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VALORIZACIÓN DE ESCORIAS OBTENIDAS TRAS EL PROCESO DE
RECICLAJE DE BATERÍAS AUTOMOTRICES MEDIANTE LIXIVIACIÓN
DEL PLOMO RESIDUAL EMPLEANDO SOLVENTES EUTÉCTICOS
PROFUNDOS (DES)

TESIS PREVIA A LA OBTENCIÓN DEL TÍTULO DE MAGISTER EN
METALURGIA

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DEDICATORIA

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Valorización de Escorias Obtenidas Tras el Proceso de Reciclaje de Baterías Automotrices Mediante Lixiviación del Plomo Residual Empleando Solventes Eutécticos Profundos (DES)

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Resumen: El reciclaje de baterías automotrices figura entre los procesos más contaminantes del mundo debido a la generación y acumulación de desechos peligrosos como la escoria de fundición. En el presente estudio se plantea una alternativa económica y segura para la remoción y recuperación de plomo a partir de dicha escoria. Mediante análisis de extractos TCLP se demostró que las muestras no cumplen con los límites permisibles de la normativa internacional. El plomo fue determinado por FRX/DRX en concentraciones hasta 5.4% principalmente a manera de anglesita (PbSO₄). Para el procesamiento hidrometalúrgico se emplearon solventes eutécticos profundos (DES), que son reconocidos principalmente por ser biodegradables y seguros. Se evaluaron 6 variables operativas: tipo de muestra, solvente, concentración, temperatura, tiempo, y aplicación de presión. Empleando un solvente preparado a base de cloruro de colina y glicerina en relación molar 2:1, fue posible disolver 95% del plomo presente en una muestra de carácter ácido. Se logró esta eficiencia de lixiviación aplicando temperatura de 90 °C, agitación de 470 rpm, porcentaje de sólidos del 5% y dejando transcurrir un tiempo de 5 h. Además, se comprobó que no es necesario aplicar presión hidrotermal para la obtención de resultados favorables. También se demostró la capacidad de recuperar 55% del plomo en solución al colocarse en una celda de electrowinning. Los solventes eutécticos profundos resultaron ser apropiados para descontaminar a la escoria de manera que se pueda cumplir la normativa, recuperar el metal valioso y dar un nuevo uso al material remanente.

Palabras clave: Escoria, Plomo, Solventes Eutécticos Profundos

Recovery of Residual Lead from the Slag of Automotive Recycling Process Applying Deep Eutectic Solvents (DES) as Leaching Agents

Abstract: The recycling of automotive batteries is one of the most polluting processes in the world due to the generation and accumulation of hazardous waste such as foundry slag. In the present study, a relatively cheap and safe alternative is proposed for the removal and recovery of lead from samples of said slag. Through analysis of TCLP extracts, it was found that the samples did not comply with the permissible limits of international regulations. Lead was found by XRF/XRD in concentrations up to 5.4% mainly as anglesite (PbSO₄). For the hydrometallurgical processing, deep eutectic solvents (DES) were used, mainly recognized for being biodegradable and safe. Six operational variables were evaluated: type of sample, solvent, concentration, temperature, time, and pressure application. Using a solvent prepared based on choline chloride and glycerin in a 2:1 molar ratio, it was possible to dissolve 95% of the lead present in an acidic sample. This leaching efficiency was reached by applying a temperature of 90 °C, agitation of 470 rpm, pulp concentration of 5% and allowing a time of 5 hours to elapse. In addition, it was verified that applying hydrothermal pressure was not necessary in order to obtain favorable results. An optimized lead solution was placed inside of an electrowinning cell achieving 55% of lead recuperation on the cathode. The ability of DES to decontaminate slag was demonstrated so that the company complies with regulations, recovers the valuable metal, and grants the remaining material new possibilities of application.

Keywords: Foundry Slag, Lead, Deep Eutectic Solvents

1. INTRODUCTION

1.1 Lead and its application on automotive batteries

Lead is a silvery gray non-ferrous metal belonging to group 14 of the periodic table and represented by the symbol Pb. Its atomic number is 82 and it is considered a heavy metal due to its atomic mass of $207.2 \pm 0,1 \text{ g}\cdot\text{mol}^{-1}$. It has 4 stable or very long half-life isotopes ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb in addition

to numerous known radioisotopes (International Union of Pure and Applied Chemistry, 2021). Chemically it is relatively inert, not being attacked by air, water, and non-oxidizing acids (Peña, 2013). The most outstanding physical properties are ductility, malleability, high density, and corrosion resistance (Yang & Reddy, 2014).

This metal was one of the first materials processed by humans since 3500 BC. The previously described properties of lead are the main reason for its commercial relevance and various applications such as the manufacture of alloys, pigments, ammunition, and gasoline additives (Kreusch et al., 2007). However, the application of greatest interest is in the manufacture of electrodes for automotive batteries.

The estimated amount of lead produced exceeds 9 million tons per year from which 86% is destined to the manufacture of electrodes for Lead-Acid Batteries (J. Pan et al., 2012). These batteries are the primary source of power that starts vehicle engines. In this type of battery, sponge Pb and slurry-like PbO₂ act as anode and cathode respectively. During discharge, both electrodes are transformed to Pb₂SO₄.

Despite being an essential device, these batteries could also represent an important hazard due to their toxic components including lead itself as well as sulfuric acid (Liao et al., 2016). Every year, 100 million batteries run out and cannot be easily disposed of on common garbage dumps or sanitary landfills. That's the main reason why more than 90% of them need to be recycled (Veloz, 2018). Over half of the lead produced in the world comes from secondary sources whose processes consume less energy than the primary extraction from ores (mainly galena rich PbS). However, they are not exempt from having an intense environmental impact (Smaniotto et al., 2009). According to Pure Earth, (2016), Lead-Acid Battery Recycling is listed as one of the top ten most polluting industrial processes.

1.2 Automotive Battery Recycling Process

The recycling process can be defined as the transformation of waste, within a production process, for its initial purpose or for other purposes. It usually has a positive impact because it protects the environment and reduces carbon emissions. This type of gaseous emissions is the main cause for greenhouse effect and global warming. Recycled materials such as spent automotive batteries provide a more sustainable alternative than mining lead from natural resources or ores (Institute of Scrap Recycling Industry, 2022).

For materials such as batteries, the recycling process consists of three main stages:

- Dismantling: selective disassembly, targeting the mechanical separation of different components, especially safe from hazardous, or valuable from non-valuable.
- Upgrading: using mechanical, physical, and metallurgical processing to obtain lead before refining.
- Refining: final treatment of the recovered metal so it can return to its life cycle.

(Cui & Forssberg, 2003).

Wasted batteries are usually collected from industrial economy through reverse distribution channel principally after car dismantling on local auto-shops and garages (Ellis & Mirza, 2010). Industrial plants that recycle lead from batteries

generally operate through pyrometallurgical extraction. This process involves the manual opening of battery caps to extract electrolyte (H₂SO₄) through physical decantation, which is then stored in a collection tank and neutralized with the use of calcium carbonate CaCO₃. Once the acid has been separated from the batteries, the casings are cracked-open to remove the lead electrodes and paste that are accumulated in separate containers for later management. Polypropylene cases are rinsed off and isolated before being sent to waste managers or plastic recycling industries (Veloz, 2018). Finally, the metallic residues are placed on metallurgical furnaces where carbon-based reduction occurs aided by fluxing and slagging agents (Santacruz Torres & Torres Agredo, 2019).

1.3 Secondary lead slag

For every ton of lead produced, 300 to 350 kilograms of slag are generated (Kreusch et al., 2007) and stacked in the open air lacking proper treatments (Sun et al., 2020). This residue is a by-product whose composition depends on the operating variables such as: furnace temperature, heat transfer efficiency and atmospheric pressure, as well as the additives that are incorporated into the mixture. Fluxing agents are intended to lower the melting point, reduce lead and separate it from the other components that end up composing the slag. (Santacruz Torres & Torres Agredo, 2019).

The typical chemical composition of secondary slag has been described by D. Pan et al., (2019) as following: 20.1-55.7% of Fe; 1.3-22.4% of Ca; 2.6-20.6% of Si; 0.1-1.1% of Zn; 1.1-21.9% of Pb; 0.3-1.3% of Cu and 0.5-20.5% of S.

Also, the major compounds have been determined through X-Ray Diffraction by (Kim et al., 2017) who found high concentrations of iron complexes like wustite (FeO), pyrrhotite (FeS) and minor quantities of fayalite (Fe₂SiO₄). Abundant concentrations of erdite (NaFeS₂·2H₂O) have also been discovered (Lassin et al., 2007). Lead was encountered as traces of galena (PbS), anglesite (PbSO₄), litharge (PbO) and metallic Pb (Gomes et al., 2011).

Since the presence of heavy metals (Fe, Zn, Pb) in the slag is unavoidable, many organizations such as the Environmental Protection Agency have classified these residues as subject to control and monitoring. According to Ecuadorian's national environmental law: Acuerdo Ministerial 142 (Ministerio del Ambiente, 2012) lead smelting slag is catalogued as a hazardous waste by specific source and toxic elements must be kept under the permissible limits given internationally by the CODE OF FEDERAL REGULATIONS, (CFR Title- 40), Subpart C or the NOM-052-SEMARNAT-2005 (Norma Oficial Mexicana, 2005).

Despite extensive reprocessing attempts, some lead will always remain in the residue. Being a toxic and persistent metal in the environment, it is considered a contamination factor for air, soil, and water (Santacruz Torres & Torres Agredo, 2019). Small particles can be carried by the wind, damaging the quality of the air and surroundings where this dust get deposited (Karali et al., 2020). The soil where the slag

is discharged suffer the penetration of the contaminant, which is also spread through rain and other processes towards groundwater and surface water. On human beings, continuous exposure to this metal can be prejudicial for health, leading to kidney, liver, and nervous system failure. In addition, lead can infiltrate plant roots, making its way up to the food chain and posing a threat to all forms of life (Matlock et al., 2002).

The large amount of slag produced introduces heavy metals into the environment and represents a significant loss of resources. For this reason, it is essential to seek sustainable alternatives to recover the lead stored in the slag, while simultaneously decontaminating it for a safe final disposal.

1.4 Stabilization/Solidification processes for lead slag

Most studies focus on developing stabilization/solidification (S/S) processes that seek physical encapsulation of the slag within building materials such as geopolymers, concrete aggregates, asphalt mixtures, refractories and ceramics (Sun et al., 2020). The objective of stabilization/solidification is to reduce the chemical reactivity of the slag while taking advantage of its mechanical properties. However, there's still risk of natural leaching of toxic elements which highlights the need of removing heavy metals initially. Even though lead presents a low leaching rate in weak acid environment, long term exposure to water can lead to a significant release of this element (D. Pan et al., 2019).

Sun et al., (2020), managed to enhance the stabilization/solidification process of lead slag within geopolymers through microwave irradiation. The investigators were able of shortening the polymerization period from 28 days to 15 minutes achieving an optimum compressive strength of 18.8 MPA and an s/s efficiency of 98.7%. Another attempt of giving slag a practical use was in the fabrication of ceramic bricks. The results of the study showed the feasibility of replacing 15% of clay with slag improving the resistance to compression of the brick pieces. The partial immobilization of lead, arsenic and selenium was also achieved (Santacruz Torres & Torres Agredo, 2019).

With the same lead slag that was investigated in this study, corresponding to a local automotive battery factory, that will be referred to as Sample 1, a previous study was developed by Veloz, (2018). The aim was to determine the feasibility of incorporating it into an asphalt mix. The author determined that this material presents a very high percentage of water absorption which makes it difficult for the homogeneous mixture to be compacted. Nevertheless, the modified mixture presented an increase of 30% in stability improving the overall mechanical properties and resistance.

The prior removal of heavy metals from secondary lead slag could improve its quality and saleability expanding its applications and diminishing disposal costs (Lupi & Pescetelli, 2008).

1.5 Typical lead extraction processes and disadvantages

There are three extraction routes in which the recovery of lead has been studied. First, pyrometallurgy, that is, reprocessing within smelting furnaces. But a larger volume of slag is generated, and energy consumption does not make it economically viable. Also, given the great presence of sulfides on the secondary slag, pyrometallurgical reprocessing may be unsuitable for lead recuperation (D. Pan et al., 2019).

The second route involves bioleaching, which consists of using degrading microorganisms to convert metal compounds into recoverable, soluble, and extractable forms (Pollmann et al., 2018). Cheng et al., (2009) managed to recover up to 80% of Al, As, Cu, Mn, Fe and Zn from Pb/Zn smelting slag taking advantage of the metabolic activity of moderate-thermophilic bacteria (Gammaproteobacteria and Betaproteobacteria). Unfortunately, these type of processes are still currently limited to laboratory scale (D. Pan et al., 2019).

Finally, there's hydrometallurgy, where leachants are used to dissolve metal compounds, which are then recovered by electrodeposition or solvent extraction.

Lead from a slag sample can be dissolved by concentrated acetic acid with 95% of efficiency. This solvent demonstrated an elevated selectivity towards lead instead of iron. The optimal conditions for this process were $T=25$ oC, $t=2$ h and $L/S= 20$ ml.g⁻¹. Sulfuric acid is then added for the recovery and precipitation of PbSO₄, but this method wouldn't be suitable for secondary slag as it can only recover lead in a reduced state (Forte et al., 2017). Other leaching agent studied involves a mixture of HNO₃-NaCl which can transform lead from slag into the form of [PbCl₄]²⁻. These ions are then converted to PbC₂O₄ by the addition of sodium oxalate. Lead oxide powder can be later obtained via calcination (Shu et al., 2015), but this means that the process isn't entirely hydrometallurgical.

The typical route for the recovery of lead from battery scraps involves leaching with ammonium carbonate (NH₄)₂CO₃ and ammonium bisulfite NH₄HSO₃ in order to transform sulfates (PbSO₄) and dioxides (PbO₂) into lead carbonates (PbCO₃). These carbonates precipitate in the form of a sludge which is then leached with hydrofluorosilicic acid H₂SiF₆. It has been shown that by carrying out an electrowinning process in this solvent and by adding a small amount of phosphorus, it was possible to prevent the formation of lead dioxides at the anode. Almost 99% of antimony-free lead was recovered at the cathode (Cole et al., 1985).

Unfortunately, the most frequently used solvents on hydrometallurgy are not environmentally friendly and have a certain degree of toxicity.

1.6 Ionic Liquids and its applications

Recently, a branch known as ion metallurgy has been developed where solvents are replaced by ionic liquids (IL) and molten salts (Abbott, Capper, Davies, et al., 2006). Ionic

liquids are usually defined as compounds completely composed of ions with a hybrid organic-ionic nature and melting points below 100 °C. There are numerous combinations of cations and anions whose diverse behaviors can be useful for multiple applications in chemical engineering, materials science and environmental science (Lei et al., 2017).

Preliminary studies have shown the potential of ILs as solvents for the extraction of gold and silver in minerals (Whitehead et al., 2004), also for uranium and plutonium in spent nuclear fuel (Abbott, Capper, Davies, et al., 2006). In the case of lead, Tan et al., (2021), evaluated the use of N,N,N-Dimethylbutylammonium Methanesulfonate to extract and act as an electrolyte for the deposition of Pb from lead-acid batteries in the form of Pb²⁺ from PbCO₃. The electrochemical kinetics of lead's reduction showed fast deposition and the possibility of up-scaling the electrowinning process in industry (Tan et al., 2021).

The disadvantages of ILs are their high cost, low availability, sensitivity to moisture, and the requirement of an inert environment for the electrodeposition (Yang & Reddy, 2014).

1.7 Deep Eutectic Solvents

As an alternative, Deep Eutectic Solvents (DES) have begun to be studied, whose dissolution properties are similar to IL's, but by not being hygroscopic makes them easier to synthesize and use (Yang & Reddy, 2014). The main reason why DES are not considered within the IL group is because they are not entirely composed of ionic species and they can also be obtained from non-ionic species (Zhang et al., 2012).

A DES is usually composed of two or three components on a certain proportion capable of associating with each other through hydrogen bond interaction forming eutectic mixtures. They are characterized by a melting point lower than that of each individual component, between 70 and 150 °C (Zhang et al., 2012). Most of them consist of quaternary ammonium salts whose freezing point is lowered by complexing the anion with a hydrogen bond donor for effective charge delocalization (Abbott, Capper, Davies, et al., 2006).

There are four types of Deep Eutectic Solvents described in literature:

- Type 1: quaternary ammonium salt + metal halide (not considered environmentally friendly)
- Type 2: quaternary ammonium salt + hydrated metal halides (considered costly)
- Type 3: quaternary ammonium salt + hydrogen bond compound (most frequently used)
- Type 4: Metal halide + Lewis acid or Brønsted base (Zhang et al., 2012)

Most of the compounds that put together DES are safe, biodegradable, and increasingly available (Abbott, Capper, et al., 2007). The main characteristics of deep eutectic solvents can be listed as the following: elevated viscosity, high surface

tension (Abbott, Capper, Davies, et al., 2006), low melting points, solubility and chemical inertness in water and relative easiness to synthesize (Ru, Hua, Xu, Li, Li, Wang, Qi, et al., 2015), they are also safe, stable, non-volatile and non-flammable (Zhang et al., 2012).

DES can donate or accept electrons or protons to form hydrogen bonds, which confers them an anionic character and excellent dissolution capacities. They can be tunable for specific physical or chemical requirements by using different hydrogen bond donors or mixtures depending on the metal of interest. The working principle of DES consists of the available protons acting as oxygen acceptors and breaking the metal-oxygen bonds. Once the oxide is protonated, intermediate species are formed and can act as active sites for ligand complexation (Pateli et al., 2020). Another theory has been described where oxygen remains attached to the metal center and the hydrogen bond donors act as a ligands (Abbott et al., 2005).

Solubility can be influenced by pH. More acidic DES are better solvents because of a higher H⁺ activity. However, the solubility is also influenced by the Gibbs energy, formation energy and lattice energy of the metal oxide that must be overcome. Other factors such as changes in speciation and coordination number of the metal cation in the produced intermediate compound also affect solubility (Pateli et al., 2020). Temperature can also be considered as a solubility factor because as it increases, pH decreases linearly (Jančíková et al., 2022). High temperature also diminishes viscosity of the solvent which can elevate the reaction rate as well as the mobility of species (Zhang et al., 2012).

Typically, the quaternary ammonium salt that is used for the preparation of deep eutectic solvents is Choline Chloride (C₃H₁₄ClNO), which can be expressed with the abbreviation ChCl. This abundant, inexpensive and safe compound can be either extracted from biomass or synthesized from fossil reserves (Zhang et al., 2012). The hydrogen bond compounds that will be investigated in the present study are Urea and renewable polyols such as Ethylene Glycol and Glycerol. ChCl-Urea is also known as reline, ChCl-Ethylene Glycol is known as ethaline and ChCl-Glycerol goes by the name of glyceline. The selected DES's physical properties are summarized in Table 1.

1.7.1 Application of Deep Eutectic Solvents

Reline, ethaline and glyceline have been tested as possible leaching agents for the processing of an Ecuadorian polymetallic concentrate coming from Portovelo. This material was mainly composed by Cu, Fe, Pb sulfides and metal oxides. Lead content of the sample was found at 8,5% mostly in the form of anglesite (PbSO₄). The leaching of metals was increased over time performing assays from 1 to 24 h and high lead recovery values were obtained: 95% in reline, 96% in ethaline and 93% in glyceline. According to the author, these results were related to the form in which lead appeared in the concentrate (PbSO₄).

Table 1. Physical properties of DES

DES	Viscosity (cP)	Density (ρ , g.cm ⁻³)	pH	Conductivity (k , mS.cm ⁻¹)	Freezing Point (°C)	Reference
Reline (ChCl-Urea)	750 (at 25 °C)	1.24 (at 25 °C)	10.387	0.20 (at 40 °C)	12	(Abbott et al., 2003), (Abbott, Capper, & Gray, 2006), (Mjalli & Ahmed, 2016)
Ethaline (ChCl-Ethylene Glycol)	52 (at 20 °C)	1.14 (at 20 °C)	4.676	6.17 (at 20 °C)	-66	(Shahbaz et al., 2012), (Abbott, Harris, et al., 2007), (Mjalli & Ahmed, 2016)
Glyceline (ChCl-Glycerol)	376 (at 20 °C)	1.19 (at 20 °C)	7.543	2.03 (at 20 °C)	-40	(Shahbaz et al., 2012), (Abbott, Harris, et al., 2007), (Mjalli & Ahmed, 2017)

However, different deep eutectic solvents are more likely to solubilize lead from different compounds. For instance, reline proved more efficient on oxides or sulfurs while ethaline worked better on sulfates. On the other hand, glyceline presented a similar behavior for various carrier sources. The ChCl-based DES achieved better recoveries on lead than other metals: zinc (40%), copper (30%) and iron (10%). Selectivity of DES towards lead could make them interesting for its application in other Pb-rich materials (Aragón Tobar, 2022).

Another study demonstrated that the ChCl-Urea system is applicable to the following lead compounds: PbSO₄, PbO₂ and PbO, all presenting similar solubility and electrochemical behavior (Liao et al., 2016). A group of investigators demonstrated the possibility of producing lead powders with specific morphologies and sizes by performing electrodeposition in reline. Rods, wires, needles, and dendritic shapes were formed by varying the concentration of PbO in the solution (Ru, et al., 2015). A similar study was performed employing ethaline to verify the dissolution-electrodeposition pathway and bulk porosity of in situ electrochemical reduction of PbO. When adding an amount of NH₄HCO₃ a faster diffusion of ions and a higher solubility was obtained favoring the posterior deposition process (Ru et al., 2016).

1.8 Lead recovery through electrowinning processes.

Electrowinning involves electrolytic deposition. It is the conventional process of coating a thin layer of the desired metal on top of a different metal (cathode) using electrical current to reduce cations from an electrolyte (leach solution). Then, the deposited metal dust can be mechanically removed from the cathode and smelted easily into a more usable form. In order to negatively charge the cathode, positive electrodes (anodes) are placed on solution where the excess of anions are exchanged by electrons moving towards the cathode (Smith & Means, 1994).

In the case of Pb from spent acid batteries, Xing et al., (2019) managed to produce lead powders with a purity of 99,6% via electrowinning. To achieve this, researchers applied CaCl₂ in solution as a leaching agent with ferrous ion as a reducing agent. Leaching conditions were T=90 °C, pH=1, t=2h and stirring=500 rpm. The appropriate minimum Pb concentration and the optimum current density were determined to be 10 g. L⁻¹ and 200 A.m² respectively. Given that chloride also acts as the anion for various selected DES a recovery path similar to this study can be potentially investigated.

Despite the fact that very little information has been found regarding the electrowinning of Pb from DES, there are studies where deep eutectic solvents have been applied in the electrolytic recovery of other metals. One example is the application of reline for the dissolution and electrowinning of zinc from electric arc furnace dust. Using cyclic voltammetry, cathodic sweeps were performed, where two deposition peaks were found, one at -0.46 V corresponding to lead and another at -1.56 V corresponding to zinc. These results were confirmed when the zinc electrodeposit was characterized because it presented an elevated content of lead impurities. The author concluded that the decontamination of the dust was possible and that the impure zinc-lead obtained could still have an application within the alloy industry (Bakkar, 2014).

Most of the research in this area focuses on analyzing the electrochemical behavior of lead deposition from the eutectic solvents using pure reagents. The application of choline-chloride-based solvents in complex matrices such as secondary lead slag has been little explored.

In the present study, the feasibility of employing DES to dissolve lead from battery slag was analyzed. The slag characterization was carried out in order to determine the concentration and chemical forms in which lead is found. To optimize this process, the best experimental conditions were established such as sample type, temperature, time, pulp concentration and pressure application. Also, a preliminary electrowinning assay was tested to evaluate this possible recovery path.

