



Pressure oxidation leaching of an enargite concentrate in the presence of polytetrafluoroethylene beads



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ABSTRACT

Polytetrafluoroethylene (PTFE) is a promising additive in medium-temperature pressure oxidation leaching of high sulfide copper ores. In this article, we present a systematic study on the performance of pressure oxidation leaching of an enargite concentrate in the presence of PTFE beads. The effects of various leaching conditions, including leaching solution composition, temperature, oxygen overpressure, initial pulp density, and an addition of varying amounts of PTFE beads, on copper leaching kinetics have been systematically investigated. Our results show that, with the use of PTFE beads, the rate of leaching and ultimate extraction of copper can be significantly enhanced, over the temperature range of 150–210 °C and an oxygen overpressure range of 50–120 psi, compared to otherwise similar conditions without the addition of PTFE beads. Results of analysis of the surface adsorbates on the PTFE beads suggest that, during the initial stages of leaching, PTFE beads capture hydrophobic sulfide minerals on their surface. Leaching of the minerals then progresses on the surface of the beads, producing elemental sulfur. The molten sulfur is partially drawn away from the mineral/electrolyte interface to the PTFE surface, mitigating the agglomeration of the mineral particles and facilitating their further oxidation. In addition, the PTFE beads have been found to be highly reusable with identical performance maintained for at least 6 cycles of leaching experiments without the need of any special surface regeneration treatment. Arsenic deportment was tracked by XRD and ICP-MS analysis of both the resulting leaching solution and residue. The majority of arsenic (about 96%) was converted to a stable solid scorodite product, thus facilitating its safe disposal.

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1. Introduction

Due to the gradual depletion of conventional high-grade copper ores, there is growing interest in the processing of complex metallurgically challenging lower-grade ores and minerals, such as those rich in enargite (Cu_3AsS_4). Pyrometallurgical smelting is the widely used process to extract copper from copper concentrates containing relatively low enargite content. Concentrates having a high content of enargite, however, pose a problem for conventional pyrometallurgical processing due to fugitive emissions of arsenic compounds and the adverse effect of arsenic on the quality of the final copper product produced in the electrorefining stage (Conner and Anderson, 2013; Safarzadeh *et al.*, 2014). Hydrometallurgical techniques appear to have several advantages over conventional pyrometallurgical techniques for the processing of these types of minerals, especially in avoiding emissions of arsenic and SO_2 (Berezowsky and Trytten, 2002). In the hydrometallurgical processing of enargite-rich ores, arsenic can be precipitated as a stable oxide (ferric arsenate) within the leaching reactor, facilitating its safe disposal, while sulfur is converted to sulfate, rather than SO_2

gas, and ultimately precipitated as gypsum (Dutrillac and Jambor, 1988; Swash and Monhemius, 1994).

Despite the potential advantages, the technology for hydrometallurgical treatment of arsenic-rich enargite ores is still evolving and is not without challenges (Safarzadeh *et al.*, 2014), such as incomplete or slow copper extraction, copper losses associated with the coprecipitation with iron compounds, and complex recovery of precious metals and elemental sulfur from the leaching residue (Dreisinger, 2006). Enargite is often considered as a refractory mineral for copper extraction in aqueous media (Safarzadeh *et al.*, 2014). Relative to other copper sulfide minerals such as chalcopyrite, covellite, and chalcocite, hydrometallurgical copper extraction from enargite ores is more difficult. Nevertheless, several hydrometallurgical processes, including atmospheric leaching, pressure oxidation, and bio-oxidation, have been considered for the processing of enargite concentrates (Safarzadeh *et al.*, 2014).

Previous investigations showed that the dissolution rate of enargite is very slow in sulfate media under atmospheric conditions when using either oxygen or ferric ions as an oxidant (Brown and Sullivan, 1934; Gupta, 2010). Brown and Sullivan reported that acidic ferric leaching of enargite at 35 °C resulted in only 33% copper extraction after 60 days. Gupta investigated the dissolution of enargite in sulfate

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media using shake flasks and stirred tank reactors in the presence of ferric or ferrous ions (Gupta, 2010). Gupta confirmed the beneficial effect of ferric ion on enargite leaching while also reporting on improved leaching performance from particle size reduction, chloride addition, lower pH, and increasing temperature. However, although leaching conditions could be selected such that the initial rate of enargite leaching was relatively fast, ultimately only ca. 40% copper extraction was achieved, possibly due to formation of a Cu_2S intermediate that passivated the enargite surface (Gupta, 2010). Rivera-Vasquez investigated the effect of electrochemical aspects on enargite dissolution in acidic ferric sulfate media (Rivera-Vasquez, 2011). Enargite dissolution was found to start at ca. 300 mV (vs. SCE) but passivated at ca. 700 mV (vs. SCE). Rivera-Vasquez concluded that the passivation was due to the formation of elemental sulfur on the enargite surface rather than by a Cu_2S product. Up to this point, published research indicated that incomplete leaching of enargite in sulfate-based electrolytes under atmospheric conditions was unavoidable. However, recent studies (Ghanad, 2011; Ghanad and Dixon, 2011) have reported that the addition of activated carbon during atmospheric ferric sulfate leaching of enargite can lead to complete extraction of copper in less than 24 h. This suggests that solid additives can interfere with the passivation process and act as catalyst for enargite leaching.

