



The fate of the sulfide ion in galena leaching with neutral citrate media

El destino del ion sulfuro en la lixiviación de galena en medio neutro con citrato

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Abstract

Lead recovery from sulfides is traditionally associated with pyrometallurgical processes that involve elevated capital costs and the generation of harmful gases that, if not adequately treated, can cause severe environmental damage. For this reason, alternative methods are needed for lead recovery from this type of mineral. A hydrometallurgical approach could permit the use of environmentally friendly organic reagents, citrate in this case, to leach lead from galena in neutral media. The effects of pH, the mineral/solution ratio, and the hydrogen peroxide concentration as an oxidant in lead leaching at room temperature were studied. The results show that, at low citrate to lead ratios (~2) and a H₂O₂/Pb ratio between 2.3 and 2.5, complete lead dissolution is possible, due to the formation of soluble sulfur oxyanion species (S₄O₆²⁻, SO₃²⁻, S₂O₃²⁻) in the near-neutral solutions. The proposed system limits the irreversible oxidation of sulfur species, liberated during galena leaching, to the sulfate ion (SO₄²⁻), which decreases the solubility of lead in solution.

Keywords: Galena leaching, Citrate, Sulfur species, Lead, Neutral media.

Resumen

La recuperación de plomo a partir de sulfuros se asocia tradicionalmente a los procesos pirometalúrgicos que implican costos elevados de capital y la generación de gases nocivos que, si no se tratan adecuadamente, pueden causar graves daños ambientales. Por esta razón, se necesitan métodos alternativos para la recuperación de plomo a partir de este tipo de minerales. Un enfoque hidrometalúrgico podría permitir el uso de reactivos orgánicos respetuosos con el medio ambiente, en este caso el citrato, para lixiviar el plomo a partir de galena en medio neutro. Se estudiaron los efectos del pH, la relación mineral/solución y la concentración de peróxido de hidrógeno como oxidante en la lixiviación de plomo a temperatura ambiente. Los resultados muestran que, a bajas relaciones entre citrato y plomo (~2) y una relación H₂O₂/Pb entre 2.3 y 2.5, es posible la disolución completa del plomo, debido a la formación de especies solubles de oxianiones de azufre (S₄O₆²⁻, SO₃²⁻, S₂O₃²⁻) en soluciones cercanas a la neutralidad. El sistema propuesto limita la oxidación irreversible de especies de azufre liberadas durante la lixiviación de galena al ion sulfato (SO₄²⁻), el cual disminuye la solubilidad del plomo en solución.

Palabras clave: Lixiviación de galena, Citrato, Especies de azufre, Plomo, Medio neutro.

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1 Introduction

Lead has various applications due to its resistance, density, and reactivity; it is used in the manufacture of containers for the discharge of radioactive material and recently in lead phosphate glass, vanadyl glass, batteries, alloys in the form of tetraethyl lead, and lead silicate (Rammah *et al.*, 2020). Unfortunately, its presence is a significant problem in public health (O'Connor *et al.*, 2018). Global lead mine production in 2022 was led by China with more than two million tons, leaving Australia in second place and the Latin countries with a production of less than 25%. The largest reserves of this metal are in Australia, followed by China with 37 and 12 million tons, respectively (USGS, 2023).

Lead represents 0.0013% of the earth's crust and is commonly found in nature as galena (PbS), anglesite (PbSO₄), and cerussite (PbCO₃), although galena is the principal mineral for lead extraction. Depending on its formation process, it can contain traces of silver, copper, zinc, cadmium, antimony, and/or arsenic. Traditionally, lead has been obtained by concentration processes, such as flotation. However, because lead is associated with other sulfides and oxides, processing the ore leads to low recovery (Javadi Nooshabadi and Rao, 2016). To adequately separate the mineral of interest, a prior ultrafine grinding process may be carried out (Zhang *et al.*, 2019). Once the concentrate is obtained, the recovered lead goes to a new concentration and refining process by pyrometallurgy, which can produce volatile ash and generate environmental problems if not handled properly. Despite those drawbacks, this process predominates in lead recovery from ores as well as in recycling (Chen *et al.*, 2016; Tang *et al.*, 2019). Lead sulfide is one of the most insoluble lead minerals with a solubility product (K_{ps}) of 10^{-28.3}; however, in highly oxidizing environments the sulfide oxidizes to sulfate, releasing only a small part of the lead into solution (Hsieh and Huang, 1989), since the K_{ps} of PbSO₄ is 10^{-6.2}. The practical consequence is that when the sulfate concentration is increased in the solution, the free lead ion (Pb²⁺) concentration decreases.