2. EXPERIMENTAL

2.1 Sampling

Three samples of battery slags were provided from the stockpiles of a local automotive battery factory located in Quito, Ecuador. This samples (5 kg each) were transported to the laboratory for proper homogenization and size reduction.

Sample 1 corresponds to the slag that leaves the process directly to the pile without any type of treatment. Sample 2 was treated on site with lime solution for neutralization and Sample 3 had the same treatment as Sample 2 but was also left to dry and oxidize in the stockpile for a period of 6 months.

2.2 Sample Preparation

Initial sample preparation consisted of homogenization, crushing, drying, and grinding (<100 µm). Representative portions of 500 g were taken for the corresponding physical, chemical and mineralogical analyses.

For the leaching assays, samples had to be washed with hot distilled water to minimize the presence of soluble species that could saturate the deep eutectic solvents. Roasting at 300 °C, below the melting point of lead 327.4 °C (Haynes et al., 2017) was intended for its transformation into oxides (PbO, PbO₂), as well as sulfates (PbSO₄). According to literature, these are the most soluble forms of lead in the deep eutectic solvents (Liao et al., 2016).

2.3 Sample Characterization

Water content was analyzed through conventional stove drying method. Samples were dried on the stove (BINDER, FD 115) for 2 h at 105 °C and the weight difference between container with wet sample and dry sample was determined using an analytical balance (SARTORIUS, CPA42025) with a resolution of 0.01 g. Loss in ignition, as well as the ash content were analyzed via calcination. Samples were placed on a muffle furnace (SNOL, 8.2) for 3-6 h at 950 °C and the weight difference between the tared crucible with uncalcinated sample and calcinated sample was determined using an analytical balance with a resolution of 0.0001 g (KERN, ARJ 220-4M). For pH and conductivity analysis, 2:1 extracts with deionized water were prepared by agitating for 1 hour and centrifuging for 2 minutes at 1500 rpm. The measurements were made by immersing calibrated electrodes of a pHmeter (inoLAB pH/ION Level 2) and a conductivitymeter (inoLAB Cond Level 2) into the obtained extracts. It was important to perform such analysis in order to determine the influence of these parameters on lead dissolution. Finally, density was measured by relating the weight of the samples with its occupied volume within a graduated cylinder.

Elemental analyses were performed through X-Ray Fluorescence (Bruker S8 Tiger unit with Spectra Plus program) in order to determine the percentage of lead and other abundant elements on the slag. Pressed tablets were prepared using 9 g of each sample with 1 g of a binder. To analyze possible crystalline phases, the X-Ray Diffraction technique was applied (D8 Advance). In this case, samples were prepared by regrinding small portions on an agate mortar. The qualitative and semi-quantitative analysis of the obtained diffractograms were carried out with the assistance of the EVA program and the TOPAS software. The objective of these tests was to find the concentration and mineralogical phases in which Pb is present, as well as other elements that could possibly interfere with the leaching of lead.

In addition, full scan analysis of TCLP extracts (Toxicity Characteristic Leaching Procedure) were carried out by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) (Agilent, 7850) to evaluate the possible toxicity of the leachates when simulating the worst probable natural

conditions. This analysis allowed to determine the mobility of any hazardous elements that could be present on the slag samples. The procedure employed to prepare leachates is described by reference method EPA 1311.

2.4 Deep Eutectic Solvent Synthesis

Deep eutectic solvents were prepared based on Choline Chloride systems (98+%, Sigma Aldrich) in a 1:2 molar ratio with three hydrogen bond donors: Anhydrous urea for reline, Ethylene glycol (99% Sigma Aldrich) for ethaline and Glycerin (99,5% Fischer Scientific) for glyceline. The mixed reagents were heated on a beaker, and continuously stirred at 80 °C for 2 hours until transparent liquids were obtained. Iodine (Baker) was added to the solvents (1 M) to maximize the oxidizing effect. Jenkin et al., (2016) proved that the use of this oxidizing agent can selectively increase the recovery of certain metals.

2.5 Conventional Leaching Assays

A weighted amount of sample was added to each deep eutectic solvent container. Then, each flask was placed in water baths with magnetic stirring at 470 rpm. After the necessary time had elapsed, aliquots were taken to measure the lead concentration through atomic absorption (Perkin Elmer AA 300). To determine better leaching conditions, assays were repeated at different temperatures, time periods and pulp concentrations.

2.6 Pressure Leaching Assays

Pressure leaching or hydrothermal leaching is conventionally used to operate at temperatures above regular boiling point, increasing the reaction rates and the selectivity for the metals of interest (Berezowsky et al., 1991).

A weighted amount of sample with a specific volume of each deep eutectic solvent was added to hydrothermal reactors and introduced into a stove for a period of 24 hours. Then, aliquots were taken for the measurement of lead concentration through atomic absorption in order to determine the influence of pressure on the leaching process. Different tests were carried out setting the stove temperature at 90 and 120 °C.

2.7 Electrowinning Assay

For the electrowinning test a volume of 100 mL of lead leachate was prepared based on the best previously determined conditions of time, temperature, type of sample, and DES. Vacuum filtration was required in order to remove solids (0.45 µm). Then, taking advantage of its solubility, a 20:80 leachate-water solution was prepared and poured into an electrolytic cell. The objective of diluting the leachate in water was to reduce its viscosity and to favor the electrowinning process. Inside the cell, a stainless-steel cathode was placed between two carbon graphite anodes and an electric current of 4.32 V was allowed to pass between the electrodes with an amperage of 0.1 A. The electric current condition was the same as the one employed on the typical electrowinning route for lead from hydrofluorosilicic acid (Cole et al., 1985).

Every 15 min of the electrowinning process, aliquots of the leachate were collected in order to measure the loss in lead concentration by atomic absorption spectrometry. The lead content was also measured in the sludge residue that precipitated to the bottom of the electrolytic cell. A series of calculations were used to account for the distribution of lead throughout the process and also to determine the final recovery percentage.

3. RESULTS AND DISCUSSION

3.1 Sample characterization

In the development of this research, three different samples were investigated. All samples received the same treatment prior to lixiviation: hot water washes and roasting at 300 °C. Table 2 shows the comparison between the physical and chemical properties of the samples with this treatment and without it.

Every sample shows a considerable decrease on its pH values after pretreatment, perhaps due to the partial calcination of basic components added as fluxing and neutralizing agents during the pyrometallurgical process. Sample 1 presented the lowest pH value of 2.87 after thermal treatment. This was an expected result given that no neutralizing agent was added to this slag portion on the recycling plant. On both samples 2 and 3, sodium and calcium bicarbonates had been incorporated as an environmental measure for neutralizing the slag of the stockpiles, resulting in elevated pH values. Since deep eutectic solvents have higher solubility for metal oxides on acidic medium, it can be expected that a higher lead quantity will be leached when treating sample 1. On lower pH, the concentration of H⁺ ions increase, and these protons can act as O²⁻ acceptors breaking the metal-oxide bonds and driving the solubilization process forward (Pateli et al., 2020).

Conductivity of all samples was similar around 94 mS.cm⁻¹ lowering to 24 mS.cm⁻¹ after pretreatment. The decrease in conductivity is explained by the hot deionized water washes which were able to remove a considerable portion of the

soluble components present in the slag samples. Fortunately, lead oxides and sulfates have negligible or inexistent solubility on water. It can be implied that the overall leaching process will be optimized since the deep eutectic solvents won't be saturated with different cations aside of lead.

Moisture content of sample 1 was the lowest because no liquid agents were added. Sample 2 presented the highest moisture content of 18.32% by being the freshest sample treated with lime milk. Sample 3 was also treated with lime milk but most of the water must have been lost by drying in the pile exposed to ambient conditions during a period of six months.

As far as the ash content and the loss for ignition analysis can tell the three slag samples are mainly constituted by inorganic and non-volatile components (>80%). This was later verified through the elemental and compound analysis performed through X-ray Fluorescence and X-ray Diffraction.

The elemental analysis presented in Table 3 is consistent with the typical composition for this type of slag reported in literature which is characterized by a CaO-FeO-SiO₂ system (Gregurek et al., 2015).

Even though the metal of interest which is lead can be found in percentages between 1.9% and 5.4% (for treated samples), the most abundant element present was iron with concentrations between 24.1% and 26.3%. The presence of iron comes from ironstone which is added during the smelting process to displace lead from sulfides, releasing it on a reduced state. Sulfur comes from the PbSO₄ and PbS wasted electrodes as well as the remaining sulfuric acid from the used batteries (9.6-10.3%). Calcium and sodium are usually added to the process in the form of CaO, NaCO₃ or Na₂B₄O₇ as typical fluxing agents capable of lowering the melting temperature and transporting unwanted metal oxides to the slag. Finally, aluminum and silicon are components of sand which is also incorporated to the mix in order to fix impurities in the calcium/sodium silicate matrix of the slag (D. Pan et al., 2019)

Table 2. Characterization of the slag samples before and after pre-treatment (hot water washes and roasting).

	Sample 1		Sample 2		Sample 3	
	Before Treatment	After Treatment (Water washes and 300 °C roasting)	Before Treatment	After Treatment (Water washes and 300 °C roasting)	Before Treatment	After Treatment (Water washes and 300 °C roasting)
pH	8.53	2.87	9.85	4.81	9.96	3.70
Conductivity (mS.cm ⁻¹)	94.57	23.43	94.17	26.67	93.63	24.00
Moisture Content (%)	3.49		18.32		9.28	
Ash Content (%)	95.34		81.52		88.79	
Loss in ignition (%)	0.043		0.063		0.038	
Density (Kg.m ⁻³)	1251.6	1355.8	990.7	1356.8	1127.0	1218.9

Table 3. X-Ray Fluorescence analysis of the slag samples before and after pre-treatment (hot water washes and roasting).

Element	Sample 1		Sample 2		Sample 3	
	Before Treatment (%)	After Treatment (Water washes and 300 °C roasting) (%)	Before Treatment (%)	After Treatment (Water washes and 300 °C roasting) (%)	Before Treatment (%)	After Treatment (Water washes and 300 °C roasting) (%)
Fe	25.1	26.3	23.7	24.6	21.6	24.1
S	11.1	9.6	9.7	9.7	10.9	10.3
Na	10.8	11.7	10.5	11.7	11.9	15.3
Pb	3.6	5.4	3.5	4.5	0.9	1.9
Si	1.9	2.1	2.4	2.4	1.8	2.1
Al	0.6	0.8	0.9	0.9	0.7	0.8
Ca	0.5	0.6	0.5	0.6	0.4	0.5
Ba	0.4	0.3	0.4	0.4	0.4	0.4
Sn	0.3	0.3	0.3	0.4	0.2	0.2

According to Zhang et al., (2012) aluminum and silicon oxides (Al_2O_3 , SiO_2) are insoluble in deep eutectic solvents, whereas calcium oxide barely has a solubility of 6 ppm on reline (Abbott et al., 2005). These compounds will fortunately not act as interferences in the leaching process. Given that choline chloride systems are selective for metallic elements, it can be inferred that silicon and sulfur won't interfere with lead solubilization. Iron oxides are the only compounds that can provide a significant impact on the leaching of lead by also being solubilized in the deep eutectic solvents. In the case of reline, Fe_2O_3 has an experimental solubility of 49 ppm, and Fe_3O_4 of 40 ppm. However, the solubility of lead oxide PbO_2 is considerably higher at 9157 ppm (Abbott et al., 2005). It is important to mention that PbO and $PbSO_4$ have proven to behave similarly to PbO_2 (Liao et al., 2016).

Given the amount of amorphous material present in the samples, no compounds could be recognized in a preliminary XRD analysis. By calcinating the samples above 950 °C it was possible to identify and quantify certain minerals listed in Table 4.

Table 4. X-Ray diffraction analysis of the slag samples calcinated over 950 °C.

Name	Compound	Sample 1 (%)	Sample 2 (%)	Sample 3 (%)
Hematite	Fe_2O_3	58	53	60
Thenardite	Na_2SO_4	30	36	36
Anglesite	$PbSO_4$	10	5	<1
Maghemite	Fe_2O_3	<1	4	2
Plagioclase Group	$(Na,Ca)Al(Si,Al)Si_2O_8$	2	2	2

All samples presented hematite (Fe_2O_3) as its most abundant component. This result agrees with the one obtained by FRX analysis where elevated concentrations of iron were demonstrated. Hematite and other iron oxides such as maghemite have significant solubilities on DES, meaning that they could possibly interfere with the lixiviation of lead. Nevertheless, iron may be present in other forms when samples are not calcinated. Wustite (FeO) and pyrrhotite (FeS) are some examples of other possible iron compounds that could be found on secondary

lead slag (Lassin et al., 2007). Sulfur and sodium were also abundant elements that were discovered in the form of sulfates such as thenardite (Na_2SO_4) and anglesite ($PbSO_4$). In agreement with previous studies, lead was found in the form of anglesite, fortunately one of the most soluble forms on DES (Liao et al., 2016). If lead is also present in the form of sulfate during leaching tests, elevated recovery results could be expected. Finally, it can be inferred that the plagioclase groups found on the slag samples come from the sand incorporated to the mix during the pyrometallurgical processing which was previously discussed.

Full scan ICP-MS analysis were performed on TCLP extracts from the three untreated slag samples. The reference method EPA 1311 procedure was used so that the results could be compared to the CFR Title- 40 regulation. Elements that leached with a concentration of 0.1 $mg.L^{-1}$ or more are listed in Table 5.

Table 5. ICP-MS Elemental Analysis of TCLP leachates of the untreated slag samples.

Element	Sample 1 ($mg.L^{-1}$)	Sample 2 ($mg.L^{-1}$)	Sample 3 ($mg.L^{-1}$)
S	4217.0	4094.0	15782.0
Ca	185.0	189.0	69.0
Fe	136.0	82.0	<0.1
Pb	26.0	14.0	7.0
Si	24.0	44.0	8.2
K	22.0	26.0	19.0
Mg	10.0	15.0	0.9
Mn	9.8	5.6	0.7
B	2.2	2.8	0.3
Zn	2.6	1.6	<0.1
Ni	1.3	1.5	<0.1

Note: The values corresponding to sulfur are considered referential since they exceed the application range of the method.

Even though Sample 3 presented the highest concentration of sulfur 15782.0 $mg.L^{-1}$, it mobilized the least amount of metals. It presented almost a third part of calcium and much lower values of lead, magnesium, and manganese in relation to the other samples. These results show that the oxidation of the slag contributed to the stabilization of the elements within the

silicate matrix. However, this sample cannot be considered safe since, like the others, surpasses the permissible limit for lead which is $\geq 5 \text{ mg.L}^{-1}$. Sample 2 mobilized higher quantities of elements compatible with a basic pH medium such as calcium, magnesium, and potassium. This can be explained by the fresh lime milk that was poured on the stockpile. Finally, sample 1 proved to be the most hazardous for the environment given the elevated concentration of lead in its leachate (26.0 mg.L^{-1}). It exceeds twice that of sample 2, triples that of sample 3 and five times the permissible limit of regulations. This is due to the affinity of lead for the acidic medium. Despite being the worst possible source of contamination, sample 1 may be more suitable for the leaching process with deep eutectic solvents due to the abundance of lead and the excess of H^+ ions.

Once again, the importance of decontaminating secondary slag waste has been demonstrated so that earthly resources are not threatened by the natural leaching of lead. The prior removal of lead is essential so that the battery recycling company complies with the regulations and permissible limits.

3.2 Conventional leaching assays

Figures 1, 2 and 3 show the combined effect of temperature and lixiviation time for lead from the three samples on three DES: ethaline, glyceline and reline. These assays were carried out at three different temperatures (30, 60 and 90 °C) during a period of 8 hours. Pulp concentration of 2% (low viscosity required) and magnetic stirring of 470 rpm was maintained constant for all these tests. Aliquots were taken every hour to carry out the analysis of dissolved lead by AAS

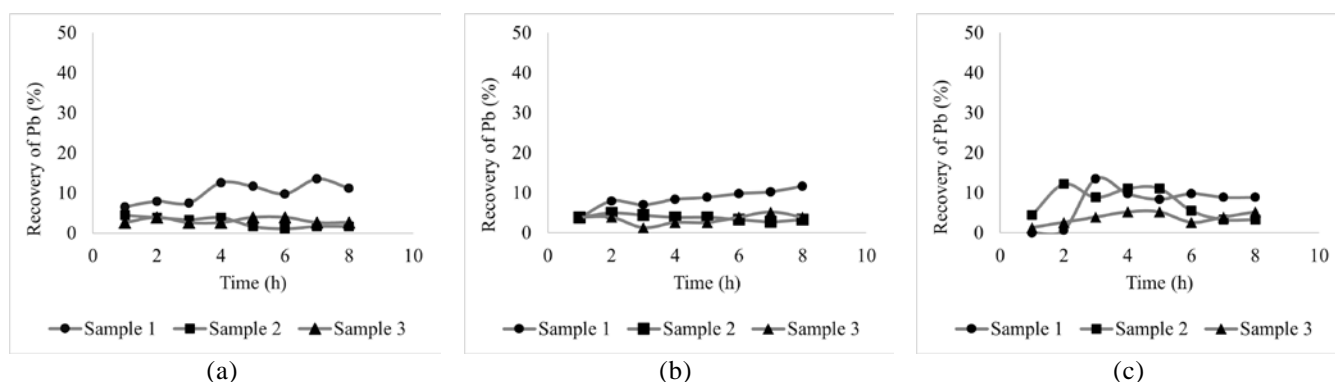


Figure 1. Leaching recovery of Pb (%) from the three different lead slag samples by lixiviation at 30 °C employing different deep eutectic solvents: (a) Ethaline, (b) Glyceline, (c) Reline. Percentage of solids = 2%.

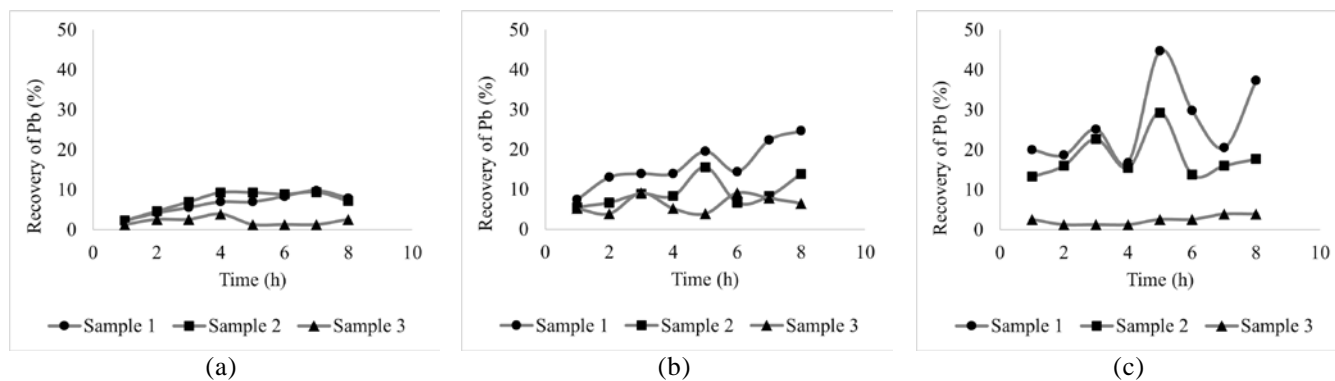


Figure 2. Leaching recovery of Pb (%) from the three different lead slag samples by lixiviation at 60 °C employing different deep eutectic solvents: (a) Ethaline, (b) Glyceline, (c) Reline. Percentage of solids = 2%.

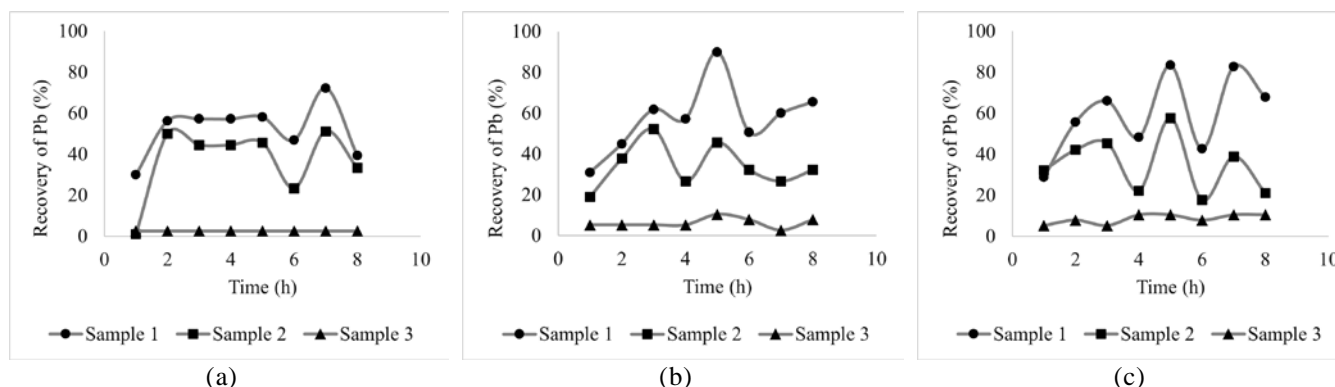


Figure 3. Leaching recovery of Pb (%) from the three different lead slag samples by lixiviation at 90 °C employing different deep eutectic solvents: (a) Ethaline, (b) Glyceline, (c) Reline. Percentage of solids = 2%.

At 30 °C, lead leaching recovery did not exceed 14% because the temperature wasn't high enough to induce mobility of species and decrease the viscosity of the solvents (Zhang et al., 2012). On ethaline, Figure 1 (a), samples 2 and 3 maintained a constant leaching recovery between 1.1% and 4.4% without showing any upward trend. On the other hand, sample 1 started with a value of 6.5% reaching a maximum of 13.5% after 7 hours of lixiviation. In the case of glyceline, Figure 1 (b), the leaching recovery of samples 2 and 3 remained below 5.2%, but sample 1 presented a clear ascending trend throughout the assay, reaching a leaching yield of 11.6% after 8 hours. And finally, employing reline as a solvent, it can be seen on Figure 1 (c) that the process did not present any clear trends. Unlike the other solvents, the leaching recovery on reline was a bit higher for sample 2, which after just 2 hours of lixiviation reached a maximum of 12.2% decreasing again at the sixth hour. Sample 1 also rose at the third hour up to 13.5% decreasing again by the fourth hour and remaining constant until the end of the assay. Sample 3 presented the highest resistance to lixiviation in every case. This may be due to the fact that the sample had a lower concentration of lead in relation to the other samples.

By carrying out the test with a temperature of 60 °C, lixiviation of lead on sample 1 could be favored by increasing its concentration on the deep eutectic solvents. Unfortunately, this increase could not be seen for samples 2 and 3. A similar behavior was expected for the three samples on both ethaline and glyceline because their hydrogen bond donors have similar characteristics as polyols. Meanwhile urea that is present in reline is a carbamide characterized by amino groups instead of alcohols. However, the behavior of the samples in glyceline turned out to be more similar to that of reline than of ethaline. Sample 1 presented the highest recovery, around 44.8% after 5 hours reline – Figure 2 (c). Sample 2 also achieved maximum recoveries at 5 hours on glyceline and reline, 15.6% and 29.3% respectively. At this temperature, reline proved to be the most effective deep eutectic solvent.

