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Oxidative leaching of refractory sulphidic gold tailings with an ionic liquid

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Abstract

The effect of temperature in the range of 20-65 °C on gold extraction from refractory gold tailings containing pyrite in 20% (v/v) of 1-butyl-3-methylimidazolium hydrogen sulphate [$Bmim^{+}HSO_4^{-}$]-water solution with thiourea as complexing agent and iron(III) sulphate oxidant, at pH of 1 was examined for 12 h leaching time intervals. The experimental results revealed that the extraction of gold improved by increasing the temperature. The effect of time showed that a substantial amount of gold extraction took place during the first day of extraction and thereafter very little gold extraction occurred. The ionic liquid [$Bmim^{+}HSO_4^{-}$] is water soluble and in aquatic solution can act like a Brønsted acid by releasing H^{+} ions. The apparent activation energy (E_a) was calculated based on the Arrhenius theory and it suggests that the kinetic process of gold leaching with this acidic ionic liquid follows shrinking core model with mixed and diffusion controlled reaction regions having E_a of 17.97 kJ/mol and 27.17 kJ/mol, respectively. In the SEM image of the solid residue of the leached sample some pores appeared on the reactive pyrite particles, whereas the pyrite particles in the unleached sample looked smooth. Additionally, Raman spectra detected sulphur shifts in the recorded spectra of the solid residue after leaching which can be an indication of the formation of a product surface layer of elemental sulphur, which supports the diffusion through a product layer in the kinetic model.

Keywords: Refractory sulphidic low-grade gold tailing, Acidic ionic liquid, 1-butyl-3-methylimidazolium hydrogen sulphate, Gold leaching, Pyrite, Raman spectra.

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1. Introduction

Precious metals, particularly gold, have attracted worldwide attention due to their unique physicochemical properties, which provide a wide range of practical applications in modern industry (Syed, 2012). Moreover, there is a large universal demand from modern growing industries that consume significant quantities of gold. Such a demand coupled with the exhaustion of high-grade gold ore sources, and the difficulty associated with the processing of refractory low-grade gold ores, which cannot be treated in an environmentally friendly way by traditional processes like cyanidation, have created noteworthy challenges in the gold supply market. Thus, currently, increasing importance is being attached to hydrometallurgical processing of refractory gold ores containing sulphide minerals, such as arsenopyrite (FeAsS) and pyrite (FeS_2), as well as tailings so as to fulfil the demand for gold in the world.

To date, several techniques have been developed to extract gold from ores, such as cyanide leaching (Dadgar, 1989; Azizi and Ghaedrahmati, 2015), bioleaching (Lynn, 1997; Deng and Liao, 2002), acid thiourea leaching (Lacoste-Bouchet et al., 1998; Ubaldini et al., 1998; Örgül and Atalay, 2002; Murthy et al., 2003; Li and Miller, 2006; Li and Miller, 2007; Gönen et al., 2007) and pressure oxidative leaching (Long and Dixon, 2004; Rusanen et al., 2013). Cyanide leaching is the most common amongst these other processes. However, because of the highly toxic nature of cyanide and its severe environmental impact, this is not an environmentally favourable process. Therefore, it is imperative to investigate new leaching agents which act in a more environmentally friendly manner (Tian et al., 2010).

At the moment, an attractive substitute processing route to cyanide leaching is the use of ionic liquids as solvents. Ionic liquids are relatively new emerging solvents, and as their names suggest, they are liquids at ambient temperature. They have many fascinating physicochemical properties such as unmeasurable vapour pressure, low melting point and high thermal stability which allow them to remain in liquid form over a wide temperature range (Whitehead et al., 2009). These features make them promising solvents for different types of ores, including extracting gold in a manner that may not pose a threat to the environment (Jenkin et al., 2016).

The scientific community recently focused their attention on research that investigates the capability of ionic liquids to extract gold from sulphidic gold ores. For example, the ionic liquid, 1-butyl-3-methylimidazolium hydrogen sulphate [$Bmim^+HSO_4^-$], has been investigated in research by Whitehead et al. (2004). The reseaerchers investigated the recovery of gold and silver from a gold-containing ore by employing [$Bmim^+HSO_4^-$] as a nonconventional solvent with thiourea as complexing agent and iron(III) sulphate oxidant (Whitehead et al., 2004). Additionally, a comparative dissolution of gold and silver from sulphidic ores using an aqueous sulphuric acid H_2SO_4/thiourea/$Fe_2(SO_4)_3$ mixture with [$Bmim^+HSO_4^-$]/thiourea/$Fe_2(SO_4)_3$ has been reported (Whitehead et al., 2007). The results revealed that the recovery of silver was improved significantly with [$Bmim^+HSO_4^-$] (>60%) compared to aqueous sulphuric acid (<10%), although the gold recovery was relatively similar (>85%) in both systems (Whitehead et al., 2007). Furthermore, the recyclability of the [$Bmim^+HSO_4^-$] solution without decomposition or significant changes in extraction effectiveness have also been demonstrated (Whitehead et al., 2004). Other studies also used ionic liquids for the leaching of various ores. For example, Dong et al. (2009) studied the leaching of chalcopyrite concentrate with an aqueous solution of [$Bmim^+HSO_4^-$], at ambient pressure for the extraction of copper in the temperature range of 50-90 °C.

According to previous work by researchers (Crowhurst et al., 2003; Dong et al., 2009), a mixture of the ionic liquid [$Bmim^+HSO_4^-$] with water has the capability to produce H^+ ions due to its anion's [HSO_4^-] dissolution in aqueous solution following the equilibrium presented in Eq. (1).

$$[Bmim]^+ \ldots\ldots\ HSO_4^- \leftrightarrow [Bmim]^+ + H^+ + SO_4^{2-} \qquad (1)$$

$$K = \frac{[\,Bmim]^+\,[\,H^+]\,[SO_4^{2-}]}{[[\,Bmim]^+ \ldots\ldots HSO_4^-]}$$

where K is the dissociate equilibrium constant. Based on the equation, by increasing the concentration of the ionic liquid, the concentration of [H^+] will rise as well, which leads to higher acidity in the aqueous solution (Crowhurst et al., 2003). Thus, this acidic ionic liquid can reduce the pH of a leaching solution like a typical inorganic acid (Chen et al., 2015).