Lead solubility can be improved by forming soluble complexes with inorganic and organic ligands. Investigations into the recovery of lead through hydrometallurgical routes have been reported using ultrasound-assisted leaching and chlorides (John *et al.*, 2020; Xie *et al.*, 2022), direct electrolysis from chlorides (Fan *et al.*, 2021), alkaline media (Seyed Ghasemi and Azizi, 2018), nitric acid (Oh *et al.*, 1999; Kim *et al.*, 2017; Ichlas *et al.*, 2020), trichloroacetic acid (Adebayo Albert *et al.*, 2021), acetic acid (Osasona *et al.*, 2021), chloride (Kobayashi *et al.*, 1990; Wang *et al.*, 2003; Adebayo and Olasehinde, 2015; Wang *et al.*, 2015; Nikkhou *et al.*, 2020) and some organic agents such as ethylenediaminetetraacetic acid, EDTA (Smaniotto *et al.*, 2009; Cheikh *et al.*, 2010), citric acid (Arwidsson *et al.*, 2010; Kumar, 2017), sodium citrate (Zárate-Gutiérrez and Lapidus, 2014; Zárate-Gutiérrez *et al.*, 2015; Solís-Marcial *et al.*, 2022), among others.

Citrate (cit) is an organic ion used in the pretreatment of gold-bearing minerals and materials because of its effectivity in removing certain base metal phases, such as those of copper and lead, from the system before the gold leaching process with thiourea (Torres and Lapidus, 2020; Segura-Bailón and Lapidus-Lavine, 2023); it can also be used in recycling lead from discarded car batteries (Sonmez and Kumar, 2009a) and lead recovery from oxidized minerals such as anglesite (Zárate-Gutiérrez and Lapidus, 2014). Citrate leaching is an attractive alternative because it forms stable complexes with lead (Table 1), although at temperatures above 30°C, citrate can be degraded (Torres *et al.*, 2018).

Figure 1 shows the predominance zones of the complexes formed between citrate and lead with respect to the pH and potential of the system. However, an oxidizing medium is necessary to transform the sulfide ion, allowing the formation of Pb-complexes; this can be achieved with the addition of hydrogen peroxide (H₂O₂). It is important to mention that the figure does not consider the maximum sulfate concentration because this investigation presents the identification of sulfur species released during galena leaching. However, the predominance zone of the principal lead complex (Pb(cit)₂⁴⁻) does not change significantly in the pH range of 6-8 contemplated in this study.

Table 1. Thermodynamic constants for the reactions of the Pb-citrate system at 25 °C.

Reaction	Log K	Reference	Ec.
$\text{Pb}^{2+} + 2\text{cit}^{3-} = \text{Pb}(\text{cit})_2^{4-}$	6.84	Puigdomenech (2004)	(1)
$\text{Pb}^{2+} + \text{cit}^{3-} = \text{Pb}(\text{cit})^-$	4.44	NIST (2004)	(2)
$\text{Pb}^{2+} + \text{H}^+ + \text{cit}^{3-} = \text{Pb}(\text{Hcit})$	8.30	NIST (2004)	(3)
$\text{Pb}^{2+} + 2\text{H}^+ + \text{cit}^{3-} = \text{Pb}(\text{H}_2\text{cit})^+$	11.14	NIST (2004)	(4)
$\text{Pb}^{2+} + \text{H}^+ + 2\text{cit}^{3-} = \text{Pb}(\text{Hcit})(\text{cit})^{3-}$	10.61	NIST (2004)	(5)
$2\text{Pb}^{2+} + 2\text{cit}^{3-} = \text{Pb}_2(\text{cit})_2^{2-}$	10.70	NIST (2004)	(6)

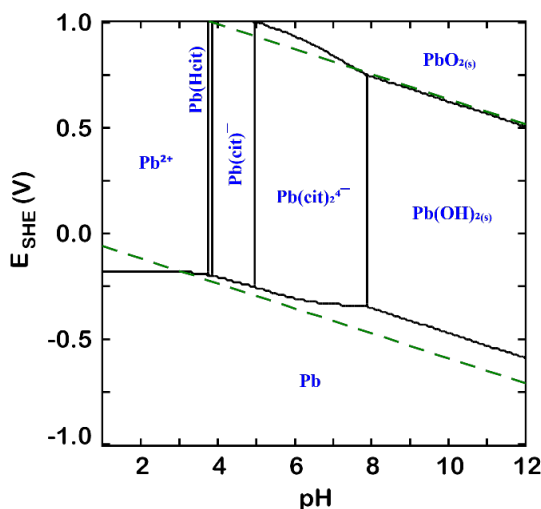


Figure 1. Eh-pH diagram for the Pb-cit system at 25°C. Total Pb and citrate concentrations: 0.01 and 0.2 M, respectively.

