



RESEARCH REPOSITORY

This is the author's final version of the work, as accepted for publication following peer review but without the publisher's layout or pagination. The definitive version is available at:

https://doi.org/10.1016/j.hydromet.2017.12.005

Truong, H.T., Lee, M.S. and Senanayake, G. (2017) Separation of Pt(IV), Rh(III) and Fe(III) in acid chloride leach solutions of glass scraps by solvent extraction with various extractants. Hydrometallurgy.

http://researchrepository.murdoch.edu.au/id/eprint/39904/

Copyright: © 2017 Elsevier B.V It is posted here for your personal use. No further distribution is permitted.

Accepted Manuscript

Separation of Pt(IV), Rh(III) and Fe(III) in acid chloride leach solutions of glass scraps by solvent extraction with various extractants



Hoai Thanh Truong, Man Seung Lee, Gamini Senanayake

S0304-386X(17)30808-3
doi:10.1016/j.hydromet.2017.12.005
HYDROM 4709
Hydrometallurgy
25 September 2017
23 November 2017
2 December 2017

Please cite this article as: Hoai Thanh Truong, Man Seung Lee, Gamini Senanayake, Separation of Pt(IV), Rh(III) and Fe(III) in acid chloride leach solutions of glass scraps by solvent extraction with various extractants. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Hydrom(2017), doi:10.1016/j.hydromet.2017.12.005

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Separation of Pt(IV), Rh(III) and Fe(III) in acid chloride

leach solutions of glass scraps by solvent extraction with

various extractants

Hoai Thanh Truong^a, Man Seung Lee^{a*} and Gamini Senanayake^b

^aDepartment of Advanced Materials Science & Engineering, Institute of Rare Metal,

Mokpo National University, Jeollanamdo 534-729, Korea

^bChemical & Metallurgical Engineering & Chemistry, School of Engineering & Information Technology, Murdoch University, 90 South Street, Murdoch, WA 6150, Australia

*Corresponding author. Tel.: +82 61 450 2492; fax: +82 61 450 2498.

E-mail address: mslee@mokpo.ac.kr (M.S. Lee).

Abstract

Solvent extraction experiments were conducted to recover pure Pt(IV) and Rh(III) from the chloride leach liquor of glass industry scraps containing a small amount of Fe(III) using Alamine 336, TOPO, TBP and Cyanex 923. The Pt(IV) and Fe(III) were selectively extracted by Cyanex 923 leaving Rh(III) in the raffinate, while only Fe(III) was extracted by TBP. The Pt(IV) in the loaded Cyanex 923 phase was first selectively stripped over Fe(III) by NaSCN and then the remaining Fe(III) was stripped by HCl solution. The Fe(III) in the loaded TBP phase was easily stripped by dilute HCl solution. The McCabe-Thiele diagrams for the extraction of Pt(IV) by Cyanex 923 and of Fe(III) by TBP were constructed. Based on the obtained results, a flowsheet for the separation of three metals from the real leaching solution of glass industry scraps was proposed.

Keywords: Glass industry scrap, Recovery, Platinum, Rhodium, Cyanex 923, Solvent Extraction.

1. Introduction

Platinum group metals (PGMs) have specific physical and chemical properties and thus the demand for PGMs is increasing (Rovira et al., 1998; Gupta et al., 2014). Since the ores containing PGMs become exhausted, it is desirable to develop an efficient process to recover PGMs with high purity from secondary resources such as spent catalysts, and glass industry scraps. In glass industry, platinum and rhodium are used in some glass melting equipment, such as crucibles, tank linings, plungers, and thermocouple owing to their high melting points and resistance to corrosion (Fischer et al., 1999; Worrell and Reuter, 2014). Since pure platinum metal cannot keep its mechanical properties at high temperature, 10% of rhodium is added to platinum to improve the properties of the resulting alloys and thus to expand their service life at high temperature (Stokes, 1987).

In order to recover pure Pt and Rh from the glass industry scraps, the scraps are generally treated by aqua regia and then the nitric acid is recovered from the leach liquor. A small amount of iron(III) is contained in the leach liquor (Nowottny et al., 1997; Schrei`er and Edtmaier, 2003; Maeda et al., 2017). The purity of Pt and Rh should be higher than 99.9% for them to be reused in the manufacture of crucibles for glass industry. Therefore, Pt(IV), Rh(III) and iron(III) in the leach liquor should be separated. Solvent extraction is widely employed for the separation of these ions from concentrated acidic solutions (Cieszynska and Wisniewski, 2011; Lee et al., 2008, 2009; Mavhungu et al., 2013).