Considering this feature, a leaching system containing the aqueous solution of acidic ionic liquid [$Bmim^+HSO_4^-$] as solvent with thiourea and $Fe_2(SO_4)_3$ can be similar to an acidic thiourea leaching system [H_2SO_4/thiourea/$Fe_2(SO_4)_3$] for gold extraction. Hence, this acidic ionic liquid can be a replacement for sulfuric acid in thiourea leaching method in order to provide the acidic medium. On the other hand, one of the drawbacks of the latter method is the high consumption of reagents like thiourea (Hilson & Monhemius, 2006; Syed, 2012), which can be overcome by this similar method of leaching with an acidic ionic liquid comprising [HSO_4^-] as its anion. However, this speculation need to be evaluated.

Jenkin et al. (2016) examined the use of a deep eutectic solvent (DES), a type of room temperature ionic liquid, to dissolve electrum by an oxidation and reduction process followed by the recovery of gold by electrodeposition. Amino acids, particularly glycine, has been investigated with hydrogen peroxide as an oxidant in alkaline medium to extract gold (Eksteen & Oraby, 2015; Oraby & Eksteen, 2015; Perea & Restrepo, 2018).

Following on the previously reported work, this investigation explore a mixture of [$Bmim^+HSO_4^-$]-water as solvent, thiourea (complexing agent) and iron(III) sulphate oxidant, as an application to the treatment of flotation concentrated cyanide tailings for gold extraction. In this work an acidic medium is required to ensure the stability of thiourea and ferric ions. In acidic medium, the aqueous form of thiourea act as a ligand to form a stable cationic complex with gold. Moreover, ferric ions are stable at $pH<2$ and precipitate as hydroxyl species (ferric hydroxide) as the pH increases (Whitehead et al., 2007). A 20% (v/v) [$Bmim^+HSO_4^-$] aqueous solution has a similar pH value than 0.5 M H_2SO_4 solution, due to the proton activity of its anion [HSO_4^-] in solution (Aguirre et al., 2016). Considering this, the [$Bmim^+HSO_4^-$] aqueous solution can be a possible replacement for sulfuric acid to provide an acidic medium of $pH=1$ (Carlesi et al., 2016). Mineralogical analysis indicated that a substantial portion of the gold was locked up in the pyrite fraction. Therefore, the purpose of the study was to determine the oxidative leaching kinetics of the sulphidic gold tailings with the acidic ionic liquid [$Bmim^+HSO_4^-$] to estimate its suitability and potential to extract gold compared to conventional cyanidation.

2. Experimental procedure

2.1. Ore sample

The sample used was cyanide tailings that was collected through a flotation process and the flotation concentrate of the tailings were used in this work. Thus, it was rich in sulphides, and of a refractory in nature with micro-dessiminated gold mainly in pyrite. The sample was obtained from the ERGO plant, operated by DRDGOLD (Pty.) Ltd, in South Africa. The as-received material having hard lumps of solids was dry milled in a roller ball mill to break up the conglomerates. The resulting fine material was subsequently dried in an oven for 1 h at 105 °C to remove any moisture. The dried sample was blended and classified into different size fractions using an electronic sieve shaker (Model ES 200) with stainless steel sieves. The finest size fraction (-45 μm containing 2.84 g/t Au) was used in the leaching experiments due to greater exposed surface area for the experiments. Table 1 represents the mineralogical analysis of the gold-bearing pyrite flotation concentrate of the cyanide tailing sample by XRD. According to the results, the predominant mineral components of the sulphidic gold tailing sample were quartz and pyrite at 45.1% and 36.3%, respectively. It is worth noting that in this refractory sulphidic tailing sample, approximately 60% of the total gold was enclosed in pyrite.

Table 1. Mineralogy of flotation concentrate of cyanide tailing.

Mineral	Chemical Formulae	Mass%
Quartz	SiO_2	45.1
Pyrite	FeS_2	36.3
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	5.3
Chlorite	$(Mg,Fe^{2+})_5AlSi_3Al_2O_{10}(OH)_8$	4.1
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	4.1
Other	-	5.0

2.2. *Reagents*

The ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulphate [$Bmim^+HSO_4^-$] was chosen with thiourea $SC(NH_2)_2$ and a source of ferric ions, $Fe_2(SO_4)_3$, for the investigation. All the required chemicals and reagents were purchased from Merck and Sigma Aldrich in South Africa. The reagents were all of the analytical grade and used as received without further purification.

2.3. Leaching tests

The leaching conditions used in this investigation were derived from an earlier optimisation study which is described in detail in Teimouri et al. (2020). A closed Schott bottle with 50 mL capacity was used for each sample for leaching experiments. In each experiment, 1.25 g of flotation concentrate cyanide tailings, which was refractory low gold-bearing pyrite (fraction size -45 µm), 20 g/kg tailing of thiourea and 1 g/kg tailing of iron (III) sulphate were used. These were added to a 10 mL mixture solution of [$Bmim^+HSO_4^-$] with deionized water (20% v/v) resulting in a solid to liquid ratio of 1:8 at a pH of 1. The closed Schott bottles were then shaken in a platform incubator at 250 rpm, in the temperature range of 20–65 °C. A bottle of each sample was removed at different time intervals (20 min, 40 min, 1 h, 3 h, 5 h, 7 h and 12 h) throughout the trial. The pregnant solution was filtered and analysed with an atomic absorption spectrophotometer (AAS) to determine the amount of extracted gold.

3. Results and discussion

3.1. Effect of Temperature

The influence of temperature was studied at four different temperature values (20, 35, 50 and 65 °C) to determine its effect on extracting gold in the acidic ionic liquid aqueous solution. Fig. 1 shows the Au concentration (mg/L) vs time (h) and Fig. 2 shows the gold extraction profiles as %gold extraction vs time (h) at different temperatures during the leaching period under study. The results generally revealed that the rate of gold extraction improved as the temperature increased. This may be the result of higher reaction rates, improved leaching kinetics and the change in viscosity of the [Bmim$^+$HSO$_4^-$]-water solution. It should be noted that [Bmim$^+$HSO$_4^-$] is a viscous solvent (900 mPa) when compared to water (1 mPa) (Whitehead et al., 2007), thus the viscosity of the ionic liquid aqueous solution reduces with rising temperature and this may result in better mass transfer or diffusivity in the solution and ultimately better extraction of gold. In general, from the graphical illustrations the rate of gold extraction is initially faster and then it decreases with increased leaching time. Possible reasons for this can be a reducing the amount of gold that can be extracted from the refractory sulphidic low-grade gold tailing, and the reagents get consumed as well which may lead to decreasing the rate of gold extraction.

