EFFECT OF OXIDIZING AGENTS ON THE TREATMENT OF A COLOMBIAN LEAD ORE BY ALTERNATIVE HYDROMETALLURGICAL PROCESSES

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Abstract

The metallurgy of lead presents significant environmental and public health challenges due to its toxicity. This is why it has been necessary to develop hydrometallurgical processes as alternatives for obtaining metal with a more sustainable and environmentally safe approach. However, these processes may involve complex chemical reactions and the use of specific chemical reagents, which may require rigorous control and monitoring to ensure the efficiency of the process and the safety of the personnel involved.

In this research, the recovery of lead from a Colombian mineral with low metal content was studied by hydrometallurgical processes in carboxylic media under ambient conditions. A preliminary chemical treatment was necessary to improve the metal extraction. For this purpose, two hydrometallurgical treatments were used: i) pneumatic agitation with ozone injection and ii) mechanical agitation with hydrogen peroxide dosing. The lead extractions from the pretreated ore were similar to those from the leach without pretreatment. This situation attributed the dissolution of the lead to the complexing effect of the carboxylic agent rather than to the effect of the pretreatments. The direct addition of peroxide to the citrate leach resulted in an extraction of 50% of the metal, an improvement of more than 30% over the leach without the addition of the oxidizing agent.

The leaching of the ore with 0.5M citrate and pH 4.5 yielded a redox potential of 926 mV, which ensured the high activity of the electrons in the chemical reaction and therefore the lead ions dissolution.

Keywords: Hydrometallurgy; Pretreatment; Ozone; Hydrogen-peroxide; Citrate; Lead

1. Introduciton

Due to the numerous applications of lead, its extraction from ores has been an important activity for centuries. However, this practice has significant challenges and limitations [1]. Lead mining faces technical, economic and environmental barriers that can make it difficult to process and affect both mining operators and the surrounding environment [2].

From a technical point of view, the extraction of lead is associated with difficulties due to the complexity of its minerals. Therefore, careful concentration and separation processes are required to obtain a final product of acceptable quality and purity. These processes can be expensive and require specialized technologies, which represents a significant technical challenge [3].

In addition, there is an economic limitation associated with lead mining. As high-grade ore deposits are depleted, lead mining becomes more expensive and less profitable. The high extraction costs, combined with the variability of lead prices on international markets, can affect the economic viability of mining [4], and limit the interest of mining companies in investing in new metallurgical operations.

In the past , the process of obtaining the metal was carried out through pyrometallurgical processes , which include several stages of ore preparation, melting, separation of impurities until obtaining metallic lead. However, it is important to note that lead pyrometallurgy can generate polluting emissions and residues, such as fumes and slags that contain heavy metals. Therefore, it is essential to apply environmental control measures and follow strict regulations to minimize negative impacts [5].

For these reasons, the metallurgical industry has made efforts in obtaining the metal through aqueous processes. In this processthe finely particulate ore is mixed with an aqueous solution containing leaching agents, which dissolve lead and other metals present in the ore, forming metal ions in the solution. The

separation of impurities is carried out using techniques such as selective precipitation, filtration, and chemical purification [6-8], to eliminate other unwanted metals and obtain a purer lead solution.

Studies have shown that once the solution is purified, metallic lead is recovered by precipitation processes. Agents such as sodium sulfide (Na_2S) or sodium carbonate (Na_2CO_3) [6,9] are used to convert lead ions into insoluble compounds, such as lead sulfide (PbS) or lead carbonate ($PbCO_3$). The precipitate obtained, it is subjected to additional smelting and refining processes to obtain high purity metallic lead. These processes may include the precipitate melting, impurities removal by pyrometallurgical processes and electrorefining.

