



Experimental Investigation of Pb Release Characteristics in Zn-Pb Mine Tailings under Simulated Leaching Conditions, Anguran, Iran

Ahmad Akhavan[✉] | Ahmad Golchin

Soil Science Department, Faculty of Agriculture, University of Zanjan, P.O.Box 38791-45371, Zanjan, Iran

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ABSTRACT

The aim of this research was to use a variety of leaching methods to see how different parameters affected the amount of lead leaching from tailings. Synthetic precipitation leaching procedure, toxicity characteristic leaching procedure, leachate extraction procedure, and field leach test protocols were utilized to assess the toxicity of the tailings. The impact of the liquid-solid ratio, particle size, contact time, and pH on lead release from tailings was also investigated. According to the findings, pH entirely effects on the release of lead from the tailings, and amphoteric leaching behavior was observed. The tailings were classified as hazardous material as a result of the TCLP leaching protocol's findings. S1 and S2 samples had lead mobility indexes of 51% and 5.6%, respectively. The solubility process influenced the discharge of lead from the tailings. In the particle size ranges of 0.3-0.5 mm and 0.6-1.0 mm, respectively, the maximum amount of lead was released from S1 and S2 samples. Various experiments have shown that the interaction between different factors will have complex and strong effects on the leaching process. To that end, managing of tailings and preventing lead emission into the environment necessitates a unique technique. Leachability is affected by a number of factors and often multiple factors can produce synergistically different releases than would be predicted by each factor alone. However, validation of the leaching approaches to field-collected and monitored cases indicates that combined effects are either captured by the test data or can be considered through fate and transport modeling.

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INTRODUCTION

In recent years, the environmental impact of mining activities has been overshadowed by economic factors and little attention has been paid to the environment. Considering that Iran produces a large volume of tailings in different parts of the country, it is not surprising that these tailings will have many environmental effects. The major portion of these tailings arises from metallurgical extraction (Çoruh et al., 2013). This process produces two products: a valuable concentrate containing the desired element and a discarded product containing different type of pollutants, particles and chemicals known as tailing (Hudson, 2001; Younger and Wolkersdorfer, 2004; Lottermoser, 2010; Zhang et al., 2019). Tailings are mostly rich in toxic metals such as As, Pb, Cu, Ni, Mn, Cd, Cr, etc (Mendez and Maier, 2007; Yang et al., 2013; Uguwanga and Kgabi, 2020). Pollution of the environment, water and land resources by mining has increased in recent decades (Al-Jabri et al., 2006; Hudson-Edwards and Dold, 2015).

The presence of heavy metals in the environment due to mining activities, especially lead, has attracted great attention due to its toxicity to human life (Roussel et al., 2000; Montanaro et al.,

*Corresponding Author Email: ahmad.akhavan@znu.ac.ir

2001; Moors and Dijkema, 2006, Ye et al., 2015; Nurcholis et al., 2017). The tailings of lead and zinc mines are packed with heavy metals, such as zinc and lead, but contain little macronutrients, little physical structure, and are highly salinized (Khan et al., 2019). Lead leaches from tailings and gets into water and soil through two important processes: solubility and mobility. According to some scientists, lead is known to cause various diseases when it is introduced into the human food chain, including the most sensitive brain, abdominal pain symptoms, constipation, headaches, irritability (Schreck et al., 2012), memory problems, inability to conceive children, and tingling in the hands and feet (Jaishankar et al., 2014). Heavy metals (Pb, Zn, Cd) concentrations in lead and zinc mine tailings are naturally greater than the earth's crust (Wani et al., 2015). While the maximum allowable concentration of lead in drinking water is 10 mg/L (WHO, 2008). The average concentration of lead in tailings dam seepage water is more than 500 mg/L (Lottermoser, 2010). Kovács et al. (2013) stated that AMD's exit from an abandoned lead-zinc mine would severely affect the Toka River and cause water pollution. They reported that tailings neutralization is not so effective process in reducing the environmental risk of tailings. In running waters from metal mine sites, for instance tailings pond water from Jumna Tin Mill; mine site drainage water from Montalbion Silver Mine; and tailings dam seepage water from Mary Kathleen Uranium Mine, lead concentrations varied between 607, 36, and 450 $\mu\text{g/L}$, respectively. In studies by Omanović; et al. (2015), it was found that heavy elements released from lead and zinc tailings by entering the river initially form ferric oxyhydroxides. Also in their study, the speciation of elements with DGT technique revealed that Mn, Co, Pb, Cd and Zn are present in the available and bioavailable forms and are fully susceptible to leaching and transfer to lower areas. Tailings are rich in sulfides, which comprise a complex mixture of sulfides with metals (zinc, lead, copper). Consequently, acid mine drainage (AMD) and environmental damage can occur. Pb reactivity and mobility in lead and zinc mine tailings depends on the physicochemical structure and properties of tailings (Falagán et al., 2017).

Ma et al. (2019) suggest that the concentration and distribution of lead in tailing particles is the main factor determining the amount of lead released into the environment by leaching. Heavy metal concentrations in leachate solutions are affected by the physical-chemical properties of the tailings, including pH, particle size, water to tailing ratio, heavy metal fractionation, mineralogy, chemical composition, and contact time between particles and water (Karaca et al., 2016). In many studies, these factors contribute greatly to the determination of the toxicity of mineral tailings when used in various environmental scenarios (Grathwohl and van der Sloot, 2007; Grathwohl and Susset, 2009; Guyonnet, 2010; Liu et al, 2017). The leaching of contaminants from tailings directly affects groundwater sources, especially if the pollutants (such as lead) are easily transported by acid rain or any other flowing water and discharged to surface and groundwater sources (Uugwanga and Kgabi, 2020).

The environmental impact of Zn-Pb mine tailings has not been fully assessed, and it remains unclear how lead is released from these tailings. Therefore, it is essential to understand the leaching characteristics of lead in order to enhance the controlled handling of Zn-Pb mine tailings. Therefore, in this paper, lead release behavior from tailings and mechanisms affecting this process was tested. In order to determine whether the liquid-solid ratio, pH, contact time, and particle size affect lead release from mine tailings, batch leaching tests were conducted. The toxicity level of tailings were investigated by synthetic precipitation leaching procedure (SPLP), toxicity characteristic leaching procedure (TCLP), field leach test (FLT), & leachate extraction procedure (LEP) and the sequential extraction procedure was also applied to evaluate the mobility behavior of lead in tailings.