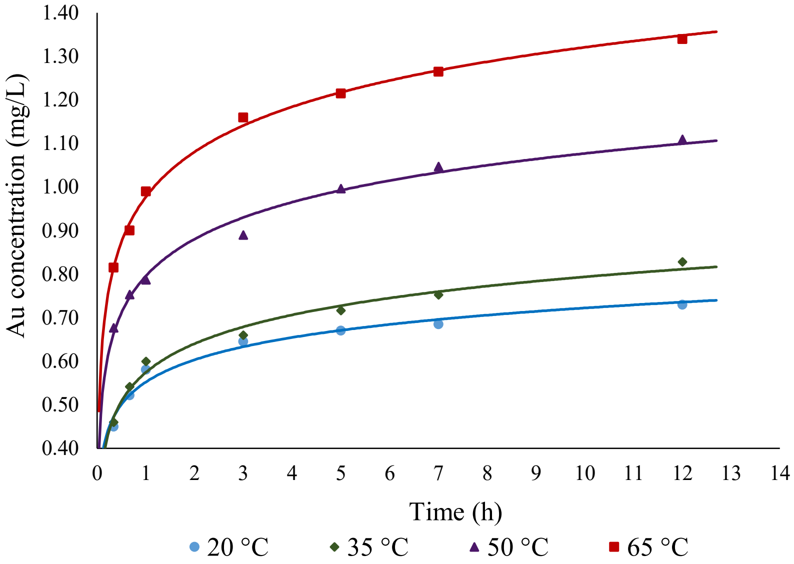

Fig. 1. Effect of temperature on the gold extraction (Au concentrtion). Conditions: [Bmim$^+$HSO$_4^-$]-water solution (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

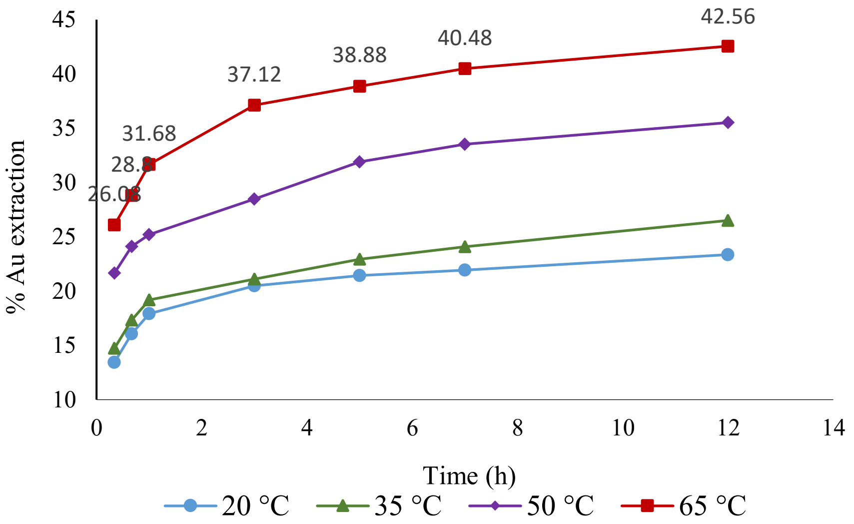

Fig. 2. Effect of temperature on the gold extraction (%Au extraction). Conditions: [$Bmim^+HSO_4^-$]-water solution (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

3.2. Effect of Time

In order to verify whether the influence of prolonged time on the extraction kinetics were negligible or not, longer extraction experiments were performed. The gold extraction from the refractory sulphidic gold tailing by [$Bmim^+HSO_4^-$]-water solution 20% (v/v)/thiourea/ferric ion was conducted at longer extraction times of 1 day, 2 days, 3 days and 5 days at pH=1, temperature 60 °C and shaking speed of 250 rpm. Fig. 3 demonstrates the gold extraction at longer leaching times. It indicates that the gold extraction increased only slightly and then reached a plateau. The magnitude of changes in the percentage of the extraction was minimal and an additional 4% leaching yield increase was observed after 5 days of extraction. It can therefore be concluded that most of the extraction took place during the first day of extraction and thereafter very little gold extraction occurred.

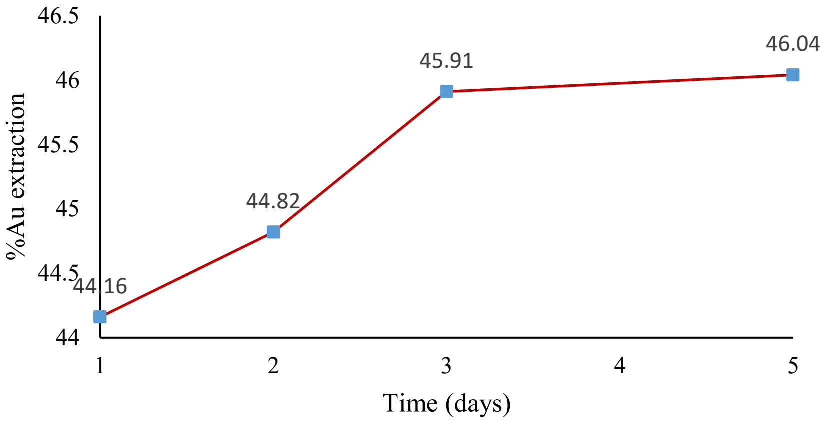

Fig. 3. Effect of time on the gold extraction. Conditions: [$Bmim^+HSO_4^-$]-water solution (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

3.3. Kinetic study

Typically dissolution of solid particles (minerals) in a fluid medium is a heterogeneous reaction. According to the shrinking core model, a heterogeneous process can be controlled by chemical surface reaction, diffusion and/or both to control the process (mixed control model). A mixed control model is a hybrid of diffusion and chemical surface reaction (Baba et al., 2012). One way to determine which model controls the reaction rate in a system, is plotting the results based on the standard equation. A linear relationship between the reaction time and the left side of the standard equation represents the fitted model (Chen et al., 2015).