Some investigations show the effects of the citrate concentration, pH, temperature, and solid/liquid ratio for lead leaching. For anglesite (PbSO_4) leaching with 0.1 M citrate from pH of 3 to 7, lead recovery increased from 10.5% to 94%, respectively, related to the formation $\text{Pb}(\text{cit})_2^{4-}$. In the pH range 8 to 10, the recovery decreased to 60% due to lead hydroxide formation. As the ratio S/L increased to 30 g/L, the extraction declined to <70% due to solution saturation (Zárate-Gutiérrez and Lapidus, 2014).

Although the citrate ion is necessary to increase lead dissolution, its concentration is also an important factor since excess citrate has been shown to decrease lead dissolution due to the formation of solid lead citrate (Sonmez and Kumar, 2009b). This behavior was observed with galena, as well as with recycled lead-acid batteries (Villa *et al.*, 2018).

On the other hand, lead dissolution from the oxidation of a Pb-Ag-Zn sulfide concentrate is limited by the low solubility of lead sulfate (Zárate-Gutiérrez *et al.*, 2015). The sulfide ions, liberated into solution from galena, and other reactive sulfides, have only been studied during the cyanidation process in the presence of sulfide minerals (Hewitt *et al.*, 2009); in other systems, such as in citrate leaching, the identification of sulfur species has not been undertaken, despite the fact that their presence is relevant in lead leaching because some species can suppress its solubility. The present study offers an option to recover lead in a neutral to slightly alkaline medium with a low concentration of citrate (0.2 M) as a complexing agent and hydrogen peroxide as an oxidant; the effects of hydrogen peroxide concentration, pH, and solid/liquid ratio and the species of sulfides liberated from galena were determined in the leaching system at 25°C.

2 Experimental

2.1 Mineral characterization

The mineral sample was obtained from a Mexican mineral processing plant in the state of Zacatecas-Mexico. The size fraction $-53/+44 \mu\text{m}$ ($-270/+325$ mesh) was employed. The lead, iron, and copper contents were determined by atomic absorption spectrometry (Varian SpectraAA 220FS) after acid digestion with aqua regia, and the mineralogical species present in the sample were identified by X-ray diffraction (D8 Advance) in the range of 2° - 90° for a 2θ angle at a speed of $8^\circ/\text{min}$.

2.2 Materials and equipment

All solutions were prepared with chemical grade reagents, deionized water, sodium citrate ($\text{NaH}_2(\text{C}_3\text{H}_5\text{O}(\text{COO})_3)$, 99%), hydrogen peroxide (H_2O_2 , 30%), hydrochloric acid (HCl, 36%), nitric acid (HNO_3 , 76%), sulfuric acid (H_2SO_4 , 98%), sodium hydroxide (NaOH, 97%), potassium permanganate (KMnO_4 , 99%).

For the leaching system, a mechanical stirrer (Caframo BDC-250) at 600 RPM was used, coupled to a heating system with a Thermo-super nova 20536 hotplate to maintain a constant temperature. The control of the temperature, pH, and ORP was carried out with the multiparameter meter, Hanna S5521. The leaching system and the sampling were carried out in a Pyrex® glass reactor with a plastic lid where the electrodes were mounted to monitor the system stability.

The experimental conditions to evaluate the effects of pH, solid/liquid ratio, and H_2O_2 concentration on lead leaching with sodium citrate are presented in Table 2; these were selected on the basis of a previous thermodynamic analysis of sulfur species distributions (not shown here). The pH was regulated with dilute sulfuric acid and sodium hydroxide; samples were taken during the leaching process at a set time, and all were analyzed by atomic absorption spectrometry.

Peroxide quantification was performed through titration (T_0) of 1 mL of the test solution (filtered leach solution) with 25 mL of deionized water and 5 mL of 9 M H_2SO_4 .

Table 2. Conditions for PbS leaching tests.

Parameter	Range
Temperature, °C	25
pH	6, 7, 8
$\text{NaH}_2(\text{C}_3\text{H}_5\text{O}(\text{COO})_3)$, M	0.2
H_2O_2 , M	0.019, 0.078, 0.097
Mineral/Solution, g/L	3, 5, 10, 30

The titration solution consisted of 0.004 M potassium permanganate, and the endpoint was indicated by a change to a faint pink color.