MATERIALS AND METHODS

Study region

Samples of tailings from the lead-zinc mine of Anguran (Figure. 1) were taken by researchers in Mahnanshah city, Zanjan province, Iran ($36^{\circ} 37'$ north, $47^{\circ} 24'$ east). A semi-arid climate

surrounds this region and Angoran mine reserves include 8 million tons of zinc in the open field and 4 million tons of zinc in the subterranean section (average grade of 28% zinc and 6% lead). Iran's Angaran lead and zinc production plant is the largest producer of lead and zinc in the world, and the largest mine in the Middle East with about 80% of its reserves in carbonate and 20% in sulfide (Borg, 2005). The first exploitation license of the Angoran mine was issued in 1922. The average annual precipitation, temperature, and humidity in this region are 295 mm, 10.9 °C and 54% respectively. The groundwater around this mine is at a depth of 50 meters above the ground. The Anguran ore is located among the limestone gems and the main geology is composed of Precambrian felsic gneiss. In this mine, 7 types of minerals including hard carbonate mineral, soft carbonate mineral, shear carbonate, calamine, very low-grade mineral, sulfide mineral and carbonate sulfide mixture have been identified by Iran Lead and Zinc Company. Geochemical characteristics of sulfide and non-sulfide minerals of Angoran lead and zinc mine (mg/kg) were presented in Table 1. More details on the geology and processing methods of the Anguran deposits were provided by Daliran et al. (2013).

Sphalerite (46.1%), galena (31.2%), Smith zonite (17.1%) and quartz (5.5%) are the most important sulfide ore minerals. Non-sulfide ores also include the minerals of Smith Zonite, Arsenopyrite, Greenocite, Serosite, Pyromorphite, Hemorphite, Clay minerals and Apatite. Exploitation of Angoran mine is done by open pit extraction method in carbonate section and underground extraction method in sulfur section. The host rock of the Anguran mineral zone is located in a metamorphic complex of Neoproterozoic to Cambrian age, which has been deformed during the Lower Miocene by extensional processes in the region (Sharafi et al., 2020).

Sample collection and preparation

Two kinds of mineral tailings generated from different extraction processes were sampled from Angoran lead-zinc mine in May 2019. The lead-zinc plant created two types of tailings during the processing of deposits, hot filter cake or cobalt cake (sample S₂) and cold filter cake or nickel cake (sample S₁). In order to extract zinc from high-grade ores, sulfuric acid and chemicals such as manganese dioxide, iron sulfate, and aluminum sulfate are added to the solution. By continuing the route, lime is used to neutralize these materials, and a leached filter cake (leach cake) is produced by filtering the neutralized solution. At this phase, various impurities precipitate and some metals, like lead and iron, accumulate in the leaching filter cake (leach cake). In the subsequent step, potassium permanganate is added to the solution to precipitate the cobalt metal. A hot filter cake is formed as a result of this process. A cold filter cake is produced by adding zinc powder and copper sulfate to the solution obtained from this step. In order to conduct this research, both types of tailings (cold and hot filter cakes) were sampled. Following transfer to the laboratory, samples were air dried for two weeks, sieved through a 2 mm sieve, and kept in a desiccator for the duration of the test.

Hazard Assessment

The following leaching processes were performed in this study to determine the hazardousness of tailing samples.

TCLP (Toxicity Characteristic Leaching Procedure): this technique is used to determine

Table 1. Geochemical characteristics of sulfide and non-sulfide ores of Angoran lead and zinc mine (mg/kg).

Element	Zn	Pb	As	Co	Cu
sulfide	377000	10000	760	403	250
non-sulfide	266000	52000	6100	490	400

whether or not a waste should be disposed of in a landfill and classed as hazardous. If the tailings have an acidic pH, extraction fluid No. 1 with a pH of roughly 4.93 was utilized, as stated in the TCLP procedure. In a one-liter volumetric flask, combine 5.7 mL glacial $\text{CH}_3\text{CH}_2\text{OOH}$ with 500 mL deionized water to generate extraction fluid No. 1. Then add 64.3 mL of 1N sodium hydroxide and deionized water to bring the container to a one-liter capacity. The ultimate pH of this solution should be 4.930.05 after it has been correctly prepared. The tailings samples were passed through a 10 mesh aperture lab standard test sieve stainless steel before beginning the extraction process. The liquid to solid ratio in this experiment was 20:1, and the suspension was agitated for 18 hours at 30 rpm using a rotary agitation equipment. Once the mixture has been centrifuged, the extract is stored in the refrigerator (USEPA, 1992).

SPLP (Synthetic Precipitation Leaching Procedure): designed to simulate the leaching of heavy elements from waste that are on the ground surface or in the ground and exposed to rain (neutral to weakly acidic). This approach uses acidified deionized water as the extraction fluid, with the goal of simulating acid rain in natural conditions. The SPLP leaching technique provides a straightforward method to analyze metal mobility in the environment since it simulates natural rainfall and describes the leaching potential of contaminants from waste. The extraction fluid has a pH of 4.2 and is made up of a 60:40 ratio of sulfuric acid to nitric acid (by weight). In this process, 10 g of tailings samples were combined with 200 mL of extraction fluid and agitated for 18 hours at 30 rpm, identical to the TCLP procedure. This part will be followed by another. To separate the liquid from the solid part, the samples were centrifuged at 4000 rpm for 10 minutes (USEPA, 1994).

FLT (Field Leach Test) was designed to quickly assess, estimate, and compare the geochemistry of leachate from mineral tailings accumulation masses.

This method replicates the interaction between water and various materials and is quick, high-quality, and low-cost. This approach has been used to evaluate a variety of materials, including biosolids, dust, flood sediments, solid sewage sludge, municipal wastes, and others (El-Kamash et al., 2005; Hageman, 2007). The FLT method is performed by weighing 50 grams of the sample and mixing it with one liter of deionized water in a one-liter bottle (liquid to solid ratio 20 to 1). The bottle was then capped and forcefully shaken by hand for 5 minutes. Allow 10 minutes for the contents of the bottle to settle after shaking. The leachate was then filtered

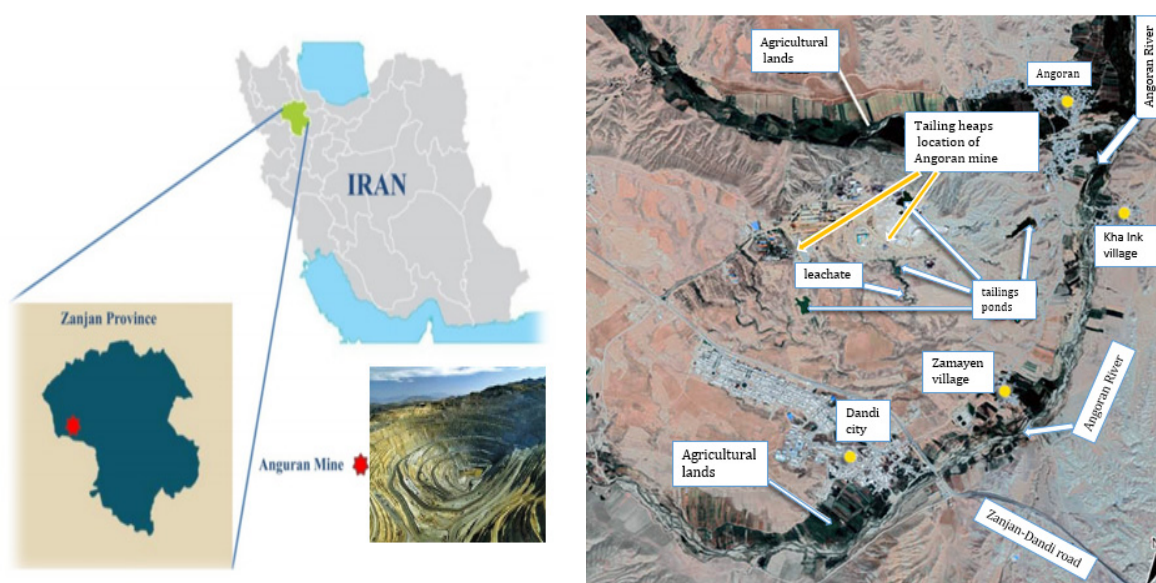


Fig. 1. Location of Angoran lead and zinc mine in relation to Zanjan province and Geographical details of the river, villages, farmlands and tailings

using Whatman filter paper grade 42. (Hageman and Briggs, 2000).

