Recovery of platinum, palladium and rhodium from acidic chloride leach solution using ion exchange resins

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A B S T R A C T

The objective of this study was to investigate the applicability and performance of the selected ion exchangers with different physicochemical characteristics and functional groups to simultaneously recover three different platinum group elements (PGE), platinum(IV), palladium(II) and rhodium(III), present in a chloride solution produced by the leaching of spent automotive catalysts. The tested ion exchangers included a resin with a quaternary ammonium functional group (Lewatit MonoPlus (M+ ) MP 600), a resin with a polyamine functional group (Purolite S985) and a resin with a thiouronium functional group (XUS 43600.00). The study also focused on the achievable desorption from the loaded resins using different eluent systems. The leach solution was chlorine-saturated and contained 2.35 mol/L hydrochloric acid, platinum and palladium in concentrations of 0.13 mmol/L, and rhodium 0.03 mmol/L. It was found that XUS 43600.00 showed the best adsorption performance for platinum(IV) and palladium(II) chloride complexes among the investigated resins, but weak affinity for rhodium(III) chloride complexes was observed for all three resins. The adsorption kinetics were found to obey the Ho pseudo-second order expression. For Lewatit MonoPlus (M+ ) MP 600 and Purolite S985 the adsorption was best described by the Freundlich isotherm, while for XUS 43600.00 the Langmuir isotherm was more apt. Desorption of the PGE was examined using four different elution agents: sodium thiocyanate (2 mol/L), hydrochloric acid (2 mol/L), thiourea (1 mol/L) in hydrochloric acid (2 mol/L), and thiourea (1 mol/L) in sodium hydroxide (2 mol/L). The results showed that platinum and palladium can be fully eluted with the acidic thiourea but desorption of rhodium proved difficult with all the eluents.

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1. Introduction

In recent years, the recycling of platinum group elements (PGE) has become an increasingly important topic, both as a potential strategy for maintaining the supply of these metals and in terms of converting a previously disposable material into a valuable renewable resource (Barakat and Mahmoud, 2004; Bernardis et al., 2005; Faurie, 2011; Gaita and Al-Bazi, 1995; Magilligan et al., 2011; Senthilingam, 2011; Zolotov et al., 2003). The growing demand for potential secondary sources of PGE has intensified research and development work which aims to recover PGE from wastes or spent materials. These secondary sources can include spent automotive catalysts, catalysts from the chemical industry, electronic scrap, exhausted nuclear fuel, military equipment and even tailings from ore-dressing plants for noble metals-containing deposits (Barakat and Mahmoud, 2004; Belyaev, 2003; Matthey, 2011; Rao and Reddi, 2000; Zolotov et al., 2003).

A patented work at Murdoch University was recently published to provide an innovative process for recovering PGE from spent automotive catalysts (Nicol and Nikoloski, 2011). Nicol and Nikoloski (2011) showed that platinum (Pt), palladium (Pd) and rhodium (Rh) can be extracted with effectiveness which compares well to other extraction methods using much more rigorous conditions, e.g., high pressure, high temperature and prolonged reaction times. Subsequently, all three PGE from the leachate solution were successfully recovered by means of precipitation or cementation. Though no comparison was made, the authors suggested that the resulting leachate solution may be subjected to other recovery techniques, e.g., electrowinning, solvent extraction, gas-reduction or adsorption to recover the desired PGE from the leachate solution.

The recovery and separation of PGE in precious metal refineries had been achieved by a series of precipitation processes until the 1970s when other effective and promising techniques, i.e., solvent extraction and ion exchange, were introduced and adopted by the refineries (Bernardis et al., 2005; Edwards et al., 1985, p.2; Renner et al., 2012; Warshawsky, 1987, p.157). These advanced techniques offer a number of advantages which the classical methods were lacking, such that higher selectivity of PGE and higher metal purity can be obtained (Bernardis et al., 2005; Cieszynska and Wiśniewski, 2012; Rengaraj...
et al., 2001). As a result of these significantly improved features, solvent extraction and ion exchange are recognised by many as potentially more efficient and economically justified, even for application with leachate solutions containing very low PGE concentration. For that reason, an alternative approach based on ion-exchange (IX) technology was proposed in this study to investigate the recovery of PGE from the chloride leach solution of spent automotive catalyst.

The use of IX for metal recovery and separation is not an unproven technology but is dated back to its unique success achieved in the late 1940s. Early examples include the separation of rare earth elements (Harris and Tompkins, 1947; Ketelle and Boyd, 1947; Marinsky et al., 1947; Spedding et al., 1947a,b), separation of sodium and potassium (Cohn and Kohn, 1948; Schubert, 1949) and amino acids (Cleaver and Cassidy, 1950). Today, IX technology is well established, with modern applications, such as, the recovery of precious metals (e.g., gold, silver, PGE), base metals (e.g., copper, zinc, nickel and iron) and uranium, removal of trace level impurities from aqueous systems for pollution control, and in pharmaceutical and chemical processing techniques for the production of pure and ultrapure water (Green et al., 1998, 2002; Haines, 1978; Hubicki et al., 2008; Mendes and Berni, 2009; Rousseau, 1987; Zagorodni, 2007). The literature also suggests that a wide range of specific functionalised resins have been studied extensively and demonstrated to be feasible in their application for selective recovery of PGE (Hubicki et al., 2008; Kononova et al., 1998, 2007, 2008, 2009, 2010a,b,c, 2011, 2013; Mel'nikov et al., 2012a,b; Nikoloski and Ang, 2014; Wołowicz and Hubicki, 2011; Wołowicz et al., 2011).