It is important to highlight that lead hydrometallurgy can vary depending on the specific characteristics of the material and the processing objectives, since the extraction of the metal today is carried out both from low-grade ores and from industrial residues [10,11]. These materials, having a complex chemistry therefore require strong oxidizing agents that help to increase the extraction percentages of the metal of interest [12]. Additionally, in aqueous media, variables such as pH and oxidation potential are determining factors for the definition of stability zones and, therefore, for the chemical reactions to take place.

Conventionally, oxidizing agents such as hydrogen peroxide and salts such as chlorine dioxide, among others, are used in these routes. However, using alternative oxidizing agents with characteristics that allow sustainable processes, that is, of high technical efficiency and low or null environmental impact, has been ventured. Ozone has multiple advantages to be used as a leaching reagent, highlighting the high oxidizing power that makes it thermodynamically capable of oxidizing a lot of substances and/or chemical elements [13].

In the dissolution of metals such as germanium, zinc and copper, oxidation with ozone in a sulfuric acid system has improved the kinetics of the chemical reactions involved, increasing solubility and favoring greater efficiency in the metals extraction. Atomic force microscope observation reveals notable alterations in the materials surface morphology after oxidative leaching [14]. Ozone in solution plays a key role in the rapid oxidation of the sulfide structures allowing the release of the encapsulated metals [15]. The ozone-sulfide system is at least three orders of magnitude more reactive than a comparable system with oxygen alone [16,17]. Ozone in chlorinated medium is effective for the extraction of gold and platinum group metals from magnetite ore with extractions of 50, 70 and 90% for Au, Pd and Pt respectively [13]. On the other hand, ozone in synergy with ultrasound used in the pretreatment stage of the leaching of a refractory mineral, notably increases the leaching percentage of precious metals such as gold (from 49.12% to 93.52%) and silver (from 4.01% to 61.25%) after 4h. The ozone oxidized sulfide enclosure, effectively damaged sulfide enclosure and restrain secondary enclosure within a short time [17].

An additional advantage that ozone offers in hydrometallurgical processes is that its degradation product is gaseous oxygen which can be recirculated to another process with less oxidizing requirements or released into the environment without harmful consequences.

The present study proposed demonstrating the effect of two oxidizing agents (ozone and hydrogen peroxide) as a pretreatment for lead leaching from an ore sample. Both agents were evaluated based on their characteristics. For ozone, it was necessary to manufacture a laboratory-scale prototype of a Pachuca tank to ensure greater time and area of contact between ozone and the solution. The aim was to take advantage of the tank's length so that ozone had more time to dissolve in the solution and thus react with the mineral, according to Henry's Law. With the use of this gas-stirred reactor, it ensures that the main process requirements are governed by the velocity and turbulent distribution of kinetic energy within the tank, that is, by mass transfer and particle suspension [18-20]. Subsequently, leaching with sodium citrate of the pre-treated mineral was carried out. For hydrogen peroxide, doses were required every hour during the direct leaching process with sodium citrate to have a more precise control over the concentration and distribution of the oxidant in the leaching solution. The effect of the oxidizing agents was determined through selective lead extractions. Citrate was chosen because it is an alternative to conventional leaching (inorganic acids) in hydrometallurgical processes. Its carboxylic characteristic (COOH) makes it attractive from an environmental perspective due to its decomposition into carbon dioxide and water at high temperatures [21].

Its high capacity to form soluble complexes with heavy metals has allowed the authors to test the reagent in various minerals and waste materials treatment, obtaining successful results [22-24].

This research aimed to study less polluting aqueous processes under moderate operating conditions, with study recovery efficiencies similar to traditional methods for obtaining lead such as: i) sintering and roasting of concentrates, ii) refining and melting of untasted concentrates, iii) roasting of lead smelting dust [25], iv) alternative hydrometallurgical treatments for mixed lead concentrates including leaching PbS with sulfuric acid, to generate lead sulfate for subsequent treatments [26], and v) leaching anglesite with citrate solutions [27], among others.

2. Experimental

The ore sample used in this study is from Colombia. The vendors did not provide the exact location of the mine.