Thus, the kinetic data of the gold dissolution was scrutinized using the shrinking core model applying the standard equations (2, 3 and 4) for diffusion, chemical reaction and mixed control, respectively.

$$1-3(1-X)^{2/3}+2(1-X) = k_d\, t \tag{2}$$

$$1-(1-X)^{1/3} = k_r\, t \tag{3}$$

$$(1-2/3X)-(1-X)^{2/3}+B(1-(1-X)^{1/3}) = k_m\, t \tag{4}$$

where X is the fraction of gold extracted at any time (t), k_d ,k_r and k_m are rate constants for the diffusion, chemical reactions and mixed control, respectively and B is a ratio of k_r/k_d in the mixed control equation (Baba et al., 2012).

In this case it was noted that the slope of the trendlines were sharper during the first hour (first zone) than the rest of the leaching reaction period up to 12 h (second zone) at the investigated temperatures, as is demonstrated in Fig. 4. The reason for this could be a higher amount of reagents and also more accessible gold for extraction leading to a faster rate of extraction represented by the sharp slope of the straight line at intervals during the first hour of leaching. The slope reduced as the leaching time is extended up to 12 h. This can be due to falling accessibility of gold for extraction because of the refractoriness of the tailings used, as a substantial amount of gold was micro-disseminated with limited available free gold in the tailings.

In order to examine the rate controlling step, the experimental results at different temperatures were plotted in terms of the standard equations and it was found that the results obtained during the first hour of the reaction for the intervals 20 min, 40 min and 1 h, fitted a mixed controlled model (both chemical reaction and diffusion) (Fig. 5). Subsequently, the data for the second zone of the leaching reaction period up to 12 h indicated control by a diffusion process (Fig. 6).

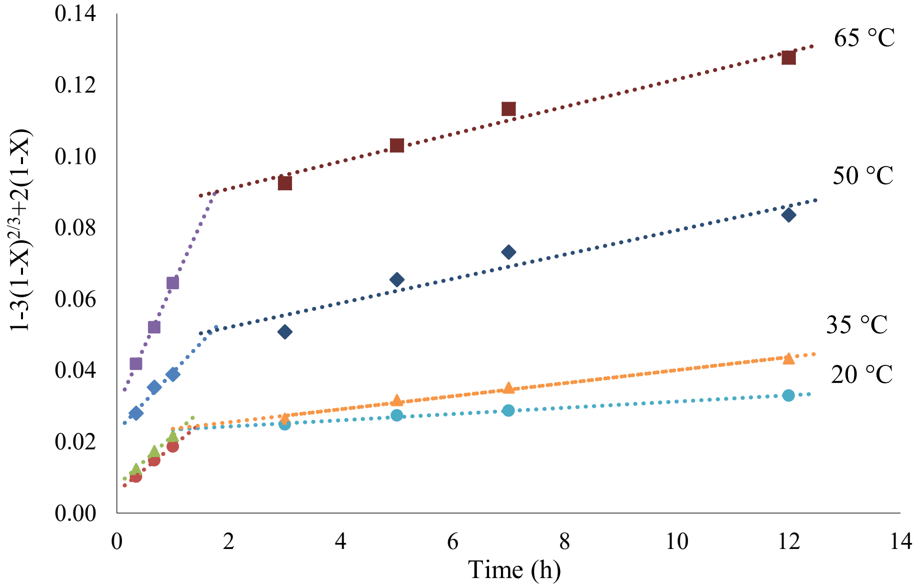

Fig. 4. Shrinking core diffusion rate control plot of gold extraction for the first and second zone at different temperatures. Conditions: [Bmim$^+$HSO$_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

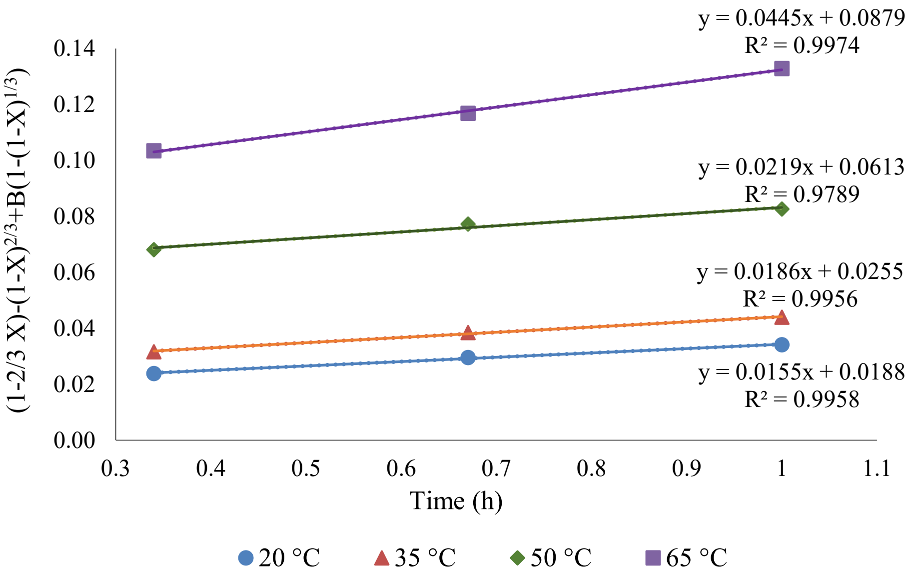

Fig. 5. Shrinking core mixed control plot of gold extraction at different temperatures. Conditions: [$Bmim^+HSO_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

