Literature has stated when aiming to extract Averrhoa bilmbi pectin (ABP) with DES ChCl: critic acid monohydrate at different ratios in an alkali and water solutions showed when the ChCl was in excess, bigger branch sizes and low linearity, the extraction of the AMP was at its lowest (349). This was because the bigger branches make it harder for the water and alkaline solution to attach to the pectin backbone (349).

The differences between the crushed and uncrushed leaching was benign; however, when a sample is crushed for leaching, the fraction of leachable species that is accessible to the solvent; which is not seen is this work. It can be assumed the reason the crushed samples do not show any major differences between the recovery rates could be due to preg-robbing phenomenon. When the particle size became too small; the finer particles meant that the surface area increased are inherently, where the favourable metals are readsorbed onto the particles. Preg-robbing is mainly seen in the cyanidation of gold when the gold complex formed ($Au(CN)_2^-$) is removed from solution by the ore (350). This occurs when the ore contains active carbon that absorb the gold from the pregnant solution (351). This occurrence seen in section 3 could be examined by the RAMAN spectra with the carbon peaks being similar to those of graphite, with a high percentage of both samples of amoxis being made up of carbon (Table 17) it is very possible that the carbon from the amoxis readsorbed the PGMs.

Another assumption could be as ChCl: EG has high surface tension, leading to weak intermolecular forces, the weaker intermolecular forces could more readily bind with the Rh or Pt. Additionally, it can only be assumptions in the reason the crushed samples does not show any major differences between the recovery rates. One of those assumptions could be due to preg-robbing phenomenon when the particle size became too small; the finer particles meant that the surface area increased are inherently, where the favourable metals are readsorbed onto the particles.

With limited developments into industrial uses of PM recovery from waste expect and low recovery yields of this research the main improvements using this current DES system instead of using highly concentrated acids or hazardous reagents such as cyanide and aqua regia are that less hazardous by-products are formed during this process and compared with the use of aqua regia that often needs a catalyst to speed up the reaction. The addition of the oxidants which acted like a catalyst for the DES systems decreased the recovery amount across all DES investigated (313).

Additionally, the reusability of the DES system has been investigated and determined that the efficiency of using recycled DES did not significantly decrease (352). With the recycling method research by Yan et al involving the addition of biomass and heating to 80°C (352). The decrease was minimal from 72.83% and 68.83% for glucan digestibility and glucose recovery using ChCl: oxalic acid (OX) then after using the same recycled DES system it decreased to 66.23% and 64.43% (352). In comparison, to the reusability of aqua regia is no viable with either adding an extreme amount of the nitric acid to get back the original or just making a new batch of aqua regia required to ensure that toxic gases do not form when stored for another use (353).

## 4.4. Addition of Oxidants.

Comparing leaching experiments, it is clear that the addition of $I_2$ has a significant impact on solubilisation of Pt. However, in all other cases, there was no significant difference in solubilisation compared to the same DES system without additional oxidant.

There have been very few investigations into DES and the addition of $I_2$ nor has there yet to be in literature on DES and $Na_2O_2$ as an oxidising agent. Despite both the reduction potentials being positive from the data shown in section 3.3, the addition of oxidants has not aided in the reaction between the PGMs and DES. The reduction potential only predicts the reaction possibilities and not the rate of reaction. The reduction of Pt ($Pt^{2+} + 2e^- \rightleftharpoons Pt(s)$) is +1.2V and $Rh^{3+} + 3e^- \rightleftharpoons Rh(s)$ is +0.8V, with these potentials are lower than the $I_2$ but higher then $Na_2O_2$ which explains why the dissolution of Rh, Pt and Co are higher using $I_2$ and $Na_2O_2$.

Jenkin et al investigated the addition of $I_2$ into the leaching *via* electrolysis of gold (Au) and other minerals from gold ores (183). This work showed that a common feature amongst the mineral structures investigated pyrite, sperrylite, ditellurides, calaverite and moncheite they may be resistant to iodine oxidation (183). The recovery of platinum group metals via potassium iodide (KI) was investigated (153). It was shown that the combination of concentrated aqua regia and KI extracted 98.7% and 96.7% for untested and end-of-life Pt (153). Despite the high recovery of Pt that was determined it can be attributed to the aqua regia more than the KI; it was determined that with the increasing concentration of KI resulted in minor improvements, with mass removed of Pt electrode with 5 mM and 15 mM being 158.2 μg and 278.8 μg respectively (153). There is limited research into $I_2$ and Rh; however, there are two patents from the 1970s and 1990s that involved the use of methyl iodide and hydrogen iodide in terms of regeneration and recovery of Rh from spent catalytic solution (354; 355). Despite these two patents showing high recovery yields/regeneration of Rh these methods involved other reagents such as water, acetic acid and metallic corrosion products and water and methyl acetate (354; 355). However, there is currently no literature describing the mechanism that is involved into the mythologies used in either patent.

There is currently no literature investigating DES and $Na_2O_2$ interaction in extraction of metals. However, literature has shown in the presence of other metals such as iron and nickel $Na_2O_2$ has no affinity towards Pt (356). In other literature it was shown with the combination of scandium (Sc) with $Na_2O_2$ which corrected the ion special interferences achieved recovery rates of 110%, 100% and 103% for Rh, Pt and Pd respectively (357). This difference between recovery rates can be assumed to be caused by the lack of competing metals that may more readily interact with $Na_2O_2$, and the introduction of Sc acted as an internal standard compensated effectively for the spectral interference (357).

There currently been no research that compares the recovery of Pt and Co, however; Hahn and Sanders investigated different methods for separating group III cation *via* various reagents including sodium hydroxide, hydrogen peroxide ($H_2O_2$), $Na_2O_2$, ammonium hydroxide and ammonium benzoate (358). $H_2O_2$ and $Na_2O_2$ with recovery rate of Co being determined at 98.6% (358). However, the poorest separations attained was by the use of $Na_2O_2$ alongside with other oxidants, no discussion in attempts to describe the mechanism was given (358). Comparing this to the data shown in section 3.2 the addition of $I_2$ resulted in higher extraction compared to no oxidate being added with extraction of Rh and Pt via $I_2$ being 0.1 mg/l and 0.1.59 mg/l compared with the extraction of Rh and Pt without oxidant at 0.055mg/l and 0.019 mg/l. In comparison with $I_2$, $Na_2O_2$ extracted a lower amount of Rh and Pt at 0.05 mg/l and 0.67 mg/l.

## 4.5. Kinetic Modelling and Parameters

Determining which order the reactions fits is imperative for understanding the interactions between the metals and lixiviants with modelling fits showing both reactants participate in the reaction. This finding matches the current literature that has shown a range of different DES, including EG and U, show a high chemisorption capacity (359). A reason to why the Rh and Pt was harder to fit the models compared to Co, could be because of the possible preg-robbing that causes the Rh and Pt complexes formed are removed from solution by the constituents of the ore.

From all the shrinking models that were fitted to the data sets of all three models only the mixed-controlled model, specifically with Co. With only Co only poorly being able to fit to the mixed-controlled model it seems likely that none of the shrinking core models will describe the leaching very well. This can be seen in SEI7 where rather than a gradual leaching process, there is a long period where nothing much happens, then a big jump in [Co]. Similarly with the other metals and models there is no gradual increase with many having a straight trendline. This can be explained by the limitations that are associated with using a shrinking core model. The inherent limitations of using the shrinking core model is when the material investigated is a porous particles (360). The shrinking core model is only valid when the reaction is controlled by inward diffusion where the reaction proceeds with the amoxis structure, and the chemical reaction is irreversible (360). Additionally, it could likely that the possible preg-robbing and equilibrium of the metal complexes formed are more of a significant factor which are not accounted for by the shrinking core model.

The separation and distribution coefficient (distr. coeff.) values are fairly similar between all the lixiviants investigated. The distr. coeff. calculated of Rh over Pt leach over time for all DES and aqua regia shows that uncrushed Rh and uncrushed Pt have higher distr. coeff. values. This suggests that there is more Rh and Pt present in the DES phase compared to the solid phase with value ranges between 7 and 20 with ChCl: Lac, U and TU having the lowest values. This could mean that there are more bounds between the molecules and has a higher affinity to the DES shown in SEI5 (361).

SEI6 shows the separation factor of the highest volumes of Rh and Pt against Co, it shows that the separation factor of the uncrushed amoxis was the system that was able to separate the Rh and Pt successfully with the crushed amoxis having significantly lower distribution coefficient (362). SEI6 shows that all the DES that have been used have similar values in comparison to the distr. coeff. of aqua-regia. Which could be due to the assumed binding points of the DES with the $Cl^-$ interacting with the PMs compared to the aqua-regia where both the nitric acid ($HNO_3$) and hydrochloric acid (HCl) react with the PMs separately (363). Distr. coeff. values for the uncrushed amoxis are lower for both Rh and Pt. The crushed amoxis having a slightly higher distr. coeff. values for both Rh and Pt it can be assumed that increasing the surface area, may not greatly improve the leaching from a MoMO catalyst; this could be due to the increased surface area (364). This can be seen in literature; catalyst material surface area was increased from ~8 mesh to ~65 mesh there was no significant benefit to the reaction (364). Despite the distr. coeff. value increases it is only slightly, and recovery is not significantly better this could be due to preg-robbing which was spoken about in section 4.3.

However, it can be seen with Rh the differences between the distr. coeff. is noticeably more similar compared to the Pt, also Rh Kd values are higher than Pt, this is currently no explanation for this in literature; however, the metals ability to react with $Cl^-$ could be an explanation. As Pt can react with $Cl^-$ at raised temperature, compared to Rh can react easier with chloride to form the aqueous complex $2RhCl_3$ the ease for Rh to react with $Cl^-$, and in turn there could be more bonds being formed during the weeklong leach with there being a specification change of the one chloride complex turning into more chloride ligands (365; 366).

The half-life reactions of the critical metals were only able to be applied to Co as the data of Rh and Pt with all the lixiviants fluctuate. Half-life in conjunction with concentration can give insight into the order of reactions that are occurring during the reaction. With the data shown in section 3.4, there are multiple interactions involved with two of the variants of the shrinking-core model, mixed-control and reaction controlled, being able to fit to some of the data sets provided. This can also be seen with the half-lives with aqua regia (crushed and uncrushed), ChCl: EG and ChCl: TU (crushed). With the remaining lixiviants having half-lives roughly double that of aqua regia and ChCl: EG and ChCl: TU (crushed) it can be assumed that the aqua regia and ChCl: EG and ChCl: TU (crushed) have diffusion reaction being the leading interaction and the other showing signs of a prominent REDOX reaction (367).

# 5. Conclusions and Recommendations

The leaching efficiencies of DES in the separation of Rh and Pt from Co and the MoMO catalyst was investigated. Using kinetic experiments, all the DES used had some efficiency towards either Rh or Pt in comparison to the already industry used lixiviant of aqua regia. ChCl: Lac and ChCl: Ur show the highest recovery of Pt and Rh from an alumina support MoMO spent catalyst. With ChCl: TU also having a high Pt recovery. The addition of the oxidants $Na_2O_2$ and $I_2$ did not improve the leaching of the PMs from the amoxis. Despite all DES being able to leach Rh and Pt with no oxidants or strong acids, Co was solubilised more than the target metals. This was expected as Co will react more readily the PMs but was not the desired outcome. A pre-treatment into removing the Co from the amoxis prior to DES leaching could be investigated.

As there is extremely limited literature on the DES chosen with PMs there is little way to know how the PMs and Co interact with the DES itself or to compare the data collected to literature. Further research into ways to enhance the recovery rate should be investigated, such as, changing temperature or adding different more benign oxidants to the system. Multiple models were used in attempts to describe the mechanisms and interactions between the DES and the amoxis; however, shrinking core models were unable to accurately fit the data. Further research with attempts to fit the data is needed to be able to best describe the mechanisms using the spectroscopic study, EXAFS, of the metal complexes that formed that is currently unknown as many different complexes could be formed during this reaction.

As there was little to no major differences between the recovery rate of the uncrushed and crushed samples, with the uncrushed performing slightly better, investigation further into the reasoning of why increasing the surface area of the spent catalyst did not improve the recovery rate. Determining why this occurred would further the understanding of the complexes that are formed with spent metals that are smaller in particle size and how leaching is affected by particle size. Oxidants were also investigated to determine if the addition of oxidative elements or compounds improved the recovery of Rh and Pt. However, it was found that with the oxidants recovered lowered amounts of the metals compared to the just the DES and amoxis.

Further research into relationship of the other PMs metals and in the leaching of gold and silver, due to the PGMs having a similar reactivity towards acids, from spent catalysts is needed. Specifically, research in required into understanding the multiple mechanism and interactions that occur during the reaction between the amoxis and DES. Additionally, more research into developing DES potentially create a more environmentally sustainable method of recovery PGMs from spent catalysts. DES cannot be claimed to be completely environmentally benign; more research is needed to confirm using DES would truly be environmentally benign This could include adding chlorides to the leach to increase the amount of chloride species and in-turn that could increase the recovery of Pt and Rh as there would be more chloride species for the PMs to bind to. Another prospect that could be to look into could be the possible combination of the DES lixiviant with previous solvometallurgy methods such as ion exchange and solvent extraction. Additionally, possible research could be altering the halide used for the HBA from ChCl to ChBr or ChI as there has been literature in showing that halides other than $Cl^-$ have affinities towards PMs.

The cleanup and reusability of DES needs further development.

## Declarations of interests

RSBruce have interest in improving methods of recovering Rh and Pt of the Amoxis they supplied.

## Acknowledgments

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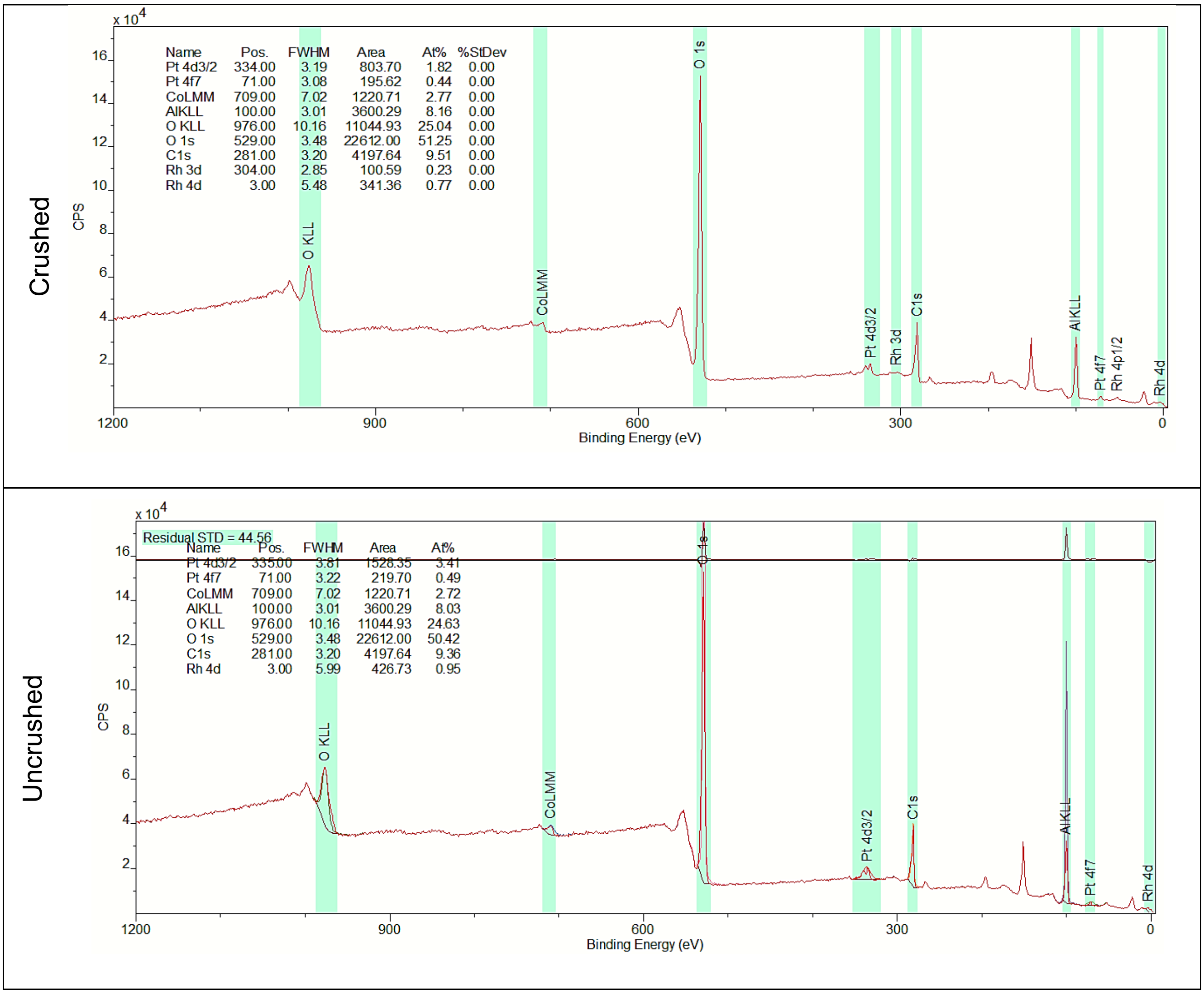
# 6.3. Supporting Electronic Information (SEI)