LEP (Leachate Extraction Procedure): This is a modern and widely used process for separating hazardous and non-hazardous material. It can also be used to simulate heavy metal leaching from hazardous waste in landfills.

To begin, 50 g of tailings are combined with 800 mL deionized water (pH= 5.0 with a 0.5 normal of acetic acid solution) and agitated at 10 rpm for 24 hours. It's important to note that the pH of the solution should be recorded multiple times by the end of the test, but not more than 5. Furthermore, the volume of 0.5 normal acids acetic supplied should not exceed 200 mL (Coruh et al., 2013).

Leaching Behavior

The following leaching protocols were used to evaluate the effect of four parameters (contact duration, particle size, liquid to solid ratio, and pH) on the amount of leached lead from tailings (Liu et al., 2017).

In pH-dependent tests, the pH of deionized water was changed to the required values of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14 by adding HCL (0.1 Molar and 1 Molar) and NaOH (0.1 Molar and 1 Molar). 1 gram of samples were weighed into polypropylene bottles, and 10 mL of deionized water with the appropriate pH values was added to the dishes. At 25 °C, the samples were agitated for 360 minutes. For the leaching time dependency experiment, 1g of each tailings sample was weighed into polypropylene bottles and 10 mL of the deionized water was added. The bottles were shaken for 0, 10, 30, 60, 100, 150, 210, 280, and 360 minutes at 30 rpm. The quantity of lead leaching from lead-zinc mine tailings to solution as a result of variations in the liquid-solid ratio was examined using the method below. To begin, 1g of each tailing sample is spilled into a centrifuge tube, and a certain amount of deionized water is added to the tubes to achieve ratios of 20:1, 20:2, 20:4, 20:6, 20:8, and 20:9. 20:10, 20:12, 20:14, and 20:16 mL/g. The samples were then shaken for 360 minutes at 25 °C. In particle size experiment test, the dried lead-zinc mine tailings were screened to 10 types of size particle (2-1.8, 1.8-1, 1-0.6, 0.6-0.5, 0.5-0.3, 0.3-0.25, 0.25-0.15, 0.15-0.075, 0.075-0.045, <0.045 mm). In a 50 mL centrifuge tube, 1g of each lead-zinc mine tailing sample with varied particle sizes was placed, and 10 mL of deionized water was added. After this, the samples were agitated on an orbital shaker for 360 minutes at 25 °C. After centrifuging the samples, the extracts were held in the refrigerator (4 °C) to determine the lead concentration.

Sequential Leaching Procedure

The sequential leaching process is a method for assessing and estimating the mobility and accessibility of metals in tailings. We adopted a 6-step sequential leaching procedure explained by Sims et al. (2008); Schultz et al. (1998) and Tessier et al. (1979). Water-soluble fraction (Wat), exchangeable fraction (Exc), carbonate fraction (Car), Fe/Mn oxide fraction (Fe/Mn), organic fraction (Org), and residual fraction (Res) are the six processes (Res). The complete schemes are listed here:

F_1 , The water-soluble fraction (Wat.) is used to determine the amount of available metal species in a solution. To begin, weigh one gram of tailings and pour it into the centrifuge tube. After that, add 25 mL deionized water. Solid and liquid components were separated by centrifugation after 2 hours of vibration at the desired temperature (25 °C) (10 minute in 4000 rpm). Save the residue for the next fraction and store the extract in the refrigerator at 4°C for subsequent analysis.

F_2 , The exchangeable fraction (Exc.) was used to extract metal species with low electrostatic absorption that are easily leached during the ion replacement process. Firstly. To separate the extract from the tailings, 10 mL of 1 mol/L magnesium chloride solution at pH= 7 was added with the remainder of the previous stage, and the resulting mixture was agitated for 1 hour and

centrifuged at 4000 rpm for 15 minutes.

F_3 , the carbonate fraction (Car.) Is concerned with metals bound to carbonate compounds. To remove lead associated to these components, a one molar sodium acetate solution is utilized. 10 mL of one molar sodium acetate solution was added to the residual component of the previous stage for this purpose. It was centrifuged for 10 minutes at 5000 rpm after stirring for 5 hours at 25 °C. The filtrate was preserved for the next fraction after the supernatants were filtered via filter paper.

F_4 , the Fe/Mn oxide bound fraction (Fe/Mn) is a crucial chemical structure for many heavy metals found in various waste products. The residual carbonate fraction was treated for 6 hours in a bain-marie (96 °C) with 20 mL of 0.04 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) acetic acid and special shaking. After that, the samples were centrifuged for 10 minutes at 5000 rpm.

F_5 , The organic fraction (Org.): the leftover Fe-Mn oxides fraction was treated for 5 hours in a bain-marie (85°C) with 20 mL of 30% hydrogen peroxide. After cooling the centrifuge tubes, 20 mL of 3.2 mol/L NH_4OAc (pH= 2, set by HNO_3) was added and the tube was shaken continuously at 25 °C for 1 hour. After that, the samples were centrifuged for 10 minutes at 5000 rpm.

F_6 , To extract the lead in the structural part (residual), 20 mL of Aqua Regia solution was added to the remaining component of the previous stage and placed in a bain-marie (85 °C) for 12 hours to extract the lead.

Total metal content: to extract the total lead in the tailings, 12.5 mL of 6 Molar nitric acids was added to the samples, and the centrifuge tube was placed in the bain-marie (25 °C) for 12 h (Sposito, 1982).