Pressure oxidation leaching of enargite in acidic sulfate and chloride media has been studied by a number of investigators to improve copper extraction. Ruiz *et al.* studied the effects of oxygen pressure, temperature, and pyrite addition on copper extraction from enargite in sulfuric acid medium. Copper extraction from pressure oxidation of pure enargite (loading: 0.2 wt.%) in aqueous sulfuric acid leaching solution (sulfuric concentration: 20 g/L) at 180 °C reached 25% after 60 min of leaching, whereas copper extraction was complete within 60 min in the presence of ferrous ion or pyrite (Ruiz *et al.*, 2011). Their results confirmed that ferric ion (produced by reaction of oxygen with either ferrous ions or pyrite) was an oxidant for enargite dissolution during pressure leaching of the concentrate. But the study was restricted to a single relatively low pulp density and was mainly focused on a relatively high pressure oxidation temperature of 180 °C. Low pulp densities and high temperatures enhance leaching kinetics, partly, by mitigating mineral agglomeration through reducing the frequency of mineral/mineral collisions and increasing the rate of oxidation of elemental sulfur that is formed during leaching, respectively. One can operate at high pulp densities at higher temperatures (> 200 °C) where rapid oxidation of elemental sulfur avoids mineral agglomeration, but complete oxidation of sulfur to sulfate necessitates a corresponding addition lime, CaO, to fix it as gypsum. Operating under medium temperature conditions (120–170 °C), where elemental sulfur is relatively stable, offers the possibility reducing the requirements for lime while producing a saleable elemental sulfur by-product. However, the elemental sulfur generated under medium temperature conditions often retards mineral oxidation by a combination of retarding mass transfer of oxidants through the sulfur layer on the mineral surface and agglomeration of the mineral particles due to the sticky nature of the molten sulfur. Chloride ions have been reported to adsorb on molten sulfur surface, restricting the oxidation reaction of molten sulfur to sulfate and enhancing the dispersion of molten sulfur (McDonald and Muir, 2007) possibly by electrostatic repulsion. In the absence of chloride ions, the sulfur coating around mineral particles tends to lead to their agglomeration, retarding further leaching.

In recent years, researchers have focused on developing effective sorbents for molten sulfur in medium-temperature pressure oxidation processes. In the previous studies (Govindaiah *et al.*, 2015; Guerra and Shepherd, 2011; Guerra, 2012; Nuo and Guerra, 2012), polytetrafluoroethylene (PTFE) has been demonstrated as an effective solid additive in medium-temperature pressure oxidation leaching of nickeliferous pyrrhotite and chalcopyrite concentrates in sulfate media. Its role in enhancing leaching kinetics is attributed to the work of adhesion of molten sulfur on PTFE being much larger than on sulfide mineral

surfaces (Mathew *et al.*, 2010; Tong and Dreisinger, 2009). This large difference in work of adhesion allows PTFE to draw molten sulfur from mineral surface to its own surface, which mitigates passivation and allows further oxidation of the mineral so as to enhance the leaching kinetics and metal extraction. In addition, PTFE is able to survive at the relatively high temperature in corrosive acidic leaching solutions for recycling due to its excellent thermal and chemical stability.

In this current work, the effects of PTFE addition on copper extraction in pressure oxidation of an enargite concentrate were studied, with the aim of achieving high copper extraction along with fixation of arsenic in a form that is safe for disposal. The effects of various leaching parameters on copper extraction kinetics from the enargite concentrate have been systematically investigated, including: leaching solution, temperature (130–210 °C), PTFE/enargite mass ratio (from 2:1 to 4:1), initial pulp density (5–20 wt.%), and oxygen overpressure (50–130 psi). Optimum leaching conditions for nearly complete copper extraction has been established. The residues and solutions obtained after leaching were analyzed by ICP-MS to account the deportment of arsenic, sulfur, copper and iron. Meanwhile, the reusability of PTFE beads has also been studied.

2. Experimental

2.1. Materials and procedures

The enargite concentrate used in this work was the +55 μm fraction of an enargite/pyrite flotation concentrate obtained from Barrick Gold Corporation, Canada. The mineral and chemical compositions of the concentrate are listed in Table 1 and Table 2, respectively. Spherical PTFE beads with a diameter of 3 mm (US Plastic Corp., USA) were used as received. Sulfuric acid (certified ACS, 95–98%), nitric acid (certified ACS Plus, 70%), acetone (certified ACS, >99.5%), hydrochloric acid (ACS reagent, 37%), and sodium chloride (>99%) were purchased from Fisher Scientific. Sodium hydroxide standard solution (1.029 N) was purchased from Sigma Aldrich. Deionized (DI) water was generated in-house using a Barnstead Nanopure II water purification system.

Solution samples collected during the pressure oxidation experiments were filtered with a 0.45 μm PTFE syringe filter (Fisher Scientific) and subsequently analyzed for copper concentration using a Perkin Elmer AAnalyst 400 atomic absorption spectrometer (AAS). The sulfuric acid concentration in the leaching solution samples was determined by titration with a 0.5 N NaOH solution, prepared by dilution of the 1.024 N NaOH stock solution, using a pH meter. The sulfur content in the leaching residue was analyzed with a CS844 carbon and sulfur analyzer at Ontario Geological Survey Geoscience Laboratories (Sudbury, Canada). X-ray diffraction (XRD) patterns of the concentrate, leaching residues, and the solid residues collected from the surface of PTFE beads were recorded using an X'Pert Pro diffractometer with $\text{Cu K}\alpha$ radiation (wavelength 1.54 Å) at room temperature. The step scan powder XRD data were collected over a 2θ range of 5–70°. The procedure for acid digestion of the residues was to dissolve 0.5 g of dried sample in aqua-regia with subsequent dilution to 100 mL using DI water. The Cu, Fe, and As concentrations in the leaching solution and residue samples

Table 1
Mineralogical composition of the enargite concentrate.

| Mineral | Chemical Formula | Content (mass %) |
|-----------------|--|------------------|
| Enargite | Cu_3AsS_4 | 45.6 |
| Pyrite | FeS_2 | 43.0 |
| Covellite | CuS | 0.5 |
| Bornite | Cu_5FeS_4 | 0.8 |
| Tennantite | $(\text{Cu, Fe})_{12}\text{As}_4\text{S}_{13}$ | 1.5 |
| Chalcopyrite | CuFeS_2 | 2.4 |
| Sphalerite Iron | $(\text{Zn, Fe})\text{S}$ | 2.6 |
| Quartz | SiO_2 | 2.5 |
| Other | | 1.1 |

Table 2
Partial chemical composition of the enargite concentrate.

| Element | Content (mass %) |
|---------|------------------|
| Cu | 25.57 |
| S | 37.77 |
| Fe | 20.07 |
| As | 8.53 |
| Zn | 1.14 |

were analyzed with a Varian 810 inductively coupled plasma mass spectrometer (ICP-MS).