For the determination of the sulfur species released during the leaching of galena, an iodometric titration system was implemented in an acid medium to quantify the species such as sulfide (S^{2-}), thiosulfate ($S_2O_3^{2-}$) and sulfite (SO_3^{2-}), and the quantification of tetrathionate ($S_4O_6^{2-}$) with permanganate, on the other hand, the determination of sulfate (SO_4^{2-}) by turbidimetry (Clesceri *et al.*, 1999). Therefore, four independent titrations were carried out on each aliquot from the leaching. The first titration (T_1) allows the quantification of intermediate sulfur species (S^{2-} , $S_2O_3^{2-}$, SO_3^{2-}), in a second titration (T_2) zinc acetate ($Zn(CH_3COO)_2$) is added in order to mask S^{2-} (Wasserlauf and Dutrizac, 1982; Kohr, 1997) and the concentration of S^{2-} is determined by difference from the previous titrations ($S^{2-} = T_1(S^{2-}, S_2O_3^{2-}, SO_3^{2-}) - T_2(S_2O_3^{2-}, SO_3^{2-})$), the third titration (T_3) was implemented to the determination of thiosulfate with $Zn(CH_3COO)_2$ and formaldehyde (CH_2O) to masks S^{2-} and SO_3^{2-} , respectively (Kilroy, 1979; Rolia and Barbeau, 1980), the concentration of sulfite is determined by difference ($T_2 - T_3$). The quantification of tetrathionate ($S_4O_6^{2-}$) and polysulfides (S_x^{2-}) are determined like $S_4O_6^{2-}$ (T_4) with permanganate due to its oxidizing power, it oxidizes all intermediate species, including $S_4O_6^{2-}$ (Miura *et al.*, 1991), and tetrathionate is determined by the difference in the concentration of intermediate sulfide ($S_4O_6^{2-} = T_4(S_4O_6^{2-}, S^{2-}, S_2O_3^{2-}, SO_3^{2-}) - T_1(S^{2-}, S_2O_3^{2-}, SO_3^{2-})$). Finally, the concentration of SO_4^{2-} was determined by turbidimetry (Clesceri *et al.*, 1999), and a balance between Pb concentration and total sulfur species in solution corroborates the concentration of all sulfides. It is important to mention that before the quantification of sulfur species, the solution was heated and filtered to eliminate the remaining H_2O_2 (Takagi and Ishigure, 1985). The concentration of H_2O_2 is determined by the difference between the solution from the leaching (T_0) and T_4 .

Thermodynamic modeling Eh-pH diagram for system S- H_2O was performed using the database of thermodynamic software HSC Chemistry v. 6.1, and the equilibrium speciation diagrams were constructed using the software Medusa Chemistry (Puigdomenech, 2004).

3 Results

3.1 Characterization of the mineral

X-ray diffraction of the sample revealed that galena (PbS, 01-0880) was the principal mineral phase (Figure 2). On the other hand, chemical analysis

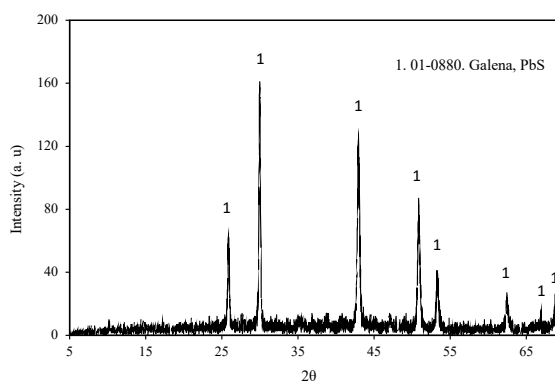


Figure 2. X-ray diffractogram of the mineral sample.

Table 3. Chemical composition of the mineral sample.

Composition (%)	
Pb	69.87
Cu	0.28
Fe	0.18

showed that the lead, copper, and iron content was 69.87, 0.28, and 0.18%, respectively (Table 3).

3.2 Citrate leaching

Leaching tests were performed to dissolve lead, evaluating different values of pH, hydrogen peroxide concentration, and the solid/liquid ratio.

3.2.1 pH effect

Figure 3 shows the results of the leaching tests, where it is observed that, as the pH increases from pH 6 to 8, there is only a slight difference in the amount of lead dissolved at a solid/liquid ratio of 3 g/L in 0.097 M of H_2O_2 after 15 minutes. At shorter times, a slight increase in the lead dissolution rate can be noted for the most alkaline pH (pH 8). The lead dissolution rate for the three cases is high, where more than 90% extraction is attained after 5 minutes and complete dissolution at 20 minutes.