After crushing, grinding, and sieving, 1 kilogram of ore in the size range of 600-300 μm was obtained.

The ore was chemically and mineralogically characterized. The elemental composition was made by conventional acid digestion with aqua regia and analyzed by atomic absorption in the Perkin Elmer 3110 spectrophotometer, using lamps and calibration standards suggested by the manufacturer. The mineralogical characterization was carried out by X-ray Diffraction in the Panalytical X'pert Pro using X'pert highScore Plus software ®.

Pretreatments were performed using deionized water, 0.1 M hydrogen peroxide (50%) dosages, and ozone injection in situ. The oxidants behavior was verified under different pH conditions: natural conditions of deionized water plus the ore (pH 6.2), basic pH (10) and acidic pH (4). In each case, the experiments were started with gas sparging and/or peroxide dosing, after which aliquots were withdrawn every hour for metal quantification. At the test end, the liquid-solid suspension was filtered and air-dried for subsequent leaching with sodium citrate. It was necessary to adjust the pH of the pretreatment solutions to 4 and 10 with a dilute solution of nitric acid (HNO_3) and sodium hydroxide (NaOH) to verify their effect.

A prototype Pachuca tank was built and put into operation for ensure adequate superficial gas velocity in the pneumatic agitation process. Optimizing the design of the Pachuca tank in terms of its length improves the efficiency and effectiveness of ozonization due to the hydrodynamics and mass transfer within the tank [18].

The construction of the prototype (Figure 1) included an external tube and a concentric tube which was attached to the gas diffuser stone which in turn, was connected to the ozone generator (domestic generator model N1668) using a hose.

The quantification process of dissolved ozone in solution was carried out according to the iodometry analytical course [28] (eq.1).

$$6KI + 3H_2SO_4 + O_3 \rightarrow 3K_2SO_4 + 6I + 3H_2O \quad (1)$$
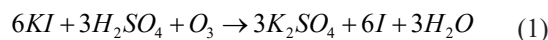
For this, deionized water, 1 ml of sulfuric acid and 2 grams of analytical grade potassium iodide were used to manufacture 1 L of analyte. Additionally, a 0.005 N sodium thiosulfate solution and 50 ml of starch (potato) were used as titrant and indicator respectively.

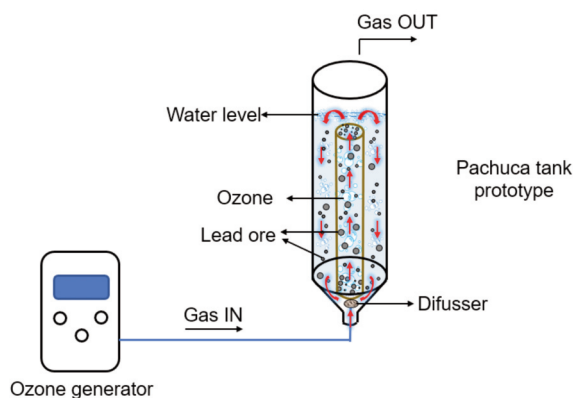Since this research aimed to analyze the effect of oxidizing agents as a pretreatment to lead ore

Figure 1. *Scheme of the experimental set-up*

leaching, many of the leaching parameters, such as temperature and agitation speed, were kept constant. All the leaching experiments were carried out at ambient temperature and pressure (Tunja-Colombia city; 17 °C and 551 mmHg). Mechanical agitation at 250 rpm (model 50006-03 - COLE-PARMER mechanical agitators) was used, with a constant solid-liquid ratio of 50 g ore per liter of leaching solution.

Leach solutions were prepared with 0.5 M sodium citrate dihydrate ($C_6H_5Na_3O_7.2H_2O$). The solution pH was adjusted to 4.5 with dilute HNO_3 solution. The pH value was changed according to the zones of formation of soluble complexes of the citrate with lead (Figure 2), since the stability of these complexes depends on the pH. This behavior is due to the fact that the H^+ ion is an important competitor of the binding sites (the functional groups involved in chelation) [28].