2.2. Pressure oxidation leaching experiments

The pressure oxidation leaching experiments were conducted in a 1.8 L Parr floor-stand Model 4574 titanium-coated autoclave equipped with a standard temperature/speed controller, Parr Model 4843. The general procedure for all pressure oxidation experiments was as follows: a prescribed amount (42.5, 85, or 170 g) of the enargite concentrate was added into the autoclave, along with 850 mL of leaching solution (composition as noted in the Results and Discussion Section). If PTFE beads were used, then they were simply poured into the autoclave. The autoclave was then sealed and heating was initiated. Once the temperature set-point was reached, the prescribed overpressure was applied using compressed oxygen and stirring was set to 900 rpm. The time when the oxygen pressure was applied marked the starting point of an experiment. Kinetic samples were collected from the autoclave at prescribed times by using the pressure in the autoclave to force the slurry out from a dip-tube connected to a bleed valve and external cooling coil. At the end of the experiment, heating and oxygen were turned off and tap water was sent through the internal cooling coils to rapidly cool the contents of the autoclave. When the slurry was sufficiently cooled, stirring was stopped, the autoclave was disassembled, and a small sample of the solution was taken, filtered using a syringe filter, and set aside for wet analysis. The remaining slurry was washed out of the autoclave onto a vacuum filter using a squeeze bottle filled with deionized water. If PTFE beads were used, then the beads were captured using a sieve (Fisher Scientific, opening size 1.18 mm) before they ended up on the filter. The slurry was filtered and the resulting cake was dried overnight at 80 °C and weighed.

2.3. Flotation procedure

Flotation experiments were performed at room temperature with a Denver Laboratory D1 model flotation machine to separate elemental sulfur and/or sulfide from oxides in selected leaching residues. The leaching residue used for the flotation was repulped to about 20 wt.% in DI water. One drop of Dow Froth 250C was used as a frother. The stirring speed was fixed at 1300 rpm. The pulp was then conditioned in the flotation cell for 5 min for each test before air was introduced. Flotation (concentrate collecting) time was set at 10 min for each test.

3. Results and discussion

3.1. Effect of leaching solution composition

Leaching experiments of the enargite concentrate were first carried out at 150 °C under 100 psi of oxygen overpressure in four different leaching solutions, including DI water, and aqueous solutions containing 7 g/L of Cl⁻ (as NaCl), or 20 g/L of H₂SO₄, or both, to investigate the effect of leaching solution composition on copper leaching kinetics. An initial pulp density of 10 wt.% (i.e., enargite concentrate loading of 85 g in 850 mL of leaching solution) was used in these experiments. Parallel experiments were undertaken with or without the use of PTFE beads (PTFE/enargite mass ratio of 4:1). Fig. 1 shows the percentage of

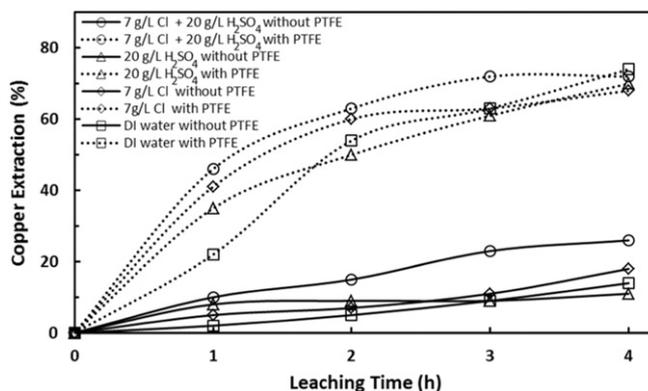


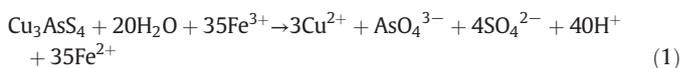
Fig. 1. Copper leaching from enargite concentrate in various leaching solutions (0.85 L) at 150 °C with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1 (when used), and 100 psi of oxygen overpressure.

copper extraction as a function of time in these experiments. In the experiments undertaken in the absence of PTFE beads, the rate of copper leaching from the enargite concentrate appears to be very slow and the final percentages of copper extraction (at 4 h) are all low (11–26%). In contrast, the use of PTFE beads is found to markedly improve copper leaching in all four leaching solutions, both in terms of rate and final percentage of copper extraction. For example, the addition of PTFE beads increases the percentage of copper extraction from ca. 14% to 74% at 4 h in pure DI water. Also of note is that, though the more complex leach solutions offer initially faster leaching kinetics (most likely owing to their higher ferric iron solubility at the outset of leaching), the final copper extractions at 4 h are similar (about 74%) for all four leaching solutions. Given the potential corrosion issues (and increased costs in material of construction) associated with the use of acid chloride solutions in pressure oxidation processes, coupled with their apparently limited benefits, we have, thus, used pure DI water as the leaching solution for all further experiments.

The significant enhancement in copper leaching in the presence of PTFE beads is believed to begin with the adsorption of sulfide minerals onto the surface of the PTFE beads, similar to how bubbles become coated by hydrophobic minerals during flotation. Oxidation of the minerals then progresses on the surface of the beads producing molten elemental sulfur. The molten sulfur is partially drawn away from the mineral/electrolyte interface to the PTFE surface. This reduces the agglomeration of the mineral particles and their passivation by sulfur, facilitating their further oxidation.