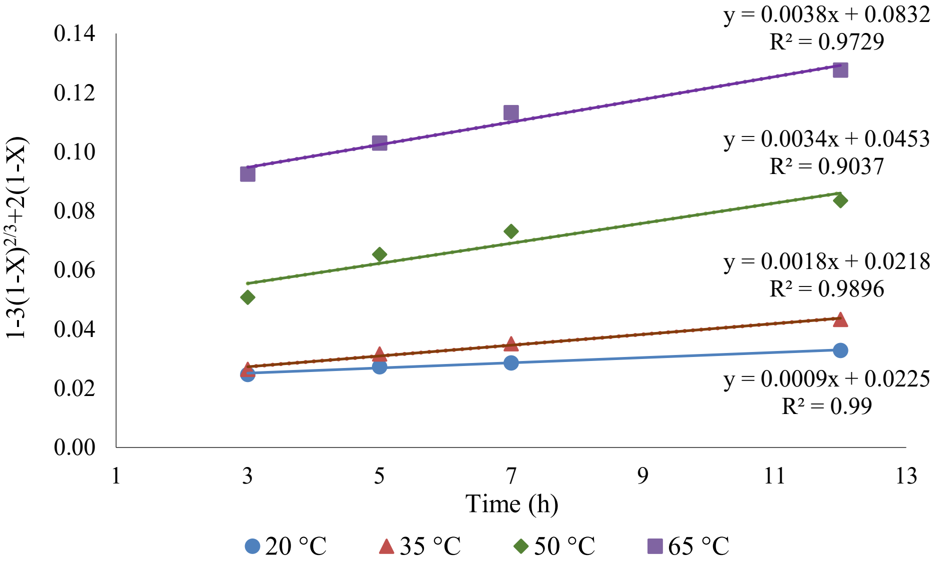

Fig. 6. Shrinking core diffusion rate control plot of gold extraction at different temperatures. Conditions: [$Bmim^+HSO_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

Based on the graphs the values for the correlation coefficient (R^2) which confirm the linearity suggest that the leaching rate of gold extraction from the flotation concentrate cayanide tailing using [$Bmim^+HSO_4^-$]-water solution/thiourea/ferric ion was mixed controlled for the initial period of the process and diffusion controlled for later stages of the reaction (see Figs. 5 and 6) in the range of the temperatures studied from 20 to 65 °C.

Determination of activation energy

The apparent rate constant *k* which was obtained from the slopes of the straight lines in Figs. 5 and 6 and were used to determine the activation energy. Using the Arrhenius equation $k=Ae^{-Ea/RT}$, the natural logarithm of the apparent rate constant, (*ln k*), was plotted against the inverse of the respective temperatures (*1/T*), as depicted in Fig. 7. According to the slopes of the straight lines in Fig. 7, the activation energy in the temperature range 20-65 °C for the mixed control region was E_a=17.97 kJ/mol and for the product layer diffusion control part of the process it was E_a=27.47 kJ/mol.

The rate controlling step can be predicted from the magnitude of the activation energy. Typically, a value below 40 kJ/mol indicates a diffusion controlled process, whereas a value higher than 40 kJ/mol represents a chemical reaction controlled one (Dong et al., 2009; Zhong, 2015; Aguirre et al., 2016; Uğuz & Geyikçi, 2019). Therefore, in this study the magnitude of activation energy in the range of 17.97-27.47 kJ/mol, confirms that the rate of leaching was mixed controlled following by diffusion in the range of the temperatures studied.

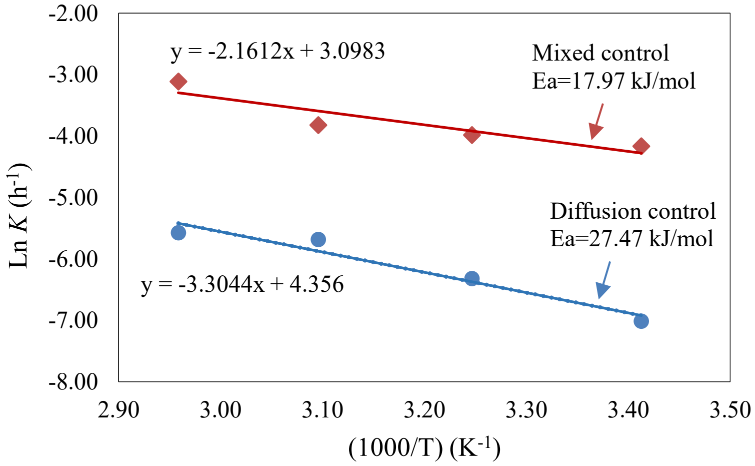

Fig. 7. Arrhenius plot for gold extraction from the tailing. Conditions: [$Bmim^+HSO_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH=1, 250 rpm.

3.4. *Solid analyses*

Scanning Electron Microscopy Analysis

The refractory gold tailings containing pyrite before and after leaching by 20% (v/v) [$Bmim^+HSO_4^-$]-water solution/thiourea/ferric ion was examined by scanning electron microscopy in the backscattered electron mode (SEM-BSE) and energy dispersion spectroscopy (SEM-EDS) (Fig. 8). As can be seen from the SEM micrographs, the surface of the pyrite particles (FeS_2) before leaching looks smooth with few defects. However, after leaching, the surface of the reactive pyrite looks rough and shows some pores, pits, and corners. This may be due to the oxidant attack and dissolution of the pyrite in which gold is "trapped" during the oxidative leaching process for a 12 h leaching time.

In fact, based on SEM examination, the oxidant mainly attack reactive sites of the pyrite surface grain with a high surface energy. These specific sites are associated with defects, corners and edges, fractures and pits which represent favourable attack/dissolution positions on specific pyrite grains where an oxidant can act. The prevalence of active sites with significant energy may differ in each pyrite grain. Thus, the oxidation reactions happens at those areas of the pyrite surface with more edges, defects, fractures and corners, signifying areas with high surface energy (Chandra & Gerson, 2010; Sun et al., 2015).

Additionally, the results for SEM-EDS analysis indicated the amount of sulphur was more after oxidative leaching (Fig. 8b) than that on the tailing sample before leaching (Fig. 8a). This high sulphur content can be associated with the formation of a slim/thin and even partial product layer of sulphur on the reactive pyrite surface. The amount of iron decreased after oxidative leaching, which can confirm possible pyrite dissolution.