During the leaching, the potential of the solutions was monitored using a saturated Ag/AgCl electrode (Oakton pH ORP 700 Benchtop Meter), later the
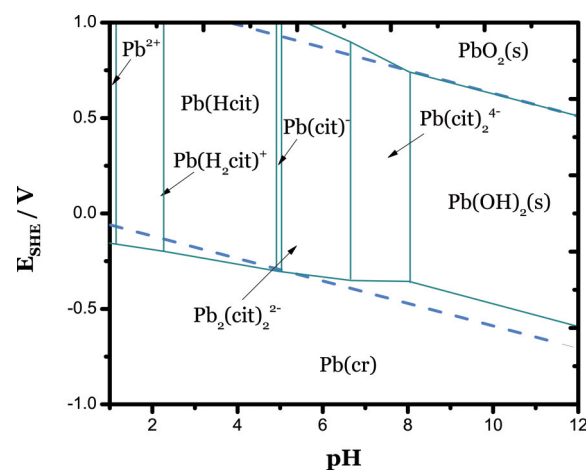

Figure 2. *Predominance diagrams for Pb in the presence of 0.5 M citrate. Designed with MEDUSA® software [29,30] using the NIST database [31] and adapted by the authors*

values were adjusted to the standard hydrogen electrode (SHE).

3. Results and discussion
3.1. Characterization of the material

The elemental composition of the mineral consists of approximately 3.92% lead, 7.57% zinc, 8.97% iron, 2.2% copper and 9.97 sulfur. These percentages allow us to assume that the study mineral is of low grade; since minerals with high metallic richness exceed 80% of Pb by weight.

For their part, X-ray diffraction tests indicate that the mineral contains crystalline silica compounds in a greater proportion, followed by lead sulfide and zinc ferrite (Figure 3).
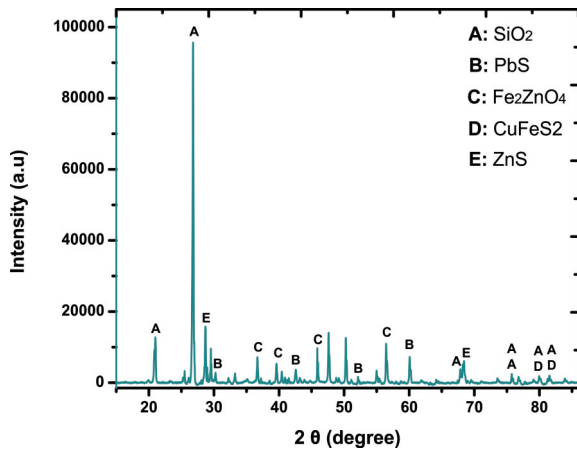

Figure 3. XRD pattern of Colombian lead ore sample

Both zinc and copper sulfide were found in lower proportions; therefore, the extraction of these metals was not the subject of this study.

3.2. Ore treatment by pneumatic agitation and subsequent citrate leaching

The results of the ozone determination in the diluted H_2SO_4 solution show that the ozone dissolved up to 105 minutes into the process (Figure 4).

After this time, saturation of the solution began to take place. The total amount of dissolved ozone was 1.03 mg. To ensure the effect of the pretreatment, the ozone injection time was set at 3 hours.