In hydrochloric acid solution, Pt(IV) exists as $PtCl_6^{2-}$, while it has been reported that aging has some effect on the stable species of Rh(III) as ionic Rh(III) is very labile (Benguerel et al., 1996). The RhCl₆³⁻ species can be transformed to RhCl₅(H₂O)²⁻ at high chloride concentration (Levitin and Schmuckler, 2003; Nguyen et al., 2016a). The reported values of relevant stability

constants for the chloro-complexes are listed in Table 1. Since both Pt(IV) and Rh(III) exist as anionic species in concentrated hydrochloric acid solutions, either amines or neutral extractants are employed to separate Pt(IV) and Rh(III) in the presence of other metal ions (Sun et al., 2011; Raju et al., 2012). Application of Kelex 100 to the concentrated hydrochloric acid solutions containing tin(IV) results in selective extraction of Rh(III) over Pt(IV) and Pd(II) but stripping of Rh(III) from the loaded organic phase is difficult (Shafiqul Alam and Katsutoshi Inoue, 1997). Although Alamine 308 is reported to be suitable for the separation of Pt(IV) and Rh(III), coextraction of Rh(III) leads to a decrease in the purity of Pt(IV) thus separated (Lee et al., 2009). A combination of precipitation and solvent extraction has been tested to recover Pt(II) and Rh(III) from the synthetic chloride solution with the following composition: 364 mg/L Pt(II), 62 mg/L Rh(III), 13880 mg/L Al(III), 6980 mg/L Mg(II), and 1308 mg/L Fe(III) (Raju et al., 2012). First, Al(III) and Fe(III) were precipitated with Na₃PO₄ and then Pt(II) was selectively extracted over Rh(III) and Mg(II) using Aliquat 336 (Raju et al., 2012). In a study to separate Pt(IV), Pd(II), Rh(III) and Ir(IV) from hydrochloric acid solutions, TBP has been used to selectively extract Pt(IV) over Ir(IV) and Rh(III) from the raffinate after extraction of Pd(II) by LIX 63 (Nguyen et al., 2016a). Compared to the number of studies devoted to the recovery of Pt(IV) and Pd(II) described above, the separation and recovery of pure Pt and Rh from the glass industry scraps has been limited (Schrei`er and Edtmaier, 2003).

In solvent extraction with amines or solvating extractants, Fe(III) is selectively extracted over Pt(IV) from hydrochloric acid solution. This work reports the results from solvent extraction experiments conducted to separate Pt(IV) and Rh(III) from the leach liquor of glass industry scraps which contained macro amount of Pt(IV) and Rh(III) in addition to the small amount of Fe(III). The three extractant Alamine 336, TOA, TBP and Cyanex 923 (Appendix 1)

were employed to determine the most suitable conditions to separate the three metal ions. Moreover, McCabe-Thiele diagrams for the extraction were constructed and a flowsheet for treating the leach liquor from glass industry scrap proposed.

2. Experimental

2.1. Chemicals and reagents

Alamine 336 and TOA were purchased from BASF Co. Korea and TBP was a product of Yakuri Pure Chemical Co. Japan. Cyanex 923 was purchased from Cytec Industries, Canada. These reagents were used without further purification. Toluene and kerosene were supplied by Daejung Chemicals & Metals Co. Korea and used as the diluents. The leach liquor of glass industry scrap digested by aqua regia was provided by DSM corp. in Korea, after removing nitric acid.

2.2. Solvent extraction procedure

The extraction and stripping experiments were carried out by mixing equal volumes (10 mL) of organic and aqueous phases in a screwed cap bottle. The mixed phases were shaken for 30 mins with a Burrell wrist action shaker (model 75 USA) and the two phases were separated using a separating funnel. All the experiments were performed at room temperature. The metal ion concentration in the aqueous phase was determined using ICP-AES (OPTIMA 4300 DV). The concentration of metal ions in the loaded organic phase was calculated by mass balance. The errors correlated with the extraction and stripping percentage of metals were within $\pm 5\%$.

In general, either amines or solvating extractants can extract Pt(IV) from concentrated hydrochloric acid solution. In order to investigate the extraction and separation behavior of the metal ions in the leach liquor, amines (TOA or Alamine 336) and solvating extractants (TBP or

Cyanex 923) of structures shown in Appendix 1 were employed in this work. The concentration of TOA and Alamine 336 was varied from 0.1 to 1 M, while that of TBP and Cyanex 923 was varied from 0.01 to 0.1 M. The volume ratio of aqueous to organic phase was unity.