## SEI1. XPS



| Name | Pos. | FWHM | Area | At% | %StDev |
|---|---|---|---|---|---|
| Pt 4d3/2 | 334.00 | 3.19 | 803.70 | 1.82 | 0.00 |
| Pt 4f7 | 71.00 | 3.08 | 195.62 | 0.44 | 0.00 |
| CoLMM | 709.00 | 7.02 | 1220.71 | 2.77 | 0.00 |
| AlKLL | 100.00 | 3.01 | 3600.29 | 8.16 | 0.00 |
| O KLL | 976.00 | 10.16 | 11044.93 | 25.04 | 0.00 |
| O 1s | 529.00 | 3.48 | 22612.00 | 51.25 | 0.00 |
| C1s | 281.00 | 3.20 | 4197.64 | 9.51 | 0.00 |
| Rh 3d | 304.00 | 2.85 | 100.59 | 0.23 | 0.00 |
| Rh 4d | 3.00 | 5.48 | 341.36 | 0.77 | 0.00 |

Residual STD = 44.56

| Name | Pos. | FWHM | Area | At% |
|---|---|---|---|---|
| Pt 4d3/2 | 335.00 | 3.81 | 1528.35 | 3.41 |
| Pt 4f7 | 71.00 | 3.22 | 219.70 | 0.49 |
| CoLMM | 709.00 | 7.02 | 1220.71 | 2.72 |
| AlKLL | 100.00 | 3.01 | 3600.29 | 8.03 |
| O KLL | 976.00 | 10.16 | 11044.93 | 24.63 |
| O 1s | 529.00 | 3.48 | 22612.00 | 50.42 |
| C1s | 281.00 | 3.20 | 4197.64 | 9.36 |
| Rh 4d | 3.00 | 5.99 | 426.73 | 0.95 |

**Figure 37 XPS spectrum of crushed and uncrushed amoxis**

## SEI2. FT-IR

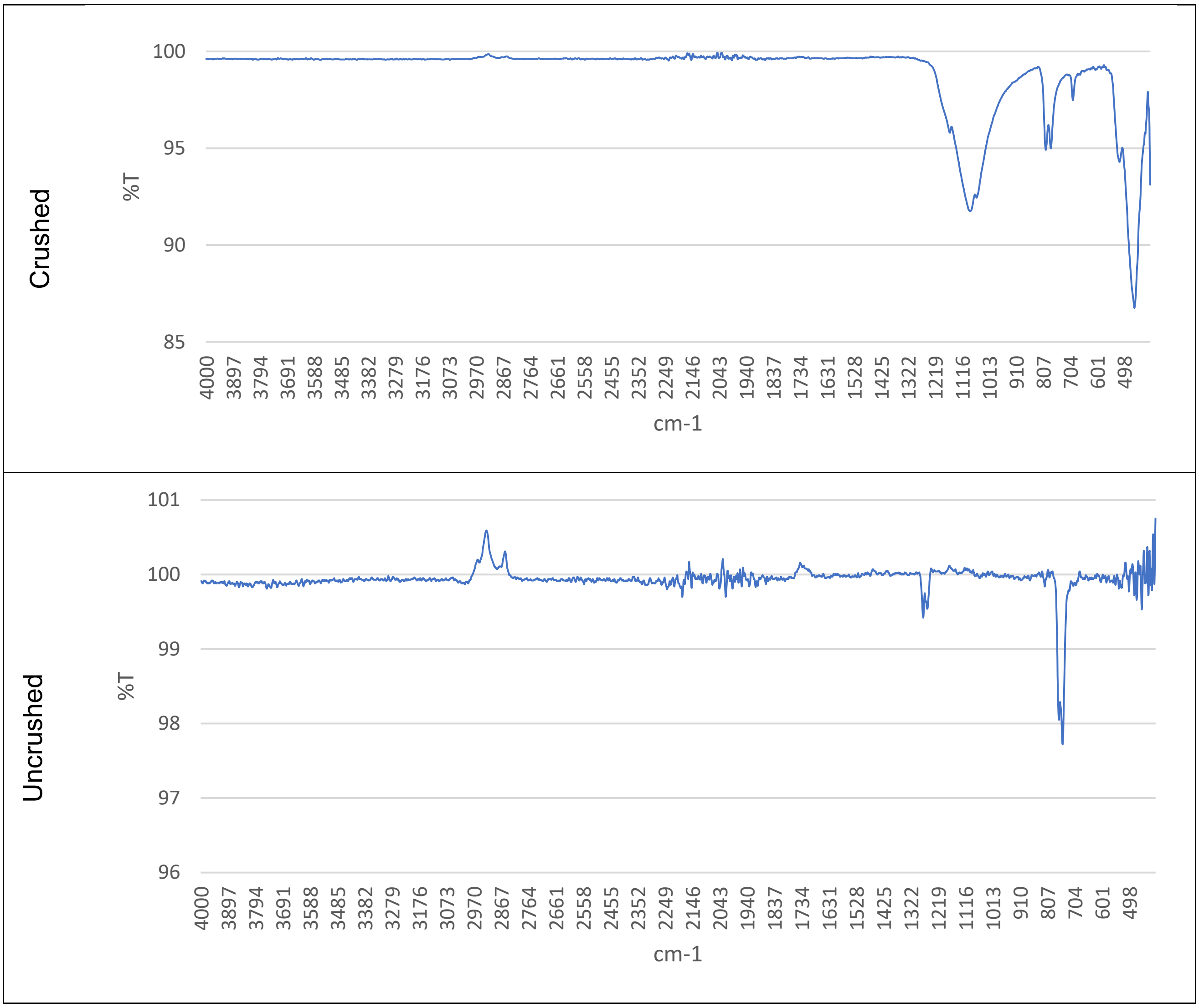


**Figure 38 FT-IR of crushed and uncrushed amoxis**

### SEI3. Equilibrium amoxis of all DES and aqua regia.

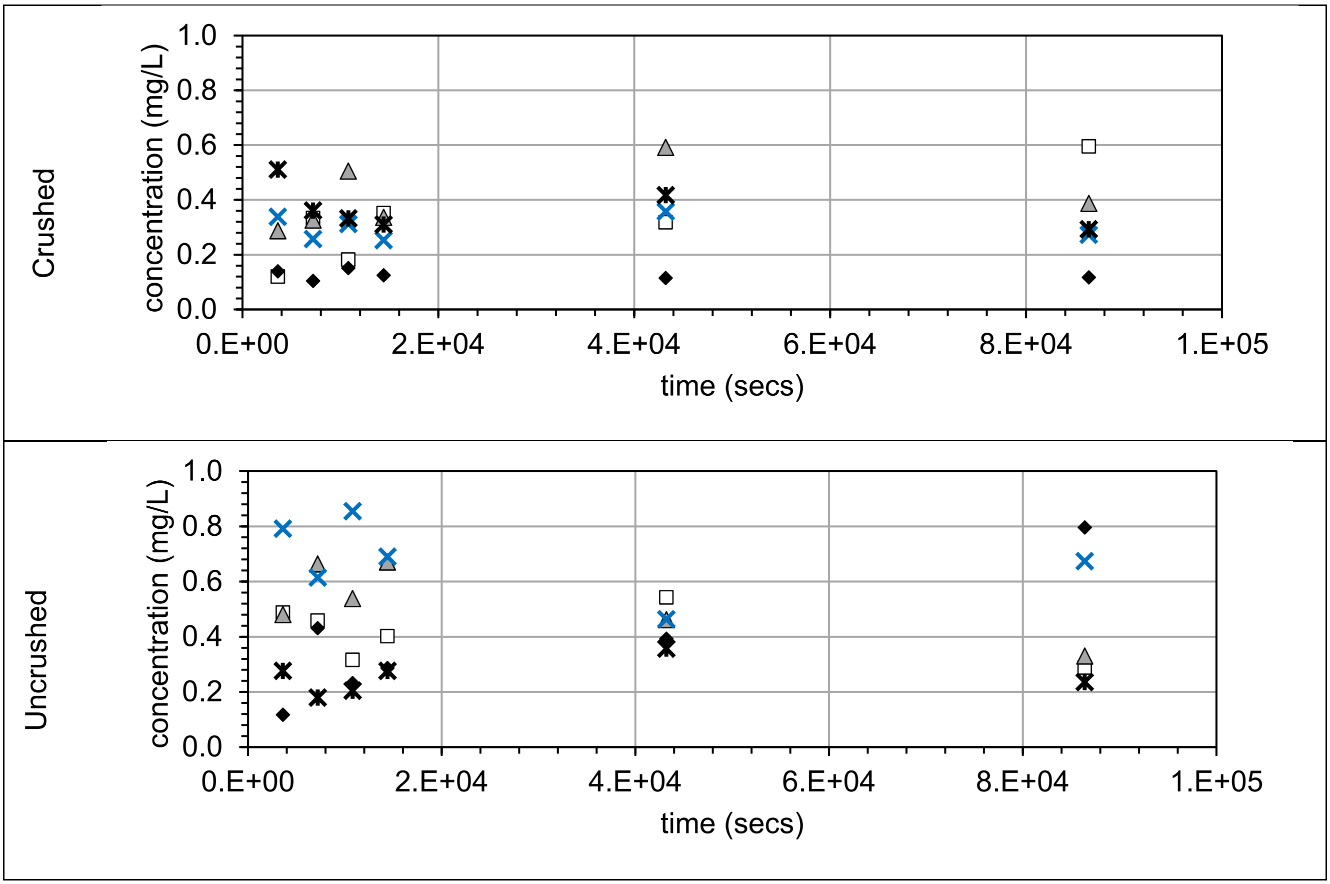


**Figure 39 Equilibrium data for the Pt at 48 hours of all lixiviants investigated. ☐ = Aqua regia, ◆ = ChCl: EG △ = ChCl: Lac ×= ChCl: TU ∗ =ChCl: Ur**

### SEI4. Leaching of uncrushed amoxis catalyst using concentrated aqua regia at different ratios.

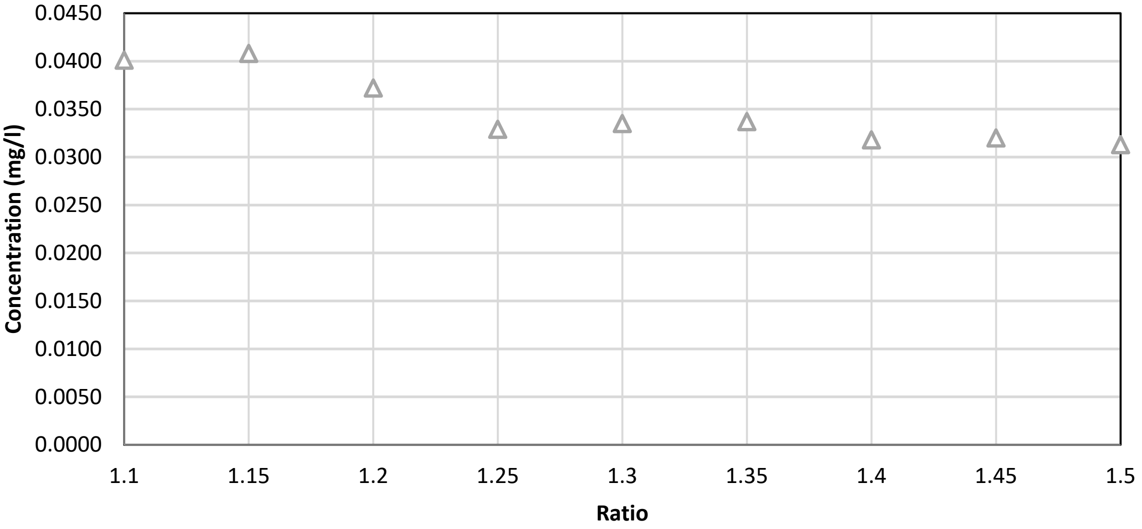


**Figure 40 Leaching of crushed and amoxis catalyst using concentrated aqua regia at different ratios. △ = Co**

## SEI5. Distribution coefficient values of Pt, Rh and Co uncrushed and crushed leaching experiments.

**Table 22 Distribution coefficient values of Pt, Rh and Co uncrushed and crushed leaching experiments.**

| $K_D$ | | Aqua Regia | ChCl: EG | ChCl: Lac | ChCl: U | ChCl: TU |
|---|---|---|---|---|---|---|
| Crushed | Co | 83.29 | 83.45 | 83.54 | 83.55 | 82.99 |
| | Pt | 17.2 | 17.1 | 11.3 | 16.6 | 20.2 |
| | Rh | 16.6 | 13.9 | 20.3 | 13.7 | 18.4 |
| Uncrushed | Co | 83.6 | 80.8 | 89.2 | 90.6 | 75.9 |
| | Pt | 10.4 | 11.4 | 7.1 | 8.02 | 12.3 |
| | Rh | 7.38 | 16.4 | 14.3 | 7.20 | 7.70 |

## SEI6. Separation Factors of Rh and Pt against Co

**Table 23 Separations Factors of Rh and Pt against Co.**

| | **α** | | | |
|---|---|---|---|---|
| **Lixiviant** | **Uncrushed Pt** | **Uncrushed Rh** | **Crushed Pt** | **Crushed Rh** |
| **ChCl: EG** | 4.97 | 4.76 | 0.153 | 0.172 |
| **ChCl: Lac** | 3.27 | 5.89 | 0.0874 | 0.177 |
| **ChCl: TU** | 5.86 | 3.98 | 0.152 | 0.0952 |
| **ChCl: Ur** | 4.82 | 4.82 | 0.0993 | 0.0890 |
| **Aqua-regia** | 4.99 | 4.82 | 0.129 | 0.0913 |