3.2. Effect of leaching temperature

Leaching experiments were subsequently carried out at different temperatures ranging from 130 to 210 °C in pure DI water with and without addition of PTFE beads. Fig. 2 shows the copper leaching kinetic curves obtained under the different conditions. In the absence of PTFE beads, leaching results were extremely poor. This was likely due to the formation of a liquid elemental sulfur coating on the enargite particles (Conner and Anderson, 2013) causing the formation of sulfur/mineral agglomerates. The marginal enhancement of copper leaching with increasing temperature in the absence of PTFE beads can be explained by the temperature effect on promoting complete oxidation of the enargite to produce sulfate rather than elemental sulfur, according to the following overall reactions (Padilla et al., 2005; Ruiz et al., 2011):



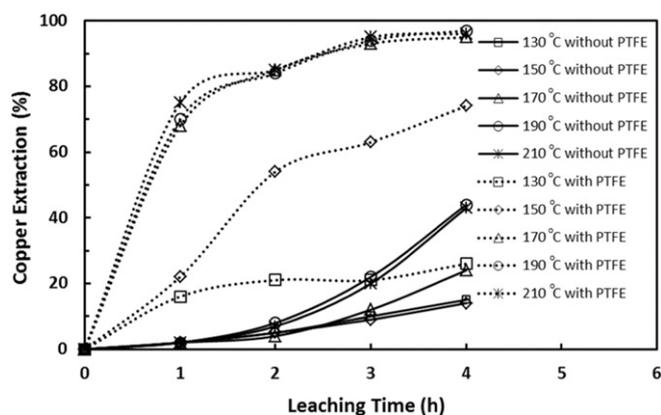
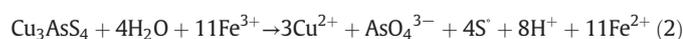


Fig. 2. Copper leaching kinetic curves at various temperatures in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1 (when used), and 100 psi of oxygen overpressure.



In fact, the complete oxidation of sulfide to sulfate likely occurs via the formation of elemental sulfur, which is then further oxidized to sulfate. The rate of the latter process depends strongly on temperature and oxygen pressure. At lower leaching temperature (<150 °C), sulfide is predominantly oxidized to elemental sulfur with little further oxidation to sulfate. At temperatures of 170 °C and higher, copper extraction is improved to some degree as a result of increasing oxidation of elemental sulfur to sulfate (Conner and Anderson, 2013). It should be noted that the extent of leaching observed in these experiments, without the use of PTFE, is much lower than those typically obtained in an industrial research setting when using deionized water as the leaching solution. The difference in leaching results can be explained by variations in the test procedure; in an industrial research setting the autoclave is typically purged with oxygen for a brief amount of time once the temperature has reached ca. 100 °C. This oxidizes the surface of the sulfide minerals to ensure they do not agglomerate during further heating of the electrolyte to the test temperature.

At each temperature, the addition of PTFE beads significantly improves copper leaching performance. At 130 °C, the percentage of copper extraction at 4 h increases from 15% to 26% with the addition of PTFE beads. At 150 °C, the percentage of copper extraction at 4 h increases from 15% to 74% with the addition of PTFE beads. The relatively smaller increase in copper extraction at 130 °C may be because the elemental sulfur produced is not molten enough to be efficiently transferred to the PTFE beads, which leads to the restricted leaching. When the temperature was between 170 and 210 °C, nearly complete copper leaching (96%) is achieved within 4 h in the presence of PTFE beads, with nearly identical copper leaching kinetic curves. From these experiments, 170 °C was selected as the most optimum temperature for the copper leaching in the presence of PTFE beads.

The surfaces of PTFE beads were examined after leaching experiments at different temperature. While the PTFE beads appeared relatively clean after the leaching at 130 °C, the beads collected after leaching at 150 °C had gained 12 g in mass and were dark colored. The adsorbed material on these beads was collected and analyzed with XRD, indicating the presence of adsorbed elemental sulfur and residual sulfides. Fig. 3 shows the XRD spectrum. An intense peak at 23° attributable to elemental sulfur (Xie et al., 2013) can clearly be observed, along with other peaks resulting from small amounts of unreacted enargite and pyrite. The XRD results support the hypothesis that PTFE beads perform as sulfur adsorbents for capturing molten sulfur to allow further oxidation of mineral particles. Meanwhile, leaching at a higher temperature of 170 °C and above resulted in beads that were only slightly darkened in color, suggesting reduced efficiency for elemental

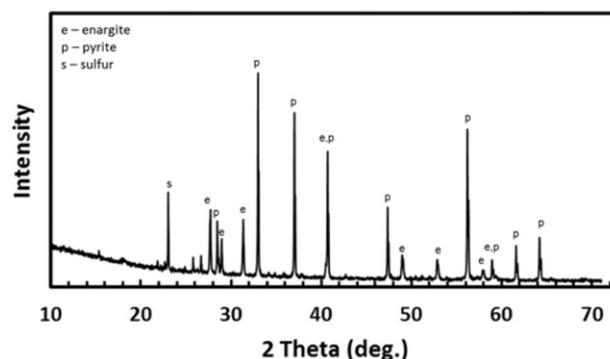


Fig. 3. XRD pattern of the surface adsorbed material on PTFE beads claimed after leaching reaction at 150 °C in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1, and 100 psi of oxygen overpressure.

sulfur collection. However, given the high percentage of copper leaching, we reason that the adsorption of elemental sulfur still occurred in these experiments but the elemental sulfur underwent further oxidation reaction to become soluble sulfate.

The acid concentration in the resulting leaching solutions after 4 h of leaching at the various temperatures was determined through titration with sodium hydroxide solution. Fig. 4 shows the acid content as a function of leaching temperature. For leaching experiments undertaken without the addition of PTFE beads, the resulting acid concentration increases from ca. 15 g/L at 130 °C to 61 g/L at 210 °C. The acid concentration is significantly higher in an experiment carried out in the presence of PTFE compared to that in the corresponding experiment undertaken in the absence of PTFE beads, and it increases continuously from 29 to 108 g/L as leaching temperature increases from 130 °C to 210 °C. The increase in acid concentration is not only indicative of the progress of mineral oxidation (according to Reactions 1 and 2), but also suggests and the increased production of sulfate (Reaction 2) rather than elemental sulfur (Reaction 1).