3. Results and discussion

3.1. Effect of different types of extractants

3.1.1 Extraction by Alamine 336 and TOA via anion exchange

The HCl concentration of as supplied leach liquor was higher than 8.5 M and the Fe(III), Pt(IV), and Rh(III) concentrations of the leach liquor are listed in Table 2. Figs. 1a and b show the variation in the extraction of Fe(III), Pt(IV), and Rh(III) with extractant concentration. While Fe(III) and Pt(IV) ions were completely extracted by Alamine 336 (Fig. 1a) and TOA (Fig. 1b) irrespective of the difference in their concentration (Table 2), the extraction percentage of Rh(III) was very low. The solvent extraction reaction of Pt(IV) and Fe(III) by tertiary amines has been generally represented by Eqs. (1) and (2) (Levitin and Schmuckler, 2003; Lee et al., 2009; Sun et al., 2011; Maeda et al., 2017), where R_3N represents the tertiary amine and the subscript aq and org represent the aqueous and organic phase, respectively.

$$PtCl_{6}^{2-}_{aq} + 2R_{3}NHCl_{org} = PtCl_{6}(R_{3}NH)_{2,org} + 2C\Gamma_{aq}$$
(1)

$$FeCl_{4aq} + R_3 NHCl_{org} = FeCl_4(R_3 NH), org + C\Gamma_{aq}$$
(2)

Benguerel et al. (1996) reported that the predominant species of Rh(III) depend on the chloride concentration as shown in Appendix 2 and RhCl₅(H₂O)²⁻ would not be extracted by amines. Selective extraction of Pt(IV) over Rh(III) by TOA and Alamine 336 agrees well with the extractability of chloro complexes of platinum group metal ions (PGMs) by amines, MCl_6^{2-}

 $>> MCl_6^{3-}$ (Nguyen et al., 2016b). During the extraction, the formation of a third phase was observed.

The purity of Pt metal should be higher than 99.9% to be recycled to the glass industry. This means that there should be no Fe(III) in Pt(IV) solution. Since Fe(III) is co-extracted with Pt(IV) by amines, the extraction and separation behavior of the metal ions in the leach liquor was investigated by employing solvating extractants, TBP and Cyanex 923.

3.1.2 Extraction by Cyanex 923 and TBP via solvation

Fig. 2a shows that as Cyanex 923 concentration increased from 0.01 to 0.05 M, the extraction of Fe(III) and Pt(IV) increased from 42 and 18% to 100 and 85%, respectively, and then was constant with the further increase of Cyanex 923 up to 0.1 M. However, no Rh(III) was extracted. The selective extraction of Pt(IV) over Rh(III) by Cyanex 923 can also be ascribed to the difference in their charge density. The charge density of RhCl₆³⁻ (54.2) is higher than that of PtCl₆²⁻ (38.2) (Nguyen et al., 2016a). In the course of solvent extraction by solvation reaction, the metal ion with higher charge density has a stronger tendency to be solvated by more water, resulting in less interaction with other species (Michael, 2012). Therefore, the extraction of Pt(IV) is higher than that of Rh(III).

Fig. 3 indicates that only Fe(III) was selectively extracted over Pt(IV) and Rh(III) by TBP and extraction efficiency increased at higher TBP concentrations. The solvent extraction reaction of Pt(IV) and/or Fe(III) with Cyanex 923 (Fig. 2a) or TBP (Fig. 3) may be represented as follows (Sun et al., 2011; Nguyen et al., 2017), where L represents the solvating extractant TBP/C yanex 923.

$$2H^{+} + PtCl_{6}^{2-}aq + mL_{org} = H_2PtCl_6 \cdot L_m, org$$
(3)

 $H^+ + FeCl_4^- + bL_{org} = HFeCl_4 \cdot L_{b,org}$

Fig. 2b shows a Log-Log plot of the distribution ratio (*D*) as a function of Cyanex 923 concentration, where D is the ratio of the concentration of Pt(IV) in organic phase to aqueous phase at equilibrium obtained in this study. A slope of 2.1 in Fig. 2b suggests a value of m equal to 2 in Eq. (3). The results in Figs. 1-3 clearly show that both Fe(III) and Pt(IV) ions were co-extracted by TOA, Alamine 336 and Cyanex 923, while only Fe(III) was extracted by TBP. The difference in the extraction behavior for Pt(IV) and Fe(III) between Cyanex 923 (Fig. 2a) and TBP (Fig. 3) might be ascribed to the fact that the interaction between hydrogen ion and Cyanex 923 is much stronger than TBP (Sarangi et al., 2006). Therefore, Pt(IV) can be readily extracted from concentrated HCl solutions by Cyanex 923.