Finally, 90°C results are presented on Figure 3 with the highest leaching recoveries observed. Also, at this temperature it was possible to better identify optimal

lixiviation times. Sample 3 was the only one that was not favored by an increase in temperature since its recoveries remained the same as at 60 °C. With ethaline, Figure 3 (a), samples 1 and 2 presented similar behaviors, remaining constant between 2 and 5 hours, reaching their maximum recovery at 7 hours and then decreasing considerably again at the eighth hour. These maximum recoveries were 72.2% and 51.2% each. With glyceline, Figure 3 (b), the best recovery of sample 1 was 90.0% at 5 hours and of sample 2 was 52.2% at the second hour. Finally, on reline, Figure 3 (c) the highest lixiviation recoveries were found after 5 hours being 83.4% for sample 1 and 57.6% for sample 2. Both samples presented similar behaviors with constant changes over time.

The most optimal combination between type of sample and solvent was obtained with sample 1 and glyceline after 5 hours of leaching. It can be inferred that lixiviation on sample 1 benefits from its low pH given the larger presence of H⁺ protons. By comparing the behavior between sample 1 (pH = 2.87) and sample 3 (pH = 3.70), the influence of pH on lead lixiviation was confirmed. As the pH increases, leaching is clearly diminished. In addition, it can be deduced that sample 3, when left to oxidize in the environment, was able to transform its chemical composition into more stable and difficult-to-leach components.

In previous studies it has been determined that as the temperature of the solvents increases, the pH also decreases. Also, temperature provides necessary energy for the formation of metal-DES complexes and reduces viscosity of the solvents, elevating the reaction rate as well as the mobility of species (Zhang et al., 2012).

The fact that some of the highest recoveries did not occur at the end of the test, but in the middle of it, can be explained by the loss of moisture that these deep eutectic solvents suffer when temperature increases, and time extends (Aragón Tobar, 2022). This loss of water also represents a loss of H⁺ ions, which decreases their complexing capacity as a consequence. Dehydration can also be the start of a degradation process. This indicates the deviation from the eutectic point that is accompanied by an evident increase in the viscosity of the solvents.

Table 6. Leaching recovery of Pb (%) from sample 1 by lixiviation at 90 °C varying the percentage of solids (1%, 2%, 5%) on the three deep eutectic solvents: Ethaline, Glyceline and Reline.

Sample	Deep Eutectic Solvent	Temperature (°C)	Lixiviation Time (h)	Percentage of Solids (%)	Recovery of Pb (%)
1	Ethaline	90	7	1	52.4
				2	66.6
				5	72.2
	Glyceline	90	5	1	67.2
				2	90.0
				5	95.0
	Reline	90	5	1	75.6
				2	83.4
				5	84.4

To evaluate the influence of the percentage of solids in the lixiviation of lead, sample 1 was used given its elevated recoveries on previous assays. Tests were carried out with the three deep eutectic solvents maintaining the temperature of 90 °C and the best recovery times (7 hours for ethaline and 5 hours for both glyceline and reline). Lead leaching recovery was evaluated when modifying the slag concentration between 1, 2 and 5% and test results are displayed in Table 6.

In every case, lead recovery by lixiviation was gradually favored by an increase in the pulp concentration. By adding 5% of slag to the three solvents, the highest recoveries were obtained (72.2% for ethaline, 95.0% for glyceline and 84.4% for reline). However, as the amount of solids increases, so does the viscosity of the leachate which can generate problems in the subsequent electrowinning test.

3.3 Pressure leaching assays

In order to analyze the influence of pressure on the lixiviation, all of the samples were introduced on hydrothermal reactors with the three DES. The percentage of solids was 2% for all cases. These reactors were placed into a stove for a period of 24 h at a temperature of 90 °C and also at 120 °C.

Hydrothermal reactors are containers designed with certain materials and technology that allows them to withstand high pressure and temperature on the inside. Hydrothermal processing can be defined as any heterogeneous reaction involving a liquid solvent under high pressure and temperature to dissolve and/or recrystallize materials that are relatively insoluble under ordinary conditions (Byrappa & Adschiri, 2007). It is worth mentioning that hydrothermal reactors have a wide range of applications. Just to name a few: the synthesis of advanced nanomaterials applied on solar cells, the production of bio-crude, the conversion of biomass into hydrogen, among others. (Hernandez-Ortiz et al., 2022). However, in current literature there are no extensive records on hydrothermal leaching with DES.

Test results for hydrothermal pressure leaching are displayed in Table 7.

Preliminary tests developed above 150 °C were discarded due to the degradation of the solvents resulting in unfavorable viscous pastes. Those results are in agreement with previous studies where it has been found by means of TGA (thermogravimetric analysis) that the decomposition temperatures of the solvents ethaline, glyceline and reline are 107.5 °C, 183.9 °C and 172.5 °C respectively (Delgado-Mellado et al., 2018). At lower temperatures, the viscosity of the leachates was also increased to a lesser extent. For this reason, aliquots had to be microfiltered before being analyzed by atomic absorption. The recovery percentages in sample 3 were not favored by an increase in pressure. Sample 1 showed better results at 90 °C than at 120 °C,

being 15.4% in ethaline and 22.4% in glyceline. In sample 2, the best recoveries were obtained, being 48.5% at 120 °C in ethaline and 61.4% at 90 °C in glyceline.

These assay results showed little repeatability due to the difficulty involved in controlling the pressure and temperature equilibrium inside of the thermal reactors. Taking this issue into consideration, as well as the fact that the recoveries did not exceed those obtained by conventional leaching, it may not be advisable to scale this procedure to an industrial level.

Table 7. Leaching recovery of Pb (%) by pressure lixiviation of the three samples with the three deep eutectic solvents. (Percentage of solids = 2%).

Sample	Deep Eutectic Solvent	Temperature (°C)	Leaching Recovery of Pb (%)
1	Ethaline	90	15.4
		120	0.0
	Glyceline	90	22.4
		120	14.5
	Reline	90	0.9
		120	3.3
2	Ethaline	90	43.1
		120	48.5
	Glyceline	90	61.4
		120	39.2
	Reline	90	3.4
		120	3.8
3	Ethaline	90	1.4
		120	6.4
	Glyceline	90	9.7
		120	6.3
	Reline	90	0.3
		120	0.0

3.4 Electrowinning assay (EW)

For the electrowinning test, 20 mL of a filtered lead leachate dissolved on 80 mL of water was poured into the electrolytic cell. The leachate was prepared by conventional lixiviation based on the best previously determined conditions: sample 1, DES = glyceline, T = 90 °C, t = 5 h, stirring = 470 rpm, percentage of solids = 5%. In this case, a stainless-steel plate was used as a cathode and the leachate as the electrolyte source of lead cations. In order to negatively charge the stainless-steel electrode, graphite anodes were also immersed in the solution. The ICP-MS analysis for the 20:80 leachate-water solution is shown in Table 8.

Table 8. ICP-MS Elemental Analysis of the electrowinning leachate.

Element	Concentration (mg)
Ba	0.75
Cu	3.00
Mn	1.00
Pb	44.50
Sb	0.20

The absence of iron ($<0.2 \text{ mg.L}^{-1}$) in this leachate indicates that lead deposition won't be interfered. In addition, the amount of lead obtained through ICP-MS (44.5 mg) agreed with the one obtained through atomic absorption (45.8 mg.L).

The stainless-steel cathode was chosen for the electrowinning process because it has an elevated reduction potential (positive). Assuming a high content of iron on its composition, then $E^\circ \approx 0.771 \text{ V}$ (Haynes et al., 2017). Graphite itself does not have a well-defined reduction potential like metal electrodes because graphite is a non-metallic material and doesn't undergo the same type of electrochemical reactions as metals do. On electrolytic cells, graphite is commonly used as inert electrodes where they don't participate in the reactions themselves but instead provide a conductive surface for electron transfer (M.Brashem, Inc, 2023).

The possible half-reactions involved in the electrolytic process are the following:

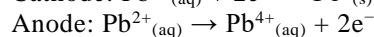
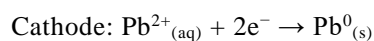


Figure 4 shows a graphical representation of the decrease in lead concentration over time during the electrowinning process. This decline can be explained by the recovery on the cathode, or by the precipitation of the valuable metal towards the anode sludge. Between 60 and 75 minutes, the total lead content remained constant (9 mg). It can be assumed that the maximum recovery had already been reached at this point of time.

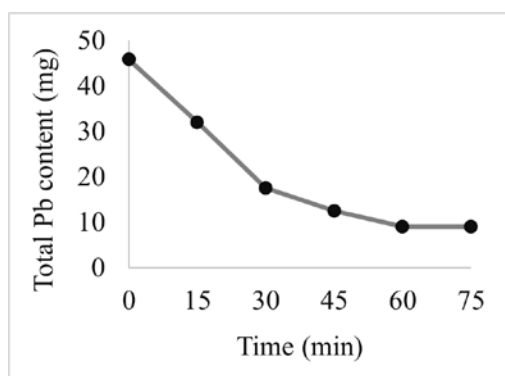


Figure 4. Lead content decrease of the 100 mL electrolyte (20:80 leachate-water solution) over time during the electrowinning development.

The total lead content distribution throughout the electrowinning process was determined. After just 60 minutes, the concentration of lead on the leachate was decreased so that only 19.7% of the total content remained in solution. This proves that the electrodeposition process occurs rapidly under the current conditions employed. However, the total recovery of reduced lead at the cathode was only 55.1% and a considerable amount (25.3%) precipitated to the anode sludge. The electrowinning test results are displayed on Figure 5.

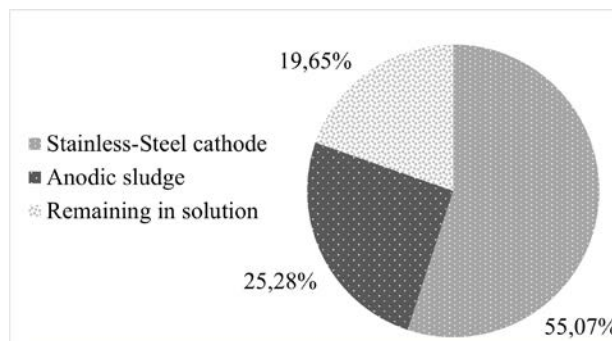


Figure 5. Lead distribution summary throughout the electrowinning process.

One of the reasons for lead loss to the anode sludge may be due to poor adherence in the cathode. To improve this adherence various agents can be added to the electrolytic solution such as lead salts (nitrate or fluoroborate). These salts are usually added in small amounts to increase the concentration of lead ions improving nucleation mechanisms. Another agent that can be used is a surfactant, such as polyethylene glycol (PEG) which can improve the wetting of the cathode surface and enhance the adhesion of the lead deposit. Surfactants also help to reduce the formation of dendritic growths when lead deposits tend to grow in a non-uniform manner (Zheng-hui, 2012). Additionally, controlling current density and temperature of the electrolyte might be necessary to find the highest current efficiency and to improve the whole electrowinning process.

After optimizing this electrolytic process, it will be possible to propose it as an attractive solution for the extraction of lead from leachates in deep eutectic solvents.

4. CONCLUSIONS

The present study proved the feasibility of applying deep eutectic solvents as leaching agents for the removal and recovery of lead from the slag generated in the automotive battery recycling process.

It was necessary to carry out the previous characterization of the treated slag where lead was found in percentages between 1.91% and 5.36% in its most probable form of anglesite (PbSO_4). This compound had an appropriate solubility for the proposed treatment as found in previous studies and later demonstrated experimentally. The only other possible interferent present on the samples was iron with concentrations between 24.10% and 26.33%, mostly in the form of oxides. These oxides have a considerable solubility on DES, but fortunately, not comparable to that of lead.

By means of TCLP extraction, it was demonstrated that none of the samples ($7.0\text{-}26.0 \text{ mg.L}^{-1} \text{ Pb}$) complies with the permissible limits of regulations ($\geq 5 \text{ mg.L}^{-1} \text{ Pb}$) for mobilizing large amounts of lead, which highlighted the importance of decontaminating the slag and recovering the valuable metal.

For the leaching process, six operational variables were evaluated: type of sample, type of DES (varying the hydrogen bond donor), temperature (30, 60, 90 °C), time (1-8 h), solids percentage (1, 2, 5 %) and pressure application. Sample 1 showed higher lixiviation recoveries due to its low pH, proving that by increasing the H⁺ concentration, breaking of metal-oxygen bonds is favored as well as the solubilization process. Glyceline was chosen as the best leaching agent after 5 hours of agitation and a temperature of 90 °C. At this temperature the solution viscosity was decreased, and the reaction rate elevated. By preparing the solution under the aforementioned conditions with a 5% solid percentage it was possible to achieve a leaching yield of 95.0%.

Through an electrowinning test, the ability to recover lead from the leachate was demonstrated with an efficiency of 55.1%. This process could be optimized in matters of current density, current efficiency, and the addition of agents in order to increase the recovery and become an attractive solution for the extraction of lead from DES leachates.

Even if the secondary slag residue does not go through a subsequent recovery process, the ability to decontaminate it has been demonstrated for compliance with regulations. The proposed methodology approaches to an environmentally friendly alternative.

5. FURTHER RECOMMENDATIONS

In this research work, the application of choline chloride with 3 hydrogen bond donors was investigated: ethylene glycol, glycerin, and urea. However, there's a wide variety of different HBDs or mixtures of them that could also be tested. Another type of operating variables could also be taken into consideration for this type of investigation. For instance, to vary the solvents pH instead of the samples pH. In addition, variation of stirring speed, type of oxidizing agent and try to optimize the surface complexation by adding coordinating ligands.

In the case of electrowinning, it is recommended to perform a complete cathodic sweep using cyclic voltammetry to find an accurate deposition peak and to select the appropriate cell voltage and current density. Exchanging the stainless-steel cathode for one of greater reducing potential could improve the electrodeposition process. A sufficient surface area of the electrode for the amount of lead present in the electrolyte should also be taken into consideration. By adding certain agents such as lead salts and surfactants, the lead adherence to the cathode could also be improved.

Finally, other forms of recovery could be explored, such as cementation. However, for any process it is important to consider ecological and economic factors such as energy consumption and reagents expenses.

6. REFERENCES

- Abbott, A. P., Capper, G., Davies, D. L., McKenzie, K. J., & Obi, S. U. (2006). Solubility of Metal Oxides in Deep Eutectic Solvents Based on Choline Chloride. *Journal of Chemical & Engineering Data*, 51(4), 1280-1282. <https://doi.org/10.1021/jc060038c>
- Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Shikotra, P. (2005). Selective Extraction of Metals from Mixed Oxide Matrixes Using Choline-Based Ionic Liquids. *Inorganic Chemistry*, 44(19), 6497-6499. <https://doi.org/10.1021/ic0505450>
- Abbott, A. P., Capper, G., Davies, D. L., Rasheed, R. K., & Tambyrajah, V. (2003). Novel solvent properties of choline chloride/urea mixtures. *Chemical Communications*, 1, 70-71. <https://doi.org/10.1039/b210714g>
- Abbott, A. P., Capper, G., & Gray, S. (2006). Design of Improved Deep Eutectic Solvents Using Hole Theory. *ChemPhysChem*, 7(4), 803-806. <https://doi.org/10.1002/cphc.200500489>
- Abbott, A. P., Capper, G., McKenzie, K. J., & Ryder, K. S. (2007). Electrodeposition of zinc-tin alloys from deep eutectic solvents based on choline chloride. *Journal of Electroanalytical Chemistry*, 599(2), 288-294. <https://doi.org/10.1016/j.jelechem.2006.04.024>
- Abbott, A. P., Harris, R. C., & Ryder, K. S. (2007). Application of Hole Theory to Define Ionic Liquids by their Transport Properties. *The Journal of Physical Chemistry B*, 111(18), 4910-4913. <https://doi.org/10.1021/jp0671998>
- Allegri Sr, T. H. (1986). The code of federal regulations—CFR Title 40. In *handling and management of hazardous materials and waste*. Boston, MA: Springer US.
- Aragón Tobar, C. F. (2022). Evaluación de la Aplicación de Disolventes Eutécticos Profundos Basados en Cloruro de Colina para la Lixiviación de Metales (Cu, Pb, Fe y Zn) Provenientes de un Concentrado Polimetálico [Tesis previa a la obtención del título de magister en metalurgia, Escuela Politécnica Nacional]. <http://bibdigital.epn.edu.ec/handle/15000/23504>
- Bakkar, A. (2014). Recycling of electric arc furnace dust through dissolution in deep eutectic ionic liquids and electrowinning. *Journal of Hazardous Materials*, 280, 191-199. <https://doi.org/10.1016/j.jhazmat.2014.07.066>
- Berezowsky, R. M. G. S., Collins, M. J., Kerfoot, D. G. E., & Torres, N. (1991). The commercial status of pressure leaching technology. *JOM*, 43(2), 9-15. <https://doi.org/10.1007/BF03220132>

- Byrappa, K., & Adschiri, T. (2007). Hydrothermal technology for nanotechnology. *Progress in Crystal Growth and Characterization of Materials*, 53(2), 117-166.
<https://doi.org/10.1016/j.pcrysgrow.2007.04.001>
- Cheng, Y., Guo, Z., Liu, X., Yin, H., Qiu, G., Pan, F., & Liu, H. (2009). The bioleaching feasibility for Pb/Zn smelting slag and community characteristics of indigenous moderate-thermophilic bacteria. *Bioresource Technology*, 100(10), 2737-2740.
<https://doi.org/10.1016/j.biortech.2008.12.038>
- Cole, E. R., Lee, A. Y., & Paulson, D. L. (1985). Update on Recovering Lead From Scrap Batteries. *JOM*, 37(2), 79-83.
<https://doi.org/10.1007/BF03257768>
- Cui, J., & Forssberg, E. (2003). Mechanical recycling of waste electric and electronic equipment: A review. *Journal of Hazardous Materials*, 99(3), 243-263.
[https://doi.org/10.1016/S0304-3894\(03\)00061-X](https://doi.org/10.1016/S0304-3894(03)00061-X)
- Delgado-Mellado, N., Larriba, M., Navarro, P., Rigual, V., Ayuso, M., García, J., & Rodríguez, F. (2018). Thermal stability of choline chloride deep eutectic solvents by TGA/FTIR-ATR analysis. *Journal of Molecular Liquids*, 260, 37-43.
<https://doi.org/10.1016/j.molliq.2018.03.076>
- Ellis, T. W., & Mirza, A. H. (2010). The refining of secondary lead for use in advanced lead-acid batteries. *Journal of Power Sources*, 195(14), 4525-4529.
<https://doi.org/10.1016/j.jpowsour.2009.12.118>
- Forte, F., Horckmans, L., Broos, K., Kim, E., Kukurugya, F., & Binnemans, K. (2017). Closed-loop solvometallurgical process for recovery of lead from iron-rich secondary lead smelter residues. *RSC Adv.*, 7(79), 49999-50005.
<https://doi.org/10.1039/C7RA09150H>
- Gomes, G. M. F., Mendes, T. F., & Wada, K. (2011). Reduction in toxicity and generation of slag in secondary lead process. *Journal of Cleaner Production*, 19(9-10), 1096-1103.
<https://doi.org/10.1016/j.jclepro.2011.01.006>
- Gregurek, D., Reinharter, K., Majcenovic, C., Wenzl, C., & Spanring, A. (2015). Overview of wear phenomena in lead processing furnaces. *Journal of the European Ceramic Society*, 35(6), 1683-1698.
<https://doi.org/10.1016/j.jeurceramsoc.2014.12.011>
- Haynes, W. M., Lide, D. R., & Bruno, T. J. (Eds.). (2017). *CRC handbook of chemistry and physics: A ready-reference book of chemical and physical data (2016.a-2017.a, 97th edition ed.)*. CRC Press.
- Hernandez-Ortiz, M., Sifuentes, C., Badillo-Almaraz, H., ruz-Domínguez, O., Barbosa, O. A., Escobedo, J., De la Rosa, J., Durán-Muñoz, H., & Cleva, M. (2022). Synthesis of ZnO:Li films using an Arduino-based Hydrothermal reactor: An application to solar cells. 10(57), 1-12.
- Institute of Scrap Recycling Industry. (2022). *Recycling's Role in Sustainability*. ISRI Voice of the Recycling Industry.
<https://www.isri.org/sustainability>
- International Union of Pure and Applied Chemistry. (2021). *Standard Atomic Weight of Lead Revised*. 43(3), 30.
<https://iupac.org/standard-atomic-weight-of-lead-revised/>
- Jančíková, V., Jablonský, M., Voleková, K., & Šurina, I. (2022). Summarizing the Effect of Acidity and Water Content of Deep Eutectic Solvent-like Mixtures—A Review. *Energies*, 15(24), 9333.
<https://doi.org/10.3390/en15249333>
- Jenkin, G. R. T., Al-Bassam, A. Z. M., Harris, R. C., Abbott, A. P., Smith, D. J., Holwell, D. A., Chapman, R. J., & Stanley, C. J. (2016). The application of deep eutectic solvent ionic liquids for environmentally-friendly dissolution and recovery of precious metals. *Minerals Engineering*, 87, 18-24.
<https://doi.org/10.1016/j.mineng.2015.09.026>
- Karali, D., Stavridis, A., Loupa, G., & Rapsomanikis, S. (2020). Dispersion Effects of Particulate Lead (Pb) from the Stack of a Lead Battery Recycling Plant. *Energies*, 13(21), 5690.
<https://doi.org/10.3390/en13215690>
- Kim, E., Roosen, J., Horeckmans, L., Spooren, J., Broos, K., Binnemans, K., Vrancken, K. C., & Quaghebeur, M. (2017). Process development for hydrometallurgical recovery of valuable metals from sulfide-rich residue generated in a secondary lead smelter. *Hydrometallurgy*, 169, 589-598.
<https://doi.org/10.1016/j.hydromet.2017.04.002>
- Kreusch, M. A., Ponte, M. J. J. S., Ponte, H. A., Kaminari, N. M. S., Marino, C. E. B., & Mymrin, V. (2007). Technological improvements in automotive battery recycling. *Resources, Conservation and Recycling*, 52(2), 368-380.
<https://doi.org/10.1016/j.resconrec.2007.05.004>
- Lassin, A., Piantone, P., Burnol, A., Bodéan, F., Chateau, L., Lerouge, C., Crouzet, C., Guyonnet, D., & Bailly, L. (2007). Reactivity of waste generated during lead recycling: An integrated study. *Journal of Hazardous Materials*, 139(3), 430-437.
<https://doi.org/10.1016/j.jhazmat.2006.02.055>
- Lei, Z., Chen, B., Koo, Y.-M., & MacFarlane, D. R. (2017). Introduction: Ionic Liquids. *Chemical Reviews*, 117(10), 6633-6635.
<https://doi.org/10.1021/acs.chemrev.7b00246>
- Liao, Y.-S., Chen, P.-Y., & Sun, I.-W. (2016). Electrochemical study and recovery of Pb using 1:2 choline chloride/urea deep eutectic solvent: A variety of Pb species PbSO₄, PbO₂, and PbO exhibits the analogous

thermodynamic behavior. *Electrochimica Acta*, 214, 265-275.

<https://doi.org/10.1016/j.electacta.2016.08.053>

Lupi, C., & Pescetelli, A. (2008, octubre). Treatment of some liquid waste associated with lead battery recycling. *TMS (The Minerals, Metals & Materials Society)*, 807-813

Matlock, M. M., Howerton, B. S., & Atwood, D. A. (2002). Chemical Precipitation of Lead from Lead Battery Recycling Plant Wastewater. *Industrial & Engineering Chemistry Research*, 41(6), 1579-1582.

<https://doi.org/10.1021/ie010800y>

M.Brashem, Inc. (2023). Why Are Graphite Electrodes Used in Electrolysis.

<https://www.mbrashem.com/why-are-graphite-electrodes-used-in-electrolysis/>

Ministerio del Ambiente. (2012). Acuerdo Ministerial 142, Listados nacionales de sustancias químicas peligrosas, desechos peligrosos y especiales. Registro Oficial No 856.

