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# Cloud Point Extraction of Platinum Group Metal solutions: Key factors in metal extraction and selective elution at low concentrations

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ABSTRACT

Platinum group metals are leached from spent autocatalytic converters and other end-of-life products, producing Platinum group metal concentrations below 500 ppm compared to 15,000 ppm from commercial concentrates. Conventional solvent extraction and precipitation methods are inefficient for processing end-of-life leachates, but Cloud Point Extraction shows promise for recovering trace Platinum group metals with minimal environmental impact. However, literature on Platinum group metal Cloud Point Extraction is limited, particularly regarding methods to elute Platinum group metals or remove co-extracted impurities from the surfactant phase. This study used design of experiments to investigate how initial solution pH, surfactant volume (10 % *w/v* Triton X − 100), complexing agent volume (1 % w/v 2-mercaptobenzothiazole, 2-MBT), metal ion concentration, and contact time affect Platinum Group Metal extraction from spent autocatalytic converters chloride leachate. Leach solutions contained 82–165 ppm PGMs and 2153–4348 ppm matrix elements. Key factors were identified to be the initial solution pH, metal ion concentration, and complexing agent volume. Interactions between initial solution pH and metal ion concentration, as well as 2-MBT and metal ion concentration, enhanced Pt, Pd, and Rh recovery, while initial solution pH–2-MBT interactions reduced Pd and Rh recovery. An increase in metal ion concentration resulted in all matrix elements being extracted to the surfactant phase. Elution of Pt and Pd from the surfactant phase with 1.0 M thiourea in 0.5 M HCl achieved 66 % and 62 % recovery, respectively, while 6.0 M HCl eluted 68 % of Rh. Attempts to achieve selective Platinum group metal elution were unsuccessful, prompting impurity scrubbing tests. Aluminium and magnesium were removed, but iron remained. These findings highlight key factors influencing Cloud Point Extraction performance and offer insights for optimizing Platinum group metal recovery by Cloud Point Extraction.

## 1. Introduction

The mining of platinum group metals (PGMs) has become increasingly costly due to the declining quality of ores, the need for deeper mining operations, and rising energy expenses [1]. Given these challenges and the critical role of PGMs in modern society, particularly in supporting the energy transition, efforts to recover them from spent autocatalytic converters (SACs) and other end-of-life (EOL) products have intensified [2,3]. The shift toward environmentally friendly transportation, such as electric and hydrogen-powered vehicles, has led to a projected decline in internal combustion engine vehicles in developed countries [4]. This transition has reduced the demand for PGMs in autocatalysts. However, demand for PGMs in clean energy applications, particularly in hydrogen production and fuel cells, is on the rise [3]. SACs are, therefore, a valuable source of PGMs for the energy transition. A study in Greece on approximately 40,000 SACs revealed an average total PGMs content of 3523 g per ton, with a distribution of 28 %, 61 %, and 11 % for Pt, Pd, and Rh, respectively [5]. Compared to primary ores, which generally contain less than 10 g of PGMs per ton, SACs represent a much more concentrated secondary source [6]. This has led to increased interest in recovering PGMs from SACs and other EOL materials, both in academic research and industrial processing [7,8,9].

Several major companies, including Umicore (Belgium), Heraeus (Germany), BASF (USA), Johnson Matthey (UK), and Nippon/Mitsubishi (Japan), have implemented commercial recycling of PGMs from SACs and other EOL sources [7]. Notably, more than 25 % of the global

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platinum (Pt), palladium (Pd), and rhodium (Rh) supply from 2018 to 2022 originated from recycled materials [10]. The recycling processes generally integrate both pyrometallurgical and hydrometallurgical methods [11]. In the initial pyrometallurgical step, SACs are melted at high temperatures with the addition of fluxes and metal collectors, resulting in a PGM-enriched alloy [12]. This alloy is then processed through hydrometallurgical techniques to recover the individual metals [12]. In the hydrometallurgical process steps, the alumina-based substrate that hosts the PGMs is dissolved using mineral acids in the presence of an oxidizing agent or, with bases [13]. This is followed by PGM recovery via methods such as hydrolysis, electro-winning, cementation, solvent extraction (SX), and ion exchange (IX) [13].

Commercial recycling of PGMs solely through hydrometallurgical methods is uncommon. Nevertheless, significant research efforts are focused on hydrometallurgical recovery of PGMs from EOL products. Hydrometallurgical processes offer several benefits over pyrometallurgical methods. These include reduced energy consumption, lower greenhouse gas emissions, and the potential for recovering additional elements [9]. However, a key drawback of hydrometallurgical processing is the generation of large volumes of wastewater and the associated treatment costs [9].

Primary commercial extraction of PGMs involves leaching concentrates containing 50–70 % PGMs in chloride media, leading to the formation of anionic chloro-complexes. PGMs are subsequently recovered from the leach solution through SX and precipitation (PPT) [14,15]. Both processes require highly concentrated leach solutions to achieve efficient recovery [15]. In contrast, leach solutions from EOL sources contain significantly lower PGM concentrations, typically below 500 ppm, as EOL materials are not as PGM-rich as ore concentrates. This low concentration makes it difficult to effectively apply SX and PPT for PGM recovery [16]. PPT also suffers from poor selectivity, necessitating multiple recycle streams that prolong the PGM retention time in refineries and increase operational costs [17]. Meanwhile, the solvents used in SX are expensive, flammable, toxic, and challenging to store, emitting hazardous fumes and posing disposal difficulties [18]. Therefore, there is a growing need for environmentally friendly, safer, and more efficient materials and methods for PGM extraction, especially at low PGM concentrations.

CPE is an efficient method for recovering PGMs at trace levels with minimal environmental impact [19,20]. It is a liquid-liquid extraction technique that employs a surfactant and a complexing agent to extract metal ions [20]. Surfactants are amphiphilic molecules composed of a polar (hydrophilic) head and a long hydrophobic tail [21]. These molecules position themselves at the interface of aqueous-air or aqueous-organic phases, with the hydrophilic head oriented toward the aqueous phase and the hydrophobic tail directed toward the hydrophobic phase [21]. When the concentration of the surfactant exceeds a threshold known as the critical micelle concentration (CMC), micelles — colloidal structures capable of binding hydrophilic or hydrophobic solutes — are formed [21]. Adding sufficient surfactant beyond the CMC to an aqueous solution results in the formation of two immiscible phases: a surfactant-rich phase (SP) and an aqueous phase [21]. In CPE, non-ionic surfactants are used, and phase separation is induced by increasing the temperature to a specific point called the cloud point temperature [22]. At this temperature, two liquid phases are formed: a SP containing the target metal ions and a second phase that is surfactant-depleted (Yamini et al., [23]; [20]).