3.2. Third phase formation and effect of diluents

Third phase formation occurred during the extraction with Cyanex 923. Addition of 1decanol as a modifier could not depress the formation of a third phase. Therefore, other diluents, such as toluene, benzene, xylene, and *n*-hexane of different dielectric constants listed in Table 3 were tested. The leach liquor was contacted with 0.05 M Cyanex 923 at an organic/aqueous phase volume ratio (O/A ratio) of 1. Results listed in Table 3 indicate that the extraction of Pt(IV) (20-90%) depended on the nature of the diluent, while there was no change in the extraction behavior of Fe(III) (100%) and Rh(III) (0%). The extraction percentage of Pt(IV) increased as the dielectric constant of the diluents decreased and the extraction order of Pt(IV) was benzene < toluene < xylene < kerosene < *n*-hexane. Although the extraction percentage of Pt(IV) was high with *n*-hexane, kerosene, and xylene as diluents, a third phase was formed during the extraction. However, no third phase was formed when toluene was employed as a diluent. Thus, toluene was used in further studies.

3.3. Effect of Cyanex 923 concentration in toluene

The effect of Cyanex 923 concentration on the extraction of the metal chloride complex ions was investigated by varying its concentration from 0.01 to 0.1 M in toluene. Fig. 4a shows that Fe(III) was completely extracted by Cyanex 923 and the extraction percentage of Pt(IV) rose from 0.3 to 63.3% as Cyanex 923 concentration was increased from 0.01 to 0.1 M. Thus, Fe(III) was selectively extracted over Pt(IV) by Cyanex 923 in toluene. Meanwhile, the extraction of Rh(III) by Cyanex 923 was negligible in the tested range of experimental conditions. When Cyanex 923 concentration for the selective extraction of Pt(IV) and Fe(III) over Rh(III) from the leach liquor. Fig. 4b shows a Log-Log plot of D as a function of [Cyanex 923] in toluene. The slope of the linear relationship indicates that the value of m in Eq. (3) is equal to 3. The difference in the value of m of Eq. (3) between kerosene (m=2) and toluene (m=3) agrees well with the higher extraction percentage of Pt(IV) from kerosene than that from toluene due to stronger solvation of the Pt(IV) species by Cyanex 923 in toluene.

3.4. McCabe Thiele diagrams

3.4.1 Pt(IV) extraction by Cyanex in toluene

To determine the number of theoretical stages required for the complete extraction of Pt(IV) from the leach liquor, McCabe-Thiele diagram for the extraction of Pt(IV) was constructed by varying the O/A ratio using 0.07 M Cyanex 923 in toluene. The extraction percentage of Pt(IV) increased from 10 to 84% with an increase of O/A ratio from 1:3 to 5:1, while Fe(III) was completely extracted at any O/A ratio. On the other hand, no Rh(III) was

extracted into Cyanex 923. Fig. 5 indicates that four counter-current extraction stages are required for the complete extraction of Pt(IV) from the initial 1514 mg/L feed solution (Table 2) at an O/A ratio of 3.5 and the concentration of Pt(IV) in the loaded organic phase is 422 mg/L.

3.4.2 Fe(III) extraction by TBP in kerosene

Unlike TOA, Alamine 336 and Cyanex 923, TBP selectively extracted Fe(III) over Pt(IV) and Rh(III) from the leach liquor (Fig. 3). Therefore, to estimate the theoretical number of stages for the extraction of Fe(III) from leach liquor, extraction isotherm for Fe(III) was obtained by employing 0.1 M TBP in kerosene. In these experiments, the volume ratio of organic to aqueous was varied from 1:3 to 3:1. The extraction percentage of Fe(III) increased from 50 to 94% as the O/A ratio was increased from 1:3 to 3:1, while no Pt(IV) and Rh(III) was extracted. Fig. 6 shows that three counter-current extraction stages are needed to extract Fe(III) from the feed solution of 1.6 mg/L (Table 2) at an O/A ratio of 1 and the concentration of Fe(III) in the loaded organic phase is 1.47 mg/L.

3.5. Stripping of loaded organic phase

It has been reported that NaSCN and dilute HCl are two solutions which can strip Pt(IV) and Fe(III) from the loaded Cyanex 923 phase (Nguyen et al., 2016; Nguyen et al., 2017). As shown in Table 1, the stability constants of $Pt(SCN)_6^{2-}(10^{33.6})$ and $Fe(SCN)_6^{3-}(10^{3.51})$ are much larger than their chloride counterparts, which will facilitate the stripping of these metal ions from the loaded organic phase. A solution of dilute HCl of low H⁺ and Cl concentration will favor the reverse reactions of Eqs. 3 and 4 and facilitate stripping due to the low stability constants of the chloro-complexes of Pt(IV) and Fe(III). Selective stripping was tested with the two stripping agents as described below.