Mjalli, F. S., & Ahmed, O. U. (2016). Physical properties and intermolecular interaction of eutectic solvents binary mixtures: Reline and ethaline: Reline-Ethaline. *Asia-Pacific Journal of Chemical Engineering*, 11(4), 549-557.

<https://doi.org/10.1002/apj.1978>

Mjalli, F. S., & Ahmed, O. U. (2017). Ethaline and Glyceline binary eutectic mixtures: Characteristics and intermolecular interactions: Ethaline-Glyceline. *Asia-Pacific Journal of Chemical Engineering*, 12(2), 313-320.

<https://doi.org/10.1002/apj.2074>

Norma Oficial Mexicana. (2005). NORMA OFICIAL MEXICANA NOM-052-SEMARNAT-2005 QUE ESTABLECE LAS CARACTERISTICAS, EL PROCEDIMIENTO DE IDENTIFICACION, CLASIFICACION Y LOS LISTADOS DE LOS RESIDUOS PELIGROSOS PREFACIO.

Pan, D., Li, L., Tian, X., Wu, Y., Cheng, N., & Yu, H. (2019). A review on lead slag generation, characteristics, and utilization. *Resources, Conservation and Recycling*, 146, 140-155.

<https://doi.org/10.1016/j.resconrec.2019.03.036>

Pan, J., Zhang, C., Sun, Y., Wang, Z., & Yang, Y. (2012). A new process of lead recovery from waste lead-acid batteries by electrolysis of alkaline lead oxide solution. *Electrochemistry Communications*, 19, 70-72.

<https://doi.org/10.1016/j.elecom.2012.03.028>

Pateli, I. M., Thompson, D., Alabdullah, S. S. M., Abbott, A. P., Jenkin, G. R. T., & Hartley, J. M. (2020). The effect of pH and hydrogen bond donor on the dissolution of metal oxides in deep eutectic solvents. *Green Chemistry*, 22(16), 5476-5486.

<https://doi.org/10.1039/D0GC02023K>

Peña, L. I. de la (Ed.). (2013). *Diccionario Esencial Química* (Primera edición). Ediciones Larousse, S. A.

Pollmann, K., Kutschke, S., Matys, S., Raff, J., Hlawacek, G., & Lederer, F. L. (2018). Bio-recycling of metals: Recycling of technical products using biological applications. *Biotechnology Advances*, 36(4), 1048-1062.

<https://doi.org/10.1016/j.biotechadv.2018.03.006>

Pure Earth. (2016). World's Worst Pollution Problems: The Toxics Beneath Our Feet. Green Cross Switzerland.

<https://www.worstpolluted.org/docs/WorldsWorst2016.pdf>

Ru, J., Hua, Y., Wang, D., Xu, C., Zhang, Q., Li, J., & Li, Y. (2016). Dissolution-electrodeposition pathway and bulk porosity on the impact of in situ reduction of solid PbO in deep eutectic solvent. *Electrochimica Acta*, 196, 56-66.

<https://doi.org/10.1016/j.electacta.2016.02.181>

Ru, J., Hua, Y., Xu, C., Li, J., Li, Y., Wang, D., Gong, K., & Zhou, Z. (2015). Preparation of sub-micrometer lead wires from PbO by electrodeposition in choline chloride-urea deep eutectic solvent. *Advanced Powder Technology*, 26(1), 91-97.

<https://doi.org/10.1016/j.appt.2014.08.008>

Ru, J., Hua, Y., Xu, C., Li, J., Li, Y., Wang, D., Qi, C., & Jie, Y. (2015). Morphology-controlled preparation of lead powders by electrodeposition from different PbO-containing choline chloride-urea deep eutectic solvent. *Applied Surface Science*, 335, 153-159.

<https://doi.org/10.1016/j.apsusc.2015.02.045>

Santacruz Torres, J., & Torres Agredo, J. (2019). Aprovechamiento de escorias de fundición secundaria de plomo en ladrillos cerámicos. *Ciencia e Ingeniería Neogranadina*, 29(1), 7-18.

<https://doi.org/10.18359/rcin.3495>

Shahbaz, K., Baroutian, S., Mjalli, F. S., Hashim, M. A., & AlNashief, I. M. (2012). Densities of ammonium and phosphonium based deep eutectic solvents: Prediction using artificial intelligence and group contribution techniques. *Thermochimica Acta*, 527, 59-66.

<https://doi.org/10.1016/j.tca.2011.10.010>

Shu, Y., Ma, C., Zhu, L., & Chen, H. (2015). Leaching of lead slag component by sodium chloride and diluted nitric acid and synthesis of ultrafine lead oxide powders. *Journal of Power Sources*, 281, 219-226.

<https://doi.org/10.1016/j.jpowsour.2015.01.181>

Smaniotto, A., Antunes, A., Filho, I. do N., Venquiaruto, L. D., de Oliveira, D., Mossi, A., Di Luccio, M., Treichel, H., & Dallago, R. (2009). Qualitative lead extraction from recycled lead-acid batteries slag. *Journal of Hazardous Materials*, 172(2-3), 1677-1680.

<https://doi.org/10.1016/j.jhazmat.2009.07.026>

BIOGRAPHY

Smith, L., & Means, J. (1994). Recycling and reuse of material found on superfund sites. Diane Pub Co.

Sun, Y., Hu, S., Zhang, P., Elmaadawy, K., Ke, Y., Li, J., Li, M., Hu, J., Liu, B., Yang, J., Liang, S., Xiao, K., & Hou, H. (2020). Microwave enhanced solidification/stabilization of lead slag with fly ash based geopolymer. *Journal of Cleaner Production*, 272, 122957.

<https://doi.org/10.1016/j.jclepro.2020.122957>

Tan, S., Bedoya-Lora, F. E., Hallett, J. P., & Kelsall, G. H. (2021). Evaluation of N,N,N-Dimethylbutylammonium Methanesulfonate Ionic liquid for electrochemical recovery of lead from lead-acid batteries. *Electrochimica Acta*, 376, 137893.

<https://doi.org/10.1016/j.electacta.2021.137893>

Veloz, C. (2018). Estudio de la utilización de desechos especiales (escoria) provenientes de baterías desechadas de vehículos en mezclas asfálticas en caliente mediante el proceso en seco [Disertación previa a la obtención del título de ingeniera civil, Pontificia Universidad Católica del Ecuador].

<http://repositorio.puce.edu.ec/handle/22000/15245>

Whitehead, J. A., Lawrance, G. A., & McCluskey, A. (2004). 'Green' leaching: Recyclable and selective leaching of gold-bearing ore in an ionic liquid. *Green Chem.*, 6(7), 313-315.

<https://doi.org/10.1039/B406148A>

Xing, P., Wang, C., Wang, L., Ma, B., & Chen, Y. (2019). Hydrometallurgical recovery of lead from spent lead-acid battery paste via leaching and electrowinning in chloride solution. *Hydrometallurgy*, 189, 105134.

<https://doi.org/10.1016/j.hydromet.2019.105134>

Yang, H., & Reddy, R. G. (2014). Fundamental Studies on Electrochemical Deposition of Lead from Lead Oxide in 2:1 Urea/Choline Chloride Ionic Liquids. *Journal of The Electrochemical Society*, 161(10), D586-D592.

<https://doi.org/10.1149/2.1161410jes>

Zhang, Q., De Oliveira Vigier, K., Royer, S., & Jérôme, F. (2012). Deep eutectic solvents: Syntheses, properties and applications. *Chemical Society Reviews*, 41(21), 7108.

<https://doi.org/10.1039/c2cs35178a>

Zheng-hui, W. (2012). FUNDAMENTAL STUDY ON EXTRACTING LEAD FROM CERUSSITE CONCENTRATE IN METHANE SULFONIC ACID BASED SOLUTION [A Thesis submitted in partial fulfillment of the requirements for the degree of Master of Applied Science]. The University Of British Columbia. <https://open.library.ubc.ca/soa/cIRcle/collections/ubctheses/24/items/1.00734>



Bruna Salgado, a graduate in Chemical Sciences from the Pontificia Universidad Católica del Ecuador, is currently pursuing a master's degree in Metallurgy at the Escuela Politécnica Nacional. Her academic journey at these esteemed institutions laid a robust foundation in chemical analysis and characterization techniques, fostering her subsequent professional development. Currently, she is dedicated to the application of chromatography in environmental samples for the detection of various contaminants. She chose to focus her research on the valorization of industrial waste as a line of inquiry that culminated in the completion of this thesis.

**SUPPLEMENTARY
INFORMATION**

PART 1: SAMPLE PREPARATION AND CHARACTERIZATION

Technical Sheet No. 1

Objective: Transform samples into a more suitable form for the analysis and leaching procedures.

HOMOGENIZATION AND SIZE REDUCTION	
Date (day/month/year):	31/01/2022
Laboratory:	DEMEX EPN
Procedure	
1) Homogenize and reduce sample size through quartering up to 1 kg. 2) Primary crushing 3) Sieve the sample in mesh 6 4) Milling 5) Pulverize up to <math><100\ \mu\text{m}</math>	



Figure TS1.1. Sample size reduction through quartering.



Figure TS1.2. Reduced samples 1, 2, 3 (left to right).

Technical Sheet No. 2

Objective: To determine the moisture content (%) present in the untreated samples.

MOISTURE CONTENT ANALYSIS	
Date (day/month/year):	17/02/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	SARTORIUS, CPA42025, (d) = 0.01 g
Stove:	BINDER, FD 115, resolution = 0.5 °C
Thermometer:	TESTO, 926, resolution = 0.1 °C
Other materials:	spatula, aluminum containers
Test Conditions	
Temperature:	105.5 °C
Sample mass:	15.00 ± 0.02 g
Drying time:	2 hours
Initial mass:	Container + Humid Sample
Final mass:	Container + Dried Sample
Procedure	
1) Weigh the previously labeled aluminum container with a precision of 0.01g. 2) Homogenize and weigh 15.00 g ± 0.02 g of the humid sample over the container, without taring the balance. 3) Place in the stove for 2 h at 105.5 °C. 4) Remove from the stove and leave to cool inside a desiccator until it reaches room temperature. 5) Weigh the container with dried sample. 6) Perform the calculations.	
Calculation Formula	
$\text{Moisture Content (\%)} = \frac{(\text{Dried Sample} + \text{Container})\text{g} - (\text{Container})\text{g}}{(\text{Humid Sample} + \text{Container})\text{g} - (\text{Container})\text{g}} \times 100$	

Table TS2.1. Moisture content analysis data.

Sample	Subsample	Container Mass (g)	Initial Mass (g)	Final Mass (g)	Moisture Content (%)	Average Moisture Content (%)
1	Replica 1	0.39	14.98	14.47	3.50	3.49
	Replica 2	0.38	15.00	14.51	3.35	
	Replica 3	0.38	15.00	14.47	3.63	
2	Replica 1	0.39	15.00	12.32	18.34	18.32
	Replica 2	0.38	14.98	12.35	18.01	
	Replica 3	0.39	15.02	12.30	18.59	
3	Replica 1	0.39	14.99	13.62	9.38	9.28
	Replica 2	0.38	15.00	13.64	9.30	
	Replica 3	0.37	15.00	13.66	9.16	



Figure TS2.1. Moisture content analysis evidence.

Technical Sheet No. 3

Objective: To determine the loss by ignition (%) present in the dried samples.

LOSS BY IGNITION ANALYSIS	
Date (day/month/year):	22/09/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Muffle:	SNOL, 8.2, resolution = 0.1 g
Thermometer:	PCE, PCE-T 1200, resolution = 0.1 °C
Other materials:	spatula, tared crucibles
Test Conditions	
Temperature:	550.0 °C
Sample mass:	2.0000 ± 0.0010 g
Drying time:	3 h
Final mass:	Crucible + Calcinated Sample
Procedure	
1) Weigh the previously tared crucible with a precision of 0.0001g. 2) Tare the balance. 3) Homogenize and weigh 2.0000 g ± 0.0010 g of the previously dried sample. 4) Place in the muffle for 3 h at 550.0 °C. 5) Carefully remove from the muffle and leave to cool inside a desiccator until it reaches room temperature. 6) Weigh the crucible with dried sample. 7) Perform the calculations.	
Calculation Formula	
$\text{Loss by Ignition (\%)} = \frac{(\text{Sample} - ((\text{Calcinated Sample} + \text{Tared Crucible}) - (\text{Tared Crucible}))\text{g}}{(\text{Sample})\text{g}} \times 100$	

Table TS3.1. Loss by ignition analysis data.

Sample	Subsample	Tared Crucible Mass (g)	Sample Mass (g)	Final Mass (g)	Loss by Ignition (%)	Average Loss by Ignition (%)
1	1st Replica	18.6436	2.0001	20.5656	0.0390	0.043
	2nd Replica	24.4513	1.9999	26.3528	0.0492	
	3rd Replica	25.6821	2.0002	27.5996	0.0413	
2	1st Replica	20.7005	2.0004	22.5753	0.0628	0.063
	2nd Replica	18.1439	1.9998	20.0149	0.0644	
	3rd Replica	28.1028	1.9994	29.9771	0.0626	
3	1st Replica	26.3683	2.0001	28.2965	0.0359	0.038
	2nd Replica	26.5453	1.9996	28.4667	0.0391	
	3rd Replica	25.2196	2.0008	27.1422	0.0391	

Technical Sheet No. 4

Objective: To determine the ash content (%) present in the untreated samples.

ASH CONTENT ANALYSIS	
Date (day/month/year):	22/09/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Muffle:	SNOL, 8.2, resolution = 0.1 g
Thermometer:	PCE, PCE-T 1200, resolution = 0.1 °C
Other materials:	spatula, tared crucibles
Test Conditions	
Temperature:	550.0 °C
Sample mass:	0.5000-1.0000 ± 0.0010 g
Drying time:	6 h
Final mass:	Crucible + Calcinated Sample
Procedure	
1) Weigh the previously tared crucible with a precision of 0.0001g. 2) Tare the balance. 3) Homogenize and weigh 0.5000 – 1.0000 g ± 0.0010 g of the humid sample. 4) Place in the muffle for 6 h at 550.0 °C. 5) Carefully remove from the muffle and leave to cool inside a desiccator until it reaches room temperature. 6) Weigh the crucible with dried sample. 7) Perform the calculations.	
Calculation Formula	
$\text{Ash Content (\%)} = \frac{(\text{Calcinated Sample} + \text{Tared Crucible})g - (\text{Tared Crucible})g}{(\text{Sample})g} \times 100$	

Table TS4.1. Ash content analysis data.

Sample	Subsample	Tared Crucible Mass (g)	Sample Mass (g)	Final Mass (g)	Ash Content (%)	Average Ash Content (%)
1	1st Replica	20.7004	1.0009	21.6576	95.6339	95.34
	2nd Replica	12.6235	1.0002	13.5774	95.3709	
	3rd Replica	23.4572	0.9999	24.4072	95.0095	
2	1st Replica	21.6314	0.9998	22.4505	81.9264	81.52
	2nd Replica	22.8095	0.9998	23.6236	81.4263	
	3rd Replica	25.2191	0.9999	26.0310	81.1981	
3	1st Replica	24.4511	0.4998	24.8958	88.9756	88.79
	2nd Replica	18.1443	0.4999	18.5855	88.2577	
	3rd Replica	18.6446	0.5006	19.0908	89.1330	



Figure TS4.1. Ash content analysis evidence.

Technical Sheet No. 5

Objective: To determine the specific gravity (Kg.m^{-3}) of the untreated and treated samples.

SPECIFIC GRAVITY ANALYSIS	
Date (day/month/year):	27/12/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Other materials:	spatula, 10 mL graduated cylinder
Test Conditions	
Sample volume:	2.0/5.0/10.0 (cm^3)
Procedure	
1) Homogenize the sample as much as possible. 2) Tare the graduated cylinder (10 mL). 3) With a spatula, fill the graduated cylinder with sample up to the desired volume. Air spaces between the soil particles should be avoided as much as possible by tapping lightly. 4) Weigh the sample container. 5) Perform the calculations.	
Calculation Formula	
$\text{Specific Gravity} \left(\frac{\text{kg}}{\text{m}^3} \right) = \frac{(\text{Sample mass})\text{g} \times 1 \text{ kg} \times 1000000 \text{ cm}^3}{(\text{Sample volume})\text{cm}^3 \times 1000\text{g} \times 1\text{m}^3}$	

Table TS5.1. Specific gravity analysis data from untreated samples.

Sample	Subsample	Sample Mass (g)	Sample Mass (kg)	Sample Volume (cm^3)	Sample Volume (m^3)	Specific Gravity (kg.m^{-3})	Average Specific Gravity (kg.m^{-3})
1	1st Replica	5.1660	0.005166	5.0	0.000005	1033.2	1251.6
	2nd Replica	7.3500	0.007350	5.0	0.000005	1470.0	
2	1st Replica	4.9889	0.004989	5.0	0.000005	997.8	990.7
	2nd Replica	4.9180	0.004918	5.0	0.000005	983.6	
3	1st Replica	2.3993	0.002399	5.0	0.000005	1199.7	1127.0
	2nd Replica	2.1088	0.002109	5.0	0.000005	1054.4	

Table TS5.2. Specific gravity analysis data from treated samples (Water washes and 300 °C roasting).

Treated Sample	Subsample	Sample Mass (g)	Sample Mass (kg)	Sample Volume (cm^3)	Sample Volume (m^3)	Specific Gravity (kg.m^{-3})	Average Specific Gravity (kg.m^{-3})
1	1st Replica	13.2141	0.0132141	10.0	0.000010	1321.4	1355.8
	2nd Replica	13.9025	0.0139025	10.0	0.000010	1390.3	
2	1st Replica	13.0535	0.0130535	10.0	0.000010	1305.4	1356.8
	2nd Replica	14.0829	0.0140829	10.0	0.000010	1408.3	
3	1st Replica	12.2203	0.0122203	10.0	0.000010	1222.0	1218.9
	2nd Replica	12.1578	0.0121578	10.0	0.000010	1215.8	

Technical Sheet No. 6

Objective: To determine the pH and Conductivity of the untreated and treated samples (2:1 Extraction).

pH and Conductivity Analysis	
Date (day/month/year):	02/04/2022, 19/09/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	SARTORIUS, CPA42025, (d) = 0.01 g
Horizontal Agitator:	Heidolph, Unimax 2010
Centrifuge:	Thermo Scientific, Heraeus Megafuge 16
Automatic Pipette (10 mL):	Socorex, Calibra 832, resolution = 0.1 mL
pHmeter:	inoLAB pH/ION Level 2
Conductivitymeter:	inoLAB Cond Level 2
Other materials:	spatula, falcon tubes, pipette tips
Test Conditions	
Sample mass:	15.00 ± 0.02 g
Water grade:	Type 1 (HPLC)
Water volume:	30 mL ± (resolucion)
Agitation time:	1 h
Agitation speed:	330 rpm
Rest time:	15 min
Centrifugation time:	3 min
Centrifugation speed:	1200 rpm
Procedure (2:1 Extraction)	
<ol style="list-style-type: none">1) Homogenize the sample as much as possible.2) Tare the balance with a falcon tube.3) Weigh 10 ± 0.02 g grams of sample inside the falcon tube.4) Add 30 ml of deionized water with an automatic pipette.5) Shake the tube for 1 h at 330 rpm on the horizontal agitator.6) Let the tube rest for 15 min and then centrifuge at 1200 rpm for 3 min.7) Submerge electrodes of a pHmeter and a conductivitymeter in the liquid part of the extracts and write down the measurements.	

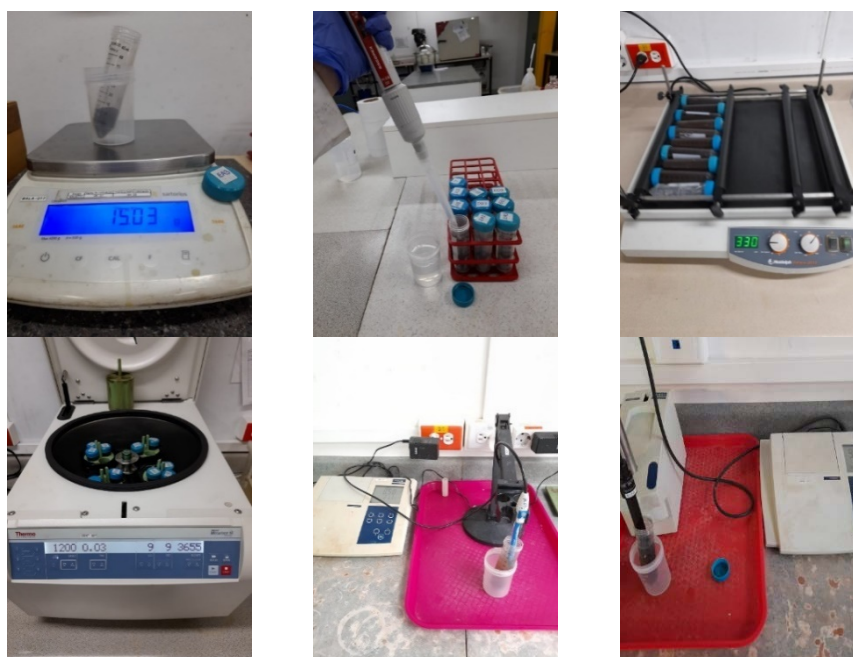


Figure TS6.1. 2:1 Extraction procedure for the analysis of pH and conductivity.

Table TS6.1. pH and conductivity analysis data from untreated samples.

Sample	Subsample	Sample Mass (g)	Deionized Water Volume (mL)	pH	Conductivity (mS/cm)	Average pH	Average Conductivity (mS/cm)
Blanco	Blanco	NA	30	7.02	0.0001	7.02	0.0001
1	1st Replica	14.99	30	8.51	93.7	8.53	94.57
	2nd Replica	14.99	30	8.57	93.8		
	3rd Replica	15.02	30	8.52	96.2		
2	1st Replica	15.01	30	9.85	95.9	9.85	94.17
	2nd Replica	15.02	30	9.85	93.4		
	3rd Replica	14.98	30	9.85	93.2		
3	1st Replica	14.98	30	9.94	94.8	9.96	93.63
	2nd Replica	14.98	30	9.98	92.4		
	3rd Replica	14.99	30	9.97	93.7		

Table TS6.2. pH and conductivity analysis data from treated samples (Water washes and 300 °C roasting).

Treated Sample	Subsample	Sample Mass (g)	Deionized Water Volume (mL)	pH	Conductivity (mS/cm)	Average pH	Average Conductivity (mS/cm)
Blanco	Blanco	NA	30	7.02	0.0001	7.02	0.0001
1	1st Replica	14.98	30	2.84	24.2	2.87	23.43
	2nd Replica	14.98	30	2.83	23.9		
	3rd Replica	15.01	30	2.93	22.2		
2	1st Replica	15.00	30	4.88	24.2	4.81	26.67
	2nd Replica	15.02	30	4.81	27.6		
	3rd Replica	9.99	30	4.75	28.2		
3	1st Replica	9.98	30	2.74	24.2	2.70	24.00
	2nd Replica	15.02	30	2.72	24.5		
	3rd Replica	15.02	30	2.65	23.3		

Technical Sheet No. 7

Objective: To determine the elemental characterization of the samples through X-Ray Fluorescence analysis.

X-Ray Fluorescence Analysis	
Date (day/month/year):	28/03/2022, 08/08/2022
Laboratory:	DEMEX-EPN
Equipment	
X-Ray Fluorescence Equipment:	Bruker S8 Tiger Unit
Equipment Program:	Spectra Plus
Other materials:	spatula
Test Conditions	
Sample mass:	9 g
Binder mass:	1 g
Procedure	
<ol style="list-style-type: none">1) Weight 9 g of the pulverized sample (<100 μm).2) Mix with 1 g of the binder powder.3) Place the mixture on a manual press.4) Compact to obtain a solid and homogeneous sample.5) Analyze on the X-Ray fluorescence equipment.	