## SEI7. Kinetic modelling of Co, Rh and Pt DES systems using the shrinking core model.

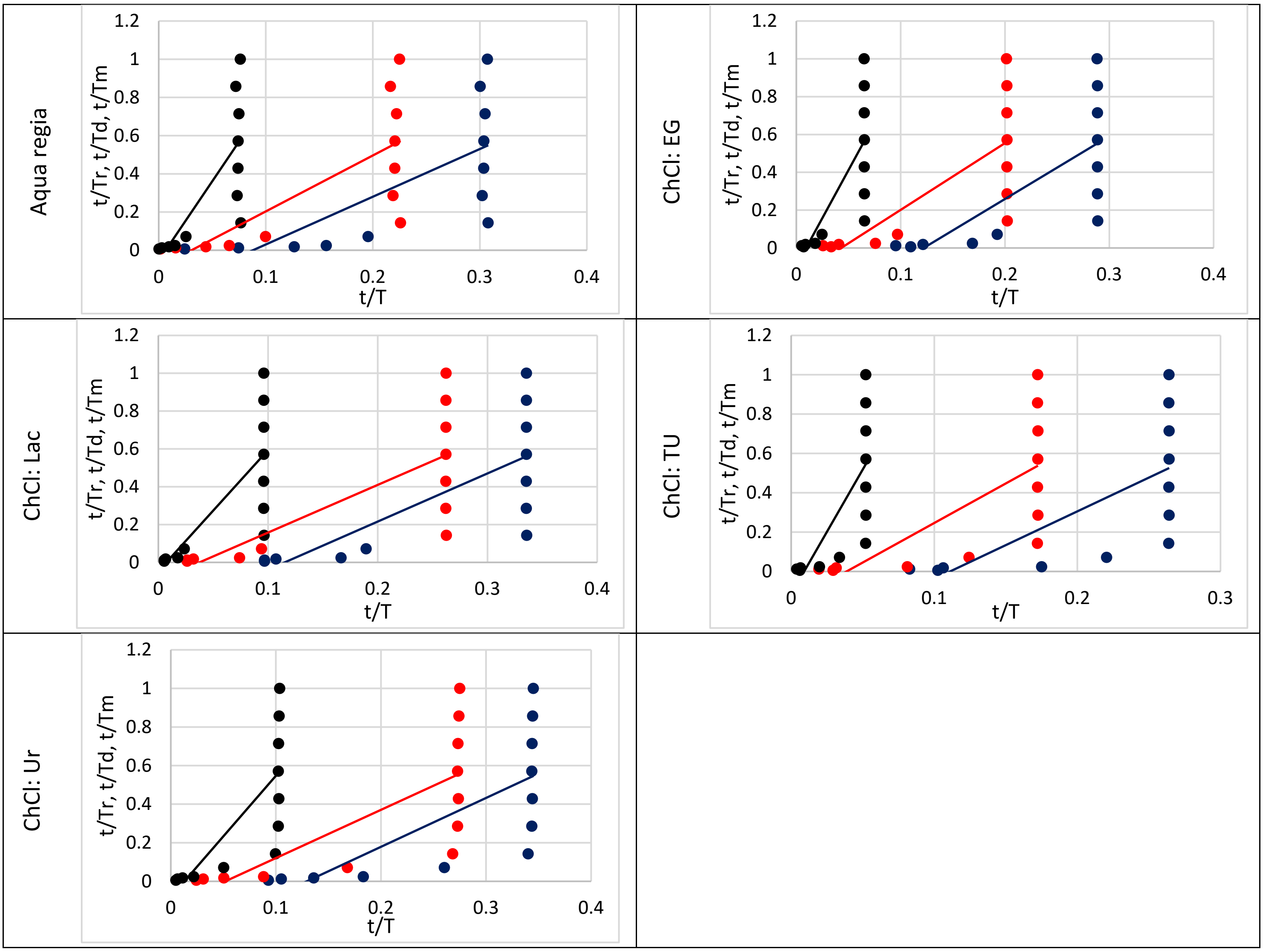


**Figure 41 (SEI7) Comparison of Cobalt Shrinking core model fitting for DES systems and aqua-regia. ●- = Mixed- Control Model ●-=Reaction-Controlled ●-=Diffusion Controlled**

## SEI8. Kinetic modelling of Rh DES systems using the shrinking core model.

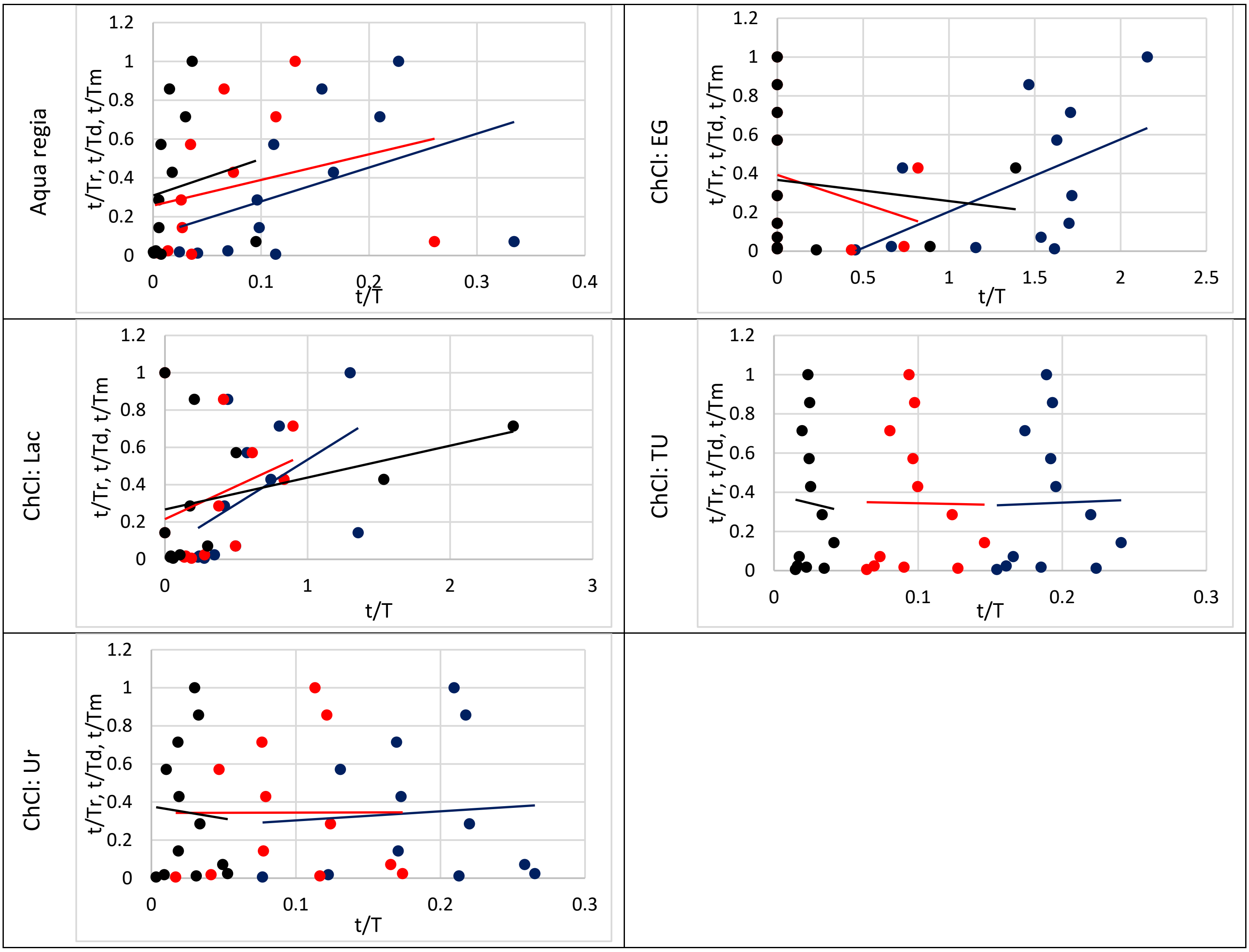


Figure 42 (SEI8) Comparison of Rhodium Shrinking core model fitting for DES systems and aqua-regia. ●- = Mixed- Control Model ●-=Reaction-Controlled ●-=Diffusion Controlled

## SEI9. Kinetic modelling of Pt DES systems using the shrinking core model.

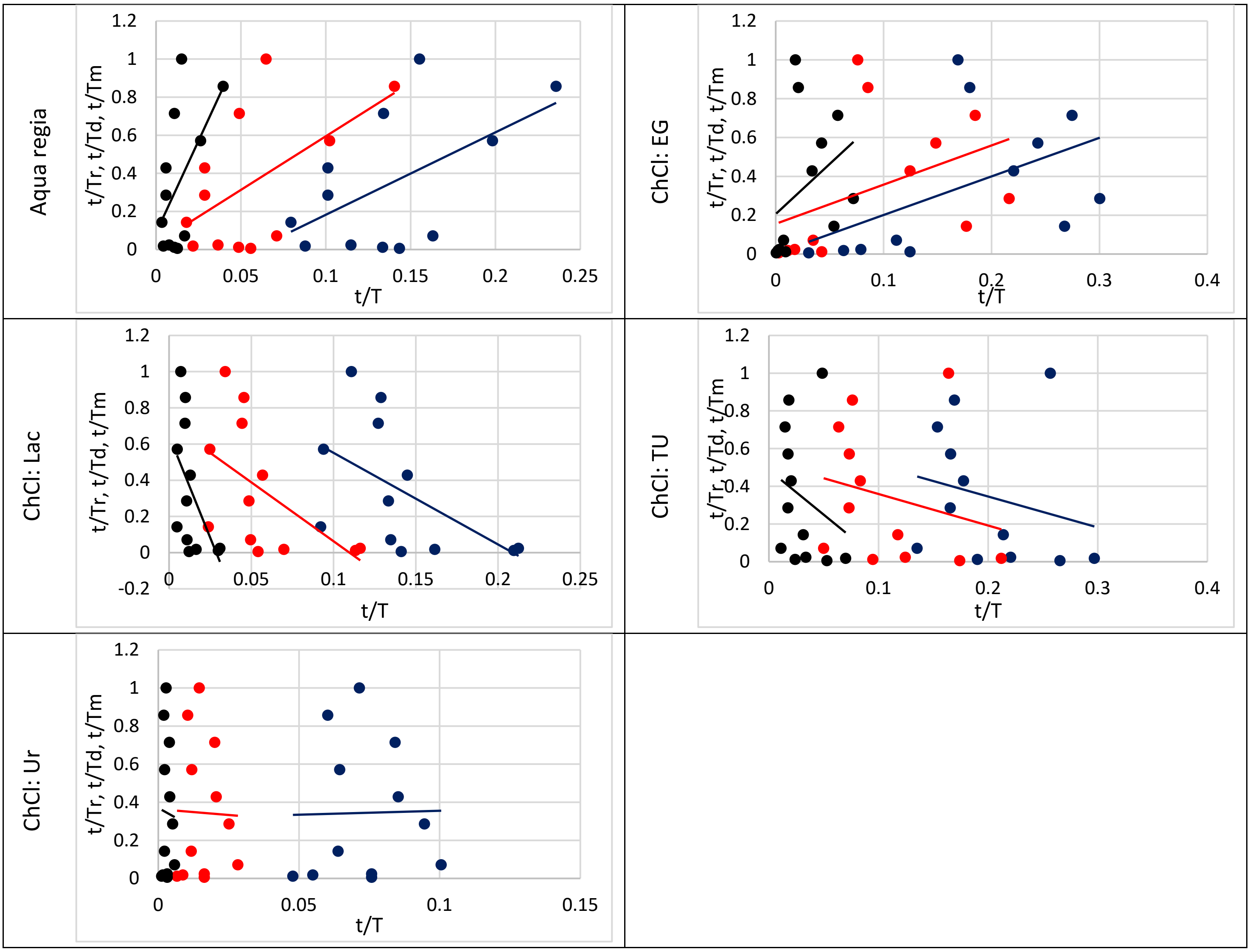


**Figure 43 (SEI9) Comparison of Platinum Shrinking core model fitting for DES systems and aqua-regia. ●- = Mixed- Control Model ●-=Reaction-Controlled ●-=Diffusion Controlled**

# CHAPTER 7: COMBINATION OF ION EXCHANGE AND DEEP EUTETIC SOLVENTS IN THEH RECOVERY OF PRECIOUS METALS FROM SPENT CATALYST.

## 7.1. Paper Overview

The combination of the two different resource recovery techniques, resin-in-leach and resin-in-pulp needs to be investigated to determine if it is possible. This paper utilises the ion exchange resins that showed the best affinity towards PMs and the DES that showed the best recovery rate for rhodium and platinum without recovering cobalt from a metal-on-metal-oxide spent catalyst.

The process of the attempts to combine DES leaching and IX resins was also investigated for the resin-in-leach and resin-in-pulp methodology. It was concluded that ion exchange resins and DES can successfully be combined into one system for full resource recovery of rhodium and platinum. The parameter investigated was temperature, it showed that from the six temperatures shown two showed the best potential for a high leaching. The two ion exchange resins, from chapter 4, that were determined to have the highest affinity towards gold was investigated. Inductively coupled plasma optical emission spectrometry (ICP-OES), and X-ray photoelectron spectroscopy (XPS) were used to obtain the amount of rhodium, platinum and cobalt on the amoxis after the leaching was completed.

The best conditions and ion exchange resin was determined with the resin-in-pulp system at 60 °C using the MTS914 resin.

This paper is expected to be submitted to the Chemical Engineering Journal.

Author contributions:

- V. R. Shields- Experimental work, data collection, data analysis and writing
- J. Miller- Hosting of V. R. Shields at RS Bruce
- O. Murray- Hosting of V. R. Shields at RS Bruce
- J. Cordiner- Manuscript review
- M. D. Ogden- Principal Investigator and manuscript review

# 7.2. Extraction of critical metals from catalytic waste by Deep Eutectic Solvents and Ion Exchange resins

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## Abstract

Currently the recovery of precious metals, particularly rhodium and platinum is processed *via* cyanidation or aqua regia which are corrosive, explosive, hazardous and toxic compounds. The possible successful combination of two different alternative recovery methods could be a major development into more sustainable recovery of rhodium and platinum from a spent catalyst compared to what is currently being used in industry. The combination of ion exchange (IX) resins and deep eutectic solvents (DES) into one system shows potential in both resin-in-pulp (RIP) and resin-in-leach (RIL) systems with varied temperatures. Six different temperatures were investigated ranging from 30°C -80°C with 30°C and 60°C showed the most potential for optimum recovery. PurometTM MTS9140 and AmberSep™ M4195 resins were investigated with DES, choline chloride (ChCl): Lactic acid (Lac), to create the system. It was found that 60°C in the RIP systems, using the resin MTS9140 was determined to be the optimum system with no rhodium or platinum found in the barren solution. In both RIP and RIL systems MTS9140 resin outperformed M-4195 resin with both MTS9140 RIP and RIL systems show no Pt and Rh in the barren solution compared to M-4195 resin with Pt concentrations of 5.14 mg/l at 60°C *via* RIP at 30°C and 60°C have concentrations of 0.17 mg/l and 0.19 mg/l, respectively. This work has shown that the combination of IX resins and DES can potentially be an environmentally sustainable recovery method for precious metals.

Keywords: platinum group metals, resource recovery, metal-on-metal catalysts, spent catalyst, deep eutectic solvents, ion exchange.

# 1 Introduction

Research into environmentally sustainable methods of recovering precious group metals (PGMs), specifically rhodium (Rh) and platinum (Pt), from waste has grown over the last couple of decades. As shown in literature and various news outlets the prices and demand of Rh and Pt have grown exponentially with a 55% increase in the price of Rh in the first month of 2020 reaching a 11-year high (280). Pt price has steadily increased with an increase of 24% in 2019 and 4% in the first month of 2020 (281). The supply has remained low with the need to recycle PGMs to meet the demand is increasing (368; 369; 370; 371; 372; 373). Extraction of Rh and Pt from other spent catalysts, has shown high recovery rates of 84%, 45% and 65% of Rh, Pt and palladium respectively (290; 289). The potential to find a method that does not involve highly toxic chemicals or produce toxic by-products for the recovering PGMs from spent catalysts is required as an environmentally sustainable alternative is required.

Ion exchange (IX) has previously been used in ionic media such as molten salts and ionic liquids (374; 375). The investigations into IX recovery *via* molten salts involve electrochemistry, specifically electroleaching and electrodeposition (376; 377; 378). However, current literature has stated that the use of molten salts produces a large quantity of chemically complex organic and aqueous liquid waste, that is created throughout the entire solvent extraction process, that is difficult and expensive to dispose of (379). Additionally, there has currently very little research into non-e-waste recovery *via* molten salts or ionic liquids.