Recovery: The following equation was used to assess the efficiency of the sequential extraction technique. In this equation, the extraction procedure is more accurately completed if the result is closer to 100 (Nemati et al., 2011; Lei et al., 2010):

$$\text{Recovery}\% = \frac{F_1 + F_2 + F_3 + F_4 + F_5 + F_6}{\text{Total concentration}} * 100$$

Mobility Index (MI): Element mobility and bioavailability are largely determined by their geochemical form (Kabala and Singh, 2001; Olajire et al., 2003). Heavy metal leaching and bioavailability are increased when there is a large percentage of heavy metals in more mobile components. The following equation was used to compute the mobility index for Pb:

$$MI = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6} * 100$$

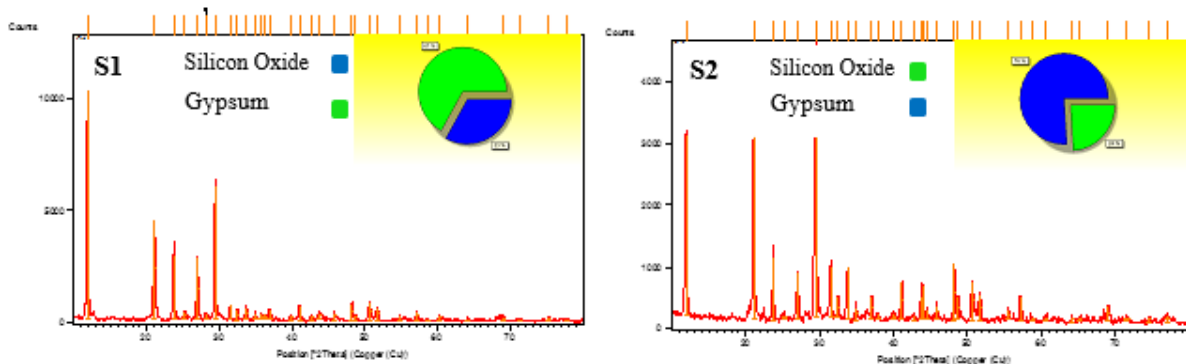
LOI, XRD, XRF and SEM analysis

Loss on ignition (LOI) is a usual procedure for measuring the amount of organic and carbonate compounds in many materials and was determined gravimetrically after heating 1 g aliquot of samples at 950 °C for 12 h. The main chemical content of tailings was specified by a Philips MagiX PRO XR spectrometer (XRF, Rigaku 2100). Crystalline minerals in the tailings were identified by X-ray diffraction spectrometer (XRD) (Philips PW1730) using Cu (K α) radiation (40 kV, 40 mA), specimen length 10mm, start Position (°2 θ): 10.0200, end position (°2 θ): 79.9800. Scanning electron microscopy (SEM, FEI Quanta-200) analysis was used to characterize the microstructures and micromorphology of tailing samples.

All experiments were performed in two replicates, and their meanings were used for analyzes and drawing graphs. The inductively coupled plasma Emission Spectrometry (ICP-OES) spectrometer was used to determine lead concentrations in the eluates (Varian series 700 model 710 Axial, Australia). Plastics, centrifuge tubes, and glassware were immersed in a 10% nitric

Table 2. The results of chemical composition analysis of lead-zinc mine tailing samples

Sample	pH	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	MgO	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI	SO ₃
	(5:1)	%	%	%	%	%	%	%	%	%	%	%	%
S ₁	6.1	14.5	4.94	5.01	16.98	0.37	0.475	0.69	0.19	0.15	0.063	28.5	24
S ₂	5.4	9.2	2.74	2.52	18.85	0.4	0.86	0.48	0.10	2.2	0.044	32.2	27

**Fig. 2.** The XRD pattern of the mine tailings

acid solution for 48 hours before being cleaned with deionized water. The lead concentration in the deionized water utilized was 0.0001 mg/L.

RESULTS AND DISCUSSION

Characteristics of lead-zinc mine tailings

In Table 2 the composition percentage and pH of samples with deionized water was shown. Calcium oxide, silicon dioxide, sulfur trioxide, ferric oxide, aluminum oxide, and iron oxide constituted the major constituents of the samples, followed by phosphorus, sodium, titanium, and magnesium oxide as minor constituents. Due to ore processing, sample S₂ exhibited a higher acidity level than sample S₁. In the waste processing of sample S₂, sulfuric acid has been used. The high SO₃ content indicates that the tailing materials are capable of producing AMD (Acid Mine Drainage). Indicators related to calculating the acid production capacity of tailing samples (NAG, NAGPH, NPR, NNP, NP, NAP, Total S %,) have also been written in the previous study (Akhavan and Golchin, 2022). Both samples had the potential to produce acid. The calculated NAG (net acid generation) values for samples S₁ and S₂ were 19.6 and 29.4 kg H₂SO₄ t⁻¹, respectively.

X-ray diffraction (XRD) patterns of tailing samples can be seen in Figure 2. XRD analyses were conducted to study the mineralogy of tailings. Based on the XRD patterns and XRF results, it appears that silicon oxides and calcium sulfate are the major phases in tailing samples. Based on the results of the present research, it was discovered that tailing chemical composition differs considerably from one type of tailing to another based on the mining process at various stages and mining methods. Chand et al. (2009) also gave similar results. Nevertheless, only quartz and gypsum have been identified as peaks.

Leaching hazard assessment

The SPLP, TCLP, LEP, and FLT methods were used to determine the leachability of lead from lead and zinc mine tailings in different scenarios and whether lead-zinc mine tailings are toxic to biological systems. Figure 3 shows the extracted lead concentration after each

leaching extraction method. The amount of leached lead varied in leaching protocols. Different particle sizes, types, and compositions of leaching agents, as well as particle contact time with leaching agents cause different amounts of leached lead from tailings. TCLP is an acetic acid extraction procedure that evaluates the potential release of contaminants from wastes through diluted acetic acid extraction. The waste material should be classified as hazardous waste if the extract obtained from the TCLP method contains a concentration greater than or equal to the USEPA-specified permissible toxic limits (Boyer, 1990). Sample S_1 released more lead in each of the four leaching tests than sample S_2 , possibly because the two samples are structurally different. The highest amount of leached lead was in the TCLP test and sample S_1 . TCLP-extractable Pb for S_1 & S_2 samples ranged from 145.2 to 50.39 mg/kg, respectively (Figure 3). As a result of different processes of tailing operations, sample S_1 had a higher released lead concentration. The leached lead concentrations in the S_1 and S_2 samples exceeded the USEPA TCLP limits (EPA, 2004; Liu et al., 2017). USEPA regulatory limit for Pb is 5.0 mg/L. Then each of the two samples qualifies as hazardous materials. Hazardous requires awareness of the danger posed by humans and the environment, assuming that all necessary transportation, storage, and organization procedures are not undertaken.

Figure 3 depicts the leached lead concentration in the SPLP test. This approach uses an extractant liquid that simulates acid rain. The simulated acid rain removed only about 24.6 and 19.8 mg/kg of Pb from the S_1 and S_2 samples, which are equal to 1.23 and 0.99 mg/L, respectively, in contrast to the significant TCLP leachability for Pb. Sample S_1 had a higher concentration of released lead than sample S_2 in the SPLP extraction test, according to TCLP. The results shown in the SPLP experiment on the lead-zinc mine tailings have indicated that lead is present in excess of the MCL (Maximum Contaminant Levels) or recommended concentration under the National Primary and Secondary Drinking Water Regulations (NPDW and NSDW). The lead standard for main and secondary drinking water is 0.015 mg/L. As a result of precipitation entering the tailings and forming leachate or fluid flow, substantial concentrations of lead can be released into the environment, resulting in high contamination over time.