The quantification of the samples taken during pneumatic agitation in the Pachuca tank prototype did not present metallic content at any of the pH values tested (Table 1). The lead present in lead sulfide could have been oxidized by ozone, forming lead sulfate and releasing oxygen and protons in the process (eq. 2).

$$PbS + 4O_3 + 2H_2O \rightarrow PbSO_4 + 4O_2 + 2H^+ \qquad (2)$$
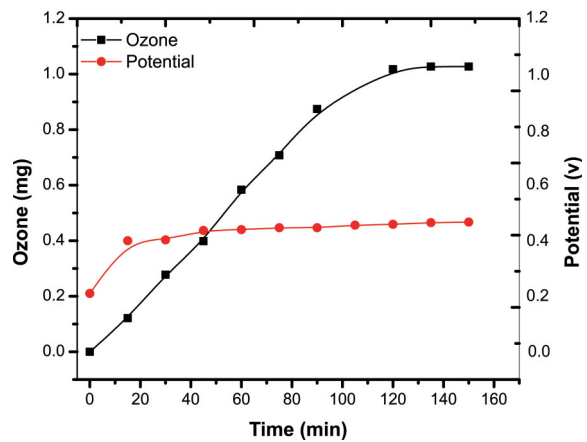

Figure 4. Milligrams of ozone dissolved in solution. Conditions: analyte pH 1.9

This situation is favorable since lead dissolution is expected to take place in secondary citrate leaching.

Table 1. Metallic extractions after treatment with O_3 and pH variation. Conditions: deionized water, 1.03 mg de O_3/3h.

	O_3 pH 7	O_3 pH 4	O_3 pH 10
Pb	0.15%	0%	0%

Citrate can form soluble complexes with covalently bound heavy metal ions [28]. Therefore, lead metal dissolution is achieved in the presence of the carboxylic agent, with the formation of a soluble lead-citrate complex.

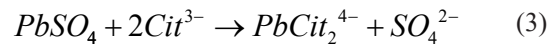$$PbSO_4 + 2Cit^{3-} \rightarrow PbCit_2^{4-} + SO_4^{2-} \qquad (3)$$

Figure 5 shows that at a given pH, as time increases, the slope of the absorption curve decreases, reaching an asymptotic value, possibly due to the consumption of H^+ ions during leaching.
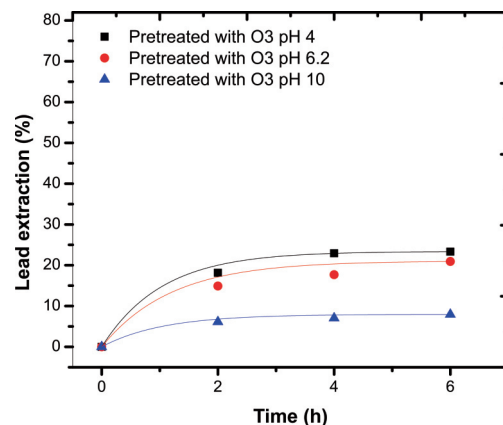

Figure 5. Lead leaching with sodium citrate. Conditions: 0.5 M Citrate, pH 4.5; S:L 50g/1L; RT; pretreated mineral without pH adjustment (6.2) and with O_3 with pH adjustment 4 and 10

Likewise, the concentration of lead dissolved in citrate decreases when the pH is increased in the pretreatment of the samples with ozone; at high pH values, the decomposition of the oxidant is induced [32]. Meanwhile, at pH values 4 and 6.2 the difference in extraction is only 2.4%. With this little appreciable difference and considering the reactions favorability occurring under neutral conditions, it would not be necessary to adjust the pH in the pretreatment.