The CPE process involves the formation of reactive PGMs-tin chloro complexes from PGMs chloro complexes using tin (II) chloride as a reducing and activating agent [24,25]. The species formed during the activation process depend on the Sn (II) / PGM ratio. When the Sn (II) / PGM ratio is <2, unreactive PGMs-tin chloro complexes are formed as shown in eq. (1). The PGMs-tin chloro complexes formed contain a greater number of unreactive $Cl^-$ ion ligands which exhibit slower exchange kinetics compared to the reactive $SnCl_3^-$ ligands as shown in eq. (1) [25].

$$[PtCl_6]^{2-}_{(aq)} + 3SnCl_3^-(aq) \rightarrow [PtCl_3(SnCl_3)]^{2-}_{(aq)} + 3Cl^-_{(aq)} + SnCl_3^-(aq) + SnCl_3^+(aq) \quad (1)$$

Eqs. (2), (3) and (4) demonstrate the activation reactions of Rh (III) and Pt (IV) when the Sn (II) / PGM ratio exceeds 6. The higher number of $SnCl_3^-$ ligands in the Rh (III) and Pt (IV) complexes, compared to $Cl^-$ ion ligands, increases their reactivity.

$$[RhCl_6]^{3-}_{(aq)} + 6SnCl_3^-(aq) \rightarrow [Rh(SnCl_3)_5]^{4-}_{(aq)} + SnCl_6^{2-}(aq) + 3Cl^-_{(aq)} \quad (2)$$

$$[PtCl_6]^{2-}_{(aq)} + 7SnCl_3^-(aq) \rightarrow [Pt(SnCl_3)_5]^{3-}_{(aq)} + 6Cl^-_{(aq)} + SnCl_3^-(aq) + SnCl_3^+(aq) \quad (3)$$

$$PtCl_6]^{2-}_{(aq)} [+ 6SnCl_3^-(aq) \rightarrow [PtCl(SnCl_3)_4]^{3-}_{(aq)} + 5Cl^-_{(aq)} + SnCl_3^-(aq) + SnCl_3^+(aq) \quad (4)$$

This leads to the formation of hydrophobic complexes with the complexing agent through a neutral complexing mechanism [26]. Eqs. (5) and (6) illustrate Rh extraction by 1-hexyl-3-methylimidazole-2-thione (HMImT), a complexing agent related to 2-MBT, which was used in this study [26].

$$[Rh(SnCl_3)_5]^{4-}_{(aq)} + 4H^+_{(aq)} \rightarrow 4H\cdot[Rh(SnCl_3)_5]_{(aq)} \quad (5)$$

$$4H\cdot[Rh(SnCl_3)_5]_{(aq)} + 2HMImT_{(org)} \rightarrow 4H\cdot[Rh(SnCl_3)_5]\cdot 2HMImT_{(org)} \quad (6)$$

The hydrophobic PGM complex is transferred to the SP; however, in the study cited in eq. (6), an organic phase was used instead, as SX was employed [26].

Research on CPE for PGMs has largely focused on their preconcentration for analysis in water and fly ash [27,28]. Available literature indicates that only a few studies, including those by Makua et al. [19], Mortada et al. [29], and Suoranta et al. [30], have explored the recovery of PGMs from SACs using CPE. These studies examined the effects of key parameters such as initial solution pH, temperature, contact time, metal ion concentration, and the volumes of surfactant and complexing agents on PGM extraction. Their findings revealed that the initial solution pH affected the formation of extractable complexes and their subsequent recovery [31]. Makua et al. [19] reported that when the water bath temperature of the CPE reaction vessel exceeded 95 °C, PGM recovery declined due to micelle breakdown. Contact time was also shown to be a critical factor, influencing both the formation of hydrophobic PGM complexes and their entrapment within the surfactant phase [32]. Metal ion concentration emerged as another key parameter, as it determines the quantity of extractable hydrophobic metal complexes formed [33]. Additionally, a sufficient concentration of 2-MBT is essential for forming adequate hydrophobic complexes with PGMs, following their reaction with PGM tin chloro complexes [34]. These hydrophobic complexes are then extracted by the surfactant's hydrophobic component. If the 2-MBT concentration is too low, the formation of extractable hydrophobic complexes is insufficient for effective transfer to the surfactant phase [34]. Despite these insights, the studies evaluated these parameters individually and did not consider possible interactions among them.

Several researchers have explored the interaction of variables in the CPE of PGMs using factorial design approaches [28,30]. Suoranta et al. [30] employed a full two-level factorial design ($2^4$) to evaluate the influence of surfactant volume (10 % *w/v* Triton X − 100), complexing

agent volume (1 % w/v 2-MBT), reducing agent volume (10 % tin (II) chloride), and metal ion concentration on the recoveries of Pd, Pt, Rh, and Ru. Key interactions identified included Triton X − 100 × 2-MBT (+), Triton X − 100 × metal ion concentration (+), and 2-MBT × metal ion concentration (−), indicating both synergistic and antagonistic effects depending on the variable pairing. Metal ion concentrations ranged from 1 to 5 ppm per metal, with a total of 20 ppm.

Similarly, Souza et al. [28] used a full $2^4$ factorial design to study Pd and Pt recovery, examining the effects of surfactant volume (Triton X − 114), complexing agent volume (2-MBT), reducing and activating agent volume (10 % tin (II) chloride/potassium iodide), and hydrochloric acid concentration. Significant interactions included tin (II) chloride/potassium iodide × HCl concentration (−), Triton X-114 × HCl concentration (+), tin (II) chloride/potassium iodide × Triton X − 114 (+), and 2-MBT × HCl concentration (+). This study was conducted at even lower metal ion concentrations (<1 ppm).

A key conclusion from both studies is that variable interactions can significantly influence PGM recovery during CPE, underscoring the importance of multivariate analysis over single-variable assessments. However, the low metal concentrations used (<25 ppm) may limit the applicability of these findings to systems with higher concentrations, such as those explored in the current study. Further investigation is needed to determine whether the observed interactions hold under more concentrated conditions relevant to industrial applications.

Furthermore, there is a notable gap in the literature regarding metal stripping or impurity removal from the metal loaded SP, which is a critical step toward the commercialization of CPE [19,30]. Only a few studies have been reported on the elution of Pt and Pd from 2-MBT-related compounds, such as 2-((2-methoxyethyl)thio)-1H-benzimidazole, 2-MBT anchored on Amberlite XAD − 1180 resin, and 2-mercaptobenzimidazole [35,36,37]. In these investigations, thiourea in hydrochloric acid was used as the eluent. Reports on Rh elution from 2-MBT are scarce. The work presented in this section was not necessarily carried out in a CPE system; however, the complexing agents used share some characteristics with 2-MBT, providing insights into the elution of PGMs from the SP in this study.

Understanding factor interactions, as well as optimizing the elution of PGMs and the removal of impurities from the metal-loaded SP, is crucial for the commercial viability of CPE. Applying design of experiments (DoE) can support systematic evaluation of these interactions, while the potential for metal recovery and impurity removal from the SP can be assessed using various stripping and scrubbing agents, respectively.

This study aimed to achieve three key objectives: (1) to identify the significant factors influencing the CPE of PGMs from a chloride leach solution of SACs and analyze their interactions using a fractional factorial design; (2) to assess the feasibility of stripping PGMs from the surfactant phase; and (3) to examine the removal of impurities from the surfactant phase.

## 2. Materials and Methods

### 2.1. Reagents

The chemical reagents used in this work were of analytical grade and were procured from Merck, Sigma Aldrich, and Ace (Pty, Ltd). Ultrapure water ($H_2O$), 32 % *w*/w hydrochloric acid (HCl), 25 % w/w ammonium hydroxide ($NH_4OH$), sodium hydroxide (NaOH), tin chloride di-hydrate ($SnCl_2.2H_2O$), triton x-100 ($C_{14}H_{22}O(C_2H_4O)_n(n = 9–10)$), thiourea ($CH_4N_2S$), palladium chloride ($PdCl_2$), platinum chloride ($PtCl_4$), rhodium chloride ($RhCl_3$), ferric chloride ($FeCl_3$), aluminium chloride hexahydrate ($AlCl_3.6H_2O$), magnesium chloride hexahydrate ($MgCl_2.6H_2O$), and 2-mercaptobenzothiazole ($C_7H_5NS_2$) were used without further purification.