The solid leaching residues obtained after 4 h of leaching at various temperatures in the presence of PTFE beads were examined. The residue obtained after leaching at 130 °C has a similar dark black color as the virgin concentrate, which corresponded to the limited progress of leaching. With increasing leaching temperature from 130 to 210 °C, the color of the residues gradually changed from black to yellowish-green to yellow. This color change suggests more complete mineral oxidation and increasing deportment of arsenic to oxides in the residues. Besides the color changes, the mass of the leaching residue also

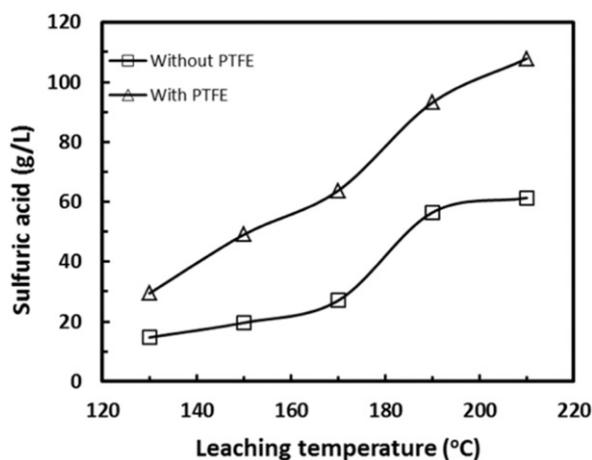


Fig. 4. Sulfuric acid concentration in the resulting leaching solution following the leaching at different temperatures in DI water (0.85 L) for 4 h with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1, and 100 psi of oxygen overpressure.

decreased significantly with the increasing leaching temperature (see Fig. 5). This is consistent with the enhanced copper leaching resulting from the use of PTFE beads. In the presence of PTFE beads, the mass of the residue decreases from 57.9 g at 130 °C to 31.2 g at 190 °C, then stays nearly constant despite the further temperature increase to 210 °C. The nearly identical residue masses at 190 and 210 °C are consistent with the observed copper extractions, suggesting complete oxidation of sulfide sulfur to sulfate (according to Reaction 1) coupled with the precipitation of arsenic as an oxide in the residues. Following this, the acid concentration in the leaching solutions resulting at 190 and 210 °C is supposed to be similar or identical, which somehow deviates from the trend noted in Fig. 4. The slight increase in acid concentration with the temperature increase from 190 °C and 210 °C (as noted in Fig. 4) possibly resulted from the enhanced water evaporation at 210 °C during the sample collection. The drop in the residue mass with the temperature increase from 170 to 190 °C, while having the same level of copper exaction, simply indicates that some portion of the mineral oxidation produced elemental sulfur at 170 °C.

The residues following leaching in the presence of PTFE beads were further characterized with XRD to identify their composition. Fig. 6 shows the XRD patterns of the various leaching residues along with that of virgin concentrate for comparison. The XRD pattern of the leaching residues at 130 °C is nearly identical to that of the virgin concentrate, showing only peaks for enargite and pyrite, respectively. This is also consistent with the very low level of copper leaching as previously described (see Fig. 2). With respect to the residue produced at 150 °C, XRD peaks attributable to elemental sulfur and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) appear in addition to the peaks belonging to enargite and pyrite. The peaks at 27.1°, 28°, and 29° are attributed to scorodite produced during leaching (Gomez et al., 2011; Xie et al., 2013). In the residues produced at 170 °C, the elemental sulfur peak significantly diminishes while the scorodite peaks become more pronounced, accompanied with almost complete disappearance of the enargite peaks and weakening of the pyrite peaks. This result supports the previously described findings of extensive copper extraction without complete sulfur oxidation. With further increases of temperature to 190 and 210 °C, the XRD patterns of the residues become mainly comprised of the peaks for scorodite, with the peaks for elemental sulfur and pyrite completely disappeared. These results are consistent with the finding of other studies of pressure oxidation of enargite at 190 and 210 °C, which reported residues that were mainly comprised of scorodite, resulting from co-precipitation of arsenic and iron after complete dissolution of the ore (Dutrizac and Jambor, 1988; Gomez et al., 2011; Swash and Monhemius, 1994). These XRD results provide further evidence confirming the complete oxidation of both enargite and pyrite with arsenic precipitation as scorodite.

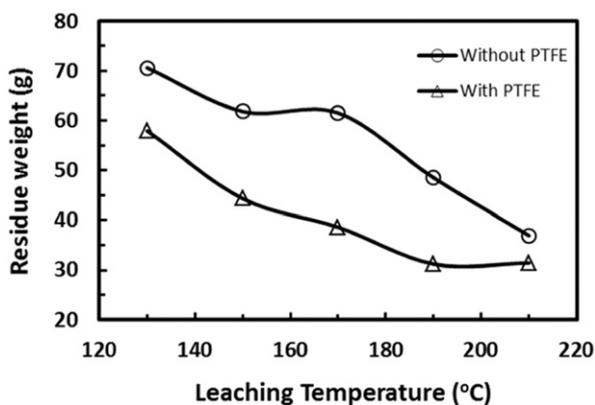


Fig. 5. Weight of leaching residue as a function of leaching temperature in DI water (0.85 L) for 4 h with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1 (when used), and 100 psi of oxygen overpressure.

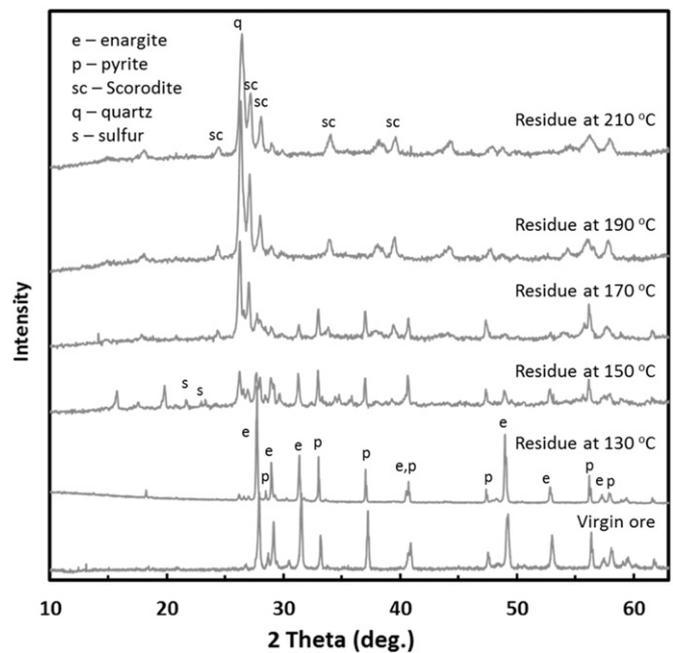


Fig. 6. XRD patterns of leaching residues yielded at various leaching temperatures in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1, and 100 psi oxygen overpressure.