3.3. Ore treatment by mechanical agitation and subsequent citrate leaching

Hydrogen peroxide acted by oxidizing the lead mineralogical phase (Figure 3). As expected, during the treatment with the oxidant, no lead extractions were achieved (in all cases it was 0%). Meanwhile, in the secondary leachings with citrate, lead dissolutions were achieved, due to the formation of complexes (Figure 6).
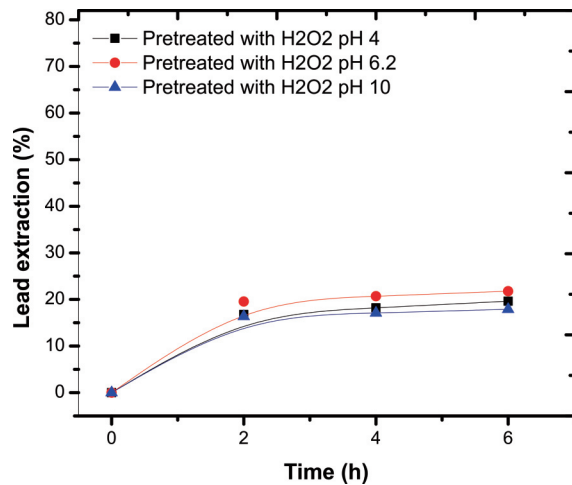
Figure 6. *Lead leaching with sodium citrate. Conditions: 0.5 M Citrate, pH 4.5; S:L 50g/1L; RT; pretreated mineral without pH adjustment (6.2) and with H_2O_2 with pH adjustment 4 and 10*

As with the mineral pretreated with ozone, the dissolution of lead is attributed to the ability of citrate to form soluble complexes with the heavy metal. The molecular structure and the presence of functional groups in the chemical composition of the carboxylic agent allow oxygen atoms with free electron pairs to act as coordination sites for Pb^{2+} ions. By pre-treating the material to acid and basic conditions, lead extraction decreases by 2.2 and 3.9% respectively; differences that apparently are insignificant in terms of extraction. The effect of the peroxide used in direct doses for leaching with citrate, was also verified (Figure 7). The results show the evident difference in the increase in lead extraction when the oxidant is dosed directly to the leach (greater than 28%). The

dissolution of the metal in the presence of hydrogen peroxide and sodium citrate is due to the high capacity of the oxidant to treat lead sulfide ores/concentrates and to the chelating agent capability of citrate [33].
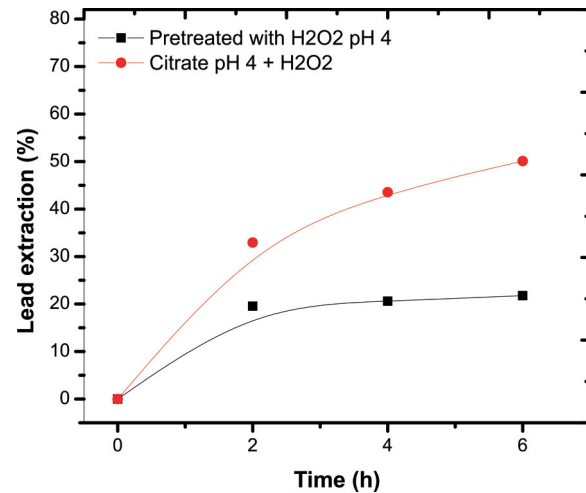
Figure 7. *Lead leaching with sodium citrate. Conditions: 0.5 M Citrate, pH 4.5; S:L 50g/1L; RT; pretreated mineral without pH adjustment (6.2) and with H_2O_2 with pH adjustment 4 and 10*

The interaction between the metal ions and the carboxylate groups of the citrate stabilize the metallic species in the solution and increase its solubility.

$$PbS + 2Cit^{3-} + 2H_2O_2 \rightarrow PbCit_2^{4-} + S^{2-} + 2H_2O + O_2 \quad (4)$$
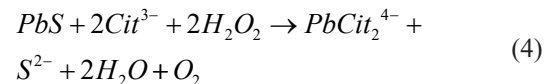
Another important difference in the ore leaching with and without pretreatment is the behavior of the extraction curves. Like the leaching of the mineral pretreated with ozone, the extraction curves (pretreated with peroxide) present an asymptotic behavior as time passes. On the other hand, with direct dosing the extraction curve presents a favorable trend, so increasing the working time or the concentration of the oxidant could achieve better percentages of lead in the citrate solution. Dissolution processes can be enhanced with an increase in the amount of peroxide; its oxidation potential ($E° = 1.77$ vs SHE) allows it to successfully oxidize sulfides, including other refractory ones such as sphalerite (ZnS) and pyrite (FeS_2) [33,34].