### 2.2. Spent autocatalytic converter chloride leach

A synthetic leach solution, modelled on the chloride leachate from spent autocatalysts reported by other researchers, was prepared as a stock solution and diluted for tests in this study [38,39]. The synthetic solution was prepared by dissolution of palladium chloride, platinum chloride, rhodium chloride, ferric chloride, aluminium chloride and magnesium chloride in HCl. The metal composition of the prepared solution and the industry leach solutions investigated by other researchers are shown in Table 1.

### 2.3. Experimental design

#### 2.3.1. Fractional factorial design

DoE can help to determine interactions between factors, and it can also help in identifying influential factors affecting a process [42]. In this study a $2^{5-1}$ fractional factorial design was used for the CPE experiments. This design aimed to determine the significant factors among the initial solution pH, volume of surfactant (10 % *w/v* Triton X − 100), volume of complexing agent (1 % *w/v* 2-mercaptobenzothiazole), metal concentration, and contact time. According to literature equilibration temperature affects CPE recovery as non-ionic surfactant molecules form micelles when the cloud point temperature is reached [21]. For Triton X − 100 the maximum PGMs recovery occurs at the equilibration temperature of 75 °C, which was used in this work. Anything below would not form adequate micelles to extract the hydrophobic PGM complexes while anything above would destroy the micelles formed lowering extraction efficiency [43,19]. The activating and reducing agent Tin (II) chloride is essential for improving the kinetics of the CPE PGMs recovery and a high amount to ensure the extraction reaches completion was used and held constant [44,22,28]. Design Expert® 13 software was used to generate the experimental design and analysis of results [45]. Preliminary studies and information from literature were used to come up with the levels for the variable and held factors [19,30]. For each variable factor under study there was a low setting coded −1 and a high setting coded +1 as shown in Table 2.

The Pt, Pd, and Rh concentration in the solution was varied from 12, 58, and 12 ppm respectively to 24, 117 and 24 ppm respectively based on literature [19,29,30].

#### 2.3.2. Methodology of Data Analysis

The normal probability plot of effects was used to analyze the fractional factorial data. When analysing un-replicated factorial designs, high order and meaningful interactions occur occasionally and there is need for selection which is provided by the normal probability plot [46]. In the normal probability plot actual value estimates of effects are plotted against their cumulative probability. The effects are ordered from low to high.

#### 2.3.3. PGMs extraction by Cloud Point Extraction procedure

A volume of 40 ml of a PGMs leach solution, at a predetermined pH, was placed in a 50 ml centrifuge tube. To it, 1 ml of the surfactant, Triton X − 100 (10 % m/v), and 1 ml of the complexing agent, 2-MBT (1 % m/v), were added and left to stand for 15 min ([30]; Niemelä et al. [47]). Afterwards 3 ml of the reducing and activating agent, tin (II) chloride di-hydrate (10 % m/v) in 6 M HCl solution was added, and the open centrifuge tubes were heated in a thermostat-controlled water bath set at 90 °C to achieve a system equilibration temperature of 75 °C for an incubation time of 1 h 55 min [30]. Due to evaporative losses, heated de-ionized water at 75 °C, which was the equilibration temperature of the CPE system, was added to ensure constant solution volume and system behaviour. A sample was collected for analysis by ICP-MS for PGMs and ICP-OES for Al, Fe and Mg. The PGMs extraction by CPE was calculated as a percentage of PGMs in the surfactant phase to that initially present in the chloride leach solution as per eq. 7.

**Table 1**
Metal concentrations (ppm) of spent autocatalyst and concentrate industrial leachates.

| Pt | Pd | Rh | Al | Mg | Fe | Composition | Reference |
|---|---|---|---|---|---|---|---|
| | | | | | | SACs | This work |
| 72 | 350 | 72 | 11,000 | 1500 | 700 | leach liquor | |
| | | | | | | Diluted SACs | |
| 12–24 | 58–117 | 12–24 | 1794–3623 | 245–494 | 114–231 | leach liquor | This work [40] |
| 246,000 | 133,000 | 41,200 | - | - | 26,000 | Industrial leachate | |
| | | | | | | SACs | [38] |
| - | 368 | 33 | 3898 | 555 | 32.2 | leach liquor | |
| 349 | 172 | 51 | 11,700 | 1704 | 520 | SACs | [39] |
| | | | | | | leach liquor | |
| 390 | 217 | – | 12,002 | 1835 | 1226 | SACs | [41] |
| | | | | | | acid leachate | |

**Table 2**
CPE variable factors and their levels.

| | Levels | | |
|---|---|---|---|
| Experimental Factor | Low (−1) | Centre (0) | High (1) |
| Initial leach solution pH (A) | 4.00 | 5.00 | 6.00 |
| Complexing agent volume/ ml (B) | 1.00 | 1.50 | 2.00 |
| Surfactant volume/ ml (C) | 1.00 | 1.50 | 2.00 |
| Metal concentration (Pt, Pd, Rh, Al, Fe, Mg) / ppm (D) | 12, 58,121,794,114,245 | 16, 78,162,285, 145,312 | 24, 117,243,623,231,494 |
| Contact time /min (E) | 115.00 | 130.00 | 145.00 |

$$E\% = \frac{C_i - C_f}{C_i} \times 100 \quad (7)$$

where $C_i$ and $C_f$ are the concentration of metal before and after extraction in the aqueous phase respectively.

#### 2.3.4. Elution of PGMs from the surfactant phase

The elution of PGMs from the surfactant phase was carried out using thiourea-hydrochloric acid, ammonia, sodium thiosulphate, and hydrochloric acid at room temperature. This involved adding the eluent to the surfactant phase followed by centrifuging at 4000 rpm for 5 min. The volume ratio of eluent to loaded surfactant phase used was 12. The tubes were cooled in a refrigerator for 30 min at 6 °C and further cooled in a freezer for 15 min at −10 °C. After cooling the aqueous phase was decanted and analysed using ICP-MS.

The stripping efficiency was calculated using eq. 8 below:

$$Stripping\ efficiency = \frac{m_{aq}}{m_{SP}} \times 100\% \quad (8)$$

where $m_{aq}$ is the mass of metal in the stripping solution and $m_{sp}$ is the initial mass of metal in the surfactant phase.

#### 2.3.5. Impurity removal from the PGMs loaded surfactant phase

The purpose of these tests was to find a suitable solution to scrub the Al, Fe, and Mg from the loaded surfactant phase. The scrubbing agents tested were $H_2O$, HCl, $H_2SO_4$, and NaOH. The volume ratio of scrubbing agent to loaded surfactant phase used was 10.The loaded surfactant phase from section **2.3.3** was mixed with one of the scrubbing agents at 25 °C and centrifuged for 60 min at 4000 rpm. After the separation of the surfactant and aqueous phase, a sample of the aqueous phase was taken using a micropipette for analysis by ICP-MS for PGMs and ICP-OES for Al, Fe and Mg.

The scrubbing efficiency was calculated using eq. 9 below:

$$Scrubbing\ efficiency = \frac{m_{aq}}{m_{SP}} \times 100\% \quad (9)$$

where $m_{aq}$ is the mass of metal in the scrubbing solution and $m_{sp}$ is the initial mass of metal in the surfactant phase.

## 3. Results and Discussion

### 3.1. Identification of significant factors

The fractional factorial CPE screening design with codified experimental factors is shown Table 3 with three replicates at the centre point to estimate the experimental error.

Table 4 shows the process pH measurements for three selected samples (3, 4, and 19) with initial leach solution pH values of 4, 6, and 5, respectively and recorded after the addition of reagents. Samples 3 and 4, which had similar metal compositions but differing initial pH values, were selected to represent the lower and upper extremes. Sample 19, with an initial pH of 5, was included for comparison. As the experiment proceeded, the process pH remained constant from 15 min into the experiment until its conclusion at 1 h and 55 min as shown in the Table 4.