Findings seen in literature, has suggested that a more environmentally sustainable lixiviant, a liquid medium used to selectively extract metals from ore bodies where they are normally found underground, such as DES can be used for the extraction and recovery of PMs from waste (380; 381). With this current information there could be a potential new methodology of combining the IX resin chosen, Puromet$^{TM}$ MTS9140 and DOWEX™ M-4195, and the DES that were found to have the best affinity towards Pt and Rh properties of both resins show in Table 24 (223; 224; 225).

**Table 24 Selected properties of PurometTM MTS9140 and DOWEX™ M-4195 used in this study.**

| Resins name | Functional group | Resin Matrix | Exchange capacity | pH range |
|---|---|---|---|---|
| Puromet® MTS9140 | Thiourea | Polystyrenic Macroporous | 1.0 eq/l | 0-14. |
| Dowex™ M-4195 | Bis-Picolylamine | Styrene-DVB | ≥0.52 g/L (Cu) | 0-7. |

The results determined in chapter 5 was four of the IX resins had shown affinity towards gold. The two shown in Table 24 were determined to have the must potential for increasing the recovery rate using more environmentally sustainable solvents when leaching precious metals from waste solutions. The methodology of the IX resin investigation was used in alternative solution to cyanide (thiourea-thiosulfate) of a simulant mining tailings. Another alternative solution to cyanidation or aqua regia is DES. The possible mechanisms that was discussed in chapter 5 in regard to MTS9140 was that the due to excess of dominant thiourea from the MTS9140 functional group and the simulant mining tailings allowed for the stable thiourea complexes, with complex stability being calculated at $[AuTU_2]^+$, $\beta_2 = 2.0 \times 10^{21}$ from both the IX resin and the mining simulant solution with the pore environment increasing further.

In comparison with the proposed mechanism of the M-4195, could be because of the nitrogen's in the BPA ligand will be positively charged and would interact with the sulfate ions to for neutralisation. In this case, the overwhelming thermodynamic stability of the reacting aqueous gold-thiourea complexes (verses copper-thiourea) would likely dominate the selectivity of the system. This makes M-4195 and TS9140 a strong candidate for gold and other precious metal recovery within this remit. The reason for the IX resin choice regards Au, Rh and Pt having similar reactivity and inertness in regard to acids and reagents for purification. The IX resin having the affinity to form the Au complexes whilst competing with other more reactive metals suggests that the IX resin being investigated would potentially have a high affinity for Rh and Pt without having an affinity towards Co which was shown in chapter 4 that both M-4195 and MTS9140 the Co in the PLS reached breakthrough in under 20 BV for both the IX resins.

Findings from chapter 6 contribute to the experimental DES chosen for this chapter with ChCl: Lac having the highest affinity towards Rh despite Lac has only been investigated into the recovery of Cu (382; 383).The data found in chapter 6 with the Rh and Pt having the highest extraction with ChCl: Lac and ChCl: TU, with recovery rates of 25.1% and 14.6% respectively (382; 380). ChCl: Lac was the final DES chosen due to the ease of making ChCl: Lac compared to the ChCl: TU which is seen in chapter 3 and 4 with the lack of a glovebox synthesising TU DES was extremely hard and required a ratio of HBA: HBD at 15:6; additionally, the price of 1L of Lac is ~£38.00 compared to ~£47.20 for 1 kg of TU and with a higher amount ratio of TU needed the price to synthesise ChCl: Lac is overall cheaper (384). ChCl: Lac it has a high affinity towards Rh in both the crushed and uncrushed amoxis, despite having a low affinity towards Pt. The current price of one ounce of Rh is more then 10x more expensive than one ounce of Pt; with a higher demand and lower supply the development into targeting Rh more the Pt is necessary (385). However, the possible interactions or mechanisms between the DES and amoxis was not determined which used the shrinking core model. The assumptions made was that the possible preg-robbing and equilibrium of the metal complexes formed are more of a significant factor and the reaction is reversible; the shrinking core model is based on the reaction being irreversible.

Two different extraction methods will be investigated, resin-in-pulp (RIP) and resin-in-leach (RIL). RIP is when the both the leaching solution and IX resin are in the same container, whereas with RIL is when the desired metal is leached out *via* the leaching solution first then run through an IX resin column. Both of are possible alternative methods to carbon-in-pulp (CIP) and carbon-in-leach (CIL) (386). Both RIP and RIL work on the same principle as CIP and CIL, which is currently used recovery gold and base metals for leached slurry *via* cyanidation that is absorbed onto activated carbon shown in chapter 2. Investigations into strong-base-resins (SBR) *via* RIL was used to combat the preg robbing phenomenon that occurs when the aurocyanide complexes gets readsorbed by the activated carbon (387).

The RIL cyanidation resulted in 70% gold recovery onto the resin compared to the >2% gold extraction *via* cyanidation of the gold ores (387). Recent developments have shown RIP to be a variable alterative to CIP with resins having a higher loading capacity, loading rates and do not require thermal regeneration and are more cost-effective despite the resins being more expensive (386). In industry IX resins are used in a pulp formation, this could be mainly due to the ease set-up and is more time-effective. RIP is more commonly seen in a commercial setting is due to the fixed bed IX resins are in an open tank compared to the more expensive pressure vessels, it offers operation cost and time savings and reduces water balance constraints (388; 389). RIL method may be less used commercially with the RIL performing 60% of that of a CIP plant (390). As literature has shown that using RIL and RIP are possible alternatives to using activated carbon and cyanidation the combination of these methods with DES-IX resin which are shown to be more environmentally sustainable compared to what is used in industry will create a completely novel recovery method of precious metals that has not yet been investigated.

Two methods that are being researched into the recovering PGMs from a spent catalyst are IX resins and ionic liquid, deep eutectic solvent (DES). Literature has proven that both IX resins and DES have the potential in recovery of PGMs not just from spent catalysts but waste in general (391; 392). Despite this, there is very little literature on the combination of DES with exchange resins; however, thus far only one literature has combined both in research of extraction, Gan et al (2016), shows the combination of DES and anion-exchange resins (AER) improved the adsorption capacity and provided a better extraction efficiency (393). The study by Gan et al. is related to biological matter and is used in SER whereas this chapter will be investigating chelating resins and a solvent impregnated resin (SIR) (393).

Literature has shown the prospect of combining DES-IX resin is a possibility and can improve a current extraction method by the improvement of steric hindrance, reduced the mass transfer limitation (394). Higher affinity and selectivity of the DES-IX resin is related to the number of binding sites for the target compound changing, leading to a rough and porous surface of the polymer, which is beneficial to release the target molecules and expected to enhance the extraction efficiency of DES-IX resin (393). Overall, the combination of DES-IX resin in literature used resins as the catalyst to improve the conversion rate and synthesis of different compounds compared to when the DES was used on its own.

**Table 25 Percentage recovery of Rh, Pt and Co of ChCl: Lac leach with amoxis.**

| **Recovery %** | | ChCl: Lac |
|---|---|---|
| Uncrushed | Co | 15.5±0.8 |
| | Pt | 8.27±0.4 |
| | Rh | 25.1±1.3 |

From the recovery rates of DES of Rh, Pt and Co from uncrushed amoxis was determined in chapter 6 and shown in Table 25. All recovery rates of metals shown in in Table 25 are low with Rh being the highest at 25%. Using the IX resins MTS9140 and M-4195 were determined to have the two highest affinities towards gold (Au) and silver (Ag), which have similar chemical properties towards Pt and Rh. The DES-IX resin research in this chapter will advance the current understanding of Pt and Rh chemistry, specifically has Rh very little literature into how it reacts with more benign solvents.

# 2. Methodology

## 2.1. Synthesis of DES

Chlorine Chloride (ChCl): Lactic acid (Lac) was synthesised by the following method: lactic acid and ChCl was dried in a vacuum oven at 50 °C for 48 and 72 hours respectively, before synthesis of the DES. HBA and HBD of ChCl: Lac weighted at a 1:2 ratio and was heated at 60°C, whilst stirring at 250 rpm using a magnetic stirrer, till a homogenous clear liquid was formed and was then kept at 80°C for another 4 hours. For both resin-in-pulp (RIP) and resin-in-leach (RIL) deep eutectic solvents (DES) was made with an experimental ratio of 1: 5 being used for Amoxis: DES + IX resin (1:4.5+0.5) for both RIP and RIL.

## 2.2. Leaching Amoxis at Different Temperatures

~0.015g of the amoxis was added to ~3ml of the synthesised DES and was left to leach for 24 hours at four different temperatures: 30°C, 40°C, 50°C, 60°C, 70°C and 80°C. After the 24 hours 1ml of the DES solution was taken and diluted to 10ml with 1% HNO3 for ICP-OES analysis.

## 2.3. Ion Exchange Resin Leach with DES

The two best IX resins that were determined to have the highest affinity towards gold (Au) and silver (Ag) from chapter one MTS9140 and M-4195 were mixed with DI water for 24hrs, then washed with deionized water for 24hrs.This allows the residual salt content to be washed out of the resins (395). For RIP and RIL 2g of each IX resin was used.

## 2.4. Leaching of Amoxis

Table 26 and Table 27 show the estimated mass per gram and concentration of each metal on the amoxis.

**Table 26 Estimated mass per gram of the metals and chemical compounds of the Amoxis (PNB 443).**

| Metal/ chemical compound | Percentage on Amoxis (%) |
|---|---|
| Co | 18.0±0.9 |
| Pt | 0.16+0.008 |
| Rh | 0.05±0.0025 |
| $Al_2O_3$ | 81.0±4.1 |

For the ICP-OES analysis of 2 samples of the alumina substrate spent catalyst, 3 ml of conc. nitric acid and 1 ml of conc. perchloric acid was added to the 0.5g of the samples and heated to 200°C, they were then made up to 50 ml using 1% conc. nitric acid before the sample could be run as the spent catalyst samples were solid a triplicate was run.

**Table 27 ICP-OES results of the Amoxis.**

| Sample | Co-59 (mg/l) | Rh-103 (mg/l) | Pt-195 (mg/l) |
|---|---|---|---|
| **Non-crushed Amoxis** | 0.13±0.006 | 0.013±0.007 | 0.059+0.003 |
| **Crushed Amoxis** | 0.33±0.02 | 0.010±0.001 | 0.036±0.002 |

### 2.4.1. Resin-in-pulp

For each DES and each IX resins ChCl:Lac DES was measured out with uncrushed amoxis/MClx with IX resins with a ratio of 1:4.5:0.5 and was left to mix with a magnetic stirrer at 250 rpm at ambient temperature for 96 hours, with 1ml samples taken after the first hour then at 24hrs then every 24 hrs afterwards. The setup of the experimental can be seen in Figure 44.

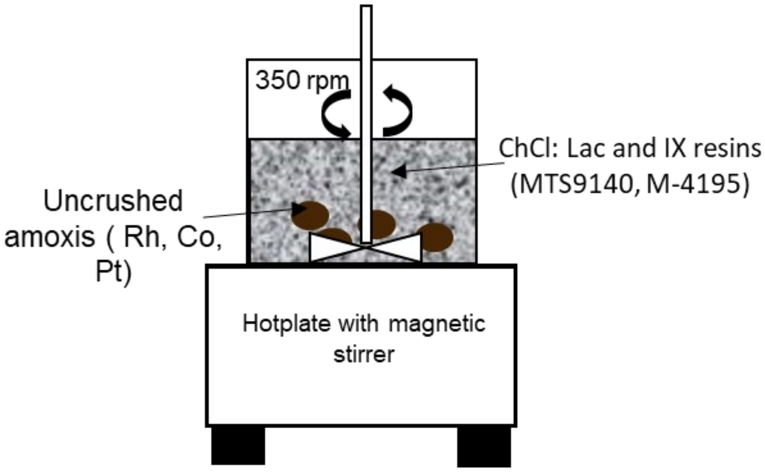

**Figure 44: Experimental set up or RIP method for extraction Rh, Pt from Co on a spent alumina catalyst.**

### 2.4.2. Resin-in-leach

Similarly, as the RIP experimental ChCl:Lac DES was measured out with uncrushed amoxis/MClx with IX resins with a ratio of 1:4.5:0.5 and left to mix for 60 hours with a magnetic stirrer at 250 rpm at ambient temperature at day five 1ml of the DES solution was taken. After those 60 hours the amoxis is removed from the DES solution and the DES with the extracted Rh, Pt and Co is run through a gravity flow IX column with 2g of the desired IX resin at a BV/h of 6 BV/h for the last 12 hours. The setup of the experimental can be seen in Figure 43 with the process of this final method being shown in chapter 4.

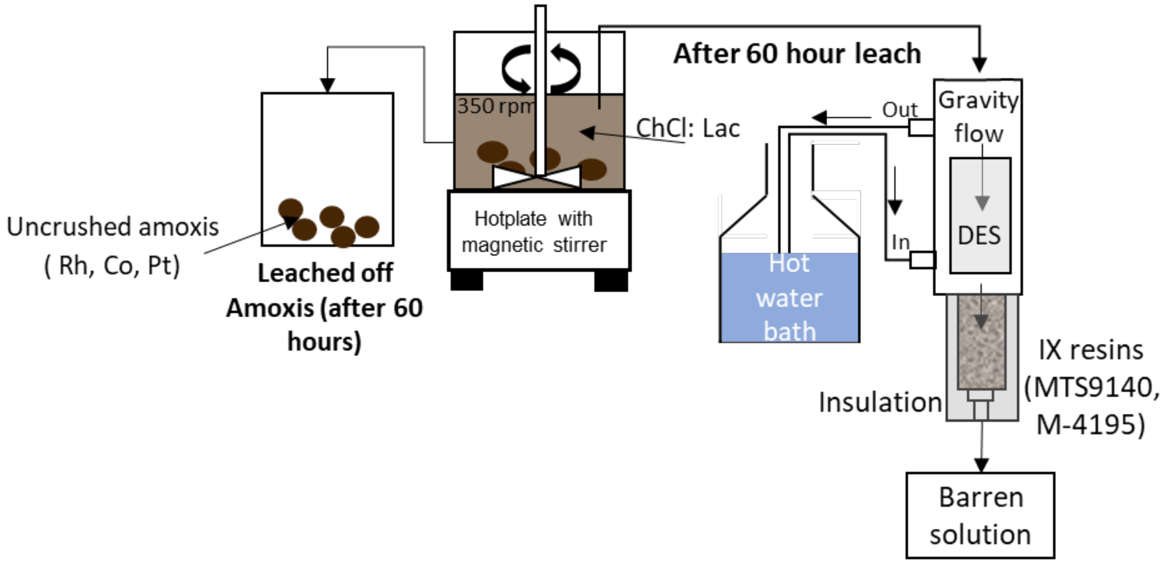

**Figure 45 Experimental set up or RIL method for extraction Rh, Pt from Co on a spent alumina catalyst.**

### 2.4.3. IX Resin State Analysis

IX resin state analysis was run after the RIP and RIL leaching. X-ray photoelectron spectroscopy (XPS) was the characteristic technique used for the solid- state analysis of the IX resin after the leaching of the amoxis leaching was run. Preparation for XPS was done by putting the crushed and non-crushed samples into a clean, high purity indium foil, separately; they were then placed on top of an adhesive carbon conductive tape.

# 3. Results

## 3.1. Temperature Impacts on Rh, Pt and Co Leaching.

Figure 44 show the different temperature increments (30°C - 80°C) and its shows that 30°C and 60°C have the highest leaching of Rh. With the 60°C and 80°C have the highest leaching of Pt.