Throughout the course of the literature review, the present authors of this study found that Purolite S985 and Lewatit MP 600 WS excel among other anion exchangers. The recovery conditions of PGE from the chloride system on anion exchangers Lewatit MP 600 WS and Purolite S985 were extensively studied by Kononova et al. (2010a,c, 2011, 2013) and Mel'nikov et al. (2012a,b). These anion exchangers were recommended because of their comparatively better sorption and kinetic properties for PGE than other investigated resins. They also exhibited promising performance in the elution of PGE. Nonetheless, both anion exchangers have yet to be tested in any hydrometallurgical leaching solution, but were only demonstrated in synthetically made solution. The scope of the investigations by these authors was also limited to the recovery of either one PGE element or a combination of two PGE elements at most in the chloride media. Thus, it was deemed useful to investigate the sorption characteristics of these anion exchangers in chloride leach solution of spent automotive catalyst for the simultaneous recovery of Pt, Pd and Rh.

In addition to these two resins, a new ion exchanger XUS 43600.00 with thiouronium functional group was developed by Dow in the recent years and it is claimed to be very selective for platinum group elements. Chelating resins containing thiouronium (thioura) or its derivatives (e.g., isothiouronium) functional groups are widely used for the separation of platinum-group metal ions from other ions (Hubicki et al., 2008). Lewatit TP-214, Purolite S-920, Srafix NMRR and Monivex are among the few thiouronium-functionalised resins that have been reported to possess promising ability to separate and recover PGE (Blokhin et al., 2007; Hubicki and Wołowicz, 2009; Hubicki et al., 1998, 2007; Warshawsky, 1987; Warshawsky et al., 1980). Nonetheless, there was no data readily available in regards to the use of thiouronium-functionalised resins in the simultaneous sorption of Pt, Pd and Rh from hydrometallurgical leaching solutions, e.g., chloride leach solution of spent automotive catalyst. Hence, it was also of great practical relevance to assess the performance of the new XUS 43600.00 thiouronium-functionalised chelating resin and to compare its performance with the other two resins.

The objective of the study therefore was to investigate the applicability and adsorption performance of the selected ion exchangers of different physical–chemical characteristics (i.e., Purolite S985, Lewatit M + MP 600, and XUS 43600.00) in recovering Pt, Pd and Rh simultaneously present in the chloride leach solution collected from leaching spent automotive catalyst. The investigation also focussed on the achievable desorption from these resins using different eluent systems. Both the rates and extents of adsorption and desorption for Pt, Pd and Rh are reported and the mechanisms of the adsorption processes are discussed using relevant models. The main difference between the ion exchanger Lewatit MP 600 WS (a heterodisperse resin) studied previously and Lewatit M + MP 600 (a monodisperse resin) used in this study is their bead size distribution.

2. Experimental materials and methods

2.1. Reagents and solutions

2.1.1. Loading solutions

Two different PGE-containing solutions were used in this study: (i) process leach solution which was a chlorine-saturated leach solution of spent automotive catalyst containing Pt, Pd and Rh and a range of impurity elements, and (ii) synthetic solution made up of analytical grade chemicals, thus containing only Pt, Pd and Rh with no other metal ion impurities.

The process leach solution was a blend of PGE-containing leach liquors from a previous project involving leaching and recovery of PGE from used automotive catalytic converters conducted by Nicol and Nikoloski (2011). To generate the process leach solution, PGE-containing feed was subjected to a treatment which involved roasting under oxidative conditions and then under reducing conditions, followed by leaching in a hydrochloric acid leach solution in the presence of an oxidising agent. The produced leach liquors were then subjected to various recovery treatments resulting in the PGE-containing leach liquors. The process leach solution contained typically 2.35 mol/L hydrochloric acid (HCl), 0.129 mmol/mL Pt and 0.125 mmol/mL Pd, and 0.033 mmol/L Rh and a range of impurity elements, as listed in Table 1.

The synthetic solution contained approximately 4 times the amount of Pt and Pd and 6 times the amount of Rh element present in the process leach solution. The synthetic solution was prepared by diluting concentrated HCl solution with deionised water, before addition of hydrated hydrogen hexachloroplatinate(IV), palladium(II) chloride, and hydrated rhodium(III) chloride salts. All chemicals used were of analytical grade. The synthetic solution was analysed and its working concentrations were reported as follows: 4.11 mol/L HCl, 0.513 mmol/mL Pt, 0.470 mmol/mL Pd, and 0.194 mmol/mL Rh. In contrast to the process leach solution, the synthetic solution contains no other metal ions.

2.1.2. Eluent solutions

The PGE-loaded resins were chemically stripped using an elution reagent (eluant). Four different eluent solutions were tested: (i) 2 mol/L NaSCN; (ii) 2 mol/L HCl; (iii) 1 mol/L thiourea in 2 mol/L HCl; and (iv) 1 mol/L thiourea in 2 mol/L NaOH. These solutions were prepared by: (i) dissolving appropriate amount of solid NaSCN in deionised water; (ii) dilution of concentrated HCl with deionised water to the desired concentration; (iii) dissolving appropriate amount of thiourea salt in deionised water.

### Table 1

<table>
<thead>
<tr>
<th>Elements</th>
<th>Concentration (mM)</th>
<th>Elements</th>
<th>Concentration (mM)</th>
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<tr>
<td>Na</td>
<td>1086</td>
<td>Fe</td>
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<tr>
<td>Mg</td>
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<td>Co</td>
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<td>265.7</td>
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<tr>
<td>Ti</td>
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<tr>
<td>V</td>
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<tr>
<td>Cr</td>
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<td>Pd</td>
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<tr>
<td>Mn</td>
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<td>Rh</td>
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