The process pH was influenced by the initial leach solution pH and was therefore excluded from the analysis of pH effects on PGM extraction. The experimental results in Table 3 were used to generate the normal probability plots in Design Expert®13 software for Pt, Pd and Rh [45]. The results are shown in Figs. 1, 2 and 3 respectively. These were used to identify the significant factors in the CPE of PGMs from an acidified chloride leach solution.

Fig. 1 shows that initial leach solution pH (A) and metal ion concentration (D) were more statistically significant for Pt recovery as they were not distributed about the fixed mean zero on the normal probability plot. The other factors such as the complexing agent volume (B), surfactant volume (C) and contact time (E) were not statistically significant for Pt CPE recovery as they were distributed near the normal distribution.

The normal probability plot for Pd recovery presented in Fig. 2 shows that complexing agent volume (B), contact time (E), and metal ion

**Table 3**
PGMs CPE results of $2^{5-1}$ fractional factorial design.

| Standard run Order | Random Run order | Experimental Factors | | | | | Recovery (%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | E | Pt | Pd | Rh | Al | Fe |
| 1 | 11 | -1 | -1 | -1 | 1 | 1 | 87.52 | 78.54 | 53.47 | 15.59 | 42.75 |
| 2 | 9 | 1 | -1 | -1 | 1 | -1 | 99.83 | 99.93 | 99.26 | 30.42 | 30.13 |
| 3 | 2 | -1 | 1 | -1 | 1 | -1 | 98.14 | 99.84 | 85.00 | 19.75 | 43.23 |
| 4 | 19 | 1 | 1 | -1 | 1 | 1 | 99.87 | 99.86 | 99.59 | 25.38 | 39.44 |
| 5 | 13 | -1 | -1 | 1 | 1 | -1 | 94.88 | 93.95 | 65.92 | 17.30 | 42.47 |
| 6 | 7 | 1 | -1 | 1 | 1 | 1 | 99.90 | 99.91 | 99.50 | 25.37 | 40.43 |
| 7 | 12 | 1 | 1 | 1 | 1 | 1 | 99.33 | 99.95 | 96.18 | 25.38 | 41.25 |
| 8 | 15 | 1 | 1 | 1 | 1 | -1 | 99.89 | 99.83 | 99.26 | 32.96 | 38.53 |
| 9 | 18 | -1 | -1 | -1 | -1 | -1 | 99.86 | 99.88 | 98.73 | 17.75 | 48.05 |
| 10 | 4 | 1 | -1 | -1 | -1 | 1 | 99.76 | 99.80 | 95.63 | 12.51 | 36.87 |
| 11 | 14 | -1 | 1 | -1 | -1 | 1 | 99.24 | 99.82 | 98.35 | 13.19 | 40.03 |
| 12 | 17 | 1 | 1 | -1 | -1 | -1 | 99.59 | 99.73 | 93.02 | 12.42 | 37.07 |
| 13 | 3 | -1 | -1 | 1 | -1 | 1 | 99.67 | 99.99 | 99.04 | 19.78 | 46.99 |
| 14 | 10 | 1 | -1 | 1 | -1 | -1 | 99.84 | 99.88 | 97.74 | 19.37 | 41.43 |
| 15 | 1 | -1 | 1 | 1 | -1 | -1 | 99.32 | 99.57 | 98.12 | 14.45 | 45.69 |
| 16 | 5 | 1 | 1 | 1 | -1 | 1 | 99.51 | 99.69 | 92.89 | 19.87 | 41.63 |
| 17 | 16 | 0 | 0 | 0 | 0 | 0 | 99.58 | 99.46 | 97.84 | 18.89 | 42.99 |
| 18 | 6 | 0 | 0 | 0 | 0 | 0 | 99.41 | 99.32 | 96.56 | 10.66 | 39.39 |
| 19 | 8 | 0 | 0 | 0 | 0 | 0 | 99.32 | 99.18 | 96.89 | 15.81 | 38.81 |

A: Initial leach solution pH; B: complexing agent volume; C: surfactant volume; D: metal concentration; E: contact time.

**Table 4**
Initial leach solution and CPE process pH at 10 % m/v tin (II) chloride.

| Standard run Order | Initial leach solution pH / Time (Minutes) | Process pH | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 15 | 30 | 45 | 60 | 75 | 90 | 115 |
| 3 | 4 | 1.10 | 1.14 | 1.12 | 1.11 | 1.13 | 1.11 | 1.10 |
| 4 | 6 | 1.67 | 1.65 | 1.66 | 1.68 | 1.69 | 1.67 | 1.69 |
| 19 | 5 | 1.36 | 1.39 | 1.37 | 1.39 | 1.40 | 1.38 | 1.39 |

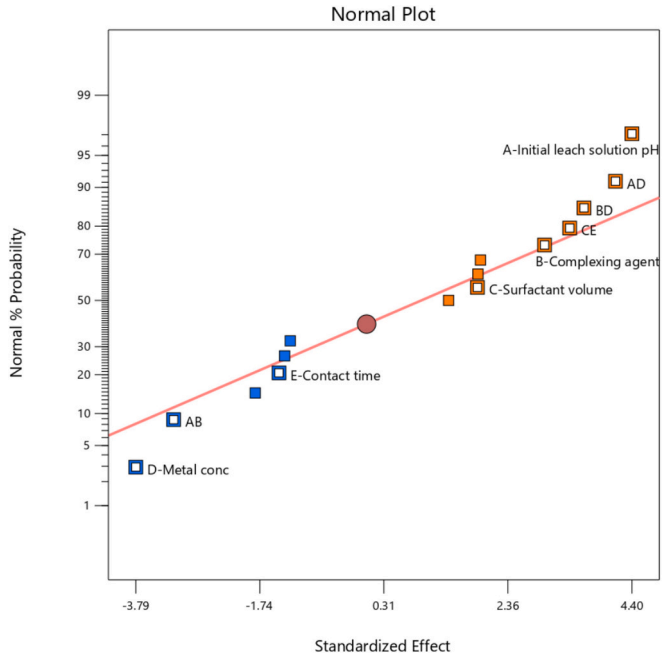


**Fig. 1.** Normal plot of effects of main factors and factor interactions from the $2^{5-1}$ fractional factorial design for Pt recovery.

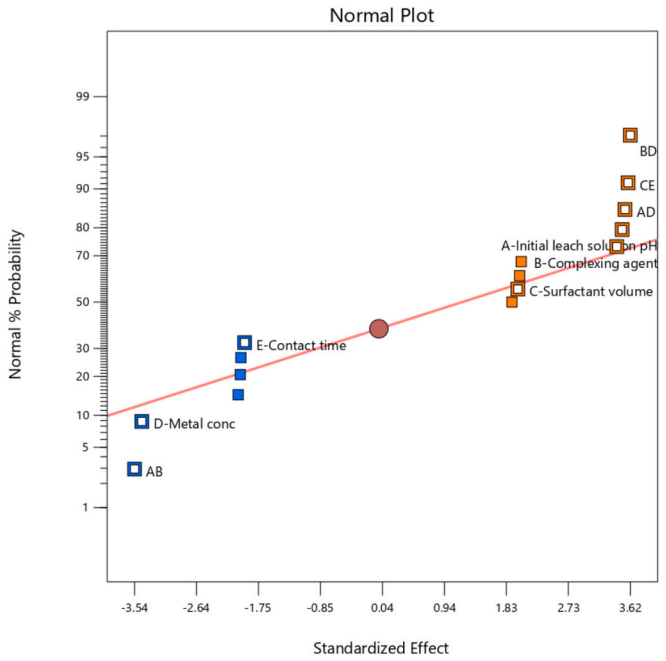


**Fig. 2.** Normal plot of effects of main factors and factor interactions from the $2^{5-1}$ fractional factorial design for Pd recovery.

concentration (D) were potentially statistically significant as they were not distributed on the normal distribution like the other factors A, and C.