Attachment TS7.1. Evidence and results of the X-Ray fluorescence analysis from untreated samples.



**ESCUELA POLITÉCNICA NACIONAL
DEPARTAMENTO DE METALURGIA EXTRACTIVA**

Resultados de Análisis

Solicitante: Lcda. Bruna Salgado

Referencia: RM - 10266

Fecha: 28/03/2022

Muestras recibidas: Tres muestras sólidas denominadas:

Muestra 1: EABS (Código registrado según cliente).

Muestra 2: EBBS (Código registrado según cliente).

Muestra 3: EOBS (Código registrado según cliente).

Resultados Análisis Fluorescencia de Rayos X

El análisis químico de la muestra se determinó en el equipo de Fluorescencia de rayos X S8 Tiger, con el programa Spectra Pluss. A continuación, se detallan los resultados obtenidos del análisis:

Elemento	Muestra 1	Muestra 2	Muestra 3
	Contenido (%)	Contenido (%)	Contenido (%)
Fe	25,06	23,66	21,62
S	11,07	9,71	10,90
Na	10,84	10,47	11,85
Pb	3,57	3,53	0,89
Si	1,92	2,37	1,81
Al	0,58	0,85	0,65
Ca	0,45	0,53	0,43
Ba	0,37	0,39	0,43
Sn	0,30	0,34	0,21
Cl	0,14	0,08	0,06
K	0,13	0,12	0,13
Mn	0,13	0,13	0,15
Cu	0,12	0,12	0,09
Mg	0,06	0,14	0,05
Ti	0,06	0,05	0,06
Zn	0,05	0,05	0,03
P	0,05	0,04	0,04
Cr	0,04	0,03	0,07
Se	0,02	0,02	0,02
Ni	0,01	---	---
Mo	---	---	0,02

Nota: La muestra fue analizada mediante pastilla prensada, por lo cual los resultados son **semi-cuantitativos**.

ERNESTO HALE
DE LA TORRE
CHAUVIN

Firmado digitalmente
por ERNESTO HALE DE
LA TORRE CHAUVIN
Fecha: 2022.03.29
10:39:42 -05'00'

Ing. Ernesto de la Torre PhD.
Jefe de Departamento



Firmado electrónicamente por:
EVELYN PAMELA
CRIOLLO TIRADO

MSc. Evelyn Criollo
Jefa de Laboratorio

Attachment TS7.2. Evidence and results of the X-Ray fluorescence analysis from treated samples (Water washes and 300 °C roasting).



**ESCUELA POLITÉCNICA NACIONAL
DEPARTAMENTO DE METALURGIA EXTRACTIVA**

Resultados Análisis Fluorescencia de Rayos X

Solicitante: Leda. Bruna Salgado.

Referencia: RM - 10266

Fecha: 08/08/2022

Muestras recibidas: Tres muestras sólidas denominadas:

Muestra 1: EACBS (*Código registrado según cliente*).

Muestra 2: EBCBS (*Código registrado según cliente*).

Muestra 3: EOCBS (*Código registrado según cliente*).

El análisis químico de las muestras se determinó en el equipo de Fluorescencia de rayos X S8 Tiger, con el programa Spectra Pluss. A continuación, se detallan los resultados obtenidos del análisis:

Elemento	Muestra 1	Muestra 2	Muestra 3
	Contenido (%)	Contenido (%)	Contenido (%)
Fe	26,33	24,57	24,10
Na	11,67	11,73	15,25
S	9,57	9,66	10,29
Pb	5,36	4,50	1,91
Si	2,13	2,44	2,06
Al	0,77	0,94	0,84
Ca	0,63	0,60	0,46
Ba	0,33	0,37	0,36
Sn	0,33	0,35	0,24
P	0,17	0,11	0,07
Mn	0,15	0,14	0,17
Cu	0,13	0,12	0,09
Ce	0,12	---	---
Mg	0,12	0,15	0,08
K	0,12	0,11	0,12
Cl	0,06	0,05	0,03
Zn	0,05	0,05	0,03
Ti	0,05	0,06	0,05
Cr	0,04	0,03	0,06
Ni	0,02	0,01	0,01
Mo	---	---	0,02
Se	0,01	0,01	0,01
V	---	---	0,01

Nota: Las muestras fueron analizadas mediante pastilla prensada, por lo cual los resultados son semi-cuantitativos.



Firmado electrónicamente por:
**EDDY FERNANDO
PAZMINO IBARRA**

Ing. Eddy Pazmiño PhD.
Jefe de Departamento (S)



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**EVELYN PAMELA
CRIOLLO TIRADO**

MSc. Evelyn Criollo
Jefa de Laboratorio

Technical Sheet No. 8

Objective: To analyze crystalline phases present on the samples.

X-Ray Diffraction Analysis	
Date (day/month/year):	08/08/2022, 07/03/2023
Laboratory:	DEMEX-EPN
Equipment	
X-Ray Diffraction Equipment:	D8 Advance
Qualitative identification software:	EVA
Quantification software:	TOPAS
Other materials:	spatula, agate mortar
Test Conditions	
Sample mass:	1 g
Particle Size	<100 μm
Detection Limit:	1 %
Procedure	
1) Weight 1 g of the pulverized sample (<100 μm). 2) Re-grind in an agate mortar. 3) Place over the sample holder and flatten slightly. 4) Analyze on the X-Ray diffraction equipment.	

Attachment TS8.1. Evidence and results of the X-Ray diffraction analysis from samples calcinated at 300 °C.



**ESCUELA POLITÉCNICA NACIONAL
DEPARTAMENTO DE METALURGIA EXTRACTIVA**

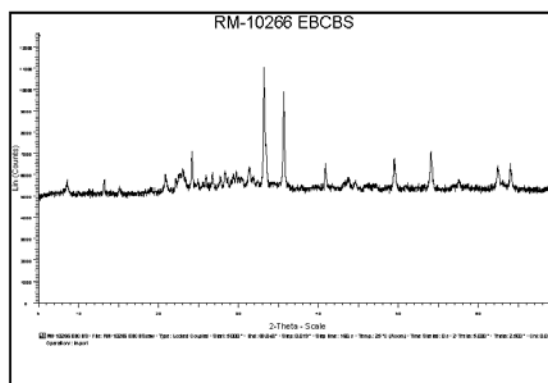
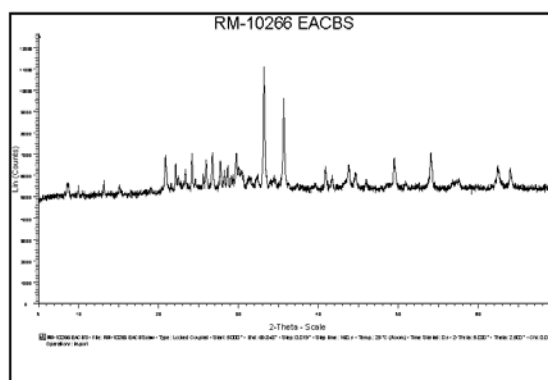


Resultados Análisis de Difracción de Rayos X

Solicitante : Ing. Bruna Salgado.
No. Referencia : RM - 10266
Fecha : 08 - 08 - 2022
Muestras recibidas : Tres muestras sólidas denominadas:
Muestras : EACBS, EBCBS, EOCBS (*Código registrado según cliente*)

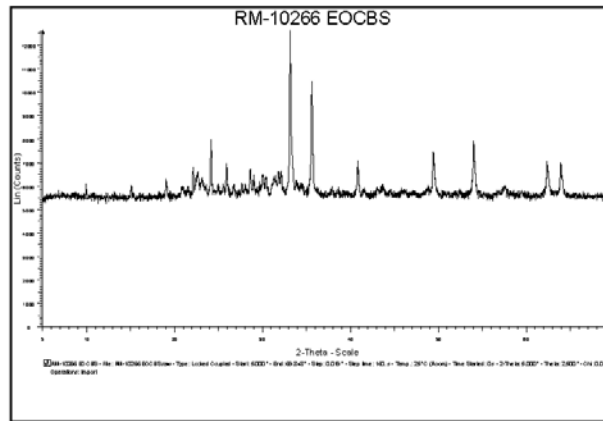
La determinación de los compuestos con cristalización definida presentes en las muestras se realizó empleando el Difractómetro D8 ADVANCE y el programa Diffrac plus (EVA) para cualificación. A continuación, se presentan los difractogramas obtenidos. Debido a las condiciones de las muestras (alto contenido de material amorfo), no permite tener una respuesta adecuada para esta técnica de análisis, sin embargo, se puede identificar presencia de: anglesita (PbSO_4), hematita (Fe_2O_3).

El límite de detección del equipo empleado es del 1% para compuestos con cristalización definida. A continuación, se adjunta los difractogramas obtenidos.





ESCUELA POLITÉCNICA NACIONAL
DEPARTAMENTO DE METALURGIA EXTRACTIVA



NOTA: Se recomienda calcinar las muestras hasta 950 °C.



Firmado electrónicamente por:
**EDDY FERNANDO
PAZMINO IBARRA**

Ing. Eddy Pazmiño PhD.
Jefe de Departamento (S)



Firmado electrónicamente por:
**EVELYN PAMELA
CRIOLLO TIRADO**

MSc. Evelyn Criollo
Jefa de Laboratorio

Attachment TS8.2. Evidence and results of the X-Ray diffraction analysis from samples calcinated at 950 °C.



**ESCUELA POLITÉCNICA NACIONAL
DEPARTAMENTO DE METALURGIA EXTRACTIVA**



Resultados Análisis de Difracción de Rayos X

Solicitante : Lcda. Bruna Salgado.
No. Referencia : RM - 10266
Fecha : 07 - 03 - 2023
Muestras recibidas : Tres muestras sólidas denominadas:
Muestra 1 : EA calcinada a 950 °C. (Código registrado según cliente).
Muestra 2 : EB calcinada a 950 °C. (Código registrado según cliente).
Muestra 3 : EO calcinada a 950 °C. (Código registrado según cliente).

La determinación de los compuestos con cristalización definida presentes en las muestras se realizó empleando el Difractómetro D8 ADVANCE y el programa Diffrac plus (EVA Y TOPAS) para cualificación y semi-cuantificación. A continuación, se detallan los resultados obtenidos del análisis.

Mineral	Fórmula	Muestra 1 Contenido (%)	Muestra 2 Contenido (%)	Muestra 3 Contenido (%)
Hematita	Fe ₂ O ₃	58	53	60
Thenardita	Na ₂ SO ₄	30	36	36
Anglesita	PbSO ₄	10	5	--
Maghemita	Fe ₂ O ₃	--	4	2
Grupo plagioclasas	(Na,Ca)Al(Si,Al)Si ₂ O ₈	2	2	2

NOTA: El límite de detección del equipo empleado es del 1% para compuestos con cristalización definida. Las muestras presentan alto contenido de material amorfo, no identificado por esta técnica de análisis.



Ing. Diana Endara PhD.
Jefa de Departamento



MSc. Evelyn Criollo
Jefa de Laboratorio

Technical Sheet No. 9

Objective: To determine the mobility of hazardous elements that could be present on the slag samples through ICP-MS analysis of TCLP extracts.

Toxicity Characteristic Leaching Procedure	
Date (day/month/year):	12/10/2021, 16/01/2023
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	SARTORIUS, CPA42025, (d) = 0.01 g
Orbital Agitator:	Heidolph, REAX 20
Centrifuge:	Thermo Scientific, Heraeus Megafuge 16
Inductively Coupled Plasma Mass Spectrometry Equipment:	Agilent, 7850
Automatic Pipette for dilution:	Socorex, Calibra 832, resolution = 0.1 mL
Other materials:	Spatula, teflon containers and lids, 500 mL graduated cylinder
CHEMICAL REAGENTS	
Sodium hydroxide:	Max 0.02 K, Merck
Acetic acid:	100% (glacial), Merck
Nitric acid:	65 %, Merck
Test Conditions	
Sample mass:	20 g
TCLP solution volume:	400 mL
TCLP solution pH	5.00
Agitation time:	18 h
Agitation speed:	30 rpm
Centrifugation time:	3 minutes
Centrifugation speed:	2400 rpm
Dilution factor:	20X with HNO ₃ 1%
Procedure	
The procedure does not present deviations from the reference method EPA-1311.	

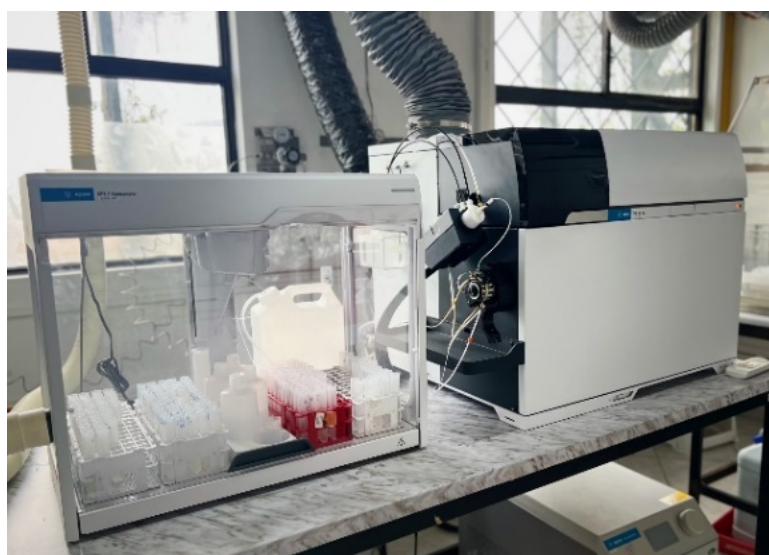


Figure TS9.1. Inductively Coupled Plasma Mass Spectrometry Equipment.

Attachment TS9.1. Evidence of the TCLP extract analysis through ICP-MS from *Sample 1*.



Ciente: Ing. Bruna Salgado Gaspar
 Quito, Francisco Andrade Marín E6-80 y Eloy
 Telf: 0990574352
Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado
Proyecto: Análisis de escoria
Fecha de Recepción: 16 Ene 2023
Tipo de Muestra b): 1 Muestra de lixiviado de cenizas
Fecha de Término de Análisis: 24 Ene 2023
Identificación Gruentec: 2301375-DS001
Fecha de Emisión del Informe: 26 Ene 2023

INFORME
 de RESULTADOS
 de ANÁLISIS

Identificación de la muestra, cliente b):	ESCORIA ÁCIDA SIN CALCINAR		
Fecha de Muestreo b):	16 Ene 2023	Fecha Medición	Método Adaptado de Referencia / Método Interno
No. Reporte Gruentec:	2301375-DS001		

Parámetros realizados en el Laboratorio
Metales en lixiviado (EPA 1311)

Aluminio mg/l ⁽¹⁾	0.16	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Antimonio mg/l ⁽¹⁾	0.0044	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Arsénico mg/l ⁽¹⁾	0.0037	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Azufre mg/l ⁽¹⁾	4217	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Bario mg/l ⁽¹⁾	0.065	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Berilio mg/l ⁽¹⁾	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Boro mg/l ⁽¹⁾	2.2	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cadmio mg/l ⁽¹⁾	0.071	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Calcio mg/l ⁽¹⁾	185	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cerio mg/l ⁽²⁾	0.013	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cesio mg/l ⁽¹⁾	0.0025	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cobalto mg/l ⁽¹⁾	0.24	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cobre mg/l ⁽¹⁾	0.061	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cromo mg/l ⁽¹⁾	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Disproσιο mg/l ⁽¹⁾	0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Erbio mg/l ⁽¹⁾	0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Estaño mg/l ⁽¹⁾	0.0051	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Estroncio mg/l ⁽¹⁾	0.63	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Europio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Fósforo mg/l ⁽¹⁾	<0.05	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Gadolinio mg/l ⁽¹⁾	0.0004	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Galio mg/l ⁽¹⁾	0.0005	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Germanio mg/l ⁽¹⁾	0.0021	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Hafnio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Hierro mg/l ⁽¹⁾	136	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Holmio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39



Cliente: Ing. Bruna Salgado Gaspar
 Quito, Francisco Andrade Marín E6-80 y Eloy
 Telf: 0990574352

Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado
Proyecto: Análisis de escoria
Fecha de Recepción: 16 Ene 2023
Tipo de Muestra b): 1 Muestra de lixiviado de cenizas
Fecha de Término de Análisis: 24 Ene 2023
Identificación Gruentec: 2301375-DS001
Fecha de Emisión del Informe: 26 Ene 2023

INFORME
 de RESULTADOS
 de ANÁLISIS



Identificación de la muestra, cliente b):	ESCORIA ÁCIDA SIN CALCINAR	Fecha Medición	Método Adaptado de Referencia / Método Interno
Fecha de Muestreo b):	16 Ene 2023		
No. Reporte Gruentec:	2301375-DS001		
Metales en lixiviado (EPA 1311)			
Lantano mg/l ⁽¹⁾	0.0090	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Litio mg/l ⁽¹⁾	0.013	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Lutecio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Magnesio mg/l ⁽¹⁾	10	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Manganeso mg/l ⁽¹⁾	9.8	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Mercurio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Molibdeno mg/l ⁽¹⁾	0.0013	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Neodimio mg/l ⁽¹⁾	0.0030	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Niobio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Níquel mg/l ⁽¹⁾	1.3	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Plata mg/l ⁽¹⁾	0.0004	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Plomo mg/l ⁽¹⁾	26	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Potasio mg/l ⁽¹⁾	22	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Praseodimio mg/l ⁽¹⁾	0.0007	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Rubidio mg/l ^(*)	0.062	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Samario mg/l ⁽¹⁾	0.0003	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Selenio mg/l ⁽¹⁾	0.17	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Silicio mg/l ⁽¹⁾	24	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Talio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Tantalio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Teluro mg/l ⁽¹⁾	0.0006	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Titanio mg/l ⁽¹⁾	<0.0005	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Torio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Tulio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Uranio mg/l ⁽¹⁾	0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Vanadio mg/l ⁽¹⁾	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Wolframio mg/l ^(*)	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39

Cliente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marín E6-80 y Eloy
Telf: 0990574352
Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado
Proyecto: Análisis de escoria
Fecha de Recepción: 16 Ene 2023
Tipo de Muestra b): 1 Muestra de lixiviado de cenizas
Fecha de Término de Análisis: 24 Ene 2023
Identificación Gruentec: 2301375-DS001
Fecha de Emisión del Informe: 26 Ene 2023

INFORME
de RESULTADOS
de ANÁLISIS

Identificación de la muestra, cliente b):	ESCORIA ÁCIDA SIN CALCINAR		
Fecha de Muestreo b):	16 Ene 2023	Fecha Medición	Método Adaptado de Referencia / Método Interno
No. Reporte Gruentec:	2301375-DS001		
Metales en lixiviado (EPA 1311)			
Yterbio mg/l⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Zinc mg/l⁽¹⁾	2.6	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Zirconio mg/l⁽¹⁾	0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39

Acreditaciones

Notas y Aclaraciones

Los ensayos marcados con (*) no están dentro del alcance de acreditación del SAE

Lugar de ejecución del Análisis: Todos los análisis presentados fueron realizados en la Matriz Quito, a excepción de los marcados con la letra (s)

a) Los equipos utilizados en los ensayos presentados cuentan con sus debidos certificados de calibración o sus homólogos, solicitar al Laboratorio en caso de requerirlos

b) Información proporcionada por el cliente, Gruentec no se responsabiliza por la veracidad de la misma.

d) Gruentec cumple con todas las condiciones ambientales requeridas para los ensayos, en caso de requerirlas, solicitar.

Porcentaje de Incertidumbre por método o analito (u)

Metales = 18%;

Valor e Interpretación de la Incertidumbre por método o analito (U)

El valor de la incertidumbre de cada medición (U) se determina mediante la fórmula $U=u/100\%C$, donde C es el valor de la medición.

El rango de incertidumbre obtenido se encuentra en el intervalo $C\pm U$

**ISABEL
LAURA
ESTRELLA
A SORIA**

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DN: cn=ISABEL LAURA ESTRELLA SORIA o=EC o=SECURITY DATA S.A. 2, ou=ENTIDAD DE CERTIFICACION DE INFORMACION
Móvil: Aprobado este documento
Ubicación:
Fecha: 2023.01.27 13:39:05:00

Ing. Isabel Estrella
Gerente de Operaciones

Nota 1: Este informe de resultados, opiniones y/o interpretaciones están basados en la información y la muestra provista por el cliente, para quien se ha realizado de manera exclusiva y confidencial.

Nota 2: La toma de la muestra, objeto de este informe fue realizada por el cliente. Gruentec no se responsabiliza por la información provista por el cliente al respecto.

Nota 3: Sin la aprobación del laboratorio no se debe reproducir este informe, excepto si se lo realiza en su totalidad.

Attachment TS9.2. Evidence of the TCLP extract analysis through ICP-MS from *Sample 2*.