The loaded organic phase was prepared by contacting the real leach liquor with 0.07 M Cyanex 923 in toluene. The concentration of Pt(IV) and Fe(III) in the loaded organic phase was 422 and 1.47 mg/L, respectively, to be consistent with the McCabe Thiele diagrams in Figs. 5 and 6, respectively. The O/A volume ratio was unity. In order to investigate the stripping behavior of Fe(III) and Pt(IV), the concentrations of NaSCN and HCl solutions were varied from 0.05 to 0.5 M and 0.01 to 1 M, respectively. The stripping percentage of Pt(IV) increased from 80 to 100% with increasing NaSCN concentration from 0.05 to 0.1 M and then remained unchanged with further increase of NaSCN concentration up to 0.5 M. However, the stripping efficiency of Fe(III) was nearly zero (see Fig. 7). Therefore, the higher stability of $[Pt(SCN)_6]^{2-}$ favors the selective stripping of Pt(IV) over Fe(III) (Ginzburg et al., 1975). Further, in terms of Hard and Soft Acid Base (HSAB) theory, Pt(IV) is a soft acid and thus has a strong tendency to form complexes with a soft base like SCN⁻, while Fe(III) is a borderline acid (Pearson, 1963).

Fig. 8 shows that the stripping percentage of Fe(III) increased from 50 to 85% as HCl concentration was increased from 0.01 to 1.0 M, whereas Pt(IV) was completely stripped irrespective of HCl concentration. According to Fig. 8 the stripping of loaded Cyanex 923 phase with NaSCN solution resulted in selective stripping of Pt(IV) over Fe(III) and thus it was possible to separate the two metal ions from the loaded Cyanex 923 phase.

Fig. 9 shows that the stripping percentage of Fe(III) from loaded TBP phase in kerosene increased from 80 to 100% as HCl concentration increased from 0.01 to 0.1 M HCl and then remained more or less constant with a further increase of HCl concentration up to 1.0 M.

3.6. Summary and proposed flowsheet

Based on the extraction and stripping results obtained, a proposed process for the separation of Pt(IV), Rh(III) and Fe(III) from the leach liquor of glass industry scraps is shown in Fig. 10. First, Fe(III) and Pt(IV) from leach liquor were completely extracted by Cyanex 923, leaving Rh(III) in the raffinate. Second, Pt(IV) was selectively stripped from the loaded Cyanex 923 phase by using NaSCN solution. The remaining Fe(III) in the loaded Cyanex 923 phase can be stripped by using HCl solution. The purity of final Pt(IV) solutions were higher than 99.9% and thus these metals can be recycled to the glass industry.

4. Conclusions

The leaching of glass industry scraps with aqua regia results in concentrated hydrochloric acid solution containing 1514 mg/L Pt(IV) and 178 mg/L Rh(III) together with a small amount of 1.6 mg/L Fe(III). The Fe(III) and Pt(IV) ions were simultaneously extracted by TOA, Alamine 336 and Cyanex 923, while only Fe(III) was extracted by TBP. The extraction percentage of Rh(III) by these 4 extractants was negligible. The Pt(IV) and Fe(III) in the loaded Cyanex 923 phase can be separated by selective stripping of Pt(IV) by NaSCN solution. The remaining Fe(III) in the loaded Cyanex 923 phase after stripping by NaSCN can be stripped by HCl solution. McCabe-Thiele diagrams for the extraction of Pt(IV) with Cyanex 923 and of Fe(III) by TBP were constructed. A process for the recovery of pure Pt(IV) and Rh(III) solutions from the leaching solution using solvent extraction was proposed.

Acknowledgements

This work was supported by the Global Excellent Technology Innovation of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource

from the Ministry of Trade, Industry & Energy, Republic of Korea (No.20165010100810). We express sincere thanks to the Korea Basic Science Institute (KBSI) for ICP data. We also thank Murdoch University for collaboration opportunities.

Scherten

References

- Benguerel, E., Demopoulos, G.P., Haris, G.B., 1996. Speciation and separation of rhodium(III) from chloride solutions: a critical review. Hydrometallurgy 40, 135-152.
- Belaustegi, Y., Olazabal, M.A., Madariaga, J.M., 1999. Development of a Modified Bromley's Methodology for the estimation of ionic media effects on solution equilibria. Part 4. The chemical model of Fe(III) with the halide ligands in aqueous solution at 25°C. Fluid Phase Equilib. 155, 21-31.
- Cozzi, D., Pantani, F., 1958. The polorographic behaviour of rhodium(III) chlorocomplexes. J. Inorg. Nucl. Chem. 8, 385-398.
- Cieszynska, A., Wisniewski, M., 2011. Selective extraction of palladium(II) from hydrochloric acid solutions with phosphonium extractants. Sep. Purif. Technol. 80, 385-389.
- Fischer, B., Behrends, A., Freund, D., Lupton, D.F., Merker, J., 1999. High temperature mechanical properties of the Platinum Group Metals stress-rupture strength and creep behaviour at extremely high temperatures. Platinum Metal Rev. 43, 18-28.
- Grinberg A.A., Busch, D.H., Trimble, R.F., 1962. An introduction to the chemistry of complex componds, second ed. Pergamon Press, London, pp.274.
- Ginzburg, S.I., Ezerskaya, N.A., Prokof eva, I.V., Fedorenko, N.V., Shlenskaya, V.I., Bel'skii, N.K., 1975. Analytical chemistry of platinum metals. John Willey & Son, New York, pp.116-143.
- Gupta, B., Singh, I., Mahandra, H., 2014. Extraction and separation studies on Pt(IV), Ir(III), and Rh(III) using sulphur containing extractant. Sep. Purif. Technol. 132, 102-109.