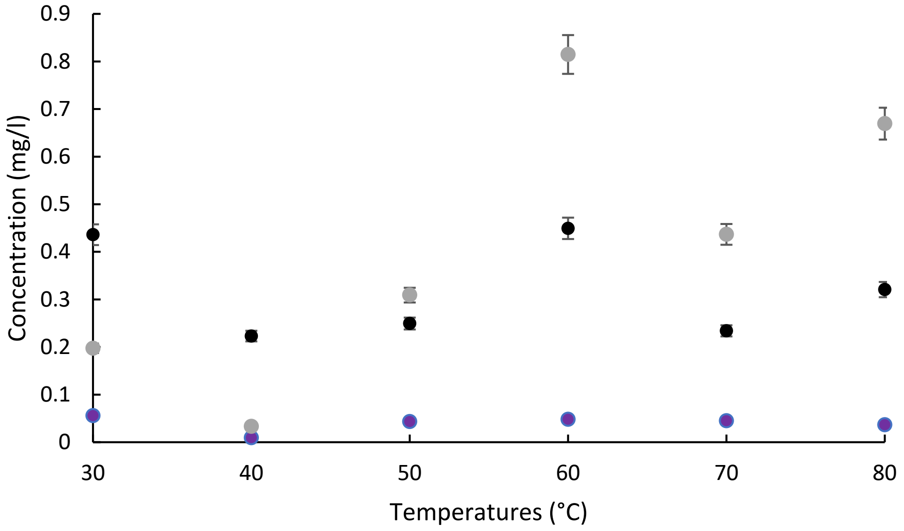

**Figure 46 ChCl: Lac DES leach of amoxis at different temperatures 30°C, 40°C, 50°C, 60°C, 70°C and 80°C Solid to liquid ratio of 1:5. Purple= Rh black= Co Grey= Pt**

Temperatures chosen for the RIL and RIP DES system extraction is based on recovery of Rh due to the it being in higher demand and lower supply in comparison to Pt (Figure 46). Two samples of each temperature was run and a triplet of both sets of data was ran through the ICP experiments. This data was used in the next set of experiments with the temperatures investigated in RIP and RIL in sections 3.2 and 3.3.

## 3.2. Resin-in-pulp

The IX resin that had the highest leaching of Rh and Pt, MTS9140 at 60°C, was chosen to do final leaching experiment for the RIP system, this system was run at two different temperatures 30°C and 60°C, show in Figure 47.

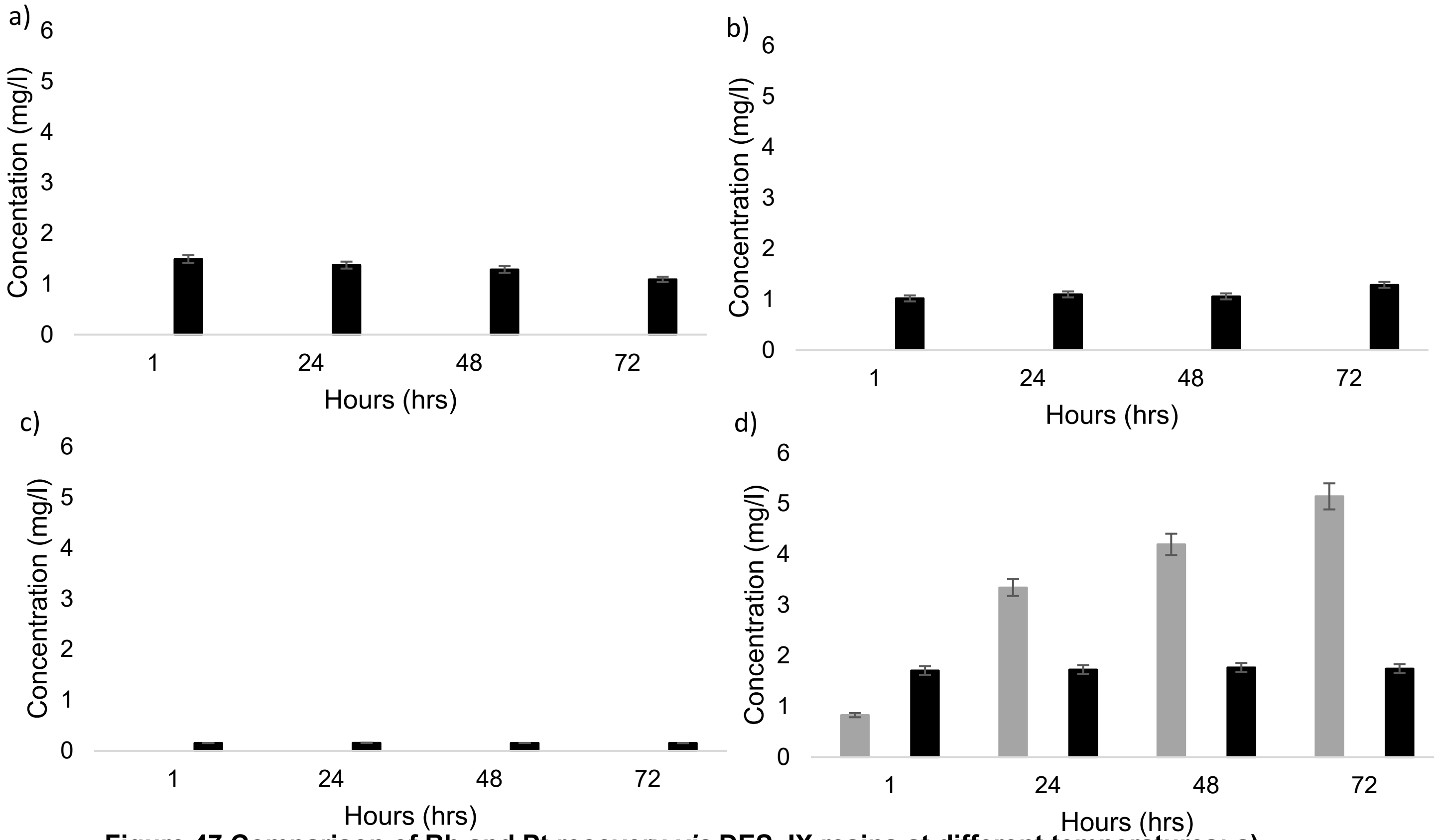

**Figure 47 Comparison of Rh and Pt recovery *via* DES, IX resins at different temperatures: a) Puromet$^{TM}$ MTS9140 at 30°C, b) Puromet$^{TM}$ MTS9140 at 60°C, c) AmberSep$^{TM}$ M-4195 IX at 30°C, d) AmberSep$^{TM}$ M-4195 IX at 60°C. Solid to liquid ratio of 1:5 Purple= Rh black= Co Grey= Pt**

Only RIP experimental that showed the PGMs with Pt being with the final concentration being 5.14 mg/l (Figure 47). It can be assumed that with the increased temperature of the M-4195 resin and DES system reduced the affinity towards Pt. Out of the two resins MTS9140 show the highest affinity towards Rh and Pt, additionally it absorbed 1.09mg/l and to at 60°C and 1.283mg/l of Co at 30°C. Compare this to M-4195 where the two differing temperature results in lowest and highest concentrations of Co that was left in the barren solution, At 30°C the final concentration *via* M-4195 is 0.15mg/l and at 60°C the final concentration *via* M-4195 is 1.75 mg/l.

## 3.3. Resin-in-leach

No Pt or Rh was seen in the RIL run expect for AmberSep$^{TM}$ M-4195 IX at 60°C which shows high concentrations of Pt which then quickly fall as more (Bed-Volumes) BVs are collected. It can be assumed that all the Rh and Pt was absorbed in the IX resin. Shown in Figure 48 and Figure 49.

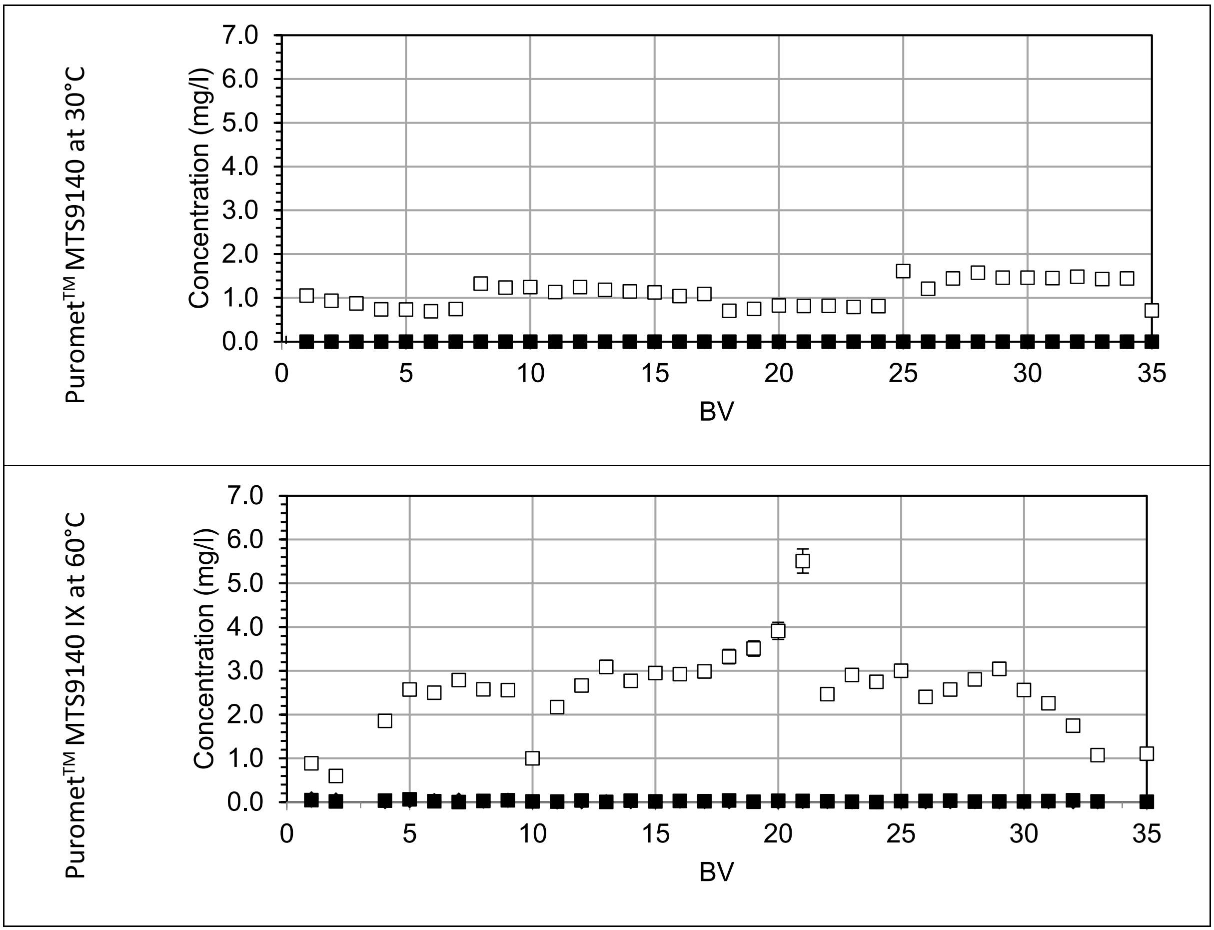

**Figure 48: Comparison of Pt, Co and Rh recovery *via* DES and Puromet$^{TM}$ MTS9140 at 30°C and Puromet$^{TM}$ MTS9140 IX resin at 60°C. Solid to liquid ratio of 1:5 □ = Co, ◆ = Rh, ■= Pt**

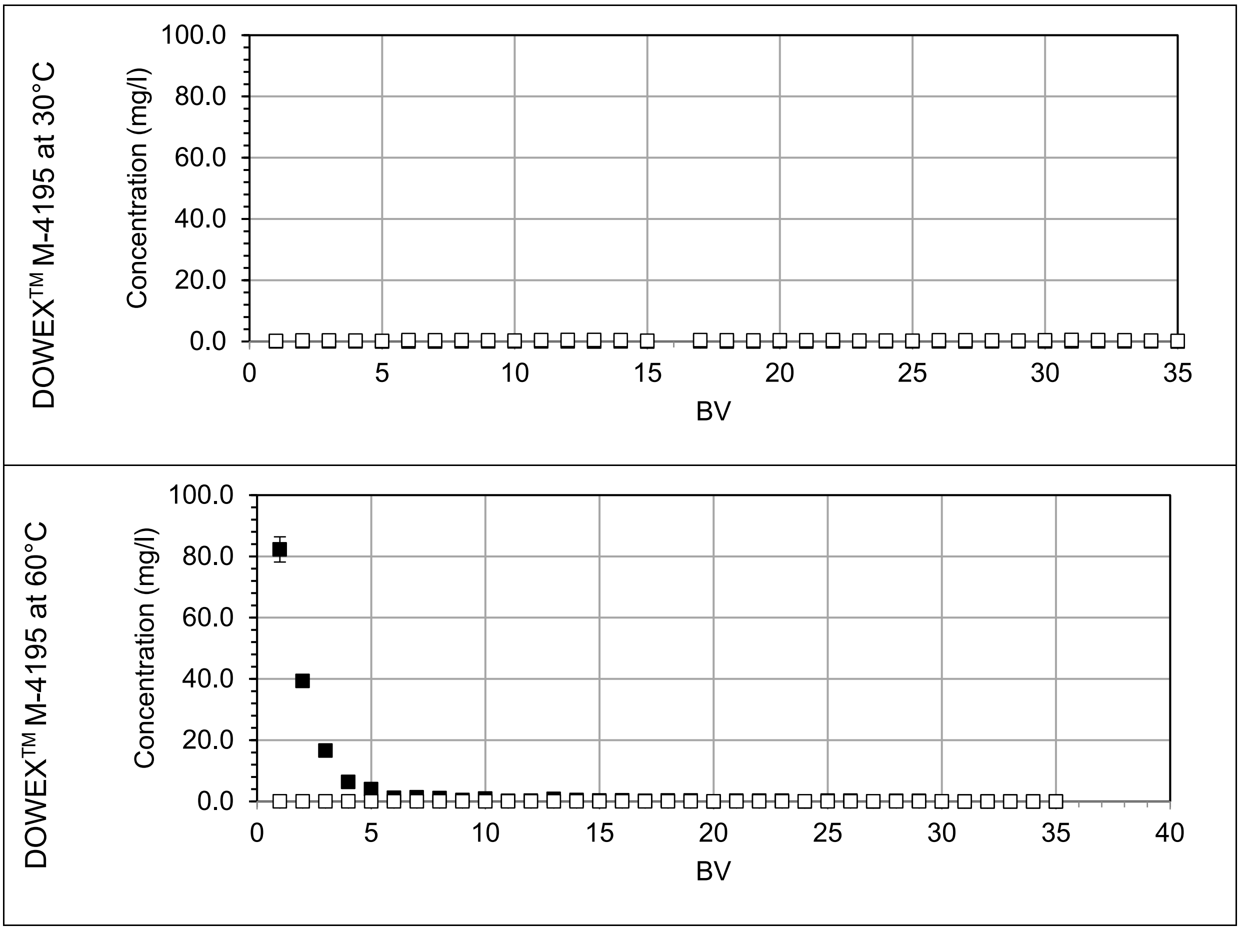

**Figure 49 Comparison of Pt, Co and Rh recovery *via* DES and AmberSep$^{TM}$ M-4195 IX at 30°C, and AmberSep$^{TM}$ M-4195 IX at 60°C. Solid to liquid ratio of 1:5. ☐ = Co, ◆ = Rh, ■= Pt**

There are similarities with the trend saw in the RIP figures (Figure 47) and data collected on the RIL systems (Figure 48 and Figure 49). RIP at 30°C the concentration of Co is lower than that at 60°C for both M-4195 and MTS9140 with Pt (Figure 49). In the barren solution of M-4195 at 60°C it shows the highest concentrations of Pt at 0.1947mg/l which is lower than what was determined in RIP system at 5.144 mg/l. However, when M-4195 was investigated in the RIL system at 30°C there was minimal concentrations of Pt and Rh that were detected, which has not been seen with any other resin or temperate none has been seen in the RIP system.