In Figure 3 the extracted lead concentration after FLT short-term extraction method presented. For rapid evaluation and comparison of quality characteristics of waste and mineral tailings, Hageman, (2007) formed the U.S. Geological Survey Field Leach Test (FLT). This protocol (FLT) is a useful tool for geochemical classification of active, easily soluble, and potentially bioavailable elements that are moveable after being leached with water. Pb release from S_1 and S_2 samples in the FLT test were similar to the SPLP test (34.7 and 25.3 mg/kg, respectively)

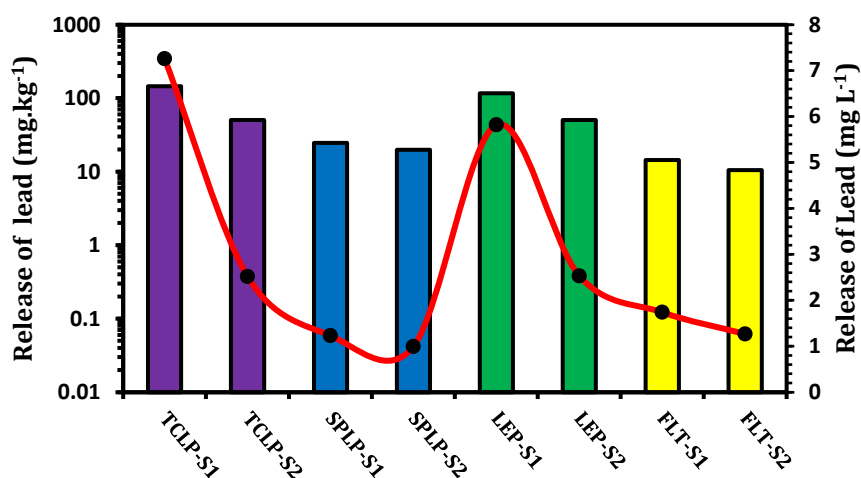


Fig. 3. The leaching of lead from tailing samples (S_1 and S_2) in leaching protocols (column mg/kg, smooth line mg/L)

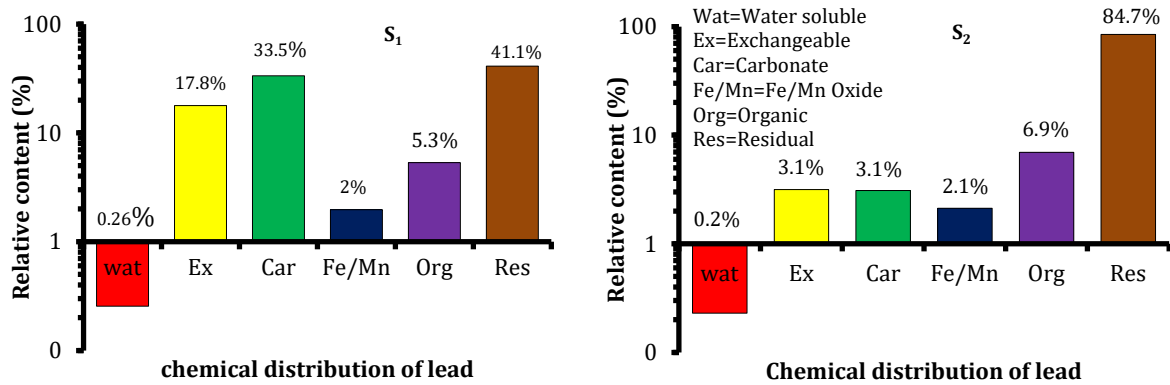


Fig. 4. Lead distribution in tailing samples (log scale)

matching to near 0.002% and 0.001% of the total Pb content in the tailings. FLT test results were similar to the previous two experiments (TCLP and SPLP), and in this experiment, more Pb was released from sample S₁. However, a lower concentration of Pb was released, due to the low acidity of the leaching solution. In compared to other methods, the FLT approach has the benefit of being able to check waste material quickly and produce nearly acceptable findings.

The Leachate Extraction Procedure (LEP) was developed to investigate the waste material in Ontario, Canada. The Canadian General Standards Board (CGSB, 1987) eventually adopted this procedure and accepted it for use in identifying wastes that are very harmful to the environment. In the LEP test, Pb was leached from lead-zinc mining tailings at concentrations of 106.4 mg/kg for sample S₁ and 50.6 mg/kg for sample S₂. Pb was discharged in larger quantities from sample S₁ than from sample S₂, as in earlier testing. The different amounts of lead released from the samples are related to the diverse metallurgical extraction techniques used in mineral processing.

Each of these approaches works on a different principle. The TCLP test creates a buffered environment in which heavy metals can be extracted. Instead, the tailings in the LEP approach are subjected to pH changes, which is more reflective of the actual environment. As a result, there's a higher chance that oxygen will get into the extraction tube, affecting the pH of the extract as well as the oxidation state of the dissolved metals. The goal of the SPLP extraction technique (solutions are unbuffered) is to imitate acidic precipitation that could occur in a situation where rainwater could pass through the tailings and into the groundwater, carrying soluble elements with it. To put it another way, the experiments described in the previous sections are often costly, time-consuming, and difficult, and they necessitate a large amount of equipment to complete. However, FLT is a low-cost, practical, and quick method for simulating probable reactions between leachant and tailings.

All of these approaches were investigated in this study, and the differences in the amount of lead leaching from lead-zinc mine tailings were related to differences in leaching solutions, time, and shaking time. All batch leach tests (from all aspects) show that tailings have the potential to release contaminants into the environment.

Partitioning of lead in samples: sequential extraction method

To determine the fractionation of lead within the tailing samples, a sequential extraction process was used. The sequential extraction approach is used to model the process of heavy metals being released into solution under various environmental conditions (Jones and Hao, 1993; Ye et al, 2022). The chemical fractions of heavy metals in tailings affect their mobility, bioavailability, and environmental stability, making them more important than the total

Table 3. Pb concentrations (mg/kg) in sequential extraction procedure applied on lead-zinc mine tailings

Sample	WSF	EXF	CRF	FE/MNF	OF	RF	Sum of all fraction	Pb Concentration in one step digestion	% Recovery	Mobility Index (%)
S ₁	43.4	3037.1	5695.5	335.1	906.6	6991.1	17008.6	16895.7	106.6	51.6
S ₂	28.9	403.5	395.6	271.3	887.2	10792.1	12788.5	11940.5	107.1	6.5