For Rh recovery initial leach solution pH (A), complexing agent volume (B), and initial metal ion concentration (D) were statistically significant as shown in Fig. 3. Factors A, B, and D were not distributed about the fixed mean zero while factors C, and E are not statistically significant for Rh extraction as they are distributed near the mean zero of the normal distribution.

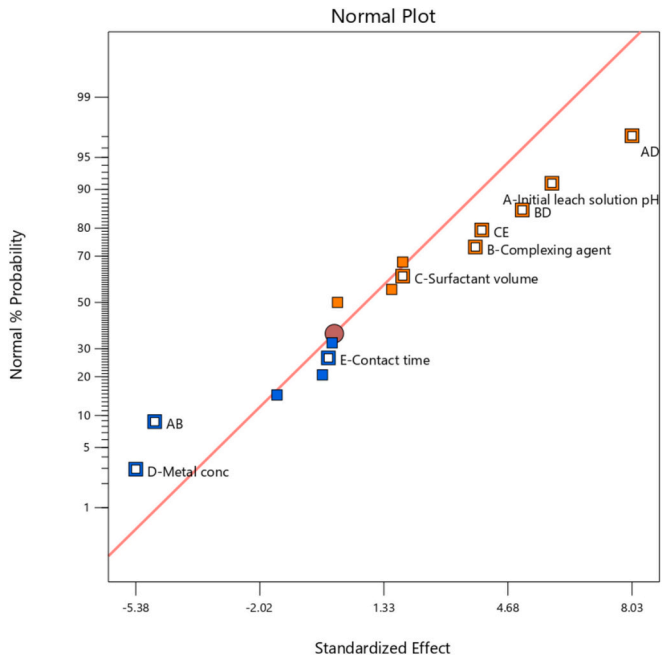


**Fig. 3.** Normal plot of effects of main factors and factor interactions from the $2^{5-1}$ fractional factorial design for Rh recovery.

### 3.2. *Influence of factors and factor interaction on PGMs adsorption*

Only in the absence of any indication that a variable interacts with other factors can the principal effect of a variable be interpreted independently. The interacting factors ought to be considered together when there is proof of one or more of these interaction effects [48]. In this investigation, the interaction between all evaluated variables was determined to be statistically significant for Pt and Rh, but not for Pd. The interaction of variables was collectively understood, as described below, therefore no study on individual factor effect on PGMs recovery was undertaken in this study.

In the DoE results of Table 3 for the recovery of the three PGMs, statistically significant interaction of factors was present and mostly involved initial leach solution pH (A) and metal ion concentration (D). These two interacted with each other and with the complexing agent volume (B). These significant interactions were AB, BD, and AD. The initial leach solution pH, A, dictates the metal species present in the CPE system, as well as the form of the complexing agent, B. When the initial leach solution pH was set high, representing a pH of 6, and the complexing agent was also at a high setting of 2 ml for standard run 4 in Table 3, both the nitrogen and sulphur electron-donating groups of the complexing agent, 2-MBT, were not protonated [49]. This enabled 2-MBT to interact with PGM species in the system, leading to high recoveries (>99 %) for Pt, Pd, and Rh. In contrast, when the leach solution pH (A) and the complexing agent volume (B) were set to low values of 4 and 1 ml, respectively, as in standard run 1 of Table 3, the recoveries for Pt, Pd, and Rh decreased to 88 %, 79 %, and 54 %, respectively. This occurred because, under acidic conditions, protonation of the complexing agent reduces the number of available bonding sites for interaction with PGM species, thereby lowering metal extraction [49].

The mechanism of extraction of anionic PGM chloro complexes by 2-MBT proceeds via a neutral complexation pathway with the PGMs anionic complex bonded via both N and S on 2-MBT, as reported in literature [50]. This mechanism is similar to the extraction of anionic Pd chloro-complexes by hydroxyoximes used in commercial PGM recovery plants, where high acidity leads to protonation of the oxime group, thereby decreasing its ability to complex with the anionic Pd chloro complex [51,52]. Additionally, elevated chloride ion concentrations suppress the forward reaction by competing with the extractant, thus slowing down the rate of Pd extraction [53]. At present the known CPE extraction mechanism of PGMs using 2-MBT contrasts with the ion-pair and solvation extraction mechanisms commonly used in commercial PGMs extraction [54]. Extractants operating via the ion-pair mechanism favour high acidity (>3 M HCl) as this enables protonation of the extractant followed by its association with anionic PGMs chloro complexes [51,55]. In this study, there was interaction between surfactant volume (C) and contact time (E), but this interaction was not as statistically significant when compared to other interactions mentioned and shown in **Figs. 1, 2, and 3**.

Table 3 presents the interactions between the initial leach solution pH (A) and metal ion concentration (D), which are also illustrated in Figs. 1, 2, and 3. These interactions had a significant positive effect on Pt and Pd extraction under the examined conditions, as evidenced by the positive standardized effect in Figs. 1, 2, and 3. This result was unexpected, given the increase in metal ion concentration in standard runs 2, 4, 6, and 8 of Table 3. Typically, a higher metal ion concentration would lead to lower metal extraction since most of the bonding sites on 2-MBT would be occupied. However, the findings suggest that sufficient bonding sites were still available and that the loading capacity of 2-MBT was not reached within the investigated metal ion concentrations.

Table 3 also highlights the interaction between the complexing agent volume (B) and metal ion concentration (D), which yielded varying results. In standard run 3, as shown in Table 3, the metal extraction efficiencies for Pt, Pd, and Rh were 99 %, 99 %, and 85 %, respectively. The lower Rh extraction may be attributed to difficulties in forming complexes with 2-MBT at an initial solution pH of 4, unlike Pt and Pd, which exhibit a stronger affinity for 2-MBT than Rh [56]. In contrast, standard runs 4 and 8 achieved metal extraction efficiencies close to 99 % for Pt, Pd, and Rh. This behaviour could be influenced by the initial solution pH setting of 6, which enhanced the availability of Sulphur (S) and Nitrogen (N) atoms, unlike in more acidic conditions where protonation occurred, as seen in standard run 3. In standard run 7, Pt and Pd extraction exceeded 99 %, but Rh extraction dropped to 96 %. This decline may be due to the initial solution pH setting of 4, which likely hindered Rh-2-MBT complex formation, leading to lower extraction.

The interaction between A and B (AB) had a negative effect on Pd and Rh recovery, as illustrated in Figs. 2 and 3, respectively. Meanwhile, the interactive effects of AD and BD were significant in Rh recovery. Figs. 4, 5, and 6 depict the interactions AB, AD, and BD for Rh recovery, which followed a similar trend to that of Pt and Pd but was more pronounced. Consequently, the corresponding plots for Pt and Pd are provided in **Figs. S1**, **S2**, **S3**, **S4**, **S5,** and **S6**.