## 3.4. IX Resin Solid-State Analysis.

XPS was run on the surfaces and internal section of the IX resins used after the leach of both the RIP and RIL experiments; however, the Co, Rh and Pt was below the datable limit. An experiment was run to determine the lowest amount that is detectable was run for both MTS9140 and M-4195. Shown in Table 28; with the full spectrums being shown in SEI1.

**Table 28 XPS of the surface of MTS9140 and M-1495 IX resins after Rh and Pt extraction is completed with elevated amount of Rh, Pt and Co (mg/l).**

| Element | MTS9140 | M-4195 |
|---|---|---|
| Pt | 3.88 | 9.23 |
| Rh | 0.29 | 6.48 |
| Co | 0.15 | 0.49 |
| Cl | 7.27 | 8.5 |
| C | 26.93 | 18.53 |
| O | 57.75 | 52.36 |
| S | 0.14 | 1.62 |
| N | 3.61 | 2.84 |

**Table 29 Mass of Rh and Pt left in barren solution of 0.5 g of Pt, Rh and Co each added to 5ml of ChCl: Lac (mg/l)**

| Element | MTS9140 | M-4195 |
|---|---|---|
| Rh | 1.68 | 0.09 |
| Pt | 6755.8 | 2485.9 |
| Co | 0.0567 | 0.0014 |

Two experiments were run after with increased amounts of Pt and Rh chloride, 0.5g each, running through the gravity flow column to determine the amount of Pt and Rh chloride gets adsorbed onto the surface of the IX resin (Table 29). There was less Rh, Pt and Co shown on the surface of the MTS9140 compared to M-4195. However, both resins show a lower affinity to Co compared to the other metals, with Co being 0.15% and 0.49% for MTS9140 and M-4195 respectively; whereas, Rh was 0.29% and 6.48%, Pt was 3.88% and 9.23% respectively. With the final amount of Rh, Pt and Co being shown in Table 28. With the excess of $Cl^-$ from the DES can be seen on both IX resins investigated with M-4195 adsorbing more than MTS9140. Where is calculated the amount of Rh and Pt that was absorbed on and into the resin.

# 4. Discussion

## 4.1. Process of Setting up Resin-in-Leach

The process to set up a successful RIL system for DES and IX resins required many alterations, this was due to many factors such as the viscosity of the DES, mass ratio of DES: amoxis: IX resin, temperature of the system. Figure 50 showing the process of the systems that were tested to get the DES and IX resin process to work.

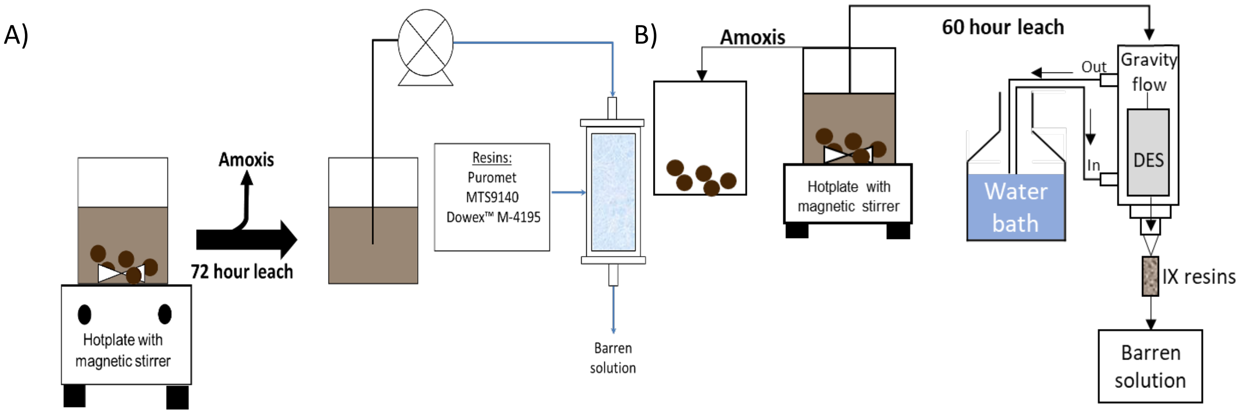

Figure 50 Process of creating the RIL process. a) First set-up, b) Second set-up

Figure 50a did not work due to the viscosity of DES being too thick this caused that was being pumped through the peristaltic pump which led to the tubing that was connecting the peristaltic to the leached amoxis and the IX resins would get clogged and eventually popped off. Also, during this system, it would not take into account the temperature that was required for the highest leach. This thought process caused a gravity-flow columns to be considered. With a gravity-flow column the factor of the DES viscosity no longer a factor and a circulating heat baths can be connected to the gravity-flow column.

Figure 50b shows the current best method of getting the gravity flow column to work. However, as the water-jacket only surrounds the column where the DES-PM solution is contained where the IX resins are packed that is left at ambient temperature, so insulation (glass wool), paper and aluminium foil was used to warp the IX resin packed column and the gravity flow column to keep and contain the temperature that is being used. Additionally, the size of filter for the IX resins had to change from the one for 2.4ml half-packed column, if the 1.4ml packed column was used the compression of the packed resins and thickness of the DES did not allow for the system to work. A 1.2ml sized filter to prevent the IX resins from flowing through the column whilst allowing the viscous DES through at a reasonable time at 3.96 BV/hr (bed-volumes per hour) (Figure 43).

As it shows in Figure 50b the was no longer a use of a peristaltic pump as the system switched to gravity flow column, despite this method allowing the DES the go through the IX resin packed column it also created an inconsistent pressure and flow rate during in section 3.3, showed a regular pattern of 7-10 7-10, which is seen with both IX resins at both temperatures. This could be due to the flow rate discrepancies which may have been caused by the gravity-flow column relying on the pressure from the air to pack the rest of the column to aid in the push of the DES down the column. This was seen in the volume of the barren solution collected with BV between the BV of 8-12, 17-21 and 28-33 for all the resins and temperatures collected 0.5ml compared to the 1.5ml that was meant to be collected.

Comparison to the flowrate of the peristaltic pump is set at 3rpm, 0.19 L/min, the flow rate of the gravity-flow column was calculated to be 0.05 L/min. This flowrate is significantly lower than using a peristatic pump, this was expected as the gravity flow is being pushed by atmospheric pressure,1.01 bar, instead of the generated pressure of up to 8.6 bar that can be seen in peristatic pumps (396). Experiments were done determine if more DES was added would that increase the flow-rate and pressure that was on the column. Volumes of 120ml were compared to the 80ml that was used in the RIL system. The BV/hr decreased from 29.64 BV/hr to 19.34 BV/hr with 80ml to 120ml, respectively. Additionally, to the differences in pressure, the viscosity of the ChCl: Lac is 12.2 cP, the higher viscosity has shown a difference in the BV/hr greatly compared to the calculated BV/hr from the peristatic pump was 3.96 BV/hr. Similarly, to what is seen in section 3 of chapter 4. The column dynamics of gold and silver *via* MTS9140 and M-4195 using the RIL system show similar data with very little PGMs being seen in the barren solution. The breakthrough column dynamics showed that the PGMs maximum capacity was not met which was also shown in sections 3.2 and 3.3.

## 4.2. Temperature Conditions

From section 3.1 was discovered that the temperature that showed the highest leaching of Rh and Pt was 30°C, 60°C and 80°C. Each temperature, resin-in-pulp and resin-in-leach experiment were repeated three times with the average recovery concentrations being presented in section 3.1 to confirm the validity of set temperature for optimum metal recovery. Despite 80°C showing high recovery of Pt the tubing used in the work thermal limit was 70°C. There is currently no literature that attempts to describe the notable reasons into why 70°C performs lower then at 60°C or 80°C, however, this pattern could be due to the different mechanism and interactions that occur between the DES and amoxis which is discussed in chapter 6. Additionally, this work is interested more into the recovery of Rh, due to the high demand, lower supply and overall higher price per oz (397). 30°C and 60°C showed the highest dissolution rate with Rh. However, in the RIP system it showed that 60°C with both resins showed a higher concentration of Co in the barren solution; compared to the data shown with the lower concentrations of Co at 30°C with M-4195 with ~0.15 mg/l of Co after 72 hours. For both the RIP and RIL systems it was determined that the MTS914 IX resin recovered the highest amount of Rh and Pt from the amoxis whilst not recovering Co. This is due to MTS9140 industrial usage is for mercury, gold, and precious metals, whereas M-4195 industrial usage is for hydrometallurgical production of copper, nickel, and cobalt (398). The functionality of M-4195 explains the data see in both sections 3.3 and 3.4 with the lowest amounts of Co being seen in the barren solution.

From the figures shown in sections 3.3 and 3.4 the metal recovery for Pt and Rh *via* the RIP system for MTS9140 at both temperatures and M-4195 at 30°C recovery rate was determined to be 100% with no Rt and Rh was analysed *via* the ICP-OES with the M-4195 at 60°C recovery rate of Pt after 72 hours was determined to be 45.55%. The recovery of Rh, Pt and Co from the resins has not been investigated but due to the high recovery rates of the metals from both IX resins the solution would need to be cycled through the resin for full and pure recovery of the metals which maintaining the resins for reuse. The recovery of the MTS9140 *via* RIL MTS9140 at 30°C and 60°C can also be seen a 100% with no Rh or Pt being present in the barren solution; however, when M-4195 shows small volumes of Rh and Pt in the barren solution when the column was run at 30°C with a recovery rate of Rh and Pt being 80% and 61% respectively. When M-4195 RIL system was run at 60°C Pt can be seen in the barren solution up till BV 30 is when it decreases to zero and no Rh is seen in the barren.

Co concentrations with MTS914 resin in the RIL system is 0.71 mg/L and 0.11 mg/L at 30°C and 60°C respectively compared to M-4195 resin is 0.01 mg/L and 0.03 mg/L at 30°C and 60°C respectively shown in Figure 48 and Figure 49. Compared to the RIP barren solution which had a higher final concentration of Co for all resins and temperatures, expect M-4195 at 30°C, MTS9140 at 1.09 mg/L and 1.28 mg/L at 30°C and 60°C respectively compared to M-4195 resin is 0.143 mg/L and 1.746 mg/L at 30°C and 60°C respectively. The chances in the data due to temperature differences could be due to the mechanism of the interactions. It was determined in chapter 6 that there are multiple interactions in play, between DES and amoxis extraction. So, it can be assumed that with the multiple interactions that are occurring in the extraction mechanism the different temperatures caused different mechanisms to become the dominate force in the extraction.

## 4.3. Deep Eutectic Solvent Combination with Ion Exchange Resins Comparison with Literature

There is currently being no literature on either RIL or RIP processes that is combined with DES in relation to the recovery of precious metals from a spent catalyst. There is literature that combines DES and IX resins in the carbohydrate conversion into 5-hydroxymethylfurfural (399). The literature showed that the combination of DES and IX catalyst was able to successfully synthesis 5-Hydroxymethylfurfural. The combination of IX resins and DES which stated how the IX resin, Amberlyst 15 a SAC resin, and various DES including ChCl: EG, $Bu_4NCl$: EG and $Bu_4PCl$: EG were investigated. It was shown that at the raised temperature of 60°C producing the highest yield using the DES $Bu_4NCl$: EG at 78% and 40°C showing the lowest yield temperature at 15% for fructose conversion (399).

This supports the temperature investigations that is seen in section 3.1, that also showed 40°C recovered the lowest amount and 60°C had the highest recovery. With ChCl: EG and $Bu_4PCl$: EG showed a yield of 40% and 50%, respectively. This literature supports the findings seen in section 3, with the optimum temperature being determined at 60°C and 40°C. It is currently unknown why 60°C is the optimum temperature for DES and IX resin work; additionally, it can be seen with other work with the use of DES in production of compounds that 60°C is the optimum temperature for higher yields (400; 401). However, the thermal stability for ChCl: Lac was found to be 196.83°C; with the degradation of a range of different organic acid DES, critic acid, Lac, oxalic acid and tartaric acid, the degradation ranged from 154.94°C to 228.61°C (402). Additionally, it has been found in literature that oxidation rates of gold *via* DES in an industrial process lower temperatures were favourable (309).

Wan et al used the combination of IX resins and DES in the synthesis of lipophilic caffeoyl alkyl ester (394). This investigated two different cation exchange resins, A-35 and NKC-9, with the DES ChCl: caffeic acid (CA) (394). It was found that the A-35 resin had a higher CA conversion rate at 95% and octodecyl caffeate yield of 91% (394). With the optimum parameters of the work being determined as 90°C, ratio of 8:1 and a catalyst load of 5% (394). Another literature by Liu et al used DES, ChCl: ethylene glycerol (EG), as an alternative to highly acidic solvents that are currently being used for electropolishing of nickel (403). It investigated with a strongly acidic cation (SAC), Amberlite IRA-200, which was wetted with the DES showed a promising alternative (403). The use the DES to wet the resin allowed a reduce of surface tension of the electrolyte and allowed the formation of tiny electrolytic cells, which weakened the polishing effect (403). Another literature that investigated the potential to remove zinc (Zn) from wastewater (404). ChCl: EG was investigated with two IX resins; one being a SAC, LEWATIT® MonoPlus SP 112, and the other was a weakly basic anion (WBA) resin LEWATIT® MP 62 (404). It was determined that the between the two resins the SAC resin SP 112 was a more successful resin in the removal of the Zn compared to the WBA MP 62 where no Zn was sorbed to the resin, due to the salts unable to be spilt by the resin (404).

Literature that has shown a different way of combining IX resins and DES systems by modifying an anion-exchange resin (AER) synthesised from ethylene glycol dimethacrylate (EGDMA), glycidyl methacrylate (GMA) and triethylamine (TEA) with ChCl: glycerol (Gyl) DES for the extraction of cleistanthol (393). It was found that the modified AER gave the highest recovery rate of 82.11% compared to the non-modified AER and octadecyl silica (ODS) recovery rate of 72.14% (393). It was determined that this was because of the [Ch]$^+$ from the ChCl can afford to interact with the charged cleistanthol through electrostatic interactions which is the major player in the affinity and selectivity of the polymer for the extraction of the cleistanthol (393). Comparing, the finding determined in this work to the findings in this work all the literature it shows that combining DES-IX resins in one system improves the recovery rate or production of the investigations and has potential to be an effective alternative to the current hazardous methods that are currently being used. However, there is very limited research into the determining why certain conditions produce the highest recovery rates, or the possible mechanisms of the interactions between the DES and IX resins.

## 4.4. Resin-in-leach and Resin-in-pulp Comparison

The Pt recovery between the two IX resins tested clearly shows that MTS9140 had a higher recovery with a no Pt or Rh was seen in the barren solution compared to M-4195 where concentrations of Pt were 5.14 mg/L at 60°C in the barren solution (RIP) and 0.19 mg/L at 60°C (RIL); however, no Rh was shown in the barren solution with any of the IX resins. When the M-4195 IX resins in the RIP systems was tested the first 1hr showed a very high recovery then a sharp decrease over the next 95 hours. This could be due to the capacity being reached between the 1st and 24th hour of the leach which can be confirmed in chapter 3 where the column experiment was run for 20 hours. Compared with the MTS9140 the Pt recovery is not gradually and inconsistent, but capacity may have been reached at 72 hours.

This is confirmed in section 3.1.2 with the best IX resin shown is also MTS9140 that is able to recover all the Rh and Pt from the amoxis with neither being shown in the barren solution with MTS9140 at 60°C. However, M-4195 has the highest amount of Co in the barren solution which can determined at out of the two resins M-4195 at 60°C has a lower affinity towards Co compared to MTS914, compared to M-4195 at 60°C having the highest affinity towards Co. Despite M-4195 at 60°C showing the lowest affinity towards Co and Pt is still shown in the barren solution which can determine that at 60°C M-4195 affinity towards Pt and potentially the other PGMs is lower compared to MTS914.