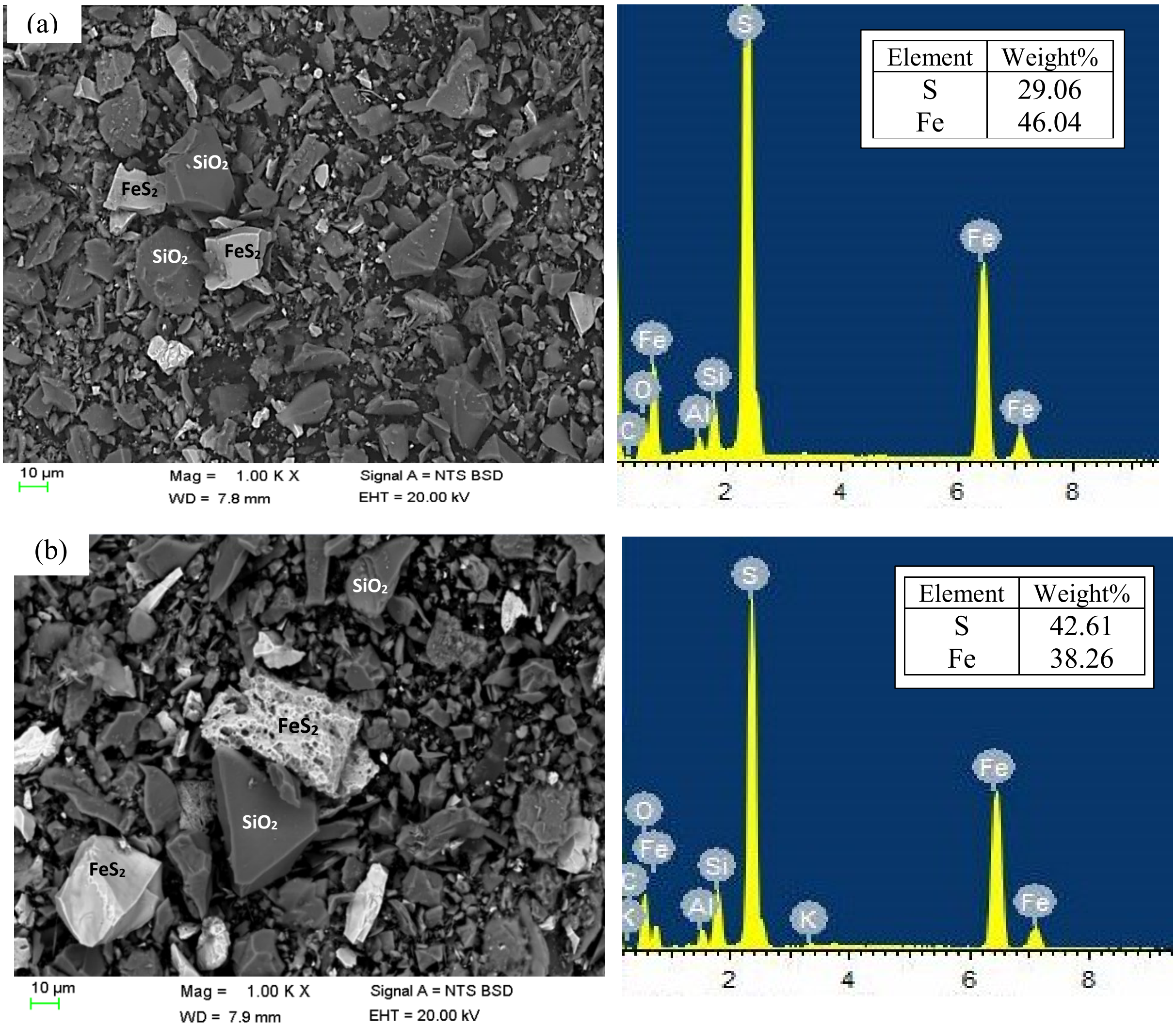

Fig. 8. SEM-BSE images and EDS of the sulphidic tailing, (a) Before leaching and (b) After leaching by [$Bmim^+HSO_4^-$]-water solution (20% v/v).

X-ray diffraction Analysis

Fig. 9 represents the X-ray diffraction (XRD) patterns of the tailings sample (pyrite concentrate) before leaching and the solid residue. As can be seen, the quartz (SiO_2) is present as the most dominant mineral and pyrite as the second major one. The gold could not be detected with the XRD, which can be due to the fact that the gold is either encapsulated (invisible) in the pyrite sample or the amount of gold present is lower than the detection limit of XRD. As revealed from the XRD patterns, there was a small decrease in the intensity of the pyrite peaks sizes after leaching, which can be due to pyrite dissolution.

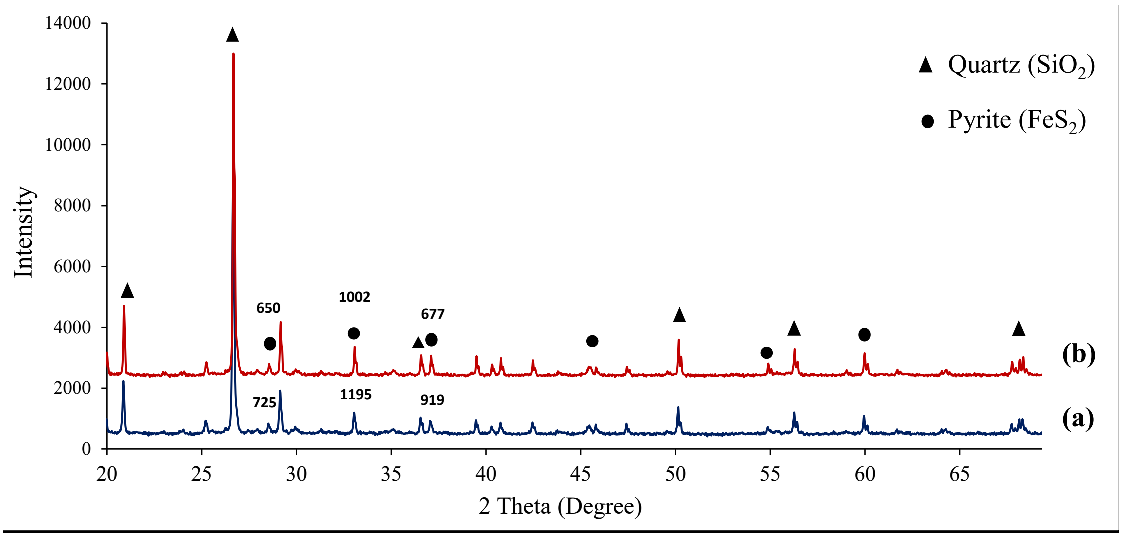

Fig. 9. XRD pattern of (a) the sulphidic tailing (before leaching), (b) the solid residue (after leaching) for 12 h leaching with 20% (v/v) [$Bmim^+HSO_4^-$]-water solution.