Cliente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marin E6-80 y Eloy
Telf: 0990574352

Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado
Proyecto: Análisis de escoria
Fecha de Recepción: 16 Ene 2023
Tipo de Muestra b): 1 Muestra de lixiviado de cenizas
Fecha de Término de Análisis: 24 Ene 2023
Identificación Gruentec: 2301375-DS002
Fecha de Emisión del Informe: 26 Ene 2023

INFORME
de RESULTADOS
de ANÁLISIS

Identificación de la muestra, cliente b):	ESCORIA BÁSICA SIN CALCINAR	Fecha Medición	Método Adaptado de Referencia / Método Interno
Fecha de Muestreo b):	16 Ene 2023		
No. Reporte Gruentec:	2301375-DS002		

Parámetros realizados en el Laboratorio

Metales en lixiviado (EPA 1311)

Aluminio mg/l ⁽¹⁾	0.85	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Antimonio mg/l ⁽¹⁾	0.0093	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Arsénico mg/l ⁽¹⁾	0.0094	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Azufre mg/l ⁽¹⁾	4094	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Bario mg/l ⁽¹⁾	0.074	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Berilio mg/l ⁽¹⁾	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Boro mg/l ⁽¹⁾	2.8	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cadmio mg/l ⁽¹⁾	0.023	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Calcio mg/l ⁽¹⁾	189	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cerio mg/l ⁽²⁾	0.019	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cesio mg/l ⁽¹⁾	0.0047	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cobalto mg/l ⁽¹⁾	0.17	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cobre mg/l ⁽¹⁾	1.3	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Cromo mg/l ⁽¹⁾	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Disproso mg/l ⁽¹⁾	0.0003	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Erbio mg/l ⁽¹⁾	0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Estaño mg/l ⁽¹⁾	0.0099	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Estroncio mg/l ⁽¹⁾	0.55	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Europio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Fósforo mg/l ⁽¹⁾	<0.05	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Gadolinio mg/l ⁽¹⁾	0.0007	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Galio mg/l ⁽¹⁾	0.0009	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Germanio mg/l ⁽¹⁾	0.0010	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Hafnio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Hierro mg/l ⁽¹⁾	82	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Holmio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39

Cliente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marín E6-80 y Eloy
Telf: 0990574352
Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado
Proyecto: Análisis de escoria
Fecha de Recepción: 16 Ene 2023
Tipo de Muestra b): 1 Muestra de lixiviado de cenizas
Fecha de Término de Análisis: 24 Ene 2023
Identificación Gruentec: 2301375-DS002
Fecha de Emisión del Informe: 26 Ene 2023

INFORME
de RESULTADOS
de ANÁLISIS

Identificación de la muestra, cliente b):	ESCORIA BÁSICA SIN CALCINAR	Fecha Medición	Método Adaptado de Referencia / Método Interno
Fecha de Muestreo b):	16 Ene 2023		
No. Reporte Gruentec:	2301375-DS002		
Metales en lixiviado (EPA 1311)			
Lantano mg/l ⁽¹⁾	0.014	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Litio mg/l ⁽¹⁾	0.011	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Lutecio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Magnesio mg/l ⁽¹⁾	15	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Manganeso mg/l ⁽¹⁾	5.6	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Mercurio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Molibdeno mg/l ⁽¹⁾	0.0018	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Neodimio mg/l ⁽¹⁾	0.0041	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Niobio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Níquel mg/l ⁽¹⁾	1.5	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Plata mg/l ⁽¹⁾	0.0057	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Plomo mg/l ⁽¹⁾	14	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Potasio mg/l ⁽¹⁾	26	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Praseodimio mg/l ⁽¹⁾	0.0011	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Rubidio mg/l ^(*)	0.066	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Samario mg/l ⁽¹⁾	0.0005	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Selenio mg/l ⁽¹⁾	0.24	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Silicio mg/l ⁽¹⁾	44	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Talio mg/l ⁽¹⁾	0.0007	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Tantalio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Teluro mg/l ⁽¹⁾	0.0006	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Titanio mg/l ⁽¹⁾	<0.0005	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Torio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Tulio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Uranio mg/l ⁽¹⁾	0.0006	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Vanadio mg/l ⁽¹⁾	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Wolframio mg/l ^(*)	<0.0002	24 Ene 2023	EPA 6020 B / MM-AG/S-39

Cliente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marín E6-80 y Eloy
Telf: 0990574352
Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado
Proyecto: Análisis de escoria
Fecha de Recepción: 16 Ene 2023
Tipo de Muestra b): 1 Muestra de lixiviado de cenizas
Fecha de Término de Análisis: 24 Ene 2023
Identificación Gruentec: 2301375-DS002
Fecha de Emisión del Informe: 26 Ene 2023

INFORME
de RESULTADOS
de ANÁLISIS

Identificación de la muestra, cliente b):	ESCORIA BÁSICA SIN CALCINAR	Fecha Medición	Método Adaptado de Referencia / Método Interno
Fecha de Muestreo b):	16 Ene 2023		
No. Reporte Gruentec:	2301375-DS002		
Metales en lixiviado (EPA 1311)			
Yterbio mg/l ⁽¹⁾	<0.0001	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Zinc mg/l ⁽¹⁾	1.6	24 Ene 2023	EPA 6020 B / MM-AG/S-39
Zirconio mg/l ⁽¹⁾	0.0003	24 Ene 2023	EPA 6020 B / MM-AG/S-39

Acreditaciones

Notas y Aclaraciones

Los ensayos marcados con (*) no están dentro del alcance de acreditación del SAE

Lugar de ejecución del Análisis: Todos los análisis presentados fueron realizados en la Matriz Quito, a excepción de los marcados con la letra (s)

a) Los equipos utilizados en los ensayos presentados cuentan con sus debidos certificados de calibración o sus homólogos, solicitar al Laboratorio en caso de requerirlos

b) Información proporcionada por el cliente, Gruentec no se responsabiliza por la veracidad de la misma.

d) Gruentec cumple con todas las condiciones ambientales requeridas para los ensayos, en caso de requerirlas, solicitar.

Porcentaje de incertidumbre por método o analito (u)

Metales = 18%;

Valor e interpretación de la Incertidumbre por método o analito (U)

El valor de la incertidumbre de cada medición (U) se determina mediante la fórmula $U=u/100\%$, donde C es el valor de la medición.

El rango de incertidumbre obtenido se encuentra en el intervalo $C\pm U$

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SORIA

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LAURA ESTRELLA SORIA
DN: c=EC, o=ISABEL LAURA
ESTRELLA SORIA snc=EC,
o=SECURITY DATA S.A. 2
entIDAD DE
CERTIFICACION DE
INFORMACION
Motivo: Aprobado este documento
Ubicación:
Fecha: 2023-01-27 13:39:05:00

Ing. Isabel Estrella
Gerente de Operaciones

Nota 1: Este informe de resultados, opiniones y/o interpretaciones están basados en la información y la muestra provista por el cliente, para quien se ha realizado de manera exclusiva y confidencial.

Nota 2: La toma de la muestra, objeto de este informe fue realizada por el cliente. Gruentec no se responsabiliza por la información provista por el cliente al respecto.

Nota 3: Sin la aprobación del laboratorio no se debe reproducir este informe, excepto si se lo realiza en su totalidad.

Attachment TS9.3. Evidence of the TCLP extract analysis through ICP-MS from *Sample 3*.



REPORTE DE ANÁLISIS

Ciente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marin E6-60 y Eloy Alfaro
Telf: 0990574352

Atn: Ing. Bruna Salgado Gaspar

Proyecto: Análisis en escoria baterías

Muestra Recibida: 12-oct.-21

Tipo de Muestra: 1 Muestra de Sólido

Análisis Completado: 21-oct.-21

Número reporte Gruentec: 2110205-DS001

Fecha de Emisión: 21-oct.-21

Identificación de la muestra:	ESCORIA BATERÍAS	Límite Máximo Permissible Desecho Sólido CODE OF FEDERAL REGULATIONS CODE OF FEDERAL REGULATIONS (CFR Title 40, Protection of Environment) ⁴¹⁾	Método Adaptado de Referencia / Método Interno
Fecha de Muestreo:	04-oct.-21		
No. Reporte Gruentec:	2110205-DS001		
Parámetros realizados en el Laboratorio			
Metales en lixiviado (TCLP EPA 1311):			
Aluminio mg/l ^(1,2)	<0.1 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Antimonio mg/l ^(1,2)	0.10 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Arsénico mg/l ^(1,2)	<0.005 ⁽¹⁾	≥5	EPA 6020 B / MM-AG/S-39
Azufre mg/l *	15782* ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Bario mg/l ^(1,2)	5.7 ⁽¹⁾	≥100	EPA 6020 B / MM-AG/S-39
Berilio mg/l ^(1,2)	<0.002 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Boro mg/l ^(1,2)	0.31 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Cadmio mg/l ^(1,2)	0.019 ⁽¹⁾	≥1	EPA 6020 B / MM-AG/S-39
Calcio mg/l ^(1,2)	69 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Cerio mg/l *	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Cesio mg/l ^(1,2)	0.0087 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Cobalto mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Cobre mg/l ^(1,2)	1.1 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Cromo mg/l ^(1,2)	<0.002 ⁽¹⁾	≥5	EPA 6020 B / MM-AG/S-39
Disproscio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Erbio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Estaño mg/l ^(1,2)	<0.005 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Estroncio mg/l ^(1,2)	0.38 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Europio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Fósforo mg/l ^(1,2)	<0.5 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Gadolinio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Galio mg/l ^(1,2)	<0.002 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Germanio mg/l ^(1,2)	<0.002 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Hafnio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Hierro mg/l ^(1,2)	<0.2 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Holmio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Lantano mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Litio mg/l ^(1,2)	0.009 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Lutecio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Magnesio mg/l ^(1,2)	0.91 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Manganeso mg/l ^(1,2)	0.73 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39

REPORTE DE ANÁLISIS

Cliente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marín E6-80 y Eloy Alfaro
Telf: 0990574352

Atn: Ing. Bruna Salgado Gaspar

Proyecto: Análisis en escoria baterías

Muestra Recibida: 12-oct.-21

Tipo de Muestra: 1 Muestra de Sólido

Análisis Completado: 21-oct.-21

Número reporte Gruentec: 2110205-DS001

Fecha de Emisión: 21-oct.-21

Identificación de la muestra:	ESCORIA BATERÍAS	Limite Máximo Permisible Desecho Sólido CODE OF FEDERAL REGULATIONS CODE OF FEDERAL REGULATIONS (CFR Title 40, Protection of Environment) ^{at)}	Método Adaptado de Referencia / Método Interno
Fecha de Muestreo:	04-oct.-21		
No. Reporte Gruentec:	2110205-DS001		
Metales en lixiviado (TCLP EPA 1311):			
Mercurio mg/l ^(1,2)	<0.001 ⁽¹⁾	≥0.2	EPA 6020 B / MM-AG/S-39
Molibdeno mg/l ^(1,2)	0.0058 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Neodimio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Niobio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Niquel mg/l ^(1,2)	<0.01 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Plata mg/l ^(1,2)	0.0028 ⁽¹⁾	≥5	EPA 6020 B / MM-AG/S-39
Plomo mg/l ^(1,2)	7.0 ⁽¹⁾	≥5	EPA 6020 B / MM-AG/S-39
Potasio mg/l ^(1,2)	19 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Praseodimio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Rubidio mg/l *	0.079 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Samario mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Selenio mg/l ^(1,2)	0.053 ⁽¹⁾	≥1	EPA 6020 B / MM-AG/S-39
Silicio mg/l ^(1,2)	8.2 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Talio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Tantalio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Teluro mg/l ^(1,2)	<0.002 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Titanio mg/l ^(1,2)	<0.005 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Torio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Tulio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Uranio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Vanadio mg/l ^(1,2)	<0.002 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Wolframio mg/l *	<0.002 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Yterbio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Zinc mg/l ^(1,2)	<0.05 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Zirconio mg/l ^(1,2)	<0.001 ⁽¹⁾	N/A	EPA 6020 B / MM-AG/S-39
Metales en peso seco:			
Aluminio mg/kg	6805	N/A	EPA 6020 A / MM-AG/S-39
Antimonio mg/kg	1472	N/A	EPA 6020 A / MM-AG/S-39
Arsénico mg/kg	955	N/A	EPA 6020 A / MM-AG/S-39
Azufre mg/kg	46156	N/A	EPA 6020 A / MM-AG/S-39
Bario mg/kg	159	N/A	EPA 6020 A / MM-AG/S-39
Berilio mg/kg	<0.1	N/A	EPA 6020 A / MM-AG/S-39

PART 2: LEACHING ASSAYS

Technical Sheet No. 10

Objective: To perform conventional leaching assays on the three samples with the three deep eutectic solvents varying the temperature and determining the leaching yield as a function of time.

CONVENTIONAL LEACHING ASSAYS	
Date (day/month/year):	28/09/2022 – 06-01-2023
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50-100 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Ethylene glycol:	99%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Urea:	Anhydrous, local brand
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Deionized water:	Type 1 (deionized)
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Synthesis Procedure	
<ol style="list-style-type: none"> 1) Weight the hydrogen bond acceptor (choline chloride). 2) Weight or take the corresponding volume of the hydrogen bond donor. 3) Mix HBA with HBD on a 2:1 molar ratio. 4) Heat the mixture on a beaker at 80 °C with continuous stirring for 2 h. 5) The synthesis is completed when a transparent liquid is obtained. 6) Add the oxidizing agent (iodine) up to 1 M. 	
Conventional Leaching Procedure	
<ol style="list-style-type: none"> 1) Weight a determined amount of sample and add to each deep eutectic solvent container. *The sample mass is determined by the percentage of solids. 2) Place each flask in temperature-regulated water baths with magnetic stirring at 470 rpm. 3) After the necessary time has elapsed, take an aliquot of the leachate and filter through paper into a round-bottom volumetric flask. 4) Wash the filtered paper with small amounts of deionized water. 5) Add nitric acid so that the final solution has a 2% concentration. 6) Complete the flask volume and homogenize the solution. 7) Transfer the solution to a 40 mL plastic container with lid. 8) Analyze the lead content of the solution through atomic absorption spectroscopy. 	
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$	
$\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$	
$\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$	
$\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Technical Sheet No. 11

Objective: To perform conventional leaching assays on the three samples with ethaline at 30 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS ETHALINE 30 °C	
Date (day/month/year):	28/09/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Ethylene glycol:	99%, Sigma-Aldrich
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	30 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Ethaline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Ethylene glycol
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS11.1 Conventional leaching assay results of the three samples on ethaline at 30 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.14	0.0070	6.52
	2	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.17	0.0085	7.92
	3	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.16	0.0080	7.45
	4	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.27	0.0135	12.57
	5	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.25	0.0125	11.64
	6	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.21	0.0105	9.78
	7	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.29	0.0145	13.51
	8	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.24	0.0120	11.18
2	1	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.08	0.0040	4.44
	2	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.07	0.0035	3.88
	3	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.06	0.0030	3.33
	4	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.07	0.0035	3.88
	5	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.03	0.0015	1.66
	6	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.02	0.0010	1.11
	7	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.03	0.0015	1.66
	8	0.2003	4.50	9.0135	10	0.1	0.0901	50	0.03	0.0015	1.66
3	1	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.02	0.0010	2.61
	2	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.03	0.0015	3.92
	3	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.02	0.0010	2.61
	4	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.02	0.0010	2.61
	5	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.03	0.0015	3.92
	6	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.03	0.0015	3.92
	7	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.02	0.0010	2.61
	8	0.2003	1.91	3.8257	10	0.1	0.0383	50	0.02	0.0010	2.61

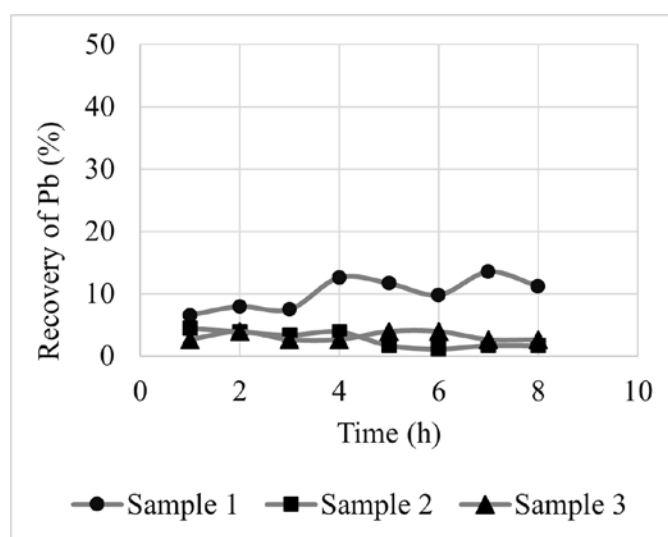


Figure TS11.1 Conventional leaching assay graph of the three samples on ethaline at 30 °C, from 1 to 8 h.

Technical Sheet No. 12

Objective: To perform conventional leaching assays on the three samples with glyceline at 30 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS GLYCELINE 30 °C	
Date (day/month/year):	28/09/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	30 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Glyceline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Glycerin
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$	
$\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$	
$\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$	
$\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS12.1 Conventional leaching assay results of the three samples on glyceline at 30 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.08	0.0040	3.73
	2	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.17	0.0085	7.92
	3	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.15	0.0075	6.99
	4	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.18	0.0090	8.38
	5	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.19	0.0095	8.85
	6	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.21	0.0105	9.78
	7	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.22	0.0110	10.25
	8	0.2003	5.36	10.7361	10	0.1	0.1074	50	0.25	0.0125	11.64
2	1	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.07	0.0035	3.88
	2	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.09	0.0045	4.99
	3	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.08	0.0040	4.43
	4	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.07	0.0035	3.88
	5	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.07	0.0035	3.88
	6	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.06	0.0030	3.32
	7	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.05	0.0025	2.77
	8	0.2006	4.50	9.0270	10	0.1	0.0903	50	0.06	0.0030	3.32
3	1	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.03	0.0015	3.91
	2	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.03	0.0015	3.91
	3	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.01	0.0005	1.30
	4	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.02	0.0010	2.61
	5	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.02	0.0010	2.61
	6	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.03	0.0015	3.91
	7	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.04	0.0020	5.21
	8	0.2009	1.91	3.8372	10	0.1	0.0384	50	0.03	0.0015	3.91

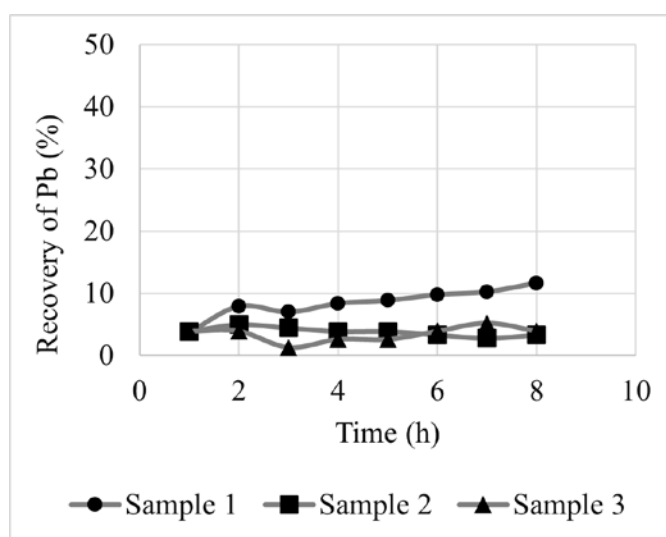


Figure TS12.1 Conventional leaching assay graph of the three samples on glyceline at 30 °C, from 1 to 8 h.

Technical Sheet No. 13

Objective: To perform conventional leaching assays on the three samples with reline at 30 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS RELINE 30 °C	
Date (day/month/year):	27/10/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Urea:	Anhydrous, local brand
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	30 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Reline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Urea
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS13.1 Conventional leaching assay results of the three samples on reline at 30 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.27	0.0135	0.00
	2	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.42	0.0210	0.65
	3	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.29	0.0145	13.52
	4	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.21	0.0105	9.79
	5	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.18	0.0090	8.39
	6	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.21	0.0105	9.79
	7	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.19	0.0095	8.86
	8	0.2001	5.36	10.7254	10	0.10	0.1073	50	0.19	0.0095	8.86
2	1	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.08	0.0040	4.44
	2	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.22	0.0110	12.20
	3	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.16	0.0080	8.88
	4	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.20	0.0100	11.09
	5	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.20	0.0100	11.09
	6	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.10	0.0050	5.55
	7	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.06	0.0030	3.33
	8	0.2003	4.50	9.0135	10	0.10	0.0901	50	0.06	0.0030	3.33
3	1	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.01	0.0005	1.31
	2	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.02	0.0010	2.62
	3	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.03	0.0015	3.93
	4	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.04	0.0020	5.24
	5	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.04	0.0020	5.24
	6	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.02	0.0010	2.62
	7	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.03	0.0015	3.93
	8	0.2000	1.91	3.8200	10	0.10	0.0382	50	0.04	0.0020	5.24

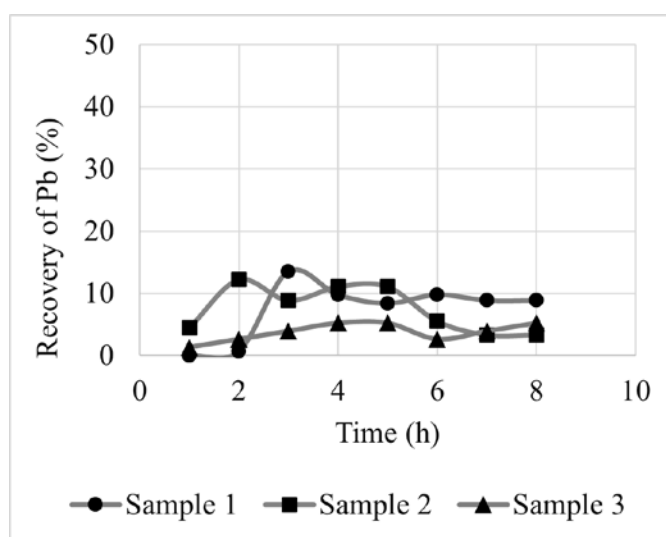


Figure TS13.1 Conventional leaching assay graph of the three samples on reline at 30 °C, from 1 to 8 h.

Technical Sheet No. 14

Objective: To perform conventional leaching assays on the three samples with ethaline at 60 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS ETHALINE 60 °C	
Date (day/month/year):	04/10/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Ethylene glycol:	99%, Sigma-Aldrich
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	60 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Ethaline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Ethylene glycol
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS14.1 Conventional leaching assay results of the three samples on ethaline at 60 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.05	0.0025	2.33
	2	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.09	0.0045	4.20
	3	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.12	0.0060	5.59
	4	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.15	0.0075	6.99
	5	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.15	0.0075	6.99
	6	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.18	0.0090	8.39
	7	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.21	0.0105	9.79
	8	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.17	0.0085	7.93
2	1	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.04	0.0021	2.34
	2	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.08	0.0042	4.67
	3	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.13	0.0063	7.01
	4	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.17	0.0084	9.34
	5	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.17	0.0084	9.34
	6	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.16	0.0080	8.89
	7	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.17	0.0085	9.45
	8	0.1999	4.50	8.9955	10	0.1	0.0900	50	0.13	0.0065	7.23
3	1	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.01	0.0005	1.31
	2	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.02	0.0010	2.61
	3	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.02	0.0010	2.61
	4	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.03	0.0015	3.92
	5	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.01	0.0005	1.31
	6	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.01	0.0005	1.31
	7	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.01	0.0005	1.31
	8	0.2005	1.91	3.8296	10	0.1	0.0383	50	0.02	0.0010	2.61

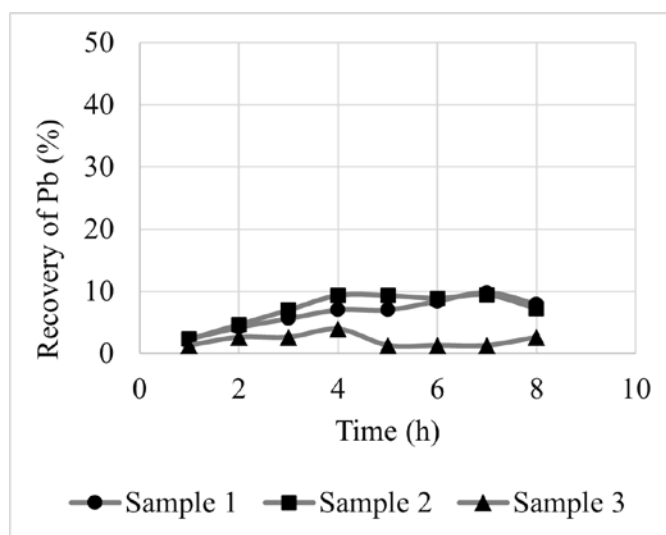


Figure TS14.1 Conventional leaching assay graph of the three samples on ethaline at 60 °C, from 1 to 8 h.