Literature has also determined when comparing RIL and RIP, the RIL system was the more favourable out of the two and determined to be a potential alternative to carbon-in-leach (386). Investigations into comparing RIL and RIP in the leaching of precious metals is very limited and only current involves gold, silver platinum and palladium and various other base metal from a cyanide heap leach solution in a RIL system. With majority of the research involving RIL or RIP being compared to carbon-in-leach (CIL) or carbon-in-pulp (CIP) systems which was already determined to be a more potential alternative (390; 405).

IX resins Minix, AuRIX and AM2B were investigated in both RIL and RIP systems into the recovery of Au with competing earth metals. All three in the RIL system was able to improve the preg-robbing that is often seen in CIL with the use of Minix resin being the optimum resin that achieved gold lading at 19,920 g/t (386). CIL and RIL had recovery rates of 80% and 87% respectively (386). The presence of a blanking agent was determined to yield the best result in addition with RIL (386). In this literature very little is discussed on the topic of RIP with it being stated that in comparison to CIP the overall gold recovery at one mine was 85-90% in comparison to 60-70% respectively (386).

Literature by Schoeman *et al.* show with four different strong base resins with ammonium functional groups, Dowex 21K XLT, Amberjet 4600, Amberlite PWA-5 and Minix, they were able to extract high levels of all the precious metals ranging between 60% to 100% in RIL systems (406). Dowex 21K XLT, Amberjet 4600 and Amberlite PWA-5 was determined to have the highest screening recoveries for Pd and Pt with recovery rates of >98% for Pt and >99% for Pd (406). It was also determined that Minix had the highest recovery for gold at 98% (406). Despite Amberjet 4600 and Amberlite PWA-5 showing high recoveries of Pt and Pd it also shows very high recoveries for other competing metals, nickel, copper and zinc with recovery rates of 85% - 100% (406). This non-selective adsorption occurs when using anion exchange resins containing high exchange capacities and small functional groups; and the lower Au affinity is due to the high ionic density of the resins which have a higher affinity towards charged anions (406). This confirms the data shown in both chapter 4 and this chapter with MTS9140 having a low ionic density had a higher affinity towards monovalent anions (407). Minix showed the highest recovery rate as similarly to MTS1940 it was developed for precious metal selectivity with Minix specifically being used for gold-selectivity for use in cyanide solutions (406).

Schoeman *et al* also investigated the difference in using acidic thiourea and potassium thiocyanate in the leaching of Au, Pd and Pt using the two resins Minix and Amberlite PWA-5 discussed earlier. It was shown that when potassium thiocyanate was used it was unable to fully elute all the metals from Minix within 20 bed-volumes (406). In comparison to when Amberlite PWA-5 was used where the elution was completed at bed-volume 15. Comparing the results seen in this chapter against the work in chapters 4 and 5 (406). However, when acidic thiourea was used complete elution was seen with Au and Pd with Minix at bed-volume 15; with the elution using Amberlite PWA-5 was slowed and was not completed at bed-volume 20 (406). No current work is able to determine the reasoning to what was seen in this work.

As discussed in chapter 6, the redox behaviour between Rh, Pt with DES has yet to be investigated. However, research into $Cl^-$ solution and Cu was investigated using MTS9140. When the $Cl^-$ and Cu are in elution it confirmed the REDOX between $ClO_3^-$ and Cu(I), whereby $ClO_3^-$ is reduced to $Cl^-$ and Cu(I) oxidised to Cu(II) (408). With Cu having similar chemical properties to PMs, it can be concluded that there is a favourable REDOX reaction that occurs between the DES and precious metals due to the $Cl^-$ being in excess thought all the reactions in this work and in chapter 6 (408). Chapter 6 shows an insight into the shifting leaching equilibrium by running it in the RIL and RIP system. This has also not yet been investigated. However, referring to chapter 6 the redox equation discussed of Pt and Rh in $Cl^-$ formed the following complexes $PtCl_6^{2-}$and $\mathrm{RhCl}_6^{3-}$ could form various complexes with the addition of MTS9140 resin such as $Pt(TU)_4^{2-}$, $[Pt(TU)_4]Cl_2$, $Rh(TU)_6^{3-}$ with the introduction of the MTS9140 resin during or after the leaching with the DES (409; 410). The redox potential ranges have not yet been investigated to determine which complex is the most stable or the preferred complex that would be made during this reaction.

When comparing the two systems based on Rh and Pt recovery it can be assumed that both systems were able to leach out more Rh and Pt without the absorption of Co. Using MTS9140 yield the best leaching with a high concentration of Co in the barren solution 1.01mg/l and 1.28mg/l for RIL and RIP, respectively. Additionally, the trend seen between the two systems show that in the RIP system the concentration of Co in the barren solution increased gradually in comparison to the RIL where the concentration vary which could be due to the flow rate discussed earlier. Another factor that could determine whether the RIL or RIP system could be chosen in an industrial setting would be ease of preparation and overall cost. RIP is a lot easier to set up and run-in comparison to RIL system used in this work.

## 4.5. X-ray Photoelectron Spectra

The first run of the IX resins after the RIP and RIL of the amoxis was run of the IX surfaces which resulted in no Co, Pt or Rh being detected, shows it can be determined that the Pt and Rh was absorbed into the IX resins shown in section 3 that there is no Rh or Pt in the barren solution of the RIL or RIP expect for Figure 48b. When 0.5g of $PtO_2$ and $Rh_2O_3$ was added to the DES and left to mix at 350 rpm for 24 hours with both MTS9140 and M-4195. The second run shown in Table 28 and SEI1 with the increased Rh and Pt allowed for them to visible using the XRD analytical technique. Comparing the atomic percentage to the percentage estimates of Rh, Pt and Co that was provided by RSBruce$^{TM}$ of 0.05%, 0.16% and 18.6% the amount of each MTS9140 resin showed a lower percentage compared to M-4195 resin at 0.29%, 3.88% and 0.15% for Rh, Pt and Co, compared to the percentage determined of Rh, Pt and Co on the M-4195 resin at 6.48%, 9.23% and 0.49% respectively. However, despite this showing that M-4195 has a higher adsorption of the metals this was an analysis of the metals on the surface of the resin; the amount of each metal absorbed into the resin is unknown.

The loading capacity calculated of each metal *via* M-4195 of 0.12 meq/l, $8\times10^{-4}$ meq/l and $5\times10^{-5}$ meq/l for Pt, Rh and Co respectively was considerably lower than the loaded capacity of MTS9140 of 0.34 meq/l, 0.016 meq/l and $2\times10^{-4}$ meq/l for Pt, Rh and Co respectively. Both resins show Co having the lowest capacity this supports the data shown though this and previous chapters of DES and IX resins having a low capacity towards Co and other transition metals with both resins investigating in chapter 4 having nearly all the Co being detected in the barren solution of the dynamic column testing (Figure 18 and Figure 19). Compared to the manufactured values all three are considerably lower with MTS9140 and M-4195 being 1 eq/l and 8.2 eq/l (Cu), from the loaded capacities of the PGMs it can determined that waste with a higher concentration of PGMs could also be used *via* this method to recovery PGMs (223; 224; 225). Additionally, at the low-grade concentrations of the metals show in this work it could be passed through the column 8 times using M-4195 and 3 times using MTS9140 before either resin is saturated with Pt. However, despite this showing that M-4195 has a higher adsorption of the metals this was an analysis of the metals on the surface of the resin; the amount of each metal absorbed into the resin is unknown.

# 5. Conclusion and Recommendations

Combining two different leaching methodologies of DES and IX into one was investigated if they could optimize the overall leaching of each method. It was determined that combining IX and DES recover Rh and Pt from Co. Various parameters were investigated to determine the optimum conditions for the leaching such as temperature and an addition of an oxidant. Resin-in-pulp was determined as the optimum method for the recovery. Two different IX resins were investigated, were Puromet™ MTS9140 and AmberSep™ M4195. With MTS9140 being determined to be the preferred IX resin, which recovered all the Rh and Pt that was on the Amoxis with only Co being seen in the barren solutions for both RIP and RIL.

Temperatures experimented, 30°C and 60°C, found that 30°C was able to recover the most amount of Rh and Pt separately from Co in both system but 60°C extracted all the Rh and Pt with leaving the highest amount of Co in the barren solution. Investigations into why Pt is seen in the barren solutions in both the RIP and RIL systems at 60°C *via* the MTS9140 and in both temperature *via* the M-195 resin is required to better understand how the temperate effect the mechanisms and interactions that extraction the Pt and Rh onto the resins. Additionally, more research into the column dynamics and mass transport behaviour of the gravity flow column and the effect that may have on the overall kinetics and recovery of PGMs from the amoxis and other spent catalysts.

A better understanding of the interactions between the DES system and IX resins prior to the MoMO being added is needed to determine the optimum conditions and into the reusability of MTS9140 with both metals until the resin gets saturated with either resin. Additionally, further investigations into the different parameters that were not investigated such as: flow rate, DES viscosity, mass of IX resin packed into the column, should be investigated to be able to determine the optimum conditions for the entire system.

## Declarations of interests

RSBruce have interest in improved methods of recovering Rh and Pt from the Amoxis they supplied.

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## 7.3. Supporting Electronic Information (SEI)

SEI1: XPS spectra of IX resins after addition of Rh and Pt chloride.

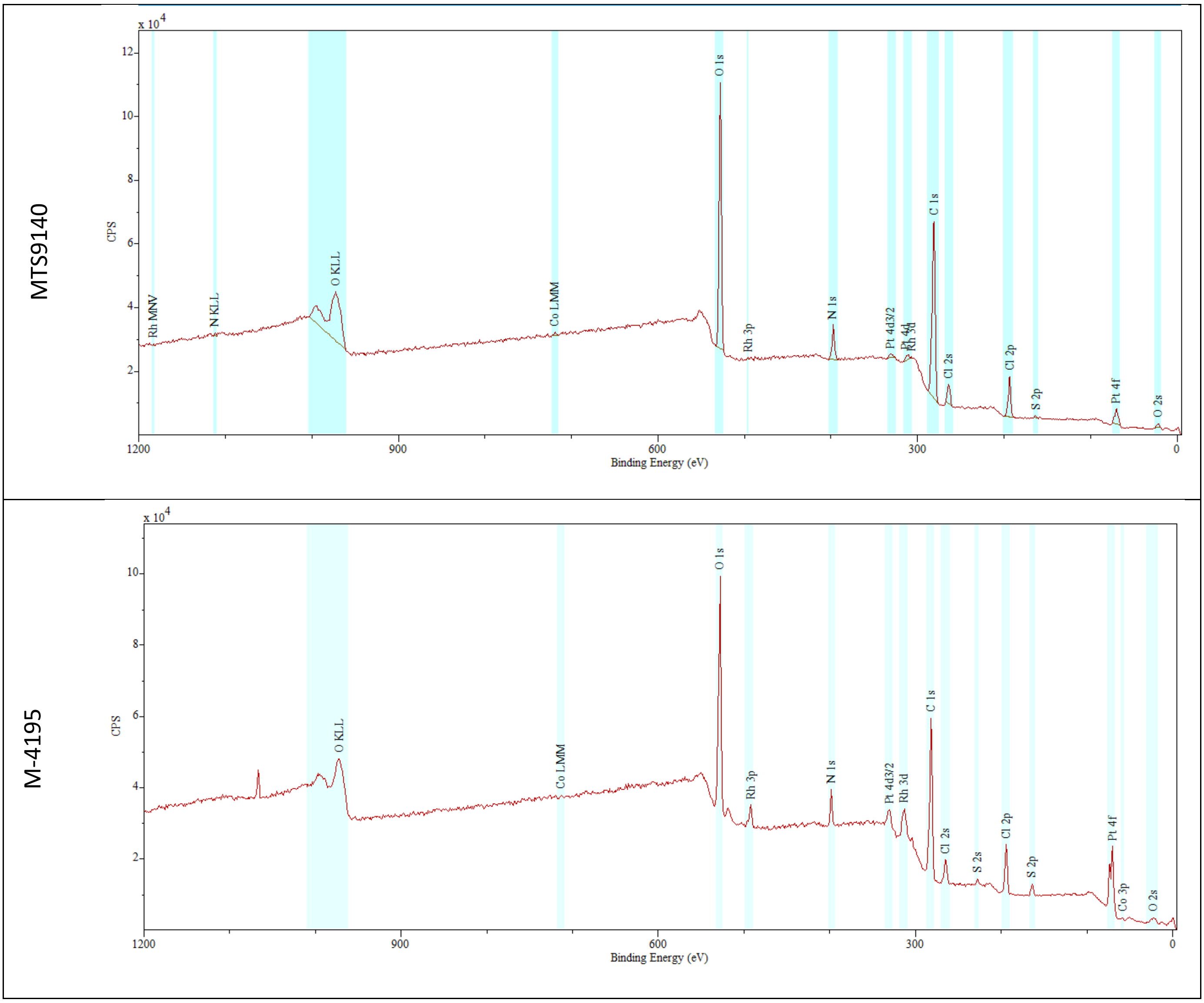

**Figure 51 SEI1: Full XPS spectra of IX resin after resin-in-pulp experimental with ChCl: Lac DES**

# CHAPTER 8: CONCLUSION AND FUTURE WORKS

## 8.1. Conclusions

The comprehensive hypothesis of this work, stated in the aim chapter 3 **"The combination of DES and IX for a more sustainable process for the recovery of precious metals from waste"**. This work focused on five different IX resins affinity towards PMs, the synthesis of four DES, DES leaching abilities of Rh and Pt and the combination of DES and IX resins leaching. It has shown the IX resin MTS9140 with the functional group thiourea has the highest affinity towards PMs; the DES ChCl:Lac showed to have the highest leaching for Rh and ChCl: TU showed a high affinity for Pt. By attempting to combine the DES and IX resins in a RIL and RIP system, it was determined that the RIL system was a more effective system for Rh and Pt recovery. Various hypothesis questions were asked in section 3, the following sections will answer each hypothesis question.

Each chapter aids the further research in the combination of DES and IX resins. Chapter 5 and 6 are the investigations for the IX resins and precious metals and the DES systems, respectively. Results were then used in the final experimental chapter 7, which combines the two approaches. The first chapter investigates Au which links to Rh and Pt in terms of similar reactivity and inertness in regard to acids and reagents for purification. The IX resin that had the best affinity towards Au could be predicted to also have a high affinity towards the PGMs that are investigated in the 7th chapter. The results discussed in chapter 5 feed into the DES systems that were chosen for chapter 6. In regards selectivity series of all the resins investigated which was Au > Ag > Cu » Co > Fe > Mg > Zn. This selectively suggested that using an IX system the MoMO catalyst metals of Pt, Rh and Co, the Pt and Rh would successfully be able to be separated from Co.

Chapter 6 links to the last combination chapter as it reveals that the recovery of the Pt and Rh from Co without the use of a strong acid (aqua regia), is possible, with all DES systems having a higher recovery rate than aqua regia for both metals. This chapter identified the best-performing DES to solubilise each metal and showed that addition of $I_2$ was beneficial for Pt solubilisation. The last chapter was a combination of the 5th and 6th chapter into a new system of RIP and RIL. The best IX and DES system that would potentially have the best recovery of Pt and Rh, with Rh being the higher priority due to the greater supply and demand disparity and the price of Rh comparison to Pt.

### 8.1.1. IX utilisation to specifically target precious metals from a complex metal mixture representative of mining waste.

The determination of commercial IX resins that have an affinity towards PMs, specifically Au, was achieved. Out of the five resins that were chosen Purolite® A200, Lewatit® MonoPlus TP 214, Dowex™ M-4195, Puromet® MTS9140 and Lewatit® VPOC 1026. The two IX resins that were found to have the highest affinity towards Au, Puromet® MTS9140 and Dowex™ M-4195, with final concentration of Au in the barren solution was 0.644 mg/l and 0.1543 mg/l, respectively. The two resins that were determined to have the highest affinity towards Au, MTS9140 had a functional group of thiourea which is known to be highly selective towards precious metals. M-4195 which is mainly used for Cu, Ni extraction but has been researched in other metals one of them being Au (243). Other IX resins that had the same functional group of M-4195 was researched in the absorption of PGMs (245).