Raman Analysis

Fig. 10 represents the spectra for a Raman analysis for the refractory gold tailing containing pyrite before and after oxidative leaching with 20% (v/v) acidic ionic liquid solution/thiourea/ferric ion. As can be seen from the spectra, it detects three shifts for the pyrite (FeS_2) centred at frequencies of about 342.8, 379.1 and 430.5 cm^{-1}, respectively. The experimentally observed shifts for the pyrite in this study were compared with the pyrite shifts in a geology investigation on some important and commonly occurring sulphidic minerals by Mernagh and Trudu (1993). The results for the pyrite shift frequencies, in cm^{-1}, are tabulated in Table 2. Additionally, there was an indication of a potential decrease in the pyrite after leaching occurred, since the intensity of the peaks declined in a similar manner as seen in the XRD pattern.

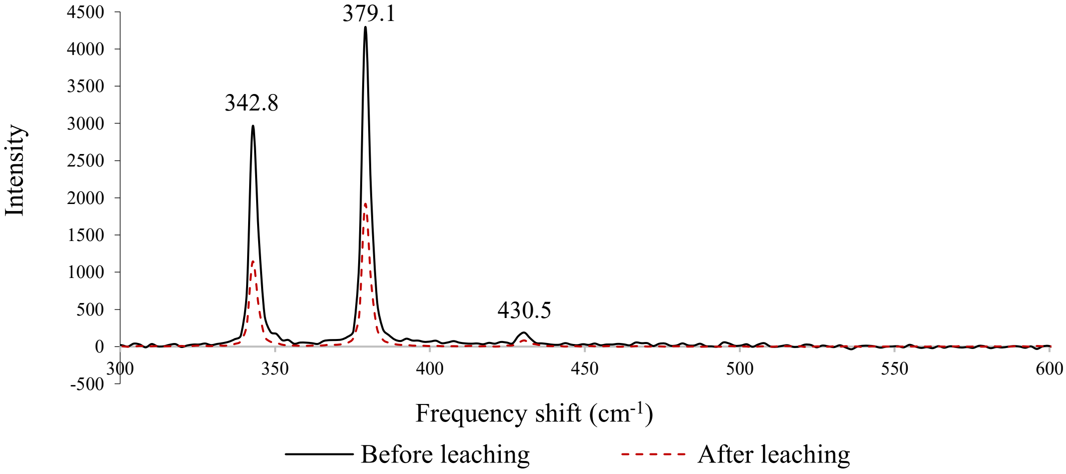

Fig. 10. Raman spectra indicating pyrite shifts of the tailing before and after oxidative leaching with 20% (v/v) [$Bmim^+HSO_4^-$]-water solution for 12 h.

Table 2. Raman frequencies (in cm^{-1}) for pyrite in this work and the Reference.

Pyrite peaks (FeS_2)	343	379	430	(This work)
Pyrite peaks (FeS_2)	342	377	428	(Mernagh & Trudu, 1993)

Additionally, Fig. 11 depicts the sulphur shifts which showed up in the residue spectra, after the oxidative leaching of the sulphidic gold tailing with Raman spectroscopy. There were three shifts for the elemental sulphur centered at approximately 153, 219 and 470 cm^{-1} in the spectra. These shifts indicate the presence of elemental sulphur in the solid residue after oxidative leaching. The observed results in the experimental analysis with Raman spectroscopy to detect the elemental sulphur shift in this work were compared with the work by Mycroft et al. (1990) (Table 3). This observation gives an indication that the diffusion through the product layer occurred in the later stages of the leaching and thus influenced the rate controlling step in this study.

Table 3. Raman frequencies (in cm^{-1}) for sulphur in the residue in this work and the Reference.

Sulphur shifts	153	219	474	(This work)
Sulphur shifts	150	218	469	(Mycroft et al., 1990)

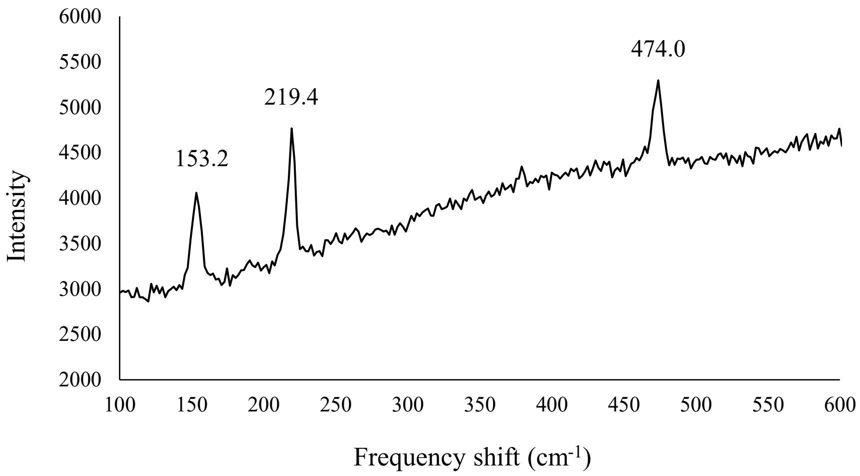

Fig. 11. Raman spectra of the solid residue after leaching with 20% (v/v) [Bmim$^+$HSO$_4^-$]-water for 12 h indicating sulphur shifts.