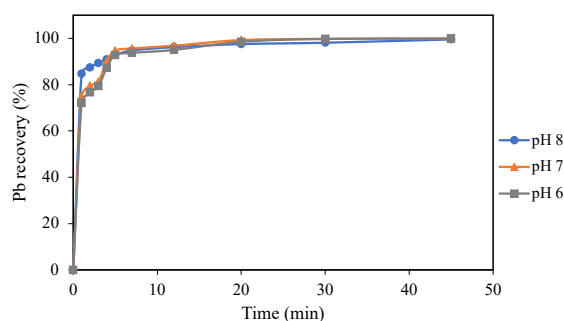


Figure 3. Lead dissolution at different pH values, 3 g/L of 0.2 M citrate, 0.097 M H_2O_2 at 25°C.

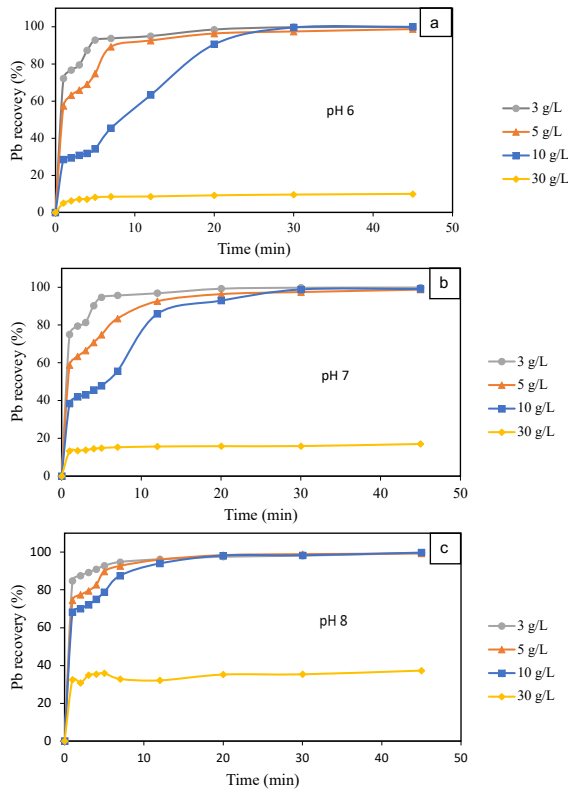


Figure 4. Lead recovery at different S/L ratios (3, 5, 10, and 30 g/L), 0.2 M citrate, and 0.097 M H₂O₂ at different pH values: a) pH 6, b) pH 7, and c) pH 8.

3.2.2 Effect of the solid/liquid ratio

The variation of the amount of mineral with respect to the volume of the citrate-H₂O₂ solution on lead dissolution was studied (Figure 4). In Figures 4a, 4b, and 4c, for a solid-liquid ratio of 10 g/L, the behavior is similar to that presented in the previous section, where the lead dissolution rate rises as the pH increases from pH 6 to pH 8; at a more alkaline pH, leached lead is greater than 95% after only 20 min; however, when the S/L ratio is increased to 30 g/L, lead dissolution decreases to 10, 17 and 37% at pH 6, 7 and 8, respectively (Figures 4a, 4b, and 4c).

As may be noted, low recoveries were obtained for the highest S/L ratio (30 g/L) at the three pH values; this behavior is related to the concentration of the oxidant in the system. For 3, 5, and 10 g/L ratios, lead concentrations of 0.010, 0.017, and 0.034 M are attained with a peroxide concentration of 0.097 M, representing 100% extraction. However, with 30 g/L the maximum Pb concentration would be 0.101 M, while only 37% of the extraction is reached (Figure 4c). At all three pH, the conversion of galena reached a stable value in less than 5 minutes.