Technical Sheet No. 15

Objective: To perform conventional leaching assays on the three samples with glyceline at 60 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS GLYCELINE 60 °C	
Date (day/month/year):	04/10/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	60 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Glyceline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Glycerin
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS15.1 Conventional leaching assay results of the three samples on glyceline at 60 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.16	0.0080	7.46
	2	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.28	0.0140	13.05
	3	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.30	0.0150	13.99
	4	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.30	0.0150	13.99
	5	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.42	0.0210	19.58
	6	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.31	0.0155	14.45
	7	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.48	0.0240	22.38
	8	0.2001	5.36	10.7254	10	0.1	0.1073	50	0.53	0.0265	24.71
2	1	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.10	0.0050	5.56
	2	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.12	0.0060	6.67
	3	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.16	0.0080	8.89
	4	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.15	0.0075	8.33
	5	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.28	0.0140	15.56
	6	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.12	0.0060	6.67
	7	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.15	0.0075	8.33
	8	0.2000	4.50	9.0000	10	0.1	0.0900	50	0.25	0.0125	13.89
3	1	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.04	0.0020	5.21
	2	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.03	0.0015	3.91
	3	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.07	0.0035	9.13
	4	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.04	0.0020	5.21
	5	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.03	0.0015	3.91
	6	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.07	0.0035	9.13
	7	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.06	0.0030	7.82
	8	0.2008	1.91	3.8353	10	0.1	0.0384	50	0.05	0.0025	6.52

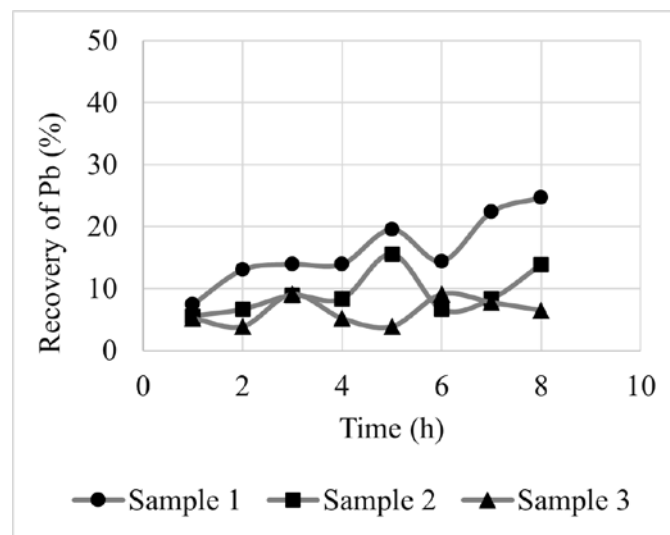


Figure TS15.1 Conventional leaching assay graph of the three samples on glyceline at 60 °C, from 1 to 8 h.

Technical Sheet No. 16

Objective: To perform conventional leaching assays on the three samples with reline at 60 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS RELINE 60 °C	
Date (day/month/year):	28/10/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Urea:	Anhydrous, local brand
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	60 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Reline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Urea
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS16.1 Conventional leaching assay results of the three samples on reline at 60 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	0.2001	1	5.36	10.7254	10	0.1	0.1073	50	0.43	0.0215	20.05
	0.2001	2	5.36	10.7254	10	0.1	0.1073	50	0.40	0.0200	18.65
	0.2001	3	5.36	10.7254	10	0.1	0.1073	50	0.54	0.0270	25.17
	0.2001	4	5.36	10.7254	10	0.1	0.1073	50	0.36	0.0180	16.78
	0.2001	5	5.36	10.7254	10	0.1	0.1073	50	0.96	0.0480	44.75
	0.2001	6	5.36	10.7254	10	0.1	0.1073	50	0.64	0.0320	29.84
	0.2001	7	5.36	10.7254	10	0.1	0.1073	50	0.44	0.0220	20.51
	0.2001	8	5.36	10.7254	10	0.1	0.1073	50	0.80	0.0400	37.29
2	0.2008	1	4.50	9.0360	10	0.1	0.0904	50	0.24	0.0120	13.28
	0.2008	2	4.50	9.0360	10	0.1	0.0904	50	0.29	0.0145	16.05
	0.2008	3	4.50	9.0360	10	0.1	0.0904	50	0.41	0.0205	22.69
	0.2008	4	4.50	9.0360	10	0.1	0.0904	50	0.28	0.0140	15.49
	0.2008	5	4.50	9.0360	10	0.1	0.0904	50	0.53	0.0265	29.33
	0.2008	6	4.50	9.0360	10	0.1	0.0904	50	0.25	0.0125	13.83
	0.2008	7	4.50	9.0360	10	0.1	0.0904	50	0.29	0.0145	16.05
	0.2008	8	4.50	9.0360	10	0.1	0.0904	50	0.32	0.0160	17.71
3	0.2006	1	1.91	3.8315	10	0.1	0.0383	50	0.02	0.0010	2.61
	0.2006	2	1.91	3.8315	10	0.1	0.0383	50	0.01	0.0005	1.30
	0.2006	3	1.91	3.8315	10	0.1	0.0383	50	0.01	0.0005	1.30
	0.2006	4	1.91	3.8315	10	0.1	0.0383	50	0.01	0.0005	1.30
	0.2006	5	1.91	3.8315	10	0.1	0.0383	50	0.02	0.0010	2.61
	0.2006	6	1.91	3.8315	10	0.1	0.0383	50	0.02	0.0010	2.61
	0.2006	7	1.91	3.8315	10	0.1	0.0383	50	0.03	0.0015	3.91
	0.2006	8	1.91	3.8315	10	0.1	0.0383	50	0.03	0.0015	3.91

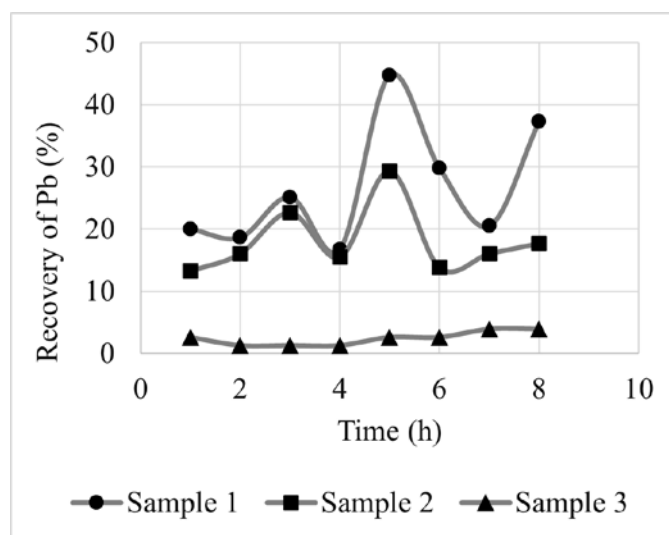


Figure TS16.1 Conventional leaching assay graph of the three samples on reline at 60 °C, from 1 to 8 h.

Technical Sheet No. 17

Objective: To perform conventional leaching assays on the three samples with ethaline at 90 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS ETHALINE 90 °C	
Date (day/month/year):	11/10/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 100 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Ethylene glycol:	99%, Sigma-Aldrich
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	90 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Ethaline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Ethylene glycol
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS17.1 Conventional leaching assay results of the three samples on ethaline at 90 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	0,1990	1	5.36	10.6664	10	0.1	0.1067	100	0.32	0.0320	30.00
	0,1990	2	5.36	10.6664	10	0.1	0.1067	100	0.60	0.0600	56.25
	0,1990	3	5.36	10.6664	10	0.1	0.1067	100	0.61	0.0610	57.19
	0,1990	4	5.36	10.6664	10	0.1	0.1067	100	0.61	0.0610	57.19
	0,1990	5	5.36	10.6664	10	0.1	0.1067	100	0.62	0.0620	58.13
	0,1990	6	5.36	10.6664	10	0.1	0.1067	100	0.50	0.0500	46.88
	0,1990	7	5.36	10.6664	10	0.1	0.1067	100	0.77	0.0770	72.19
	0,1990	8	5.36	10.6664	10	0.1	0.1067	100	0.42	0.0420	39.38
2	0,1998	1	4.50	8.9910	10	0.1	0.0899	100	0.01	0.0010	1.11
	0,1998	2	4.50	8.9910	10	0.1	0.0899	100	0.45	0.0450	50.05
	0,1998	3	4.50	8.9910	10	0.1	0.0899	100	0.40	0.0400	44.49
	0,1998	4	4.50	8.9910	10	0.1	0.0899	100	0.40	0.0400	44.49
	0,1998	5	4.50	8.9910	10	0.1	0.0899	100	0.41	0.0410	45.60
	0,1998	6	4.50	8.9910	10	0.1	0.0899	100	0.21	0.0210	23.36
	0,1998	7	4.50	8.9910	10	0.1	0.0899	100	0.46	0.0460	51.16
	0,1998	8	4.50	8.9910	10	0.1	0.0899	100	0.30	0.0300	33.37
3	0,2003	1	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	2	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	3	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	4	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	5	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	6	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	7	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61
	0,2003	8	1.91	3.8257	10	0.1	0.0383	100	0.01	0.0010	2.61

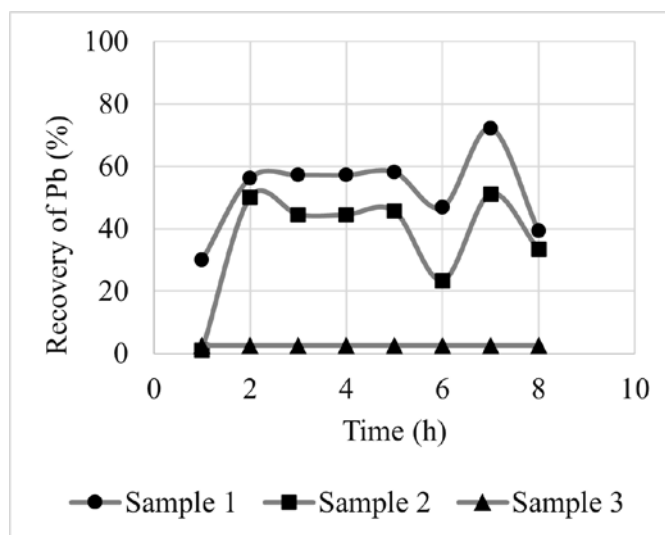


Figure TS17.1 Conventional leaching assay graph of the three samples on ethaline at 90 °C, from 1 to 8 h.

Technical Sheet No. 18

Objective: To perform conventional leaching assays on the three samples with glyceline at 90 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS GLYCELINE 90 °C	
Date (day/month/year):	11/10/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 100 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	90 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Glyceline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Glycerin
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$ $\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$ $\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$ $\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS18.1 Conventional leaching assay results of the three samples on glyceline at 90 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.33	0.0330	30.92
	2	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.48	0.0480	44.98
	3	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.66	0.0660	61.85
	4	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.61	0.0610	57.16
	5	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.96	0.0960	89.96
	6	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.54	0.0540	50.60
	7	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.64	0.0640	59.97
	8	0.1991	5.36	10.6718	10	0.1	0.1067	100	0.70	0.0700	65.59
2	1	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.17	0.0170	18.89
	2	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.34	0.0340	37.78
	3	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.47	0.0470	52.22
	4	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.24	0.0240	26.67
	5	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.41	0.0410	45.56
	6	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.29	0.0290	32.22
	7	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.24	0.0240	26.67
	8	0.2000	4.50	9.0000	10	0.1	0.0900	100	0.29	0.0290	32.22
3	1	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.02	0.0020	5.23
	2	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.02	0.0020	5.23
	3	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.02	0.0020	5.23
	4	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.02	0.0020	5.23
	5	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.04	0.0040	10.46
	6	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.03	0.0030	7.85
	7	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.01	0.0010	2.62
	8	0.2002	1.91	3.8238	10	0.1	0.0382	100	0.03	0.0030	7.85

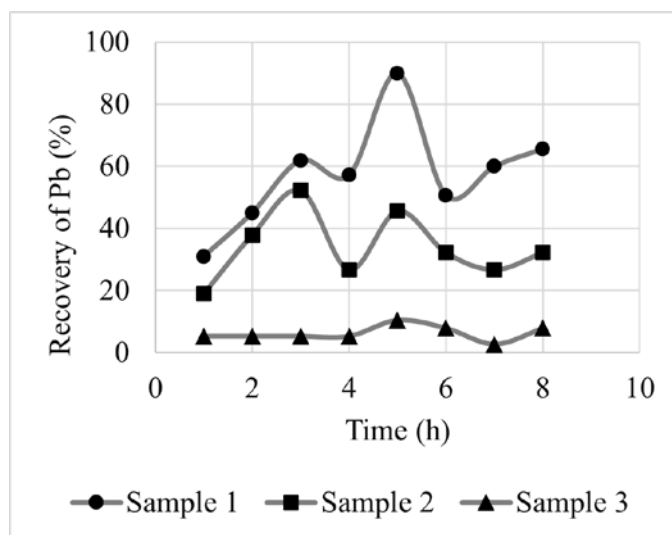


Figure TS18.1 Conventional leaching assay graph of the three samples on glyceline at 90 °C, from 1 to 8 h.

Technical Sheet No. 19

Objective: To perform conventional leaching assays on the three samples with reline at 90 °C and determining the leaching recovery yield throughout time.

CONVENTIONAL LEACHING ASSAYS RELINE 90 °C	
Date (day/month/year):	09/12/2022
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 100 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Urea:	Anhydrous, local brand
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	90 °C
Sample mass:	0.2000 ± 0.0010 g
Solids percentage:	2%
Agitation speed:	470 rpm
Deep Eutectic Solvent:	Reline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donor:	Urea
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Maximum leaching time	8 h
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$	
$\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$	
$\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$	
$\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS19.1 Conventional leaching assay results of the three samples on reline at 90 °C, from 1 to 8 h.

Sample	Leaching time (h)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES Volume (mL)	Aliquot volume (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery percentage (%)
1	1	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.31	0.0310	28.80
	2	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.60	0.0600	55.75
	3	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.71	0.0710	65.97
	4	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.52	0.0520	48.31
	5	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.89	0.0890	83.40
	6	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.46	0.0460	42.74
	7	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.89	0.0890	82.69
	8	0.2008	5.36	10.7629	10	0.1	0.1076	100	0.73	0.0730	67.83
2	1	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.29	0.0290	32.11
	2	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.38	0.0380	42.07
	3	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.41	0.0410	45.40
	4	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.20	0.0200	22.14
	5	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.52	0.0520	57.58
	6	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.16	0.0160	17.72
	7	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.35	0.0350	38.75
	8	0.2007	4.50	9.0315	10	0.1	0.0903	100	0.19	0.0190	21.04
3	1	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.02	0.0020	5.24
	2	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.03	0.0030	7.85
	3	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.02	0.0020	5.24
	4	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.04	0.0040	10.47
	5	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.04	0.0040	10.47
	6	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.03	0.0030	7.85
	7	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.04	0.0040	10.47
	8	0.2000	1.91	3.8200	10	0.1	0.0382	100	0.04	0.0040	10.47

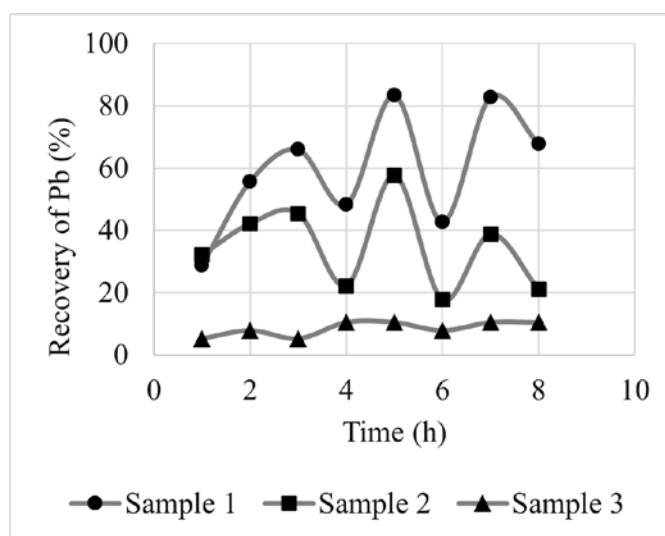


Figure TS19.1 Conventional leaching assay graph of the three samples on reline at 90 °C, from 1 to 8 h.

Technical Sheet No. 20

Objective: To perform conventional leaching assays on *sample 1* with the three deep eutectic solvents varying the solids percentage in order to determine the best leaching recovery yield.

SOLIDS PERCENTAGE ASSAY	
Date (day/month/year):	06/01/2023, 23/02/2023
Laboratory:	Gruentec Cia. Ltda.
Equipment	
Balance:	KERN, ARJ 220-4M, (d) = 0.0001 g
Magnetic Stirring Stove:	IKA, RCT basic, (-310 °C)
10 mL Automatic Pipette:	Socorex, Calibra 832, resolution = 0.1 mL
1 mL Automatic Pipette:	Eppendorf, Research, resolution = 1 µL
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50-100 mL round-bottom volumetric flasks, glass funnels, filtered paper (125 mm), 40 mL plastic containers with lids
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Ethylene glycol:	99%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Urea:	Anhydrous, local brand
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Sample:	Sample 1
Temperature:	90 °C
Solids percentage:	1%, 2%, 5%
Agitation speed:	470 rpm
Deep Eutectic Solvents:	Ethaline, Glyceline, Reline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donors:	Ethylene glycol, Glycerin, Urea
HBA to HBD Molar Ratio:	1:2
Deep Eutectic Solvent Volume:	5-10 mL
Iodine concentration:	1 M
Leaching time on Ethaline:	7 h
Leaching time on Glyceline:	5 h
Leaching time on Reline:	5 h
Aliquot volumes for AAS:	0.1 mL
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$	
$\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$	
$\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$	
$\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS120.1 Solids percentage assay results on *sample 1* with the three deep eutectic solvents.

Sample	DES	Solids (%)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES (mL)	Theoretical Pb content of the aliquot (mg)	Flask volume (mL)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery (%)	
1	Ethaline	1	0.0504	5.36	2.7014	5	0.0540	50	0.72	0.0360	66.63	
		2	0.1990	5.36	10.6664	10	0.1067	100	0.77	0.0770	72.19	
		5	0.2508	5.36	13.4429	5	0.2689	50	2.82	0.1410	52.44	
	Glyceline	1	0.0507	5.36	2.7175	2.7175	5	0.0544	50	0.73	0.0365	67.16
		2	0.1991	5.36	10.6718	10.6718	10	0.1067	100	0.96	0.0960	89.96
		5	0.2513	5.36	13.4697	13.4697	5	0.2694	50	5.12	0.2560	95.03
	Reline	1	0.0506	5.36	2.7122	2.7122	5	0.0542	50	0.82	0.0410	75.59
		2	0.1991	5.36	10.6718	10.6718	10	0.1067	100	0.89	0.0890	83.40
		5	0.2493	5.36	13.3625	13.3625	5	0.2672	50	4.51	0.2255	84.38

Technical Sheet No. 21

Objective: To perform hydrothermal leaching assays on the three samples with the three deep eutectic solvents to determine the influence of pressure on the recovery leaching yield.

PRESSURE LEACHING ASSAYS	
Date (day/month/year):	26/10/2022
Laboratory:	DEMEX EPN
Equipment	
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, microfilters, hydrothermal reactors.
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Ethylene glycol:	99%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Urea:	Anhydrous, local brand
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	90 °C, 120 °C
Solids percentage:	2%
Deep Eutectic Solvents:	Ethaline, Glyceline, Reline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donors:	Ethylene glycol, Glycerin, Urea
HBA to HBD Molar Ratio:	1:2
Sample mass:	0.2000 g
Deep Eutectic Solvent Volume:	10 mL
Iodine concentration:	1 M
Pressure leaching time:	24 h
Aliquot volumes for AAS:	0.1 mL
Round-bottom flask volume:	50 mL
Procedure	
<ol style="list-style-type: none"> 1) Weight 0.2 g of the previously homogenized sample on a hydrothermal reactor. 2) Add 10 mL of the deep eutectic solvent. 3) Close the hydrothermal reactor properly. 4) Place the reactor on a stove at a determined temperature. 5) Leave for 24 h and remove the reactor from the stove. 6) Open the hydrothermal reactor and take and aliquot of the leachate. 7) Microfilter into a round-bottom volumetric flask. 8) Add nitric acid so that the final solution has a 2% concentration. 9) Complete the flask volume with deionized water and homogenize the solution. 10) Analyze the lead content of the solution through atomic absorption spectroscopy. 	
Calculation Procedure Formulas	
$\text{Total Pb content of the sample (mg)} = \frac{\text{sample mass (g)} \times \text{Pb sample concentration FRX (\%)} \times \frac{1000 \text{ mg}}{1 \text{ g}}}{100 \%}$	
$\text{Theoretical Pb content of the aliquot (mg)} = \frac{\text{Total Pb content of the sample (mg)} \times \text{aliquot volume (mL)}}{\text{DES volume (mL)}}$	
$\text{Real Pb content of the aliquot (mg)} = \text{AAS Pb concentration of the aliquot} \frac{\text{mg}}{1000 \text{ mL}} \times \text{flask volume (mL)}$	
$\text{Leaching recovery percentage (\%)} = \frac{\text{Real Pb content of the aliquot (mg)}}{\text{Theoretical Pb content of the aliquot (mg)}} \times 100 \%$	

Table TS21.1 Pressure leaching assay results on the three samples with the three deep eutectic solvents.

Sample	DES	Time (h)	T (°C)	Sample mass (g)	Pb Sample concentration FRX (%)	Total Pb content of the sample (mg)	DES (mL)	Theoretical Pb content of the aliquot (mg)	AAS Pb concentration of the aliquot (mg.L ⁻¹)	Real Pb content of the aliquot (mg)	Leaching recovery (%)
1	Ethaline	24	90	0.20	5.40	10.72	10	0.1072	0.33	0.0165	15.39
		24	120	0.20	5.40	10.72	10	0.1072	0.00	0.0000	0.00
	Glyceline	24	90	0.20	5.40	10.72	10	0.1072	0.48	0.0240	22.39
		24	120	0.20	5.40	10.72	10	0.1072	0.31	0.0155	14.46
	Reline	24	90	0.20	5.40	10.72	10	0.1072	0.02	0.0010	0.93
		24	120	0.20	5.40	10.72	10	0.1072	0.07	0.0035	3.26
2	Ethaline	24	90	0.20	4.50	9.00	10	0.0900	7.76	0.0388	43.11
		24	120	0.20	4.50	9.00	10	0.0900	8.73	0.0437	48.50
	Glyceline	24	90	0.20	4.50	9.00	10	0.0900	11.06	0.0553	61.44
		24	120	0.20	4.50	9.00	10	0.0900	7.05	0.0353	39.17
	Reline	24	90	0.20	4.50	9.00	10	0.0900	0.61	0.0031	3.39
		24	120	0.20	4.50	9.00	10	0.0900	0.68	0.0034	3.78
3	Ethaline	24	90	0.20	1.90	3.82	10	0.0382	0.11	0.0006	1.44
		24	120	0.20	1.90	3.82	10	0.0382	0.49	0.0025	6.41
	Glyceline	24	90	0.20	1.90	3.82	10	0.0382	0.74	0.0037	9.69
		24	120	0.20	1.90	3.82	10	0.0382	0.48	0.0024	6.28
	Reline	24	90	0.20	1.90	3.82	10	0.0382	0.02	0.0001	0.26
		24	120	0.20	1.90	3.82	10	0.0382	0.00	0.0000	0.00

Technical Sheet No. 22

Objective: To perform a preliminary electrowinning test on the lead leachate prepared based on the best previously determined conditions of time, temperature, type of sample, and DES.