We have further characterized the composition of the leaching residues produced in both the presence and absence of PTFE beads through elemental analysis (sulfur analysis and ICP-MS for Cu, Fe, and As). Fig. 7 plots the chemical composition (S, Cu, Fe, As) of the residues as a function of leaching temperature, along with the mass of the elements in the original concentrate (total 85 g) for comparison. The addition of PTFE beads during leaching significantly reduces the mass of both Cu and S in the residue compared to those produced in the absence of PTFE beads at each temperature. The amount of copper in the residues yielded in the presence of PTFE beads decreases steeply (from 16 to 4.1 g) as leaching temperature is increased from 130 to 150 °C, but changes very little as the temperature is further temperature increased (3.0, 1.5 and 1.4 g at 170, 190, and 210 °C, respectively), particularly above 190 °C. The amount of sulfur in the residues also decreases sharply from 20.4 to 1.4 g with the temperature increase from 130 to 190 °C, plateauing at 1.3 g at 210 °C. These data again confirm the nearly complete leaching of copper and oxidation of the sulfide sulfur to sulfate at 190 °C or above in the presence of PTFE beads.

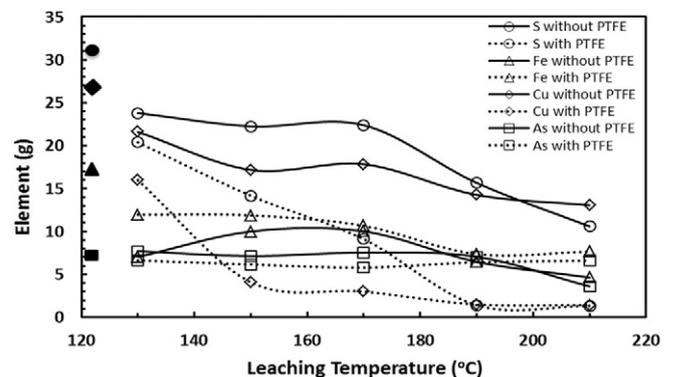


Fig. 7. Chemical composition of leaching residues produced after leaching at various temperatures in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1 (when used), and 100 psi of oxygen overpressure. Chemical composition of original enargite concentrate is indicated as sulfur (●), copper (◆), iron (▲), and arsenic (■).

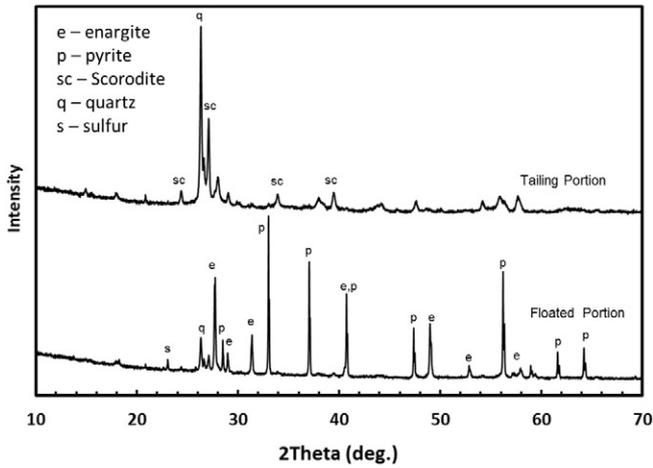


Fig. 8. XRD patterns of the floated and tailing portions of the leaching residue after flotation. The residue was yielded from the leaching reaction at 170 °C for 4 h in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1, and 100 psi of oxygen overpressure.

Elemental sulfur and pyrite are known to be hydrophobic and are expected to have excellent floatability at near neutral pH, suggesting that they can be separated from scorodite in the residues through flotation. To explore this possibility, we undertook flotation experiments on the residues produced in the presence of PTFE beads at 150–210 °C. Fig. 8 shows typical XRD patterns of the floated and tailing portions after flotation of the residue produced at 170 °C. From the XRD pattern, the floated portion consists of predominantly of pyrite, with small amounts of elemental sulfur and enargite. The tailing portion consists predominantly of scorodite and quartz. In terms of the partitioning of the residues between floated and tailing portions, for the residues produced at 150 and 170 °C, the floated portion accounted for 52 and 42 wt.% to total residue weight, respectively. On the contrary, no material was floated from the residues produced at 190 and 210 °C, indicating that the residues were completely comprised of oxides, which was consistent with complete oxidation of the concentrate. The results of these experiments suggest that flotation is a viable method to separate elemental sulfur and unreacted sulfides from oxides, namely scorodite and quartz, in the leach residues.

Another important metric of leaching performance is department of arsenic, whose residual dissolved concentration and solid form are important for safe disposal given its toxicity. Previous reports have shown that arsenic precipitates out with iron as scorodite in autoclaves operated above 150 °C (Dutrizac and Jambor, 1988; Gomez et al., 2011; Swash and Monhemius, 1994). We have analyzed arsenic concentrations in both the leaching solutions and residues. Fig. 9 shows the concentrations of Cu, Fe, and As in the various leaching solutions

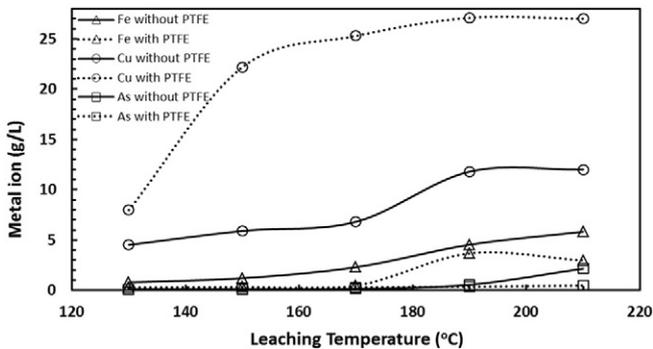


Fig. 9. Chemical composition of the resulting leaching solutions produced at various temperatures in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1, and 100 psi of oxygen overpressure for 4 h.