This behavior is related to the peroxide-galena stoichiometry, which is dependent upon the oxidation of the sulfur species released during this process. Figure 5 shows the Eh-pH diagram for the metastable S-H₂O system, showing the metastable species

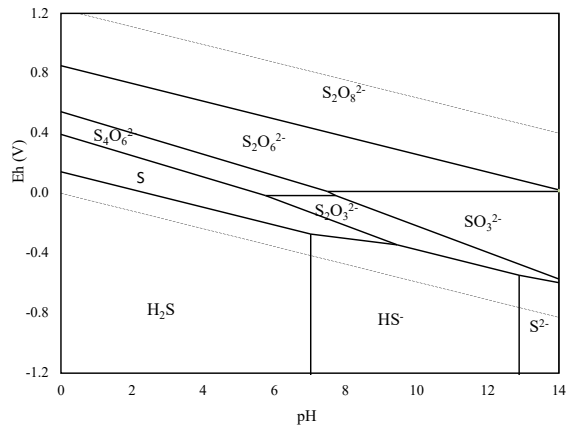


Figure 5. Eh-pH diagram for system S-H₂O at 0.01 M S²⁻, and 25°C.

present, such as thiosulfate (S₂O₃²⁻), tetrathionate (S₄O₆²⁻), and sulfite (SO₃²⁻); the stable species such as HSO₄⁻ and SO₄²⁻ have been omitted.

The metastable species shown in Figure 5 can be related to galena leaching. The formation of each sulfur species resulting from the oxidation of galena and the relationship between H₂O₂/PbS leached are presented in Table 4. These ratios could indicate the degree to which sulfur is oxidized, in the absence of auto-decomposition or consumption by competing metal sulfides. In any event, values of H₂O₂/PbS leached lower than 4 indicate that the sulfur does not completely oxidize to the sulfate ion; this situation is advantageous since PbSO_{4(s)} has an extremely low solubility (10^{-6.2}) and PbS (10^{-28.3}), as was mentioned earlier.

Table 5 shows the relationship between the initial lead present in the galena and solution at the different (S/L) ratios (3, 5, 10, and 30 g/L) at 0.097 M peroxide; in these conditions, there are H₂O₂/Pb^o ratios of 9.7, 5.7, 2.9 and 1.0, respectively for each S/L ratio. Considering the reactions in Table 4, it is crucial that the H₂O₂/Pb ratio be less than three and greater than two to avoid irreversible oxidation of sulfide to sulfate and the formation of elemental sulfur, respectively. Therefore, a ratio between 2 to 3 promotes the formation of reversible sulfur oxyanion species S₂O₃²⁻, S₄O₆²⁻ and SO₃²⁻. For the H₂O₂/Pb^o ratio of 2.9 (S/L=10 g/L in this case), these species are prevalent (see below); the other relations show an unfavorable behavior because 3 and 5 g/L imply H₂O₂/Pb^o ratios above four, and 30 g/L relationship suggest a value less than one.

These relationships were corroborated by quantifying the consumption of hydrogen peroxide, presented in Table 5, determined by titration. Except in limited cases, the (H₂O₂ consumed/Pb leached) ratio is less than 4, even though H₂O₂ is still present in the solution after 45 minutes; this may indicate that sulfur transformations to higher oxidation states get slower as the pH and solid/liquid ratio increase

(ratio $H_2O_2/Pb > 2$). It is interesting to note that at pH 8, H_2O_2 is almost completely consumed at 10 and 30 g/L. The predictions of products of sulfide ion oxidation from PbS shown in Table 5 are verified by the determination of the sulfur species by titration (Figure 6), where tetrathionate predominates under all conditions.

For these four scenarios, the H_2O_2/PbS ratio ~ 2.3 is the most favorable option for the leaching system because the tetrathionate ion can act as oxidant in a reversible reduction to thiosulfate; a similar effect is observed for sulfite (Druschel *et al.*, 2003).

3.2.3 Effect of H_2O_2 concentration

To evaluate the effect of H_2O_2 and the ratio H_2O_2/Pb necessary for galena leaching, avoiding the irreversible oxidation to sulfate, four concentrations of H_2O_2 were used (0.097, 0.078, and 0.019 M), 0.2 M citrate at 25°C. In Figure 7, lead recovery decreases as the peroxide concentration decreases; this behavior is related to the ratio $H_2O_2^\circ/Pb^\circ$ required for lead leaching and irreversible sulfide oxidation (below 3 and above 2).

Table 4. Ratio of H_2O_2/PbS for reactions present in the system PbS-Cit- H_2O_2 .