- Hogfeldt, E., 1983. Stability Constants of Metal-Ion Complexes, Part A: Inorganic Ligands, Vol. 21. Pergamon Press, Oxford, p. 216.
- Levitin, G., Schmuckler, G., 2003. Solvent extraction of rhodium chloric from aqueous solutions and its separation from palladium and platinum. React. Funct. Polym. 54, 149-154.
- Lee, M.S., Lee, J.Y., Kumar, J.R., Kim, J.S., Sohn, J.S., 2008. Solvent extraction of PtCl₄ from hydrochloric acid solution with Alamine 336. Mater. Trans. 49, 2823-2828.
- Lee, J.Y., Kumar, J.R., Kim, J.S., Park, H.K., Yoon, H.S., 2009. Liquid-liquid extraction/separation of paltium(IV) and rhodium(III) from acidic chloride solutions using tri-iso-octylamine. J. Hazard. Mater. 168, 424-429.
- Mountain B.W., Wood S.A., 1988. Solubility and transport of platinum-group elements in hydrothermal solutions: Thermodynamic and physical chemical constraints. In: Prichard H.M., Potts P.J., Bowles J.F.W., Cribb S.J. (eds) Geo-Platinum 87. Springer, Dordrecht, pp. 60.
- Michael, N.T., 2012. Computer simulations of a chromatographic column used in the separation of platinum group metal chlorinated complexes. OpenUCT, Thesis Sci. (2012), http://hdl.handle.net/11427/11810
- Mavhungu, A., Mbaya, R.K.K., Moropeng, M.L., 2013. Recovery of Platinum and Palladium Ions from AqueousSolution Using Grape Stalk Waste. Int. J. Chem. Eng. Appl. 4, 354-358.
- Maeda, M., Narita, H., Tokoro, C., Tanaka, M., Motokawa, R., Shiwaku, H., Yaita, T., 2017. Selective extraction of Pt(IV) over Fe(III) from HCl with an amide-containing tertiary amine compound. Sep. Purif. Technol. 177, 176-181.

- Nowottny, C., Halwachs, W., Schugerl, K., 1997. Recovery of platinum, palladium and rhodium from industrial process leaching solutions by reactive extraction. Sep. Purif. Technol. 12, 135-144.
- Nguyen, V.T., Lee, J.C., Chagnes, A, Kim, M.S., Jeong, J.K., Cote, G., 2016. Highly selective separation of individual platinum group metal (Pd, Pt, Rh) from acidic chloride media using phosphonium-based ionic liquid in aromatic diluent. RSC Adv. 6, 62717-62728.
- Nguyen, T.H., Sonu, C.H., Lee, M.S., 2016a. Separation of Pt(IV), Pd(II), Rh(III) and Ir(IV) from concentrated hydrochloric acid solutions by solvent extraction. Hydrometallurgy 164, 71-77.
- Nguyen, T.H., Kumar, B.N., Lee, M.S., 2016b. Selective recovery of Fe(III), Pd(II), Pt(IV), Rh(III) and Ce(III) from simulated leach liquors of spent automobile catalyst by solvent extraction and cementation. Korean J. Chem. Eng. 33, 2684-2690.
- Nguyen, T.H., Wang, L.Y, Lee, M.S., 2017. Separation and recovery pf precious metals from leach liquors of spent electronic wastes by solvent extraction. Korean J. Met. Mater, 55, 247-254.
- Pearson, R.G., 1963. Physical and inorganic chemistry: Hard and soft acids and bases. J. Am, Chem. Soc. 85, 3533-3539.
- Read, M.C., Glaser, J., Persson, I., 1994. Rhodium(III) complexes with cyanide and sulfur-donor ligands: rhodium-103 nuclear magnetic resonance chemical shift correlations. J. Chem. Soc. Dalton Trans. 0, 3243-3248.