According to Fig. 4, the initial leach solution pH had a positive effect on the extraction of the PGMs when the complexing agent volume was low. No effect was observed when the volume was high. At a low initial leach solution pH, higher proton presence could result in protonation of the sulphur group on 2-MBT (complexing agent) lowering its extraction ability as also suggested by other researchers [28]. At a high complexing agent setting, varying the initial leach solution pH did not have an observable impact. This is likely due to the sufficient availability of the 2-MBT ligand in the system for PGM complexation. Regardless of protonation at low pH, the ligand remained adequate to facilitate metal binding.

The plot in Fig. 5 shows the interaction of initial leach solution pH with metal ion concentration. The initial pH of the leach solution positively influenced the extraction of the PGMs when the metal ion concentration was high and slightly negatively influenced extraction when the metal concentration was low. The CPE studies were conducted at an initial solution pH of 4–6 where formation of hydrated PGM-chloro complexes is prevalent [17]. At low pH and high metal ion concentration (experiment 1, 3 and 5 of Table 3) the total recovery for the PGMs was lower than in other experiments. Several reasons could be attributed to this observation. When the pH is low at both low and high metal ion concentrations, the increased proton levels lead to the protonation of

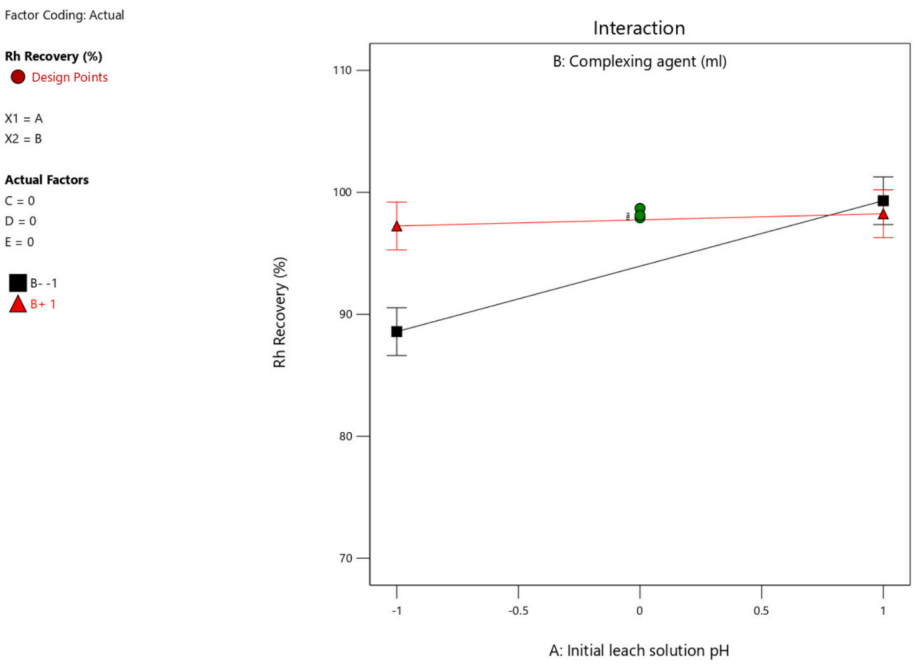


**Fig. 4.** Interaction of initial leach solution pH with complexing agent plot for Rh.

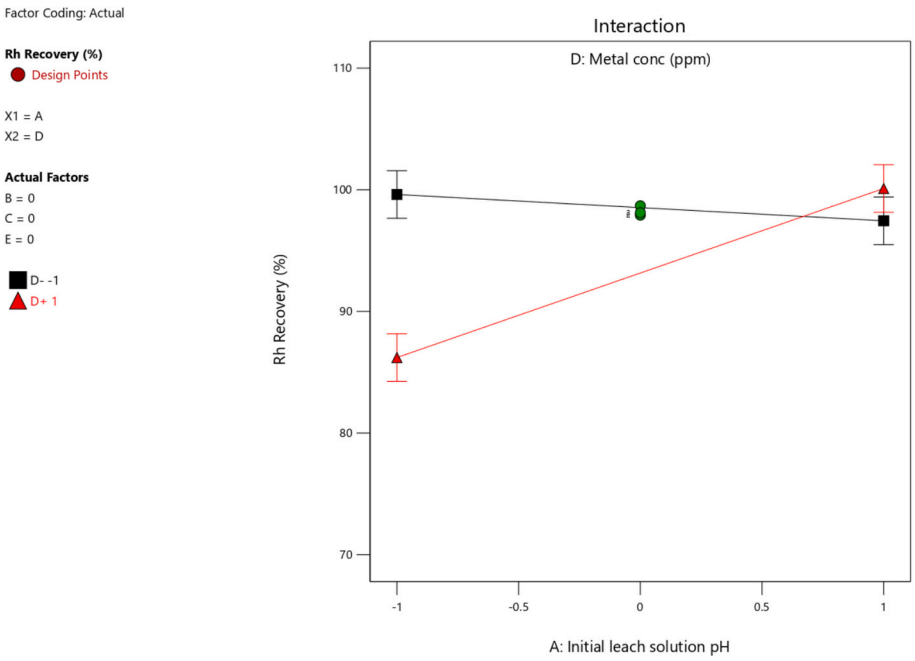


**Fig. 5.** Interaction of initial leach solution pH with initial metal concentration plot for Rh.

donor atoms on 2-MBT (the complexing agent). This reduces the number of available bonding sites on 2-MBT and thereby decreasing its metal extraction efficiency [49]. This effect was observed and more pronounced at high metal ion concentrations due to greater abundance of metal species compared to lower metal ion concentrations [28]. The lower metal extraction at initial solution pH 4 could also be due to the lower hydrophobicity of the formed PGM complexes compared to the higher hydrophobicity observed at initial solution pH 6, as reported in the literature [57]. When the initial solution pH was increased to 6, metal extraction improved due to the availability of more bonding sites on the complexing agent, 2-MBT as the number of free hydrogen ions to protonate 2-MBT was low. Tin (II) chloride is added in the CPE process to reduce Pt (IV) to Pt (II) and Rh (III) to Rh (I), to increase the extraction rate of both elements and ensure quantitative Rh extraction [22]. It is possible that in a leach solution with an initial pH of 4, the reductant generated more $SnCl_3^-$ due to the higher concentration of $Cl^-$ compared to solutions with higher initial pH values used in the study. This compound may have reacted with surfactant micelles, reducing PGMs extraction, as noted by other researchers [28].

Fig. 6 illustrates the relationship between the complexing agent and metal ion concentration. The volume of the complexing agent positively influenced the extraction of PGMs, particularly when the metal ion concentration was high. The complexing agent plays a crucial role in transforming the PGMs into a hydrophobic form, making them easily