Reaction	Ratio H_2O_2/PbS	Ec.
$2PbS + 9H_2O_2 + 4cit^{3-} + 2H^+ = 2Pb(cit)_2^{4-} + S_2O_8^{2-} + 10H_2O$	4.5	(7)
$PbS + 4H_2O_2 + 2cit^{3-} = Pb(cit)_2^{4-} + SO_4^{2-} + 4H_2O$	4.0	(8)
$2PbS + 7H_2O_2 + 4cit^{3-} + 2H^+ = 2Pb(cit)_2^{4-} + S_2O_6^{2-} + 8H_2O$	3.5	(9)
$PbS + 3H_2O_2 + 2cit^{3-} = Pb(cit)_2^{4-} + SO_3^{2-} + 3H_2O$	3.0	(10)
$4PbS + 9H_2O_2 + 8cit^{3-} + 6H^+ = 4Pb(cit)_2^{4-} + S_4O_6^{2-} + 12H_2O$	2.3	(11)
$2PbS + 4H_2O_2 + 4cit^{3-} + 2H^+ = 2Pb(cit)_2^{4-} + S_2O_3^{2-} + 5H_2O$	2.0	(12)
$PbS + H_2O_2 + 2cit^{3-} + 2H^+ = Pb(cit)_2^{4-} + S^0 + 2H_2O$	1.0	(13)

Table 5. H_2O_2 concentration consumed at different S/L ratios with an initial concentration of 0.097 M H_2O_2 .

pH	Ratio S/L, g/L	Initial Pb, M	Ratio H_2O_2/Pb	Dissolved Pb M	Consumption H_2O_2 M	%	Experimental ratio, H_2O_2 consumed/Pb dis	Species
6	3	0.01	9.7	0.010	0.041	41.8	4.1	SO_4^{2-}
	5	0.017	5.7	0.017	0.07	72.6	4.1	SO_4^{2-}
	10	0.034	2.9	0.034	0.079	81.2	2.3	$S_4O_6^{2-}$
	30	0.101	1.0	0.010	0.057	58.4	5.7	SO_4^{2-}
7	3	0.01	9.7	0.010	0.041	41.8	4.1	SO_4^{2-}
	5	0.017	5.7	0.017	0.07	71.8	4.1	SO_4^{2-}
	10	0.034	2.9	0.033	0.076	78.6	2.3	$S_4O_6^{2-}$
	30	0.101	1.0	0.017	0.054	55.2	3.1	$S_2O_6^{2-}/SO_3^{2-}$
8	3	0.01	9.7	0.010	0.041	41.8	4.1	SO_4^{2-}
	5	0.017	5.7	0.017	0.069	70.9	4.0	SO_4^{2-}
	10	0.034	2.9	0.034	0.079	81.2	2.3	$S_4O_6^{2-}$
	30	0.101	1.0	0.038	0.061	62.8	1.6	$S^0/S_2O_3^{2-}$

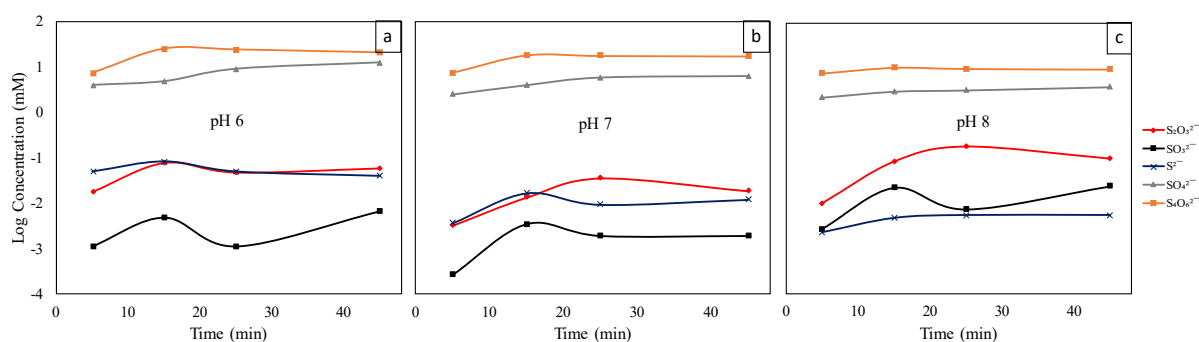


Figure 6. Products of the sulfide ion oxidation from galena (PbS) in the presence of 0.2 M citrate, at 10 g/L with an initial concentration of 0.097 M H_2O_2 , at different pH values: a) pH 6, b) pH 7, and c) pH 8.

Table 6. H_2O_2 consumption and ratio $\text{H}_2\text{O}_2/\text{Pb}$ at pH 8, 0.2 M citrate, 3.0 g/L mineral, varying the H_2O_2 concentration at 25°C.