- Rovira, M., Cortina, L., Arnaldos, J., Sastre, A.M., 1998. Recovery and separation of platinum group metals using impregnated resins containing Alamine 336. Solvent Extr. Ion Exch. 16, 1279-1302.
- Raju, B., Rajesh Kumar, J., Lee, J.Y., Knonc, H.S., Lakshmi Kantam, M., Ramachandra Reddy,
 B., 2012. Separation of platinum and rhodium from chloride solutions containing aluminum, magnesium and iron using solvent extraction and precipitation methods. J. Hazard. Mater. 227-228, 142-147.
- Stokes, J., 1987. Platinum in the glass industry ZGS materials supplement conventional alloys. Platinum Metal Rev. 31, 54-62.
- Shafiqul Alam, M., Katsutoshi Inoue., 1997. Extraction of rhodium from other platinum group metals with Kelex 100 from chloride media containing tin. Hydrometallurgy 46, 373-382.
- Saji, J., Prasada Rao, T., Iyer, C.S.P., Reddy, M.L.P., 1998. Extraction of iron(III) from acidic chloride solutions by Cyanex 923. Hydrometallurgy 49, 289-296.
- Schrei`er, C., Edtmaier, C., 2003. Separation of Ir, Pd and Rh from secondary Pt scrap by precipitation and calcination. Hydrometallurgy 68, 69-75.
- Sarangi, K., Padhan, E., Sarma, P.V.R.B., Park, K. H., Das, R.P., 2006. Removal/recovery of hydrochloric acid using Alamine 336, Aliquat 336, TBP and Cyanex 923. Hydrometallurgy 84, 125-129.
- Sun, P.P., Lee, J.Y., Lee, M.S., 2011. Separation of Pt(IV) and Rh(III) from chloric solution by solvent extraction with amine and neutral extractants. Mater. Trans. 52, 2071-2076.
- Theopold, K., Langley, R., Robinson, W. R., 2015. Chemistry. Rice University, pp.1255.

Worrell, E., Reuter, M.A., 2014. Handbook of Recycling. Amsterdam, Elsevier, pp.125.

Section Manus

Reaction	Equilibrium constant	Reference
	(log K)	
$Fe^{3+} + 4C\Gamma = FeCl_4^-$	-1.31	Belaustegi et al., 1999.
$Pt^{4+} + 6CI = PtCl_6^{2-}$	2.36	Hogfeldt, 1983
$PtCl_4 + C\Gamma = PtCl_5^-$	2.02	Lee et al., 2008.
$PtCl_5^- + C\Gamma = PtCl_6^{2-}$	2.01	Lee et al., 2008.
$Rh^{3+} + 6C\Gamma = RhCl_6^{3-}$	8.43	Cozzi and Pantani, 1958.
$RhCl_{6}^{3-} + H_{2}O = RhCl_{5}(H_{2}O)^{2-} + C\Gamma$	8.76	Read et al., 1994.
$Fe^{3+} + 6SCN^{-} = Fe(SCN)_6^{3-}$	3.51	Theopold et al., 2015.
$Pt^{4+} + 6SCN^{-} = Pt(SCN)_{6}^{2-}$	33.6	Mountain and Wood, 1988.
$Rh^{3+} + 6SCN^{-} = Rh(SCN)_6^{3-}$	35.0	Read et al., 1994.

 Table 1 Stability constants for the formation of complexes of Pt(IV), Rh(III), and Fe(III) with chloride and thiocyanate.

thiocyanate ion (SCN⁻); tetrachloroferrate(III) ion (FeCl₄⁻); hexathiocyanatoferrate(III) ion (Fe(SCN)₆³⁻); hexachloroplatinate(IV) ion (PtCl₆²⁻); pentachloroplatinate(IV) ion (PtCl₅⁻); hexathiocyanatoplatinate(IV) ion (Pt(SCN)₆²⁻); hexachlororhodate(III) ion (RhCl₆³⁻); hexathiocyanatorhodate(III) ion (Rh(SCN)₆³⁻); aquopentachlororhodate(III) ion (RhCl₅(H₂O)²⁻).

Element	Fe(III)	Pt(IV)	Rh(III)
mg/L	1.6	1514	178
mmol/L	0.03	7.76	1.73
8			

Table 2 The composition of real leach liquor of glass industry scraps in aqua regia.

Diluent	Dielectric constant	Extraction percentage, %			Formation of a
		Pt(IV)	Fe(III)	Rh(III) ^a	third phase
Toluene	2.38	13.9	100	0	No
Benzene	2.28	12.6	100	0	No
Xylene	2.27	23.5	100	0	Yes
Kerosene	2.0	88.6	100	0	Yes
<i>n</i> -Hexane	1.88	89.9	100	0	Yes

Table 3 Effect of diluents on the extraction of Fe(III), Pt(IV), and Rh(III) by Cyanex 923.

a. Concentration was too low to measure

Experiment conditions: leach liquor: [Fe]=1.6 mg/L, [Pt]=1514 mg/L, [Rh]=178 mg/L; organic phase: [Cyanex 923]=0.05 M, O/A=1.