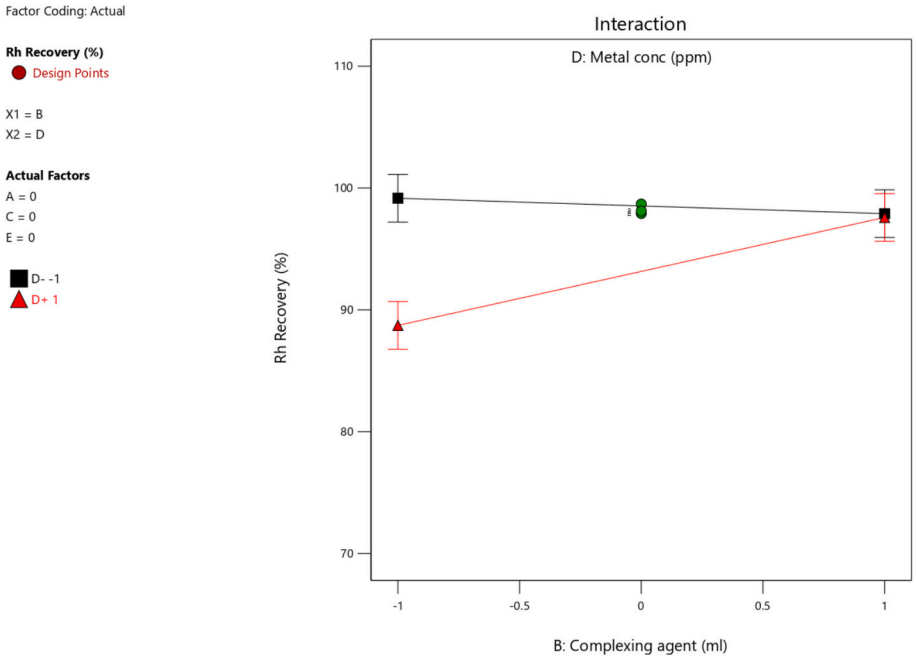


**Fig. 6.** Interaction of complexing agent with initial metal concentration plot for Rh.

extractable by the surfactant. However, when the metal ion concentration was high and the complexing agent volume was low, there were insufficient complex ligands to convert the PGMs into the 2-Mercaptobenzothiazole PGM complexes. As a result, PGM extraction was lower, as not all PGMs were in the necessary form for extraction by the surfactant.

The total PGMs recovery of 100 % was obtained at initial pH 6, 2 ml of complexing agent, 1 ml of surfactant, high metal concentration and maximum contact time. The minimum PGMs recovery of 73 % was obtained at initial pH 4, 1 ml of complexing agent, 1 ml of surfactant, high metal concentration and maximum contact time.

### 3.3. Extraction of impurity elements

Table 3 demonstrates that Al and Fe were co-extracted into the SP, while Mg was not. Feng et al. [58] conducted a study on the inhibition of Fe corrosion using 2-MBT, the same agent employed in this study and discovered that it adsorbed onto the iron surface via nitrogen and exocyclic sulphur atoms. This explains the recovery of Fe to the SP in the test work. An investigation on aluminium corrosion inhibition in 1.0 M HCl using 2-mercaptobenzothiazole-related compounds, specifically 4-[4-(1,3-benzothiazol-2-yl)phenoxy] phthalonitrile and tetrakis[(benzo[*d*]thiazol-2-ylphenoxy) phthalocyaninato] gallium(III) chloride, was also carried out, achieving efficiencies of 76 % and 83 % respectively [59].The study found that the lone pairs on the nitrogen and sulphur interacted with aluminium, chemically explaining its recovery in the present CPE study. Magnesium was not extracted at the metal ion concentrations and conditions investigated in the fractional factorial design. This could be due to it being a hard acid whose interaction with soft acids like 2-MBT is limited at the investigated metal ion concentrations in the screening test work [60].

Other researchers have conducted the CPE recovery in 1.0 M HCl to improve selectivity as the matrix (non-target) elements do not form hydroxides at such acidic conditions compared to the present study [61,30]. In their studies, they extracted about 5 % of matrix elements. Besides the high acidity, those works were also at much lower PGMs and matrix element concentrations. The PGM concentrations in those works were below 50 ppm, while matrix element concentrations were under 750 ppm. In contrast, the present study examined higher concentrations, ranging from 82 to 165 ppm for PGMs and 2200 to 4400 ppm for matrix elements. At present no work has been conducted to determine the minimum amount of the 2-mercaptobenzothiazole required to extract the PGMs from SACs leachates. The 2-MBT concentration could be a key factor in improving CPE selectivity in PGMs extraction.

The extraction results in Table 3 showed that magnesium was not extracted under the investigated metal ion concentrations and conditions. Therefore, further testwork was conducted in triplicate to study impurity behaviour. The fractional factorial design revealed that only the metal composition, initial leach solution pH, and complexing agent volume were statistically significant in the extraction of Pt, Pd, and Rh. The additional testwork investigated metal ion concentrations corresponding to a solution composition of 36.00, 175.00, 36.00, 5500.00, 350.00, and 750 ppm of Pt, Pd, Rh, Al, Fe, and Mg, respectively. An initial leach solution pH of 5 and a complexing agent volume of 1.5 ml were employed. The surfactant volume and contact time were set at 1.0 ml and 115 min, respectively. After the reagents were added, the process pH was 1.82, and the achieved extractions were 99.61 % Pt, 99.52 % Pd, 98.66 % Rh, 22.21 % Al, 52.34 % Fe, and 20.83 % Mg. The surfactant phase from this experiment was subsequently used in the elution and scrubbing testwork described in the following sections.

### 3.4. PGMs elution from the loaded surfactant phase

Elution experiments were performed according to the procedure described in section **2.3.4**. Various eluents, including thiourea in HCl, HCl, ammonia, and sodium thiosulphate, were tested. Two tests, labelled as A and B, were performed using the metal loaded SP obtained after CPE and the outcomes of these tests are detailed in Table 5.

In trial A of the elution tests, conducted with a 5-min contact time, a solution of 1.0 M thiourea in 0.5 M HCl successfully stripped over 60 % of Pt and Pd in a single stage from a loaded SP. Simultaneously, 6 M HCl stripped 52 % of Rh from a loaded SP in one stage. In a study by Zhang et al. [37], Pt(II) and Pt(IV) were extracted using 2-Mercaptobenzimidazole (2-MBI), a compound related to 2-MBT. These researchers achieved a 90 % elution for each ion using 0.1 M thiourea in 0.5 M HCl. These high results could be because there were no other metals co-extracted, unlike in the present study. Thiourea, characterized by sulphur and nitrogen donor atoms, acts as a robust soft base. According to Pearson's

**Table 5**
PGMs elution test work from loaded surfactant phase.

| | | | | % Stripping | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Trial | Contact time (Min) | Number of stages | Eluent | Pt | Pd | Rh | Al | Fe | Mg |
| | | 1 | 1.0 M Thiourea in 0.5 M HCl | 65.96 | 61.73 | 22.47 | 7.97 | 12.90 | 5.22 |
| A | 5 | 1 | 6.0 M HCl | 9.91 | 5.41 | 52.63 | 38.49 | 44.85 | 46.93 |
| | | 1 | 1.0 M $NH_3$ | 0.34 | 11.10 | 1.55 | 0.10 | 0.05 | 0.02 |
| | | 1 | 1.0 M $Na_2S_2O_3$ | 17.15 | 7.12 | 9.60 | 7.12 | 7.02 | 5.11 |
| | | 1 | 1.0 M Thiourea in 0.5 M HCl | 52.65 | 24.78 | 5.46 | 45.49 | 18.52 | 50.89 |
| | | 2 | 1.0 M Thiourea in 0.5 M HCl | 92.10 | 42.30 | 21.84 | 55.37 | 23.17 | 57.74 |
| | | 1 | 6.0 M HCl | 27.46 | 7.78 | 68.32 | 50.76 | 51.89 | 53.97 |
| B | 60 | 2 | 6.0 M HCl | 31.16 | 13.95 | 81.22 | 60.98 | 77.84 | 60.60 |

Hard Soft Acid Base theory, thiourea would then readily form stable complexes with PGMs, which are considered soft acids [60].

As per the literature, the complexes formed with thiourea for Pd (II) and Pt (II) are identified as $Pd[((NH_2)_2CS)]_4^{2+}.2Cl^-$ and $Pt[((NH_2)_2CS)]_4^{2+}.2Cl^-$ ([35]; Ruzmetov and Gevorgyan, [62]). Pd and Pt can be recovered through precipitation by adding NaOH, followed by calcination to obtain metallic Pd and Pt [26]. In this study, effective elution of Rh was achieved using 6 M HCl. However, a challenge emerged with the elution agents employed, as they also led to the elution of impurities such as Al, Fe, and Mg. Consequently, this resulted in impure PGM solutions, necessitating a scrubbing stage before PGMs elution, as discussed in section **3.5**.