However, solutions may be hindered by the decomposition of the oxidizing agent due to the presence of copper and iron cations contained in the sample, whose concentrations increase as leaching progresses. Generally, these cations can form complexes with hydrogen peroxide, leading to its premature decomposition [35].

3.4. Comparison of metallic extractions

The results of the secondary leaching with sodium citrate after pre-treating the mineral with O_3 and H_2O_2 are shown in Figure 8. The extractions in both cases are similar, as is the one achieved by leaching without pre-treatment. This situation allows us to conclude that the lead solutions are due to the complexing action of the carboxylic agent. The nature of the reagent allows it to bind with the lead cations present in the process.
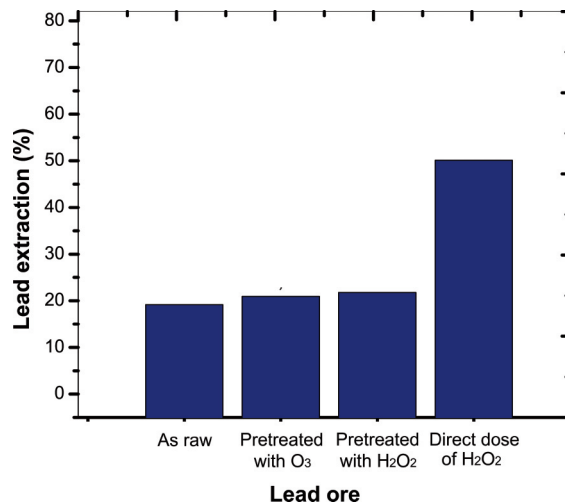

Figure 8. Comparison of lead leaching with sodium citrate. Conditions: Citrate 0.5 M, pH 4.5; S:L 50g/1L; RT

Although the presence of oxidants in the pretreatment solution was ensured, they are not enough to increase lead extraction; additionally, it must be considered that a possible layer of elemental sulfur may form on the mineral surface during treatment, hindering the action of oxidizing agents (as occurs with other polymetallic sulfides) [36]. The attack on the mineral depends to a great extent on the concentration of the oxidant dissolved in the solution; however, in the case of ozone, industrial generators are capable of producing a maximum mass flow of 6 g O_3/h [26]; This amount, compared to that reached by the domestic ozone generator, explains why the treatment is inefficient. Regarding the pH, it was expected that the acid conditions of the solution would increase the dissolution of ozone and therefore improve its interaction with the mineral; however, the limited ozone generation capacity and low flow rate of the ozonator used affected both the driving forces of the liquid and gas phases [37].

On the other hand, hydrogen peroxide is an oxidant that leads to the the mineralogical species destruction that contained lead (Figure 3), thus allowing a greater dissolution of the metal of interest.

Furthermore, by providing an additional supply of oxygen to the system, it induces acceleration of the leaching rate by increasing the Cit-Pb reaction rate. However, these benefits of hydrogen peroxide are only reflected during the direct dosing of the agent in the leaching of lead ore.

Now, we know that the ability to form soluble complexes with citrate varies depending on specific conditions such as pH and the oxidation/reduction potential of the solution. However, despite the fact that in the Cit-Pb system at pH 4.5 a single soluble species (PbHcit) is formed in a wide range of potential (Figure 4), the ORP measured in the experiments (Table 2) indicates that during the direct dosing of peroxide, the activity of the chemical reaction was much higher than when pretreatments were performed on the mineral.

Table 2. Oxidation/reduction potentials measured in citrate leaches 0.5M

As raw	Pretreated with H_2O_2	Pretreated with O_3	Direct dosing of H_2O_2
641 mV	622 mV	668 mV	884 mV
658 mV	532 mV	665 mV	908 mV
695 mV	623 mV	663 mV	926 mV

The measurement of the potential and its variations through the leaching time allows monitoring of the changes of lead oxidation states in the process, which significantly affects the leaching rate of the mineral.