(a)



Fig. 1. Effect of Alamine 336 (a) or TOA (b) concentration on the extraction of Fe(III), Pt(IV), and Rh(III). Leach liquor: [Fe]=1.6 mg/L, [Pt]=1514 mg/L, [Rh]=178 mg/L. [Alamine 336] or [TOA]=0.1-1.0 M. O/A=1. Diluent: kerosene.

Stranger



Fig. 2a. Effect of Cyanex 923 concentration on the extraction of Fe(III), Pt(IV), and Rh(III). Leach liquor: [Fe]=1.6 mg/L, [Pt]=1514 mg/L; [Rh]=178 mg/L. [Cyanex 923]=0.01-0.1 M. O/A=1. Diluent: kerosene.



Fig. 2b. Plot of log D of Pt(IV) as a function of log [Cyanex 923]. Leach liquor: [Fe]=1.6 mg/L, [Pt]=1514 mg/L; [Rh]=178 mg/L; [Cyanex 923]=0.01-0.1 M. O/A=1. Diluent: kerosene.



Fig. 3. Effect of TBP concentration on the extraction of Fe(III), Pt(IV), and Rh(III). Leach liquor: [Fe]=1.6 mg/L, [Pt]=1514 mg/L; [Rh]=178 mg/L. [TBP]=0.01-0.1 M. O/A=1. Diluent: kerosene.



Fig. 4a. Effect of Cyanex 923 on the extraction of Fe(III), Pt(IV), and Rh(III). Leach liquor: [Fe]=1.6 mg/L, [Pt]=1466 mg/L, [Rh(III)]=178 mg/L. Organic: [Cyanex 923]=0.01-0.1 M. O/A=1. Diluent: toluene.



Fig. 4b. Plot of log D of Pt(IV)as a function of log [Cyanex 923]. Leach liquor: [Fe]=1.6 mg/L, [Pt]=1466 mg/L; [Rh]=178 mg/L. [Cyanex 923]=0.01-0.1 M. O/A=1. Diluent: toluene.



Fig. 5. McCabe-Thiele diagram for the extraction of Pt(IV). Leach liquor: [Fe]=1.6 mg/L, [Pt]=1466 mg/L, [Rh]=178 mg/L. Organic, [Cyanex 923]=0.07 M. O/A=1:3-5:1. Diluent: toluene.



Fig. 6. McCabe-Thiele diagram for the extraction of Fe(III). Leach liquor: [Fe]=1.6 mg/L, [Pt]=1466 mg/L, [Rh]=178 mg/L. Organic: [TBP]=0.1 M. O/A=1:3-3:1. Diluent: kerosene.



Fig. 7. Effect of NaSCN concentration on the stripping of Fe(III) and Pt(IV). Loaded Cyanex 923 in toluene phase: [Fe]=1.47 mg/L, [Pt]=422 mg/L. Stripping agent, [NaSCN]=0.05-0.5 M. O/A=1.

Ś



Fig. 8. Effect of HCl concentration on the stripping of Fe(III) and Pt(IV). Loaded Cyanex 923 in toluene phase: [Fe]=1.47 mg/L, [Pt]=422 mg/L. Stripping agent: [HCl]=0.01-1.0 M. O/A=1.



Fig. 9. Effect of HCl concentration on the stripping of Fe(III). Loaded TBP in kerosene phase: [Fe]=1.47 mg/L. Stripping agent, [HCl]=0.01-1.0 M. O/A=1.



Fig. 10. Proposed flowsheet for recovery of Fe(III), Pt(IV), and Rh(III) from acid leaching solution of glass industry scarp by solvent extraction.

A CLARENCE



Appendix 1. Chemical formula and structure of extractants used in this study

TBP (tri-*n*-butyl phosphate), Cyanex 923 (a mixture of four trialkyl phosphine oxides), TOA (tri-

n-octyl amine), Alamine 336 (tricaprylamine).





Highlights

- A process was proposed to recover Pt(IV) and Rh(III) from glass scraps.
- The Pt(IV), Rh(III) and Fe(III) in leachate was separated by solvent extraction.
- Fe(III) was selectively extracted over Pt(IV) and Rh(III) by TBP. .
- Selective extraction of Pt(IV) and Fe(III) over Rh(III) by Cyanex 923.
- Pt(IV) and Fe(III) in loaded Cyanex 923 was stripped by NaSCN and HCl.

the second secon