Table 4. Assortment of mobility index and risk them for environment

MI (%)	stability	hazard
MI ≤ 1	No stability	No hazard
1 < MI ≤ 10	Low stability	Low hazard
10 < MI ≤ 30	Medium stability	Medium hazard
30 < MI ≤ 50	High stability	High hazard
50 < MI ≤ 75	Very high stability	Very high hazard

concentration of heavy metals from an environmental standpoint (Peng et al., 2017). Figure 4 shows the Pb concentrations in each chemical fraction as a percentage of total Pb. In the lead-zinc mine tailing samples (S₁ and S₂), the lead recovery rates were reasonable (106.6 % –107.1 %). Different distribution fractions of Pb can be found in both lead-zinc mine tailing samples. The percentages of water-soluble Pb fractions linked with F₁ in both tailing samples are the smallest and the dominant levels of lead seen in the residual fraction among the six fractions analyzed. The order of lead concentration in various factions of sample S₁ & sample S₂ as below, respectively: Residual > Carbonate > Exchangeable > Organic > Fe/Mn Oxide > Water soluble; Residual > Organic > Exchangeable > Carbonate > Fe/Mn Oxide > Water soluble. In the examined fractions, the lead concentration distribution trend was different. More than 50% of the lead in sample S₁ is in the first three components (mobile), but this number is less than 7% in sample S₂. Soluble, exchangeable, and carbonate components are generally formed by anthropogenic activities and are rapidly leached based on the binding energy of heavy elements with distinct phases (Saleem et al., 2018). The leaching of heavy and toxic metals poses a serious threat to both plant and animal life. Unlike the previous state, sample S₂ has over 85% of lead in the residual fraction, showing that sample S₂ has a lower toxicity level than sample S₁. Human manipulation does not play a significant role in the residual phase of lead, which is often related with geological and historical resources (Islam et al., 2015). Furthermore, lead-zinc mine tailings had minimal Fe/Mn oxide and organic fractions (less than 10% of total). Oxide conditions can cause the dissolution of iron and manganese oxides, as well as organic components (Karbassi and Shankar, 2005; Sundaray et al., 2011).

The mobility index was used to estimate the potential for lead mobilization (MI). Table 3 shows the MI results that were calculated. The MI, which considers just the weakly adsorbed fractions using a fractionation procedure, is a more reliable indicator. In sample S₁, the computed mobility index revealed that Pb had high mobility (MI= 51%), which was more compatible with the concentration of lead in this sample, which represents a very high environmental danger (Table 4). The mobility index of sample S₂ was low (6.5%), and this difference in the mobility index of the examined samples could be related to structural variances in the tailings and differences in the metallurgical extraction methods (Lei et al., 2010). The lead mobility index in the S₁ sample was quite high, indicating that under ideal environmental conditions, lead may easily travel and penetrate water and soil resources (See Table 4). Whatever the amount

of MI in tailings was, it demonstrated that this material poses a greater risk to the environment. Lead is an extremely hazardous element, according to the Russian general toxicological standard (Vodyanitskii, 2016). As a result, it is vital to control the amount of lead that enters the environment. The mobility of elements in the environment is determined by a number of parameters, including mobility, element concentration in tailing particles, and solubility. Although heavy metals attached to organic parts can become mobile due to prevailing oxide circumstances, metals attached to organic parts are not harmful to the environment since they are removed slowly under favorable environmental conditions. They can, however, move when the environment becomes excessively oxidized or severely reducing. Prolonged flooding caused by climatic change (e.g., rain surge) may occur in some modes due to the mobilization of trace metals and pesticides stored in soil and tailings, or the mobilization of metals adsorbed on the solid matrix (Liang et al., 2014).

Bath leaching experiments

The process of leaching elements from waste materials, which is influenced by physicochemical qualities and occurs when a leachant seeps through (e.g. soil matrix) or passes through the particles. As a result, organic and inorganic contaminants are released into the environment (Houben et al., 2013; Ye et al, 2022). The batch leaching test is one of the most important procedures for determining the leaching of components from tailings. Batch testing are similar to column leaching tests in terms of speed and simplicity. A batch leaching test is a quick and inexpensive approach to determine the toxicity of a hazardous chemical that has been dumped on the ground (Cote and Constable, 1982). Because conditions may be nearly regulated over a short period of time, the results are more repeatable than those from column leaching (Colombani et al., 2015). Shape, size, and percentage of particle porosity in waste materials are very essential physical parameters, while the most important chemical factors are temperature, contact time, liquid to solid ratio, amount of leaching agent, and pH. To mimic the effect of diverse ecological conditions on the release of contaminants from tailings, many features of batch leaching studies should be carried out. Some of the more relevant characteristics of these test conditions are investigated in this paper:

pH dependent release

The pH of the leachate is a key factor in determining the solubility of several trace elements, with more metallic cations precipitating as pH rises and anionic species such as arsenate, selenate, molybdate, borate, chromate, and vanadate appearing in more soluble forms (Spears et al, 1995). The acidity (pH) of the environment has a direct impact on cation adsorption ability or the cation exchange process on active surfaces with adsorption-desorption power. The purpose

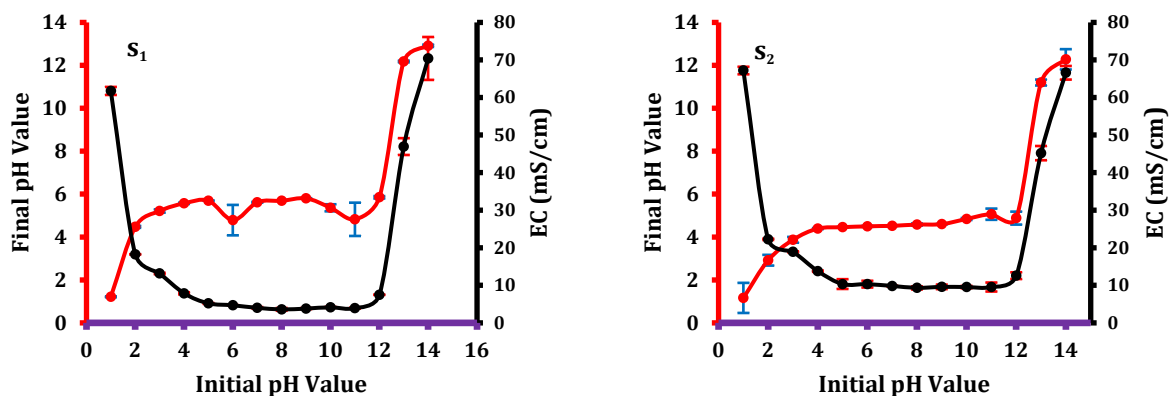


Fig. 5. The EC and pH of samples after 360 minutes of shaking time (pH = red curve, EC= black curve)