4. Conclusions

In this study, the effect of two hydrometallurgical pretreatments on a low-grade Colombian lead ore for subsequent leaching with sodium citrate was evaluated. The findings showed that both the treatment with hydrogen peroxide and ozone injection were not enough to improve the extraction of the heavy metal in carboxylic media. The limited ozone production capacity of the generator used did not ensure the mass flow necessary for mineral activation. On the other hand, the dosage of peroxide in the system was more efficient when it was carried out directly on the leaching with citrate than as a pretreatment.

The action of the leaching agent was essential for the dissolution of lead, reaching 50% extraction over 6 hours in the presence of 0.1M H_2O_2. Although the formation of soluble lead species with citrate depends on the pH and not on the redox potential, the increase in oxygen present in the system increased the activity of the electrons in the chemical reaction and therefore the dissolution of the lead ions.

Due to the behavior of the leaching curve with

direct dosing of peroxide, it is suggested to extend the working time to achieve higher metal extractions.

The method proposed here shows promise for treating low-grade lead ores since energy consumption is significantly lower compared to conventional pyrometallurgical routes. In addition, by using a leaching agent of a carboxylic nature, the environmental impacts in terms of effluent production and health and safety risks are practically nil.

Acknowledgements

Authors' contribution

J. Borda: Investigation, Formal análisis, Supervision and Writing – original draft & editing, Visualization; I.D. Salamanca: Investigation, Formal análisis and Visualization; R. Torres: Conceptualization, Methodology, Project administration, Supervision, and Writing – review.

Data availability

The study did not report any data.

Conflict of interest

The authors claim that they have no conflicts of interest.

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UTICAJ OKSIDACIONIH SREDSTAVA NA TRETMAN KOLUMBIJSKE OLOVNE RUDE ALTERNATIVNIM HIDROMETALURŠKIM PROCESIMA

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Apstrakt

Metalurgija olova predstavlja značajne izazove za životnu sredinu i javno zdravlje zbog svoje toksičnosti. Zbog toga je bilo neophodno razviti hidrometalurške procese kao alternativu za dobijanje metala sa održivijim i ekološki sigurnijim pristupom. Međutim, ovi procesi mogu uključivati složene hemijske reakcije i upotrebu specifičnih hemijskih reagenasa, što može zahtevati rigoroznu kontrolu i praćenje kako bi se osigurala efikasnost procesa i bezbednost uključenog osoblja.

U ovom istraživanju, hidrometalurškim procesima u karboksilnoj sredini u ambijentalnim uslovima proučavano je dobijanje olova iz kolumbijskog minerala sa niskim sadržajem metala. Za poboljšanje ekstrakcije metala bio je neophodan preliminarni hemijski tretman. U tu svrhu korišćena su dva hidrometalurška tretmana: i) pneumatsko mešanje sa ubrizgavanjem ozona i ii) mehaničko mešanje sa doziranjem vodonik peroksida. Ekstrakcije olova iz prethodno obrađene rude bile su slične onima iz luženja bez predtretmana. Ova situacija pripisuje rastvaranje olova efektu kompleksiranja karboksilnog agensa pre nego efektu predtretmana. Direktno dodavanje peroksida u citratno luženje rezultiralo je ekstrakcijom 50% metala, što je poboljšanje od više od 30% u odnosu na luženje bez dodavanja oksidacionog sredstva. Ispiranje rude sa 0,5M citrata i pH 4,5 dalo je redoks potencijal od 926 mV, što je obezbedilo visoku aktivnost elektrona u hemijskoj reakciji i samim tim rastvaranje jona olova.

Ključne reči: *Hidrometalurgija; Predtretman; Ozon; Vodonik peroksid; Citrat; Olovo*