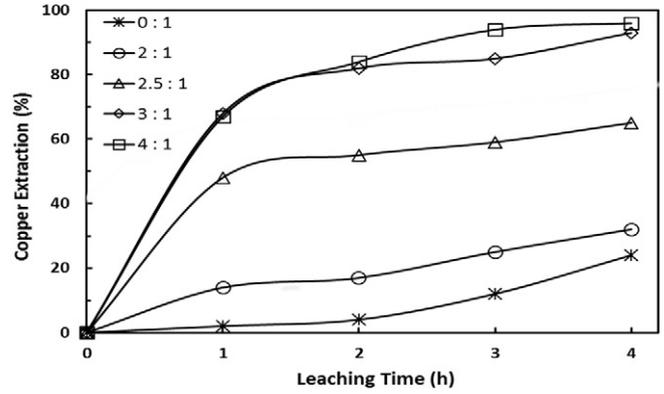


Fig. 10. Copper leaching kinetic curves by leaching at different PTFE/enargite concentrate mass ratios at 170 °C in DI water (0.85 L) with an initial pulp density of 10 wt.% and 100 psi of oxygen overpressure.

produced at different temperature after 4 h in both the presence and absence of PTFE beads. Compared to copper concentration, the concentrations of Fe and As are relatively low in the leaching solutions. For leaching experiments carried out in the presence of PTFE beads, arsenic concentrations range between 0.1 g/L (at 130 °C) to 0.46 g/L (at 210 °C), with the increase likely associated with increasing acid concentration in the leaching solution (Fig. 4). The leaching solution produced at 170 °C in the presence of PTFE beads contains 0.36 g/L of As, which corresponds to only 4% of total arsenic in the original enargite concentrate. This confirms that most arsenic has been precipitated out along with Fe as scorodite in the leaching residues.

Further leaching experiments were conducted at 170 °C in neutral water. These conditions were selected as the most promising for industrial application since they resulted in nearly complete copper leaching without complete oxidation of sulfide to sulfate, while also avoiding the use of chlorides and fixing most of the arsenic as scorodite (a form that is suitable for disposal).

3.3. Effect of loading of PTFE beads

The effect of the loading amount of PTFE beads on leaching performance has also been investigated by carrying out a series of leaching experiments at 170 °C using a fixed amount of enargite concentrate (85 g in 0.85 L of DI water) while varying the PTFE/enargite mass ratio of (2:1, 2.5:1, 3:1, and 4:1). Fig. 10 shows the copper extraction kinetic curves as a function of PTFE/enargite mass ratio. After 4 h, copper extraction reaches are 24, 32, 65, 93, and 96% at PTFE/enargite mass ratio of 0, 2:1, 2.5:1, 3:1, and 4:1, respectively. Meanwhile, the rate of copper

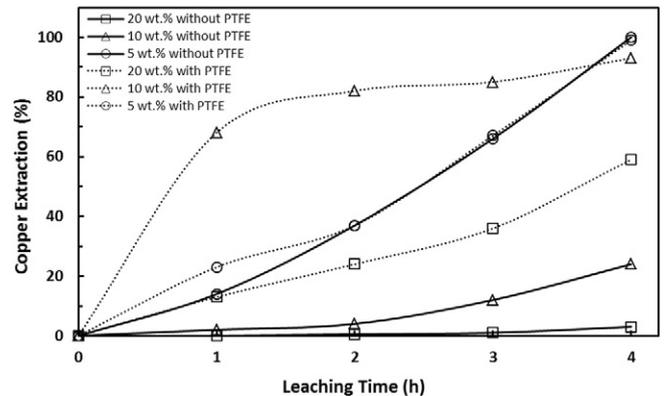


Fig. 11. Copper leaching kinetic curves at different initial pulp density (wt.%) at 170 °C in DI water (0.85 L) under 100 psi of oxygen overpressure with a PTFE/enargite mass ratio of 3:1 (when used).

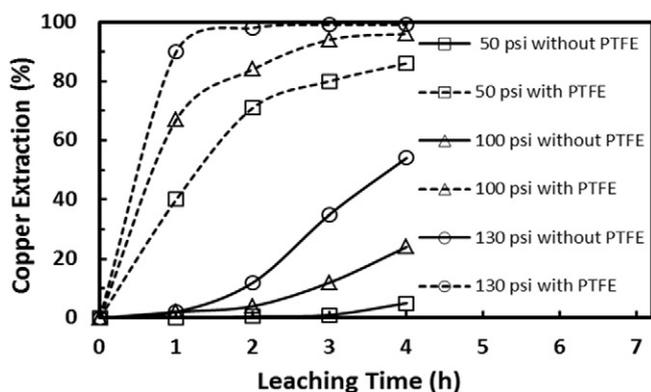


Fig. 12. Effect of oxygen overpressure on copper extraction at 170 °C in DI water (0.85 L) with an initial pulp density of 10 wt.% and a PTFE/enargite mass ratio of 4:1 (when used).

leaching within the first hour increases significantly with increasing PTFE/enargite mass ratio up to 3:1. A further increase in ratio to 4:1 results in a nearly identical leaching performance. This result suggests that a PTFE/enargite mass ratio of 3:1 provides enough surface area for adsorption of the enargite concentrate being leached. These results show that a PTFE/enargite mass ratio of *ca.* 3:1 is sufficient for near complete copper extraction from this enargite concentrate at 170 °C.