Table 5 indicates that the elution efficiency of Pt and Pd using acidified thiourea decreased over time. In a one-stage elution test with a 5-min contact time, the efficiencies were 66 % for Pt and 62 % for Pd. However, after 60 min under the same conditions, the efficiencies dropped to 53 % and 25 %, respectively. This decline suggests possible re-extraction by the surfactant phase, warranting further investigation to understand the underlying mechanism.

In contrast to Pt and Pd, Rh exhibited an increase in elution efficiency, rising from 53 % at a 5-min contact time to 68 % after 60 min. To further examine elution behaviour, a multi-stage elution trial (Trial B in Table 5) was conducted using 1.0 M thiourea in 0.5 M HCl and 6.0 M HCl. For acidified thiourea, transitioning from a one-stage to a two-stage process improved elution efficiencies from 53 % to 92 % for Pt, from 25 % to 42 % for Pd, and from 5 % to 22 % for Rh. This enhancement is attributed to increased interaction between thiourea molecules and Pt (II) and Pd(II), leading to greater formation of their respective thiourea complexes [35].

When 6.0 M HCl was used as the eluent, Pt and Pd elution efficiencies improved by less than 6 % in the second stage, whereas Rh exhibited a 12 % increase. These results highlight the need for further studies over a contact time range of 1 to 2 h to better understand PGM elution behaviour and optimize process conditions.

### *3.5. Impurity removal from the PGMs loaded surfactant phase*

The removal of impurities through scrubbing represents the reverse extraction process for Al, Fe, and Mg. Scrubbing experiments were carried out according to the procedure described in section **2.3.5**. Single-stage scrubbing tests were performed using HCl, deionized water, NaOH, and $H_2SO_4$ at a contact time of 60 min, and the results are detailed in Table 6.

The results reveal that only Al and Mg could be effectively scrubbed from the PGMs surfactant phase using 0.1 M HCl. The results in Table 6 suggest that the scrubbing process for Al would require three stages, while four stages would be necessary for Mg scrubbing; however, further tests are required to confirm this. However, the tested reagents proved ineffective in scrubbing Fe. Several factors contribute to the difficulty in scrubbing Fe. Notably, Fe's d orbitals strongly interact with S and N donor atoms in the complexing agent, 2-MBT, forming sigma bonds and pi back bonding into S and N orbitals as per literature (Rodgers, [63]). In contrast, Al and Mg only form sigma bonds with 2-MBT (Tabish et al., [64]). According to Obot et al. (2014), the binding energies of 2-MBI, a compound related to 2-MBT, on Fe and Al were 191.84 and 71.95 kJ/mol, respectively. These binding forces elucidate the challenges faced in scrubbing Fe.

The stability of the Fe complex formed with 2-MBT, compared to that of Al and Mg, may also be attributed to crystal field stabilization energy (CFSE) [65]. CFSE arises from ligands producing an electrostatic field that splits the d orbitals of Fe [65]. The redistribution of electrons in the split orbitals generates energy known as CFSE, stabilizing the complex. CFSE ranges from ten to hundreds of kJ/mol, similar in magnitude to bond energies. The absence of d orbitals in Al and Mg results in no CFSE, making their complexes less stable compared to Fe complexes, explaining the lower scrubbing efficiency of Fe compared to Al and Mg.

The high electronegativity of Fe (1.83) compared to Al (1.61) and Mg (1.31) according to the Pauling scale also plays a role. It results in stronger Fe bonds with 2-MBT compared to Al and Mg (Shriver et al., [66]). This also accounts for the challenge in scrubbing Fe from the SP compared to Al and Mg.

The scrubbing results indicated a need for improvement in the extraction conditions, particularly as scrubbing Fe posed a challenge for the leach solution processed from an initial leach solution pH of 4–6. There is need for further work at refined extraction conditions to inhibit Fe extraction.

## 4. Conclusions and Recommendations

The aim of this study was to identify the factors influencing CPE and explore how these factors interact in the CPE of PGMs from a SACs chloride leach solution, using a fractional factorial design. The study also aimed to evaluate the feasibility of stripping PGMs and removing impurities from the loaded surfactant phase. Three key factors were found to significantly impact PGMs extraction: initial leach solution pH (positive effect), complexing agent volume (positive effect), and metal concentration (negative effect). Furthermore, three interaction factors

**Table 6**
Al, Fe and Mg scrubbing from the PGMs surfactant phase.

| Scrubbing agent | % Scrubbing | | | | | |
|---|---|---|---|---|---|---|
| | Pt | Pd | Rh | Al | Fe | Mg |
| 1.0 M $H_2SO_4$ | 1.14 | 1.45 | 2.56 | 8.08 | 0.87 | 5.18 |
| 1.0 M NaOH | 0.31 | 0.18 | 0.56 | 8.31 | 0.32 | 0.02 |
| 0.1 M HCl | 0.08 | 0.21 | 0.61 | 43.50 | 3.52 | 27.98 |
| 0.01 M HCl | 0.63 | 1.28 | 2.31 | 44.99 | 0.21 | 4.90 |
| 0.001 M HCl | 0.46 | 1.11 | 2.42 | 7.86 | 0.31 | 5.08 |
| $H_2O$ | 0.96 | 2.42 | 4.18 | 12.06 | 0.32 | 7.69 |

influencing PGMs extraction were identified: initial leach solution pH and metal concentration (AD), initial leach solution pH and complexing agent volume (AB), and complexing agent volume and metal concentration (BD).

Building on the screening design studies conducted at low metal ion concentrations, additional tests were performed at higher concentrations, where all matrix elements were extracted into the SP. Elution experiments revealed that over 60 % of Pt and Pd could be recovered within just 5 min using 1 M thiourea in 0.5 M HCl, while more than 65 % of Rh was eluted after 1 h of contact with 6 M HCl. However, selective elution proved challenging due to the co-elution of impurities.

The testwork clearly showed that achieving selectivity of PGMs over Al, Fe, and Mg was a significant challenge in both the extraction and elution tests, leading to the initiation of scrubbing experiments. These tests demonstrated that Al and Mg could be fully scrubbed after three and four 1-h contacts with 0.1 M HCl, respectively. However, Fe could not be effectively removed from the PGMs SP under the tested reagents and conditions.

These findings underscore the promise and limitations of CPE for recovering PGMs from low-grade, complex feedstocks. On the one hand, the method shows strong potential for efficient, low-impact metal recovery. On the other, the lack of selectivity, particularly against iron, remains a major obstacle to commercial application.

To move CPE closer to industrial feasibility, future work should focus on tailoring extraction conditions to enhance PGM selectivity, particularly over iron, and on refining elution protocols to increase recovery rates without compromising purity. Investigating the specific role of 2-MBT in complex formation and selectivity, as well as optimizing elution variables such as contact time and temperature, could further enhance process performance. Ultimately, this study contributes valuable insights toward the development of more sustainable and efficient strategies for PGM recovery from secondary resources.

## CRediT authorship contribution statement

**C.W. Baleti:** Writing – original draft, Software, Methodology, Investigation, Data curation, Conceptualization. **A. Shemi:** Writing – review & editing. **S. Ndlovu:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2025.114683.

## Data availability

All relevant data are contained within the article and Supplementary Material.

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