Initial Pb	Initial H_2O_2 M	Ratio $\text{H}_2\text{O}_2/\text{Pb}$	Dissolved Pb, M	Consumption H_2O_2 M	Consumption H_2O_2 %	Experimental Ratio, H_2O_2 consumed/Pb dis	Species
	0.097	9.7	0.0100	0.040	41.2	4.0	$\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$
0.01	0.078	7.8	0.0100	0.042	53.9	4.2	$\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$
	0.019	1.9	0.0076	0.019	98.6	2.5	$\text{S}_2\text{O}_3^{2-}/\text{S}_4\text{O}_3^{2-}$

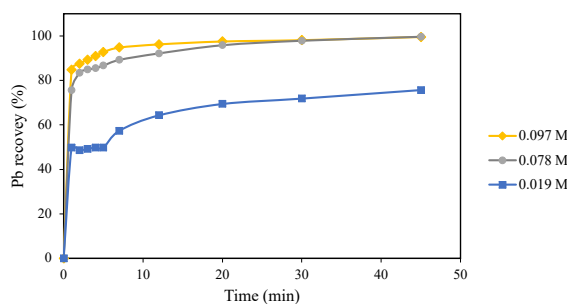
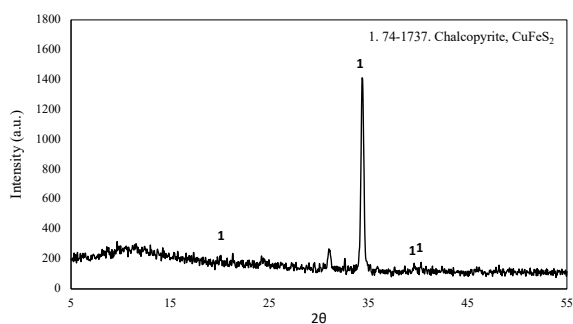
Figure 7. Recovery of lead with 0.097, 0.078, or 0.019 M H_2O_2 , 0.2 M citrate, and 3 g/L of mineral at pH 8 and 25°C.

Table 6 shows the different $\text{H}_2\text{O}_2/\text{Pb}$ ratios in the system for the three peroxide concentrations (0.097, 0.078, and 0.019 M) at the lowest S/L ratio (3 g/L). At $\text{H}_2\text{O}_2/\text{Pb}$ ratios of 9.7 and 7.8, there is an excess of peroxide, where the irreversible sulfate species is generated, and complete dissolution of the galena is achieved. However, for the ratio of 1.9, where this ratio ($\text{H}_2\text{O}_2/\text{Pb}$) is less than 2, only 76% of the lead passed into the solution. The three relationships were corroborated with the lead in solution and peroxide consumption presented in Table 6, where values of 4 and 4.2 for initial H_2O_2 concentrations of 0.097 and 7.8 M, respectively, were found. On the other hand, a ratio of 2.5 was determined for the initial H_2O_2 concentration of 0.019 M and the presence of reversible sulfur oxyanion species ($\text{S}_2\text{O}_3^{2-}/\text{S}_4\text{O}_3^{2-}$) was evidenced.

High ratios H_2O_2 consumed/Pb dissolved (≥ 4) can be associated to high consumptions of peroxide (greater than 53%) and final oxidation states of the sulfur are linked to $\text{S}_2\text{O}_8^{2-}$ and SO_4^{2-} , causing a detrimental effect on the solubility of lead, despite the presence of citrate in the alkaline solution. Only at an initial concentration of 0.019 M H_2O_2 (ratio $\text{H}_2\text{O}_2/\text{Pb} = 2.5$), a partial oxidation of sulfur to thiosulphate and tetrathionate is achieved. Finally, it is important to mention that once the pH is regulated, it remains stable throughout all the tests due to the buffering effect of citrate (Ruiz-Vela *et al.*, 2023).

The solids present after the leaching process at pH 8 and 0.097 M H_2O_2 were characterized by X-ray diffraction (Figure 8). The principal phase is chalcopyrite, which is consistent since this mineral is stable under the working conditions.

Figure 8. X-ray diffractogram of the residues obtained at pH 8 and 0.097 M of H_2O_2 .

Conclusion

Citrate is a leaching agent that facilitates lead leaching from galena at room temperature. It is possible to completely leach the lead content of the mineral at pH 8, when sufficient peroxide is present in the system for mineral oxidation due to the formation of stable complexes between citrate and lead (Pb-Cit).

Under the conditions tested, lead recovery is favored when the relation between peroxide and galena is about 2.3 to 2.5, promoting the formation of tetrathionate and other soluble sulfur species that do not suppress lead solubility. At these near-neutral pH values, the formation of dithionate and sulfate ions appears to be slowed, allowing more efficient use of the hydrogen peroxide oxidant, compared to that observed in more acid solutions.

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