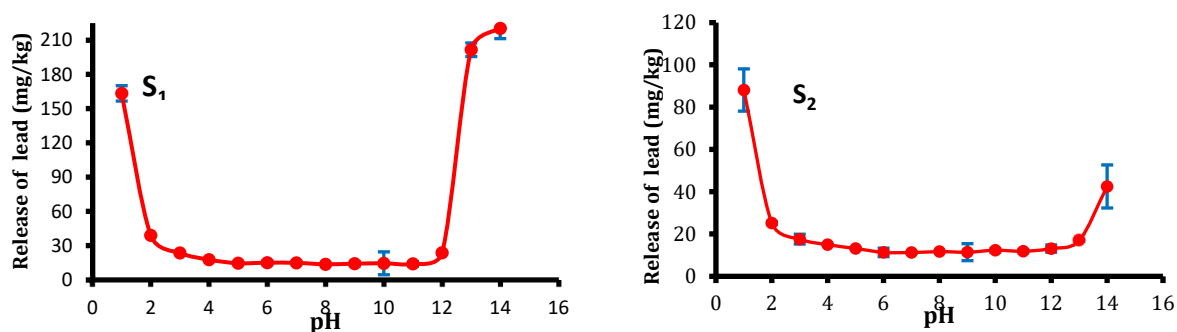


Fig. 6. Effect of pH on leaching behavior of lead from tailings

of this section is to assess the impact of pH on lead leaching behavior. The leaching technique outlined in Section 2.4 was followed, and the eluates were used to determine the concentration of lead. The mechanism of releasing lead from tailings into solution as a result of pH variations was rather different. The ultimate pH of the extracts differed significantly from the beginning pH, as seen in Figure 5. The final pH in samples S₁ and S₂ stayed about 5.6 and 4.9, respectively, within the initial pH range of 3-12. This is related to the tailing samples' buffering capacity. This is most likely due to ox-hydroxide compounds, salts with weak bases, and the dissolution-precipitation process. According to several authors (Król et al., 2020, Ye et al, 2022), the acidity of the leaching agent that comes into contact with the tailings can cause extremely considerable changes in the amounts of pollutants that can be emitted into the environment. The tailings buffering capacity was not overcome in highly acidic (pH= 1 and 2) and very alkaline (pH=13 and 14) conditions, and the pH of the solution showed abrupt swings. Changes in pH have a direct impact on the solubility of the chemicals.

Figure 5 depicts the leaching behavior of lead at different pH levels. In both samples, particularly in sample S₁, a roughly v-shaped (amphoteric) leaching behavior was observed. This indicates that the lowest and highest pH values had the most solubility. The amount of lead leached was high in both highly acidic and highly alkaline conditions, as can be seen. Although a non-negligible amount (37.5 mg/kg, approximately equal to water-soluble portion) of lead was also leached in the alkaline pH range in sample S₂, the leaching of this element increased with lowering pH in both samples. However, in sample S₁, considerably more lead was leached than in the acidic state. Because of the varied mineralogical compositions of the tailing samples, this circumstance exists (Figure 2). The threshold limit of Pb in waste samples defined by Portuguese legislation for disposal in hazardous waste landfills is 20 mg/kg. Because the tailings contain sulfide, its oxidation generates acidic circumstances that release substantial levels of lead into the environment, leached Pb concentrations much surpassed the legal limit in acidic conditions. As a result, tailings should be regarded as a potentially hazardous material. Although a higher concentration of lead is released into the solution in an acidic environment, the amount of released lead into the solution is still less (1%) than the overall concentration of Pb in the samples (Table 2). A large portion of the total lead concentration was found in the structural component of the tailings, which corresponds to the results of sequential extraction. Lead is a heavy and toxic metal that poses one of the most difficult toxic and hazardous metals to deal with in terms of possible waste environmental implications. Other studies have shown similar results for pH-dependent Pb leaching behavior (Van Herck et al., 2000; Van der Sloot et al., 2001; Boym, 2017, Król et al., 2020). Because the amount of lead concentration in the liquid phase is controlled by several minerals whose solubility is affected by pH, analysis of the acquired data revealed that the solubility process affects lead release. In this regard, Restituta Paul et al., (2018), by simulation of the eluates obtained from another tailings sample with a similar composition by Visual Minteq software, reported that the most

important phases controlling the concentration of lead in solution are: $\text{Pb}(\text{OH})_2(\text{aq})$ for acidic condition forming > 50%, while PbOH^+ forms 27%. Under the neutral conditions, carbonates ($\text{Pb}(\text{CO}_3)_2^{2-}$, $\text{PbCO}_3(\text{aq})$ & PbHCO_3^+) and chloride (PbCl^+ , $\text{PbCl}_2(\text{aq})$, ZnCl_3 & PbCl_4^{2-}) lead compound overcome the solution at 41% and 45% respectively. $\text{Pb}(\text{OH})_2$ made up roughly 80% of total soluble lead under alkaline circumstances. Cerussite is another chemical that can affect lead solubility (PbCO_3). The lead research values achieved in the experiments are consistent with previous studies (Chandler et al., 1997; Zhang et al., 2008; Fernández-Olmo et al., 2009; Kogbara, 2011).

Liquid to solid ratio

Different liquid-solid ratios were used to investigate the effect of the liquid-solid ratio on the concentrations of lead discharged into the water. In this investigation, the liquid to solid ratio ranged from 20:1 to 20:16. The results of liquid to solid ratio testing on tailing samples are shown in Figure 7. As the L/S ratio decreased, the leached concentration of lead from the tailings decreased rapidly due to an increase in viscosity. When the liquid-to-solid ratio is low, the solution thickens and the viscosity rises, causing mass transfer resistance around the tailing's particles (Liu et al., 2006). For some elements, the leachability discipline is independent of the liquid to solid ratio, whereas for others, the leaching rate is a function of L/S (Zandi and Russell, 2007). The leaching behavior of lead from tailings was found to be proportional to the liquid to solid ratio in this study. There are several factors that can influence the release of a specific component of tailings samples into the aquatic environment in general. Extremely soluble metals found on the surface of tailings typically fall into the category of available controlled leaching if the concentration leached into the extract is limited solely by the number of metals in the tailings. These elements are expected to be highly available in the aquatic environment and to be leached as soon as they reach high concentrations. Some other metals' leachability may be solubility controlled, whereas metal leachability in tailings can be described using dissolution and deposition processes. As a result, according to the definitions, the process of releasing lead from tailings is known as solubility-controlled leaching (Figure 7).

Particle size results

The size of particles is one of the primary contributors to incorrect extrapolation of metal release from tailings (Janusa et al., 1998; Karius and Hamer, 2001). The amount of adsorption and storage capacity of heavy metals on tailings is heavily influenced by particle size distribution. Figure 8 depicts the leached concentrations of lead with varying particle sizes for tailing samples (S_1 and S_2). As shown in Figure 8, the leaching behavior of the tailings varied greatly depending on particle size. The leached concentrations of lead increased first and then decreased in sample

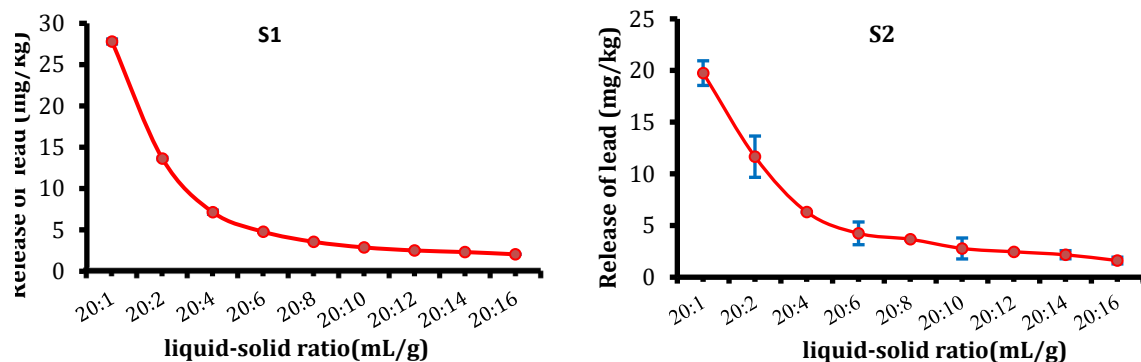


Fig. 7. The release of lead from tailings due to changes in liquid to solid ratios