Improvements to this research could be readily done for the breakthrough data for MTS9140, M-4195 and Lewatit® VP OC 1026, by running a longer leach to determine the breakthrough for the IX resins. VP OC 1026 was unable to fit any of the models; potentially by doing a longer leach and collecting more BV then the 80 collected the breakthrough could occur afterwards. MTS9140 did not reach breakthrough at 80 BV and a longer run through the packed column and peristaltic pumps to determine that breakthrough point when the capacity for Au is reached. Similarly, with M-4195 even though a breakthrough was seen, however; from the data seen in chapter 4 the capacity was not reached. Doing a longer running time for the M-4195 would be able to determine this.

The breakthrough models were a great tool in calculating the modelled 10% volume and mass. MTS910 do not fit the expected 10% breakthrough points and masses with the expected 10% breakthrough values of 247ml and 24mg respectively with the achieved 10% breakthrough points and masses with values of 0ml and 0mg. Compared with M-4195 which matched the 10% breakthrough points and masses with 80ml and 7.6mg respectively with the achieved volumes and masses at 10% breakthrough being 77ml and 7.7mg respectively. It is unclear why VP OC 1026 did not fit the modelled data points; however, this is suspected to be because of relatively weak interactions between D2HEPA and the IX resin matrix.

Out of the five resins investigated, four of them showed to have an affinity towards Au with only A200 resin being the only resin that showed the breakthrough point. This means that TP214, MTS9140, M-4195 and VPOC 1026 are all potential resins for an alternative to cyanidation *via* activated carbon with all four were determined to adsorb a high amount of the Au that was present in the PLS. It is noted that the IX resins with thiourea functional groups showed the best affinity and recovery of Au and Ag. This data and the PLS having a thiourea-thiosulphate lixiviant showed the stability of gold-thiourea (AuTU) complexes increase as more ligands of thiourea get introduced into the solution and IX resins, compared to when the other metals in the PLS were introduced to the thiourea-thiosulphate lixiviant and thiourea IX resins.

### 8.1.2. Precious metals (PMs) on metal-on-metal oxide (MoMO) catalysts be selectively dissolved in DES.

Kinetic leaching experiments was used to determine which of the four DES synthesised would be able to selectivity dissolve PMs from a MoMO catalyst. This was performed with a lixiviant that is already used in industry, aqua-regia ($HNO_3$: HCl). All the DES systems showed the ability to selectively dissolve the PMs from the MoMO catalyst. They were also all able to dissolve more than aqua-regia.

ChCl: Lac, ChCl: Ur and ChCl: TU showed the most promising DES systems for dissolving PMs. The lac and U system showed the highest selectivity towards Rh, and the TU system showed the highest selectivity towards Pt. However, ChCl: Lac was chosen over the other DES systems that showed the most selectivity towards the PMs due to the ease of synthesis without the glovebox, the costs of the reagents, thiourea, urea and lactic acid is priced at £47.20, £60.60 and £38.00 respectively and the price of Rh, £12684.07 per oz compared the price of Pt, £805.45 per oz (dated 02-01-2023), it is more economically beneficial to focus on Rh (384; 397).

None of the shrinking core models were able to accurately describe the interactions and mechanisms that occurs between the DES and amoxis. With the Rh with all three shrinking core models having $R^2$ values of 0-0.28, Pt $R^2$ values ranging between 0-0.31 and Co $R^2$ values of 0.52-0.6. The figures shown in the SEI9-SEI11 shows mixed-control shrinking core model with nothing occurring then a steep increase. The reaction-controlled and diffusion-controlled shrinking core models both shows no cohesive pattern with many of the lines of best fit deescalating or being a horizontal line. Further research with attempts to fit the data is needed to be able to best describe the mechanisms.

A parameter that was investigated in this work was the addition of oxidants, $I_2$ and $Na_2O_2$. $I_2$ was determined as the more efficient oxidant out of the two with concentrations of 0.1 mg/l, 0.29 mg/l and 1.59 mg/l for Rh, Co and Pt. Whereas, $Na_2O_2$ showed better affinity towards Co with final concentration of 0.69 mg/l after 24 hours. However, the addition of the oxidants did not improve the overall leaching of the DES leaching seen without the addition of oxidants.

### 8.1.3. IX effectively being coupled with a DES system for the development of an effective and recovery process.

The premise of this work was to determine if it was possible to successfully combine two separation techniques into one. From the work shown in chapter 7, it is possible. The process of combining the IX column experiment seen in chapter 4 and the chosen DES system from chapters 5 and 6 was investigated with various set-ups investigated to get the DES to be in contact with both the Amoxis and IX resins. Two systems resin-in-leach (RIL) and resin-in-pulp (RIP) were investigated as the standard two methods for ion exchange methodologies. The main issues that were seen with the set-up of the RIL system were regarding keeping the temperature chosen throughout the column and the viscosity of the DES. These two issues were fixed with changing from using a pessimistic pump to using a gravity flow column and insulating the water-jet and column allowed for the temperature of the remain constant to keep the IX resin column the same temperature as the DES column.

By doing both RIP and RIL experiments it was determined that the DES and IX resins can effectively be combined into one system to recover the PMs from the MoMO spent catalyst. Various temperatures were investigated for the optimum temperatures 30-80°C from which three temperatures showed the highest leaching concentrations of Rh and Pt, 30°C, 60°C and 80°C; however, at 80°C Rh had the second lowest leaching concentration with 40°C being the lowest. Co remained fairly consistent between all temperatures investigated between 0.2mg/l to 0.4 mg/l. The two chosen temperatures, 30°C and 60°C, were investigated in both leaching methods that were investigated.

From all the experiments investigated in 7th chapter lead up to the MTS9140 and M-4915 being the IX resins to be investigated at two different temperatures with ChCl: Lac in two methods, RIP and RIL. The work resulted in determining that RIP method showed to have no Rh and Pt in the barren solution expect for M-4195 at 60°C, after 72 hours 5.144mg/l of Pt was detected in the barren solution. M-4195 in the RIL system showed a similar pattern to M-4195 RIP at 60°C. Similarly, the M-4195 *via* RIL at 60°C shows Pt in the barren solution; moreover, at 30°C both Rh and Pt was shown in the barren solution. However, an interesting finding was with MTS9140 differences between the RIP and RIL minimal amounts of Pt, Rh was shown in RIL at 60°C. With all experiments both RIP and RIL all have Co in the barren solution all at ~1mg/l ~2mg/l, with the exception of M-4195 at 30°C *via* RIP with Co showed concentrations of ~0.16mg/l and MTS9140 at 60°C *via* RIL with concentrations of 1-6mg/l shown in the barren solution. Out of the two resins chosen for the DES x IX system MTS9140 *via* RIL at 60°C has shown the best highest affinity towards both Rh and Pt whilst being able to separate them from Co.

The overall research that has been completed in this thesis adds to the overgoing research into recovery precious waste from, catalytic, waste. The potential for more benign and ‘green’ solvents and reagents for the recovery of inert and unreactive metals, not just precious metals. Additionally, the whole scope of the usage of DES with metal recovery via the process of RIP or RIL could be used in a wide range of metal-containing waste forms, such as mining tailings, catalytic waste, EV or other electronic product waste that contain precious or inert metals. The current gaps in precious metal recovery are in regard to using less hazardous or highly concentrated solvents such as cyanide or concentrated acids. Additionally, the research into DES still has limited research into recovery of inert metals. The new system of combining DES and IX into one recovery method is an exciting new recovery option and has potential use for purification of newly mined metals. The potential for this new system if used in industry could reduce the overall by-products and environmental harm of the current methods used in PM mining, purification and waste recovery.

## 8.2. Future Work

There were some limitations to the work investigated in this thesis during the COVID-19 restrictions and shut down of experiments which would have greatly aided to the interpret the findings in chapter 6 and 7. The experiments that were unable to be done are a priority for future work on this project. This mainly includes a full characterisation of the spent MoMO catalysts that were used throughout this work. This includes SEM, EDXA, more fully analysed XRD, surface area analysis to determine the oxidation states of the Rh, Pt and Co.

### 8.2.1. Ion Exchange Resin Affinity towards Precious Metals

This work has confirmed some questions regarding using an alternative lixiviant to cyanide for Au from PLS. However, there are some questions that were raised during this work about the IX resin breakthrough time, the lixiviant concentrations and the parameters of the packed IX resins with the peristaltic pump. These areas need to be investigated to improve the full scope of how each IX resin interacts with Au, Ag and when the capacity is reached and the full scope of how well the alternative lixiviant of thiourea-thiosulphate interacts with PMs. This can be done by testing the following hypothesis:

- Recovery of Au and Ag can be increased by increasing flowrate, concentration of lixiviant.
    - A study comparing the recovery of Au and Ag when the flowrate of the PLS running through the packed IX resin increases would aim to answer this question.
    - A study determining if increasing the concentration of the compounds used in the lixiviant would give better understand of the complexes formed and by increasing the concentration would the capacity of Au and Ag be reached.
    - As MTS9140 was unable to reach breakthrough nor did any of the other resins tested reach capacity a longer running time would give data on how much Au and Ag can be absorbed by the IX resins before capacity is reached.

    - As well as this, solid state analysis of the IX resins after the leaching run would give better evidence into how much Au and Ag is absorbed by the IX resins.

### 8.2.2. Deep Eutectic Solvents Interactions.

The DES synthesised for Rh and Pt recovery in this work showed that they can leach out the PMs successfully in comparison to commercial use of aqua regia (HCl: $HNO_3$). Despite that, this work has raised many questions with the interactions of the DES would interact with metals specifically precious metals and how HBA and HBD of the DES interact with each other.

In particular, it is not clear what the mechanism is that allows the DES to solubilize the metal species from the spent catalyst via a leaching process. In chapter 6 the effect of adding an oxidizing agents to the DES has a minimal effect on Rh leaching performance, but addition of $I_2$ significantly increased Pt leaching. The are two possible explanations for this behaviour.

1. The DES system oxidises the metal nanoparticles effectively by a currently undetermined mechanism.
2. The metals are (partially) not present on the spent catalyst in a zero-oxidation state but have already been oxidized and are present as salts. Therefore, redox chemistry is not necessary for solubilization (this may apply more so for Rh than Pt).

The following list of questions would be needed to be answered before DES can be used on commercial or industry levels:

- Would using different halides (Br, I, F) of the chosen HBA (ChCl) affect the affinity of Rh and Pt leaching form MoMO?
- Does synthesising DES in a glovebox have an impact of the interactions between HBA and HBD and recovery of Rh and Pt?
    - The DES synthesised in this work was done without the use of a glovebox. Seeing the difference of the use of a glovebox in the synthesis and leaching would give insight into the scale up applications of using this method in industry.

- Does the ratio between the HBA and HBD affect the leaching amounts of Rh and Pt?
- What are the effects of having $H_2O$ or synthesising in the DES system with the recovery of Rh and Pt?
- What are the economic benefits of replacing aqua regia and cyanide with DES?
  - Does the price of DES and IX resin process outweigh the overall price point of cyanidation and other industrial used lixiviants?
    - Determining the cost of the DES and IX resin system
- Would addition of different oxidants improve the recovery rate of PGMs?
  - Would the potential increase of the recovery of PGMs out way the potential hazardous oxidants and by-products that will be produced?

This area needs to be investigated to be to improve our understanding of the bonding interactions between the HBA and HBD is still being debated and researched and can further develop the functionality and possible uses of DES with recovery of different metals. This knowledge could allow the current low percentage of recycled PM waste. Using EXAFS to determine the interactions of the DES and Rh and Pt would give definite data on how DES leach the Rh and Pt from the spent MoMO catalyst. Also using various other models that attempt to describe the mechanisms that occur during the reaction. An investigation that could help determine the mechanism of the DES system and the metals could be to measure whether $H_2$ is generated during the leaching process.

### 8.2.3. Combination of Ion Exchange resins and DES system.

The combination of the DES system and IX resins was able to successfully recover Rh and Pt from a MoMO spent catalyst. With both Rh and Pt being able to successfully separate from Co in the RIL system at 30°C and 60°C. However, this work has raised questions into the how to optimize the DES × IX system that were not investigated.

- Would changing the independent variables of the system improve the adsorption of the IX resin?

    - Other parameters that were not investigated such as pressure, flowrate, bed-height should be investigated to determine the optimum conditions for the DES × IX resin system.
    - If changing the ratio of the DES would improve the recovery percentage. Using a range of different ratios would greater insight into how each reagent of the DES interact with the metals and amoxis.
- Further investigations into how IX resins and DES interact prior to the addition of the Amoxis.
    - Experiments into how both RIP and RIL interact with the DES systems before the MoMO catalyst is added. Using EXAFS to determine the composition and mechanism of the interaction that occurs prior to the addition of the MoMO catalyst.
    - Solid state analysis of the IX resins before and after the DES interaction to determine how the DES effects the IX resins.
- Investigations into more sustainable ways to recovery the Rh and Pt from the IX resins used should be investigated. Current methods usually involve pyrometallurgy or high concentrations of salts or brine.
- Investigations prioritizing Pt instead of Rh would that change the IX resin would be beneficial to compare the chemistry between Pt and Rh.
    - It was shown in chapter 4 MTS9140 worked best when TU was in excess in the solution, how would have investigating DES-IX resin methodology using ChCl: TU affected the overall recovery of Rh and Pt.

### 8.2.4. Clean-up and reusability of DES.

The clean-up and reusability of DES after the use of the DES-IX system has not been investigated. There is a wide range of different methods that can be investigated in regard to the reuse and clean-up of DES after being used for the extraction of various metals. Some potential methods are solvent extraction, electrodeposition, antisolvent crystallization with the most investigated method being chemical precipitation with the most commonly used method being evaporation (411).

Recent literature has different DES solvents ChCl: EG, Lac, maleic acid (MA) and oxalic acid (OX) after the recycling of lithium (Li) battery via the extraction of Li, Co and nickel (Ni) (412; 411). Li et al investigated MA and EG DES clean-up and reusability was investigated via using precipitating out Co and Li with the addition of anhydrous OX and washing out the precipitates three times with deionized water and being left to dry in an electric oven. The recovery of the Co was calculated to be 96% with no Li being precipitated out (412). The occurrence of Li not being precipitated out can be attested to the stable complex the $Li^+$ makes with the DES; the DES was then used four more times till the Li was able to be precipitated out using the anhydrous OX at a recovery of 80.4% with the leaching efficiency of Co remaining at 90% (412). The success of the reusability of the DES systems was a saving of 105.4 USD/KG (412). The second method for the investigation of the clean-up of the DES after the recycling of Li-batteries is using $Na_2CO_3$ and $(NH_4)_2CO_3$ (411). The chemical precipitation showed an overall recovery of 94% (411). Similarly, to Li et al the ChCl:Lac with the extracted metals was cleaned with the addition of OX (411). This method also yields a high recovery of 85% (411). This investigation does not include the reusability of the DES; however, it does so the decomposition of the DES; which denotes that the decomposition can occur during the leaching and after during the precipitation phases when evaporation is used to remove the solvents that were added in the precipitation phases which can potentially lead to thermal decomposition and decrease the leaching efficiency when the DES is reused (411).

These two studies show the high possibilities of the ChCl:Lac used in the final chapter with the IX resins has potential to a good life cycle of reusability if investigated. The main method currently being investigated is chemical precipitation with OX seemingly being the most used chemical in these investigations. Granted there are a list of other methods listed previously that have been shown to have comparable results to OX; however, the saved costs, and environmental impacts of by-products should be investigated in future when the clean-up and reuse of the DES are investigated after leaching of the precious metals.

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