Previous gold leaching investigations using thiourea and ferric ion oxidant found that the oxidant can also react with thiourea to form formamidine disulphide (FD), $NH_2(NH)CSSC(NH)NH_2$. The corresponding reaction follows Eq. (5):

$$2\ SC(NH_2)_2 + 2\ Fe^{3+} \rightarrow FD + 2\ Fe^{2+} + 2\ H^+ \qquad (5)$$

FD can act as an oxidizing agent in gold leaching (Lacoste-Bouchet et al., 1998) contributing to the electrochemical reaction follows Eq. (6):

$$2\,Au + 2\,SC(NH_2)_2 + FD + 2\,H^+ \rightarrow 2\,Au(SC(NH_2)_2)_2^+ \qquad (6)$$

The overall electrochemical reaction of gold dissolution by adding equations (5 and 6) side by side can be written as Eq. (7):

$$Au + Fe^{3+} + 2\,SC(NH_2)_2 \rightarrow Au[SC(NH_2)_2]_2^+ + Fe^{2+} \qquad (7)$$

FD could decompose and lead to the irreversible formation of elemental sulphur and cyanamide in acidic medium (Eq. (8)) (Gönen et al., 2007):

$$NH_2(NH)CSSC(NH)NH_2 \rightarrow SC(NH_2)_2 + CN(NH_2) + S^0 \qquad (8)$$

Taking this into consideration there is still a possibility that the sulphur shifts which was detected in the Raman spectra can be either as a result of oxidative pyrite dissolution or thiourea decomposition. In oxidative leaching of pyrite the sulphur could form in acidic pH in the presence of ferric ion as the oxidant because of the following reaction in Eq. (9) (Feng et al., 2019):

$$FeS_2 \rightarrow Fe^{2+} + 2S^0 + 2e^- \qquad (9)$$

This could possibly explain why diffusion through a product layer was the rate controlling step in this study.

3.5. Comparison of cyanide and acidic ionic liquid gold extraction

The alkaline cyanidation gold leaching process has been used for more than 120 years without any remarkable change in the process since its first implementation. It has been accepted as the best lixiviant for extracting gold industrially due to the simple procedure and cost-effectiveness. The gold is oxidized and dissolved in alkaline cyanide solution to form the stable anionic gold-cyanide complexes $Au(CN)_2^-$, and the optimum pH for gold dissolution is in the basic range of pH=10-10.5 (Hilson & Monhemius, 2006). The overall chemical Au dissolution reaction is illustrated in Eq. (10) (Syed, 2012).

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \rightarrow 4\,Au(CN)_2^- + 4\,OH^- \qquad (10)$$

However, this technique is no longer acceptable in some countries because of it posing severe environmental problems. Recently ionic liquids were employed and considered as potential alternative solvents to extract gold from refractory gold ores. In the acidic ionic liquid

$[\mathrm{Bmim}^+\mathrm{HSO}_4^-]$ aqueous solution, the ionic liquid participate in gold extraction reaction by providing the required acidic pH, so in this leaching system with thiourea and ferric ion, gold dissolves to produce a stable cationic Au-thiourea complex.

Cyanide leaching on the same gold tailings in an optimized DRDGOLD process achieved on average 65% extraction of gold. In this investigation, the extracted gold with $[\mathrm{Bmim}^+\mathrm{HSO}_4^-]$/thiourea/ferric ion was 37.5%, which was less than in the cyanide process (Table 4). Thus, under the experimental conditions tested in this study, the acidic ionic liquid leaching was not better than cyanide in terms of gold extraction efficiency. Even though the ionic liquid mixture does not extract more gold than the cyanidation process, it does offer the advantage of a possible safer process. Furthermore, the ionic liquid can potentially be recycled after the first extraction, although this needs to be proved. Therefore, further detailed work on the oxidative leaching of refractory sulphidic tailings containing gold using ionic liquids needs to be undertaken to identify the factors that can release locked gold and achieve enhanced gold extraction.

Table 4. Comparison between cyanidation and ionic liquid $[\mathrm{Bmim}^+\mathrm{HSO}_4^-]$ gold leaching.

	Cyanidation	Ionic liquid
pH	11	1
Extracted gold	65%	42.6%
ratio	1.53	

4. Conclusions

Gold extraction from flotation concentrated tailings containing pyrite was studied in an aqueous solution of acidic ionic liquid $[\mathrm{Bmim}^+\mathrm{HSO}_4^-]$/thiourea/ferric ion system. The addition of 20% (v/v) of ionic liquid $[\mathrm{Bmim}^+\mathrm{HSO}_4^-]$ into aqueous solution provide an acidic medium of approximately pH=1, due to proton release by its anion $[\mathrm{HSO}_4^-]$, which was consistent with the pH result for 20% (v/v) of the same ionic liquid in the work by Carlesi et al. (2016). Thus, the studied ionic liquid performed like a common inorganic acid in aqueous leaching solution.

The results showed that gold extraction from refractory tailings increased with increasing temperature in an aqueous solution of acidic ionic liquid $[\mathrm{Bmim}^+\mathrm{HSO}_4^-]$/thiourea/ferric ion system. Thus, higher temperature leads to improved reaction kinetics, decrease in viscosity of the [$Bmim^+HSO_4^-$]-water solution, better mass transfer or diffusivity in the solution and ultimately enhanced gold extraction.

According to the shrinking core model, the linear relationship between the standard equation and the leaching time and also the calculated activation energy (E_a) based on the Arrhenius theory suggest that the kinetic process of gold leaching with the acidic ionic liquid was mixed controlled succeeded by diffusion with activation energies in the range of 17.97-27.47 kJ/mol.

Additionally, a solid analysis of the initial gold-bearing pyrite and the solid residue (after leaching) revealed slight differences in the overall structure and morphology of the solid sample before and after leaching. In SEM-BSE of the residue, the surface of the pyrite particle looked rough and some pores appeared. In addition, the Raman spectroscopy analysis revealed elemental sulphur shifts in the solid residue, which may indicate that the oxidative leaching of the pyrite leads to the formation of a product layer of elemental sulphur. This observation gives a possible reason for diffusion through the product layer, which was the rate controlling step in this study. This observation is in agreement with the explanation of the leaching kinetics of the gold-bearing pyrite by diffusion through the product layer.

It is expected that ultrafine grinding of the refractory sulphidic gold ore can increase the exposed surface area, and possibly expose more free gold to enhance the gold extraction yield.

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