3.4. Effect of initial pulp density

The effect of initial pulp density on copper leaching kinetics was investigated by undertaking the leaching experiments at different pulp densities (5, 10, or 20 wt.%) at 170 °C and 100 psi of oxygen overpressure. The experiments were carried out both in the absence and in the presence of PTFE beads. When PTFE beads were used, a fixed PTFE/enargite mass ratio of 3:1 was adopted. Fig. 11 illustrates the copper leaching kinetic curves from these different runs. At the lowest pulp density of 5 wt.%, the addition of PTFE beads has almost no effect, with nearly identical copper extraction curves, possibly because of less agglomeration of the mineral particles at this low pulp density. At higher pulp densities of 10 and 20 wt.%, the addition of PTFE beads markedly enhances the rate of copper leaching (within the first hour). However, while nearly complete copper extraction (93%) was achieved with PTFE beads at the pulp density of 10 wt.%, a copper extraction of only 59% was obtained at the pulp density of 20 wt.%. The lower copper extraction is probably due to increased agglomeration of the mineral

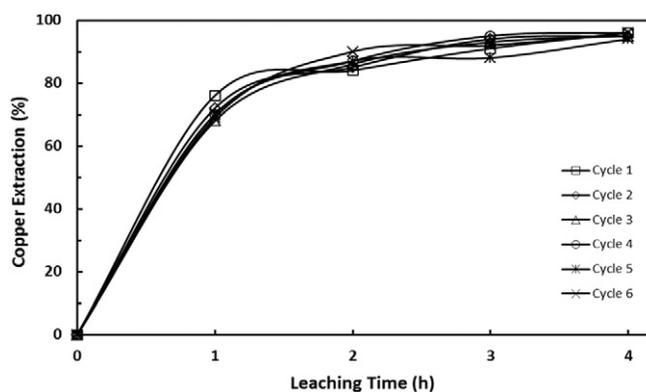


Fig. 14. Copper leaching kinetic curves for 6 continuous leaching cycles at 170 °C in DI water (0.85 L) with an initial pulp density of 10 wt.%, a PTFE/enargite mass ratio of 4:1, and 100 psi of oxygen overpressure.

particles at the higher pulp density. From the results of these experiments, it appears that 10 wt.% is near the maximum initial pulp density for leaching of this enargite concentrate at 170 °C in DI water with the addition of PTFE beads.

3.5. Effect of oxygen pressure

Fig. 12 presents the copper leaching kinetic curves obtained at different oxygen overpressure (50, 100, and 130 psi). In the absence of PTFE beads, the copper extraction at 4 h increases significantly from 6% to 55% as oxygen overpressure increases from 50 to 130 psi. Similarly, the addition of PTFE beads generally improves copper leaching, both in terms of final extraction and leaching rate. After 4 h, copper extraction reaches 86, 96, and 99% at the oxygen overpressure of 50, 100, and 130 psi, respectively. The enhanced copper leaching kinetics with increasing oxygen overpressure can be explained by noting that the equilibrium concentration of dissolved oxygen should increase proportionally with oxygen pressure and this should result in faster initial rates of mineral oxidation. In turn, oxidation of the pyrite in the concentrate generates ferric ions in solution, which is known to be the major direct oxidant in this system. In addition, previous investigators have also shown that higher oxygen partial pressures typically favor acid generation through sulfate formation rather than elemental sulfur formation (Salomon-De-Friedberg, 2014). Thus, it is likely that the elemental sulfur that is formed at higher oxygen pressure is more rapidly converted



Fig. 13. Optical images of PTFE beads after each leaching cycle at 170 °C in DI water with 100 psi of oxygen overpressure.

to sulfate, reducing its impact as a barrier to mass transport as well as mitigating agglomeration.

3.6. Reusability

All the above results confirm the effectiveness of the use of the PTFE beads to enhance the performance of pressure oxidation of the enargite concentrate. With the inherent high chemical and thermal stability of PTFE, these beads are expected to have good reusability, which makes them highly promising for commercial use. We have subsequently investigated the reusability of these beads by carrying out 6 cycles of 4 h leaching experiments at 170 °C with the same batch of beads (340 g). After each cycle of leaching, the PTFE beads were simply sieved from the leaching solution and forwarded to the next leaching cycle without further washing or surface regeneration. Fig. 13 shows the images of the beads after each cycle. With each successive leaching cycle, the color of the beads darkens only slightly. It is possible that the mineral/sulfur coatings formed on the PTFE beads during leaching shrink to a greater extent than the PTFE beads during the cooling of the slurry at the end of a leaching cycle, causing them to crack and predominantly flake off into the leaching residues. This is supported by the results of the flotation experiments, which indicated relatively easy separation of the sulfide and oxide fractions of the residues. Fig. 14 shows the copper leaching kinetic curves from the 6 cycles of leaching. Nearly identical kinetic curves can be observed, confirming that the performance of PTFE beads is maintained throughout the cycles of leaching. These data confirm the excellent reusability of PTFE beads in medium-temperature pressure oxidation of the enargite concentrate.

4. Conclusions

PTFE beads have been demonstrated to be effective sulfur/sulfide mineral sorbents for pressure oxidation of an enargite concentrate. The addition of PTFE beads greatly enhances copper leaching in terms of both the rate and final copper extraction. The condition with the leaching temperature of 170 °C and oxygen overpressure of 100 psi has been found to be optimal for high copper extraction without complete sulfur oxidation. XRD results confirm the presence of a combination of elemental sulfur and sulfides in the residues, along with scorodite, when leaching at 170 °C using DI water. The sulfur/sulfide fraction of the residues can be easily separated from the oxide fraction by flotation. At 190 °C and above, the sulfur in the concentrate is completely oxidized to sulfate. The optimum mass ratio of PTFE beads to enargite concentrate was found to be 3:1 at 170 °C with initial pulp density of 10 wt.% in DI water, in order to minimized PTFE addition without sacrificing copper extraction. Increasing oxygen pressure was also found to significantly enhance copper extraction from enargite in the presence of PTFE beads at 170 °C. The reusability of the PTFE beads was also confirmed, indicating they are suitable for reuse in multiple leaching cycles without the need of surface regeneration. This work confirms the potential for application of PTFE for pressure oxidation of enargite-rich ores.

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