ELECTROWINNING ASSAY	
Date (day/month/year):	23/04/20223
Laboratory:	DEMEX EPN
Equipment	
Electrodeposition cell and Equipment	Custom built
Atomic Absorption Spectroscopy Equipment:	Perkin Elmer, AA 300
Inductively Coupled Plasma Mass Spectrometry Equipment:	Agilent, 7850
Other materials:	100 mL erlenmeyers, 100 mL glass beakers, spatula, magnetic stirrers, parafilm, pipette tips, 50 mL round-bottom volumetric flasks, glass funnels, filtered paper (0,45 µm), electrodes, 100 mL graduated cylinder.
Chemical reagents	
Choline chloride:	<98%, Sigma-Aldrich
Glycerin:	99.5%, Fischer Scientific
Iodine:	Iodine-Iodide 0.1 N, Baker
Nitric acid:	65%, Merck
Test Conditions	
Temperature:	Environmental conditions (± 20 °C)
Solids percentage:	± 5%
Deep Eutectic Solvent:	Glyceline
Hydrogen Bond Acceptor:	Choline chloride
Hydrogen Bond Donors:	Glycerin
HBA to HBD Molar Ratio:	1:2
Sample mass:	5.009 g
Deep Eutectic Solvent Preparation Final Volume:	110 mL
Deep Eutectic Solvent Preparation Dilution:	20:80
Diluting Substance:	Water
Iodine concentration:	1 M
Cathode:	Stainless-Steel (2.8 cm x 3.2 cm)
Anodes (2):	Graphite
Voltage:	4.32 V
Electric Current:	0.1 A
Aliquot volumes for AAS:	0.1 mL
ICP/MS Pb concentration of the Anode Sludge (ug)	2315
Anode Sludge Mass Dilution ICP-MS Analysis	5
Procedure	
<ol style="list-style-type: none"> 1) Prepare 100-110 mL of a lead leachate based on the best previously determined conditions of time, temperature, type of sample, and DES. 2) Vacuum filtrate the lead leachate through a 0.45 µm filtered paper. 3) Dilute 20 mL of the lead leachate with 80 mL of water. 4) Analyze the initial lead concentration through atomic absorption spectroscopy and/or ICP-MS. 5) Place the solution into an electrolytic cell. 6) Place a stainless-steel cathode between two graphite anodes. 7) Allow an electric current of 0.1 A to pass between electrodes. 8) Every 15 minutes of the electrowinning process, take an aliquot of the solution to measure lead concentration through atomic absorption spectroscopy. 9) Mechanically remove the reduced lead adhered to the cathode and analyze through atomic absorption spectroscopy. If not possible, calculate this quantity through mass balance. 10) Centrifuge and filter the remaining solution and analyze the precipitated anode sludge through ICP-MS. 11) Design a mass balance to account for the distribution of lead throughout the process. 12) Determine the final recovery percentage. 	

Attachment TS22.1. Evidence of the ICP-MS analysis of the optimized leachate for electrowinning.



Cliente: Ing. Bruna Salgado Gaspar
 Quito, Francisco Andrade Marín E6-80 y Eloy Alfaro
 Telf: 0990574352
Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado Gaspar
Proyecto: Análisis de Lixiviado
Fecha de Recepción: 03 Ago 2023
Tipo de Muestra b): 1 Muestra de Lixiviado
Fecha de Término de Análisis: 16 Ago 2023
Identificación Gruentec: 2308040-LIX001
Fecha de Emisión del Informe: 17 Ago 2023

INFORME
 de RESULTADOS
 de ANÁLISIS



Identificación de la muestra, cliente b):	LIQ EW ICP		
Fecha de Muestreo b):	03 Ago 2023	Fecha Medición	Método Adaptado de Referencia / Método Interno
No. Reporte Gruentec:	2308040-LIX001		

Parámetros realizados en el Laboratorio

Metales en lixiviado (EPA 1311)

Parámetro	Resultado	Fecha Medición	Método Adaptado de Referencia / Método Interno
Aluminio mg/l ^(*)	<0.1	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Antimonio mg/l ^(*)	0.004	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Arsénico mg/l ^(*)	<0.005	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Azufre mg/l ^(*)	<10	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Bario mg/l ^(*)	0.015	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Berilio mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Boro mg/l ^(*)	<0.2	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cadmio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Calcio mg/l ^(*)	<0.5	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cerio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cesio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cobalto mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cobre mg/l ^(*)	0.06	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cromo mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Cromo Hexavalente mg/l ^(*)	<0.02	16 Ago 2023	EPA 3060 A / MM-AG/S-38
Disprosió mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Erbio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Estaño mg/l ^(*)	<0.005	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Estroncio mg/l ^(*)	<0.005	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Europio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Fósforo mg/l ^(*)	<0.5	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Gadolinio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Galio mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Germanio mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Hafnio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Hierro mg/l ^(*)	<0.2	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Holmio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39

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Cliente: Ing. Bruna Salgado Gaspar
Quito, Francisco Andrade Marín E6-80 y Eloy Alfaro
Telf: 0990574352

Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado Gaspar
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Tipo de Muestra b): 1 Muestra de Lixiviado
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INFORME
de RESULTADOS
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Identificación de la muestra, cliente b):	LIQ EW ICP		
Fecha de Muestreo b):	03 Ago 2023	Fecha Medición	Método Adaptado de Referencia / Método Interno
No. Reporte Gruentec:	2308040-LIX001		

Metales en lixiviado (EPA 1311)

Lantano mg/l ^(*)	<0.0001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Litio mg/l ^(*)	<0.005	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Lutecio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Magnesio mg/l ^(*)	<0.2	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Manganeso mg/l ^(*)	0.020	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Mercurio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Molibdeno mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Neodimio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Niobio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Niquel mg/l ^(*)	<0.01	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Plata mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Plomo mg/l ^(*)	0.89	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Potasio mg/l ^(*)	<0.5	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Praseodimio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Rubidio mg/l ^(*)	<0.005	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Samarium mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Selenio mg/l ^(*)	<0.01	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Silicio mg/l ^(*)	<0.5	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Talio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Tantalio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Teluro mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Titanio mg/l ^(*)	<0.005	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Torio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Tulio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Uranio mg/l ^(*)	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Vanadio mg/l ^(*)	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39

Cliente: Ing. Bruna Salgado Gaspar
 Quito, Francisco Andrade Marín E6-80 y Eloy Alfaro
 Telf: 0990574352

Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado Gaspar
Proyecto: Análisis de Lixiviado
Fecha de Recepción: 03 Ago 2023
Tipo de Muestra b): 1 Muestra de Lixiviado
Fecha de Término de Análisis: 16 Ago 2023
Identificación Gruentec: 2308040-LIX001
Fecha de Emisión del Informe: 17 Ago 2023

INFORME
 de RESULTADOS
 de ANÁLISIS



Identificación de la muestra, cliente b):	LIQ EW ICP		
Fecha de Muestreo b):	03 Ago 2023	Fecha Medición	Método Adaptado de Referencia / Método Interno
No. Reporte Gruentec:	2308040-LIX001		

Metales en lixiviado (EPA 1311)

Wolframio mg/l ⁽¹⁾	<0.002	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Yterbio mg/l ⁽¹⁾	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Zinc mg/l ⁽¹⁾	<0.05	09 Ago 2023	EPA 6020 B / MM-AG/S-39
Zirconio mg/l ⁽¹⁾	<0.001	09 Ago 2023	EPA 6020 B / MM-AG/S-39

Acreditaciones

(1) Servicio de Acreditación Ecuatoriano: Certificado No. SAE LEN 05-008

Notas y Aclaraciones

Los ensayos marcados con (*) no están dentro del alcance de acreditación del SAE

Lugar de ejecución del Análisis: Todos los análisis presentados fueron realizados en la Matriz Quito, a excepción de los marcados con la letra (s)

- a) Los equipos utilizados en los ensayos presentados cuentan con sus debidos certificados de calibración o sus homólogos, solicitar al Laboratorio en caso de requerirlos
- b) Información proporcionada por el cliente, Gruentec no se responsabiliza por la veracidad de la misma.
- c) La muestra presentó condiciones adecuadas de preservación y conservación. Llegó en envases adecuados para proteger sus características.
- d) Gruentec cumple con todas las condiciones ambientales requeridas para los ensayos, en caso de requerirlas, solicitar.

Porcentaje de incertidumbre por método o analito (u)

Cromo Hexavalente = 30%; Metales = 18%;

Valor e interpretación de la incertidumbre por método o analito (U)

El valor de la incertidumbre de cada medición (U) se determina mediante la fórmula $U = u/100 \cdot C$, donde C es el valor de la medición.

El rango de incertidumbre obtenido se encuentra en el intervalo $C \pm U$

ISABEL LAURA
 ESTRELLA
 SORIA

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 Motivo: Estoy aprobando este documento
 Ubicación:
 Fecha: 2023-08-17 17:27:05:00

Ing. Isabel Estrella
Gerente de Operaciones

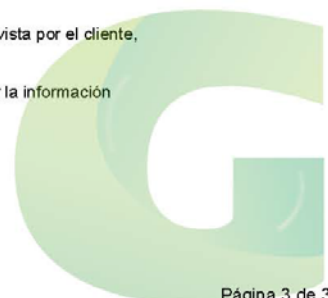
Nota 1: Este informe de resultados, opiniones y/o interpretaciones están basados en la información y la muestra provista por el cliente, para quien se ha realizado de manera exclusiva y confidencial.

Nota 2: La toma de la muestra, objeto de este informe fue realizada por el cliente. Gruentec no se responsabiliza por la información provista por el cliente al respecto.

Nota 3: Sin la aprobación del laboratorio no se debe reproducir este informe, excepto si se lo realiza en su totalidad.

 QUITO Eloy Alfaro 57-157
 y Belisario Quevedo (San Juan de Cumbaya)
 02-6014-371 / 0984680711
 info@gruentec.com

www.gruentec.com



Attachment TS22.1. Evidence of the ICP-MS lead analysis for the filter paper containing the whole anode sludge.



Cliente: Ing. Bruna Salgado Gaspar
Quito
Telf: 0990574352

Actividad principal del cliente: Investigación
Atn: Ing. Bruna Salgado Gaspar
Proyecto: Análisis en papel filtro
Fecha de Recepción: 25 Ago 2023
Tipo de Muestra b): 1 Muestra de papel filtro
Fecha de Término de Análisis: 01 Sep 2023
Identificación Gruentec: 2308300-SOL001
Fecha de Emisión del Informe: 04 Sep 2023

INFORME
de RESULTADOS
de ANÁLISIS

Identificación de la muestra, cliente b):	PAPEL FILTRO LODO ANÓDICO		
Fecha de Muestreo b):	24 Ago 2023	Fecha Medición	Método Adaptado de Referencia / Método Interno
No. Reporte Gruentec:	2308300-SOL001		

Parámetros realizados en el Laboratorio
Metales en Sólidos

Plomo ug/filtro ^(*)	2315 ^{e1)}	01 Sep 2023	IO-1/IO-5/EPA 6020B Adaptado / MM-AG/S-39
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Notas y Aclaraciones
Los ensayos marcados con (*) no están dentro del alcance de acreditación del SAE
Lugar de ejecución del Análisis: Todos los análisis presentados fueron realizados en la Matriz Quito.
n.d. - No Determinado
a) Los equipos utilizados en los ensayos presentados cuentan con sus debidos certificados de calibración o sus homólogos, solicitar al Laboratorio en caso de requerirlos
b) Información proporcionada por el cliente, Gruentec no se responsabiliza por la veracidad de la misma.
c) La muestra presentó condiciones adecuadas de preservación y conservación. Llegó en envases adecuados para proteger sus características.
d) Gruentec cumple con todas las condiciones ambientales requeridas para los ensayos, en caso de requerirlas, solicitar.
e) Diluciones:
e1) La Muestra presenta características que hicieron necesario aplicar dilución 10x.
Porcentaje de incertidumbre por método o analito (u)
Metales = 22%;
Valor e interpretación de la Incertidumbre por método o analito (U)
El valor de la incertidumbre de cada medición (U) se determina mediante la fórmula $U=u/100^*C$, donde C es el valor de la medición.
El rango de incertidumbre obtenido se encuentra en el intervalo $C\pm U$

ISABEL LAURA ESTRELLA SORIA

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Mejor: Estoy aprobando este documento
Ubicación:
Fecha: 2023-09-05 16:16:05:00

Ing. Isabel Estrella
Gerente de Operaciones

Nota 1: Este informe de resultados, opiniones y/o interpretaciones están basados en la información y la muestra provista por el cliente, para quien se ha realizado de manera exclusiva y confidencial.
Nota 2: La toma de la muestra, objeto de este informe fue realizada por el cliente. Gruentec no se responsabiliza por la información provista por el cliente al respecto.
Nota 3: Sin la aprobación del laboratorio no se debe reproducir este informe, excepto si se lo realiza en su totalidad.

 QUITO Eloy Alfaro 57-157
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Página 1 de 1

Table TS22.1 Data for the determination of the theoretical lead content in the aliquot.

Aliquot volume (mL)	0.1
Total volume of the prepared leachate (mL)	110
Sample 1 weight (g)	5.0009
Sample 1 FRX concentration (%)	5.36

Calculation TS22.1 Determination of the theoretical lead content in the aliquot.

$$\text{Theoretical Pb content in the aliquot (mg)} = \frac{\text{Sample 1 FRX concentration (g)}}{100 \text{ (g)}} \times \frac{\text{Sample 1 weight (g)}}{1 \text{ g}} \times \frac{\text{Aliquot volume (mL)}}{\text{Leachate Total Volume (mL)}} \times 1000 \text{ mg}$$

$$\text{Theoretical Pb content in the aliquot (mg)} = \frac{5.36 \text{ (g)}}{100 \text{ (g)}} \times \frac{5.009 \text{ (g)}}{1 \text{ g}} \times \frac{0.1 \text{ (mL)}}{110 \text{ (mL)}} \times 1000 \text{ mg}$$

$$\text{Theoretical Pb content in the aliquot (mg)} = 0.244$$

Table TS22.2 Data for the determination of the real lead content in the aliquot.

AAS Pb concentration of the aliquot (mg.L ⁻¹)	4.58
Flask volume (mL)	50

Calculation TS22.2 Determination of the real lead content in the aliquot.

$$\text{Real Pb content in the aliquot (mg)} = \frac{\text{AAS Pb concentration of the aliquot (mg.L}^{-1}\text{)}}{1000 \text{ (mL)}} \times \text{flask volume (mL)}$$

$$\text{Real Pb content in the aliquot (mg)} = \frac{4.58 \text{ (mg)}}{1000 \text{ (mL)}} \times 50 \text{ (mL)}$$

$$\text{Real Pb content in the aliquot (mg)} = 0.229$$

Calculation TS22.3 Determination of the lead recovery percentage in the initial electrowinning leachate.

** Previous experiment: 95.0%*

$$\text{Pb leaching recovery (\%)} = \frac{\text{Real Pb content in the aliquot (mg)}}{\text{Theoretical Pb content in the aliquot (mg)}} \times 100$$

$$\text{Pb leaching recovery (\%)} = \frac{0.229 \text{ (mg)}}{0.244 \text{ (mg)}} \times 100$$

$$\text{Pb leaching recovery (\%)} = 93.85 \text{ OK}$$

Table TS22.3 Data for the determination of the initial lead content in the diluted leachate.

Leachate volume in the electrolytic cell (mL)	100
Dilution factor	5

Calculation TS22.4 Determination of the initial lead content in the diluted leachate.

$$\text{Pb initial lead content (mg)} = \frac{\text{Real Pb content in the aliquot (mg)}}{\text{Dilution factor}} \times \frac{\text{Leachate volume in the electrolytic cell (mL)}}{\text{Aliquot volume (mL)}}$$

$$\text{Pb initial lead content (mg)} = \frac{0.229 \text{ (mg)}}{5} \times \frac{100 \text{ (mL)}}{0.1 \text{ (mL)}}$$

$$\underline{\text{Pb initial lead content (mg)} = 45.8}$$

Table TS22.4 Data for the determination of the lead content remaining in solution (after 60 min).

Leaching time (min)	60
AAS Pb concentration of the aliquot (mg.L ⁻¹)	0.18
Aliquot volume (mL)	0.1
Leachate volume in the electrolytic cell (mL)	100
Flask volume (mL)	50

Calculation TS22.5 Determination of the lead content remaining in solution (after 60 min).

$$\begin{aligned} & \text{Pb remaining in solution (mg)} \\ &= \frac{\text{AAS Pb concentration of the aliquot (mg)}}{1000 \text{ (mL)}} \times \text{Flask volume (mL)} \times \frac{\text{Leachate volume in the electrolytic cell (mL)}}{\text{Aliquot volume (mL)}} \end{aligned}$$

$$\text{Pb remaining in solution (mg)} = \frac{0.18 \text{ (mg)}}{1000 \text{ (mL)}} \times 50 \text{ (mL)} \times \frac{100 \text{ (mL)}}{0.1 \text{ (mL)}}$$

$$\underline{\text{Pb remaining in solution (mg)} = 9}$$

$$\text{Pb remaining in solution (\%)} = \frac{\text{Pb remaining in solution (mg)}}{\text{Pb initial lead content (mg)}} \times 100$$

$$\text{Pb remaining in solution (\%)} = \frac{9 \text{ (mg)}}{45.8 \text{ (mg)}} \times 100$$

$$\underline{\text{Pb remaining in solution (\%)} = 19.65}$$

Table TS22.5 Data for the determination of the lead precipitated on the anodic sludge (after 60 min).

Leaching time (min)	60
ICP-MS Pb content of the whole anodic sludge (mg)	2.315
Dilution for analysis	5

Calculation TS22.6 Determination of the lead precipitated on the anodic sludge (after 60 min).

$$\text{Pb coming from the anodic sludge (mg)} = \text{ICP/MS Pb content of the whole anodic sludge (mg)} \times \text{Dilution}$$

$$\text{Pb coming from the anodic sludge (mg)} = 2.315 \text{ (mg)} \times 5$$

$$\underline{\text{Pb coming from the anodic sludge (mg)} = 11.58}$$

$$\text{Pb coming from the anodic sludge (\%)} = \frac{\text{Pb coming from the anodic sludge (mg)}}{\text{Pb initial lead content (mg)}} \times 100$$

$$\text{Pb coming from the anodic sludge (\%)} = \frac{11.58 \text{ (mg)}}{45.8 \text{ (mg)}} \times 100$$

$$\underline{\text{Pb coming from the anodic sludge (\%)} = 25.28}$$

Calculation TS22.7 Determination of the lead recovered at the cathode (after 60 min).

Pb recovered at the cathode (%) = Initial Pb content (%) - [(Pb remaining in solution) + (Pb coming from the anodic sludge)] (%)

$$\text{Pb recovered at the cathode (\%)} = 100\% - (19.65 + 25.28)$$

$$\underline{\text{Pb recovered at the cathode (\%)} = 55.07}$$

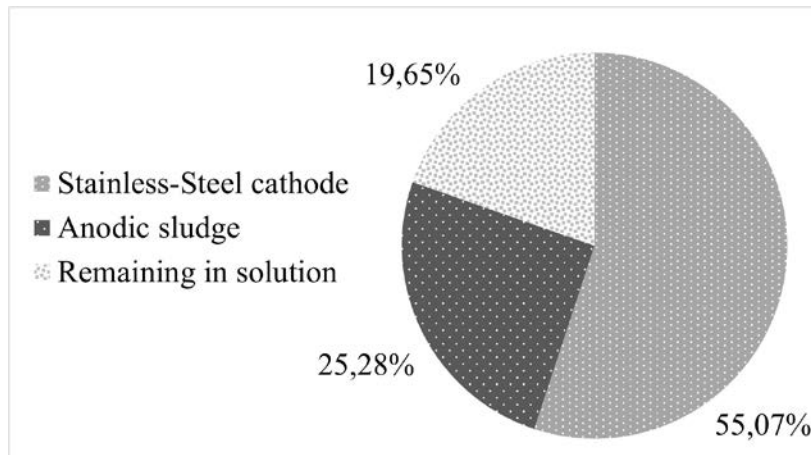


Figure TS22.1 Lead distribution summary throughout the electrowinning process.

Calculation TS22.8 Determination of the electric current to be applied for the electrowinning test.

* Electric current condition applied on the typical electrowinning (hydrofluorosilicic acid) = 170 A.m².
(Cole et al., 1985)

$$\text{Available Cathode Surface Area} = \text{lenght (m)} \times \text{width (m)}$$

$$\text{Available Cathode Surface Area} = 0.030 \text{ (m)} \times 0.028 \text{ (m)}$$

$$\text{Available Cathode Surface Area} = 0.00084 \text{ m}^2$$

$$\text{Electric Current} = \frac{170 \text{ A}}{\text{m}^2} \times \text{Available Cathode Surface Area (m}^2\text{)}$$

$$\text{Electric Current} = \frac{170 \text{ A}}{\text{m}^2} \times 0.00084 \text{ m}^2$$

$$\text{Electric Current} = 0.14 \text{ A} \approx 0.1 \text{ A}$$

Table TS22.6 Data of the lead content decrease in the electrolyte (20:80 leachate-water solution) over time during the electrowinning process.

Time (min)	Sample Weight (g)	FRX Pb Concentración (%)	Pb total theoretical content (g)	Pb total theoretical content (mg)	EW Leachate volume (mL)	Aliquot volume (mL)	Flask volume (mL)	AAS Pb (mg.L ⁻¹)	Pb total real content aliquot (mg)	Pb total real content (mg)
0	5.0009	5.36	0.2680	268.04824	100	0.1	50	0.92	0.0458	45.8
15	5.0009	5.36	0.2680	268.04824	100	0.1	50	0.64	0.0320	32.0
30	5.0009	5.36	0.2680	268.04824	100	0.1	50	0.35	0.0175	17.5
45	5.0009	5.36	0.2680	268.04824	100	0.1	50	0.25	0.0125	12.5
60	5.0009	5.36	0.2680	268.04824	100	0.1	50	0.18	0.0090	9.0
75	5.0009	5.36	0.2680	268.04824	100	0.1	50	0.18	0.0090	9.0

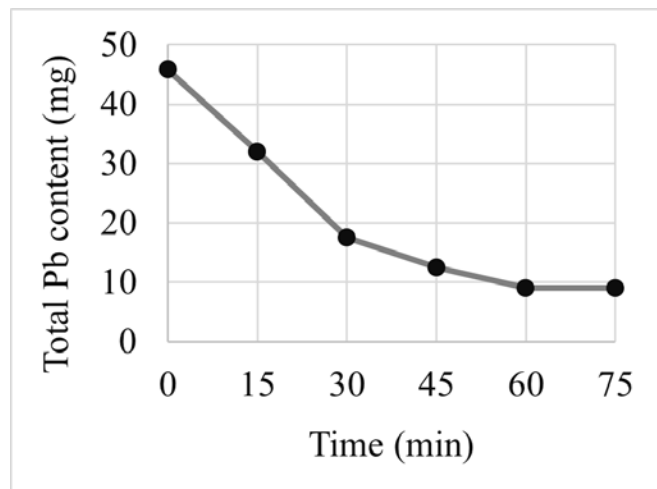


Figure TS22.2 Lead content decrease of the 100 mL electrolyte (20:80 leachate-water solution) over time during the electrowinning development.

Table TS22.7 Data for the experimental determination of the lead recovered at the cathode (after 60 min).

* Assuming that the whole deposited solid at the cathode is lead Pb.

Stainless-steel cathode initial weight (mg)	6250.5
Stainless-steel cathode final weight (mg)	6270.7

Calculation TS22.9 Experimental determination of the lead recovered at the cathode (after 60 min).

$$\text{Pb recovered at the cathode (mg)} = \text{Cathode final weight (mg)} - \text{Cathode initial weight (mg)}$$

$$\text{Pb recovered at the cathode (mg)} = 6270.7 \text{ mg} - 6250.5 \text{ mg}$$

$$\text{Pb recovered at the cathode (mg)} = 20.2 \text{ mg}$$

$$\text{Pb recovered at the cathode (\%)} = \frac{\text{Pb recovered at the cathode (mg)}}{\text{Pb initial lead content (mg)}} \times 100$$

$$\text{Pb recovered at the cathode (\%)} = \frac{20.2 \text{ (mg)}}{45.8 \text{ (mg)}} \times 100$$

$$\text{Pb recovered at the cathode (\%)} = 44.10\%$$

Calculation TS22.10 Coefficient of variation between the calculated recovered lead content vs. experimental recovered lead content.

$$\%CV = \frac{\delta}{\mu} \times 100$$

$$\%CV = \frac{\delta (55.07\% ; 44.10\%)}{\mu (55.07\% ; 44.10\%)} \times 100$$

$$\%CV = \frac{7.76}{49.59} \times 100$$

$$\%CV \approx 15.64$$



Figure TS22.3 Electro-winning assay evidence.