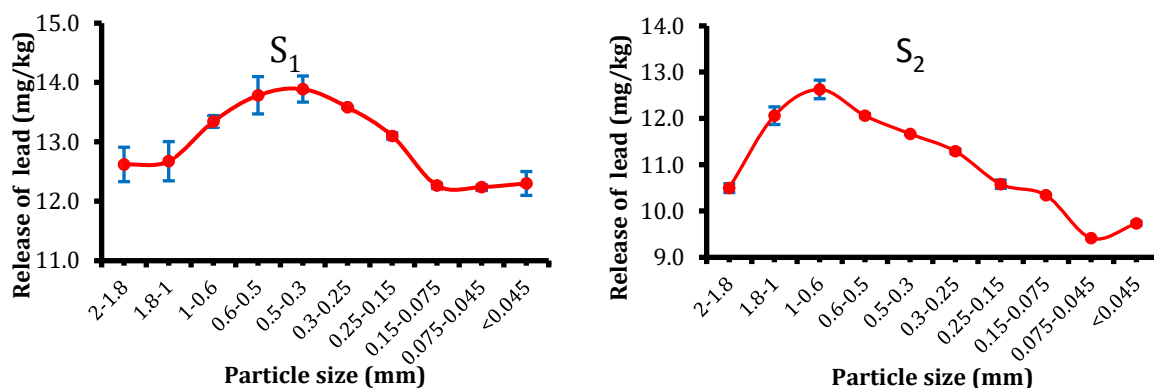


Fig. 8. Release of lead from tailings due to changes of particle sizes

S_1 as the particle size of the tailings was reduced. Lead concentrations in various particle sizes of sample S_1 were similar to the normal distribution model, with the highest concentrations (13.9 mg/kg) observed in particle sizes of 0.3–0.5 mm, and particles coarser or finer than this size had lower leached lead concentrations. The same leaching behavior was reported by Li and Chen (2017) for waste printed circuit boards. It is well established that as particle size decreases, the metal leaching rate increases because the surface area of particles increases, which is beneficial for metal leaching (Guo et al., 2020). Particle size below a critical value, on the other hand, will result in particle-particle agglomeration, impeding leaching liquid permeation through fine powders (Yang et al., 2011). Sample S_2 had a completely different leaching behavior than Sample S_1 and reduced the amount of lead released into the solution by decreasing particle size. Figure 8 shows that as particle size decreases from 1.8–2 mm to 0.10–0.6 mm, the lead leaching ratio increases from 11.5 to 12.5 mg/kg. Lead leaching rates decreased as tailing particle size was reduced further, reaching 9.5 mg/kg in particles with diameters greater than 0.045 mm. The differences in metallurgical extraction treatments and particle crushing methods result in such disparities in leaching of elements from tailings.

Leaching time results

It has been discovered that the leaching of heavy metals from materials to water resources is a very slow process, and that even with long leaching times, the balance between the solid and liquid phases cannot be achieved. Time-dependent leaching experiments are used to determine the equilibrium time and amount of lead leaching at different leaching times. On the other hand, reactions between the leaching solution and the host phase occur over time, which reduces or increases the amount of leaching. Two types of leaching behavior were observed in this study. An initial rapid release is followed by a reduction in the amount of release (100 minutes) and a slow concentration until a stable state is achieved (Figure 9- S_1). The rapid and incremental entry of lead into solution in sample S_1 can be attributed to soluble and labile lead (corresponding with sequential extraction), but the researchers concluded that the decrease of lead in solution with increasing time is due to the strong binding of this metal via adsorption processes, sedimentation, complex formation with organic matter, and cation exchange (Raskin and Ensley, 2000;). The leaching pattern in sample S_2 was completely different from that in sample S_1 . In fact, a gradual rise in lead concentration is required until a steady mood is attained. An example of complete dissolution of a component to achieve the depletion of elements (i.e.: no more concentration enhancement) on municipal solid waste ash cited by Kirby and Rimstidt (1994). Both plots show that the amount of lead released into the solution achieved a steady state almost after 280 minutes of leaching. The equilibrium condition between tailings and leachant has been achieved in steady state.

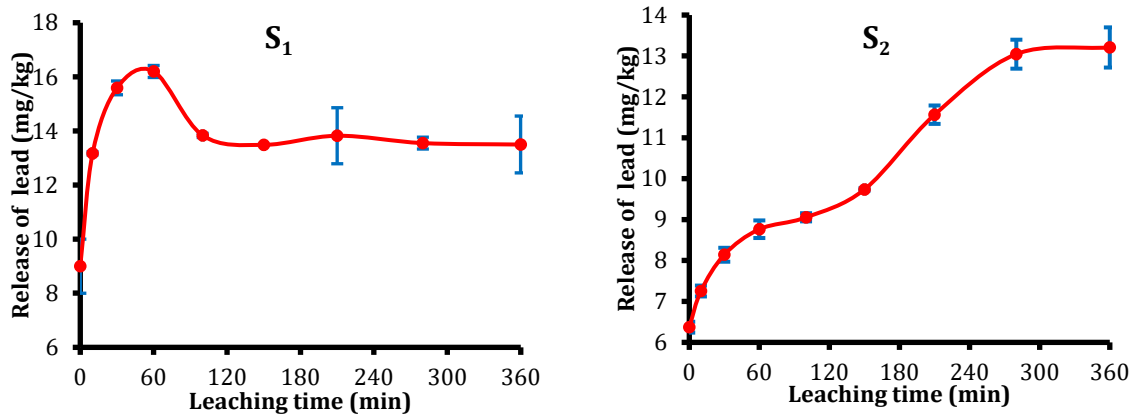


Fig. 9. The effect of contact time on release of lead.

Cappuyns et al. (2003) identified four distinct patterns of leaching as a function of time: Type 1: metals (e.g. Na, Mg, K) are promptly leached at the start of the experiment; the labile reservoir is significantly more dominating and may be related to cation exchange reactions. Type 2: some metals have a quick initial release, followed by a moderate but fundamental release in the experiment's last step. The rapidly labile reservoir is less important than the labile reservoir. This pattern represents the disintegration of inadequately firm solid forms or the more mobile elements in wastes that are simply desorbed on acidity (e.g. carbonates). Metals that are easily discharged are classified as type 3. The steadily labile reservoir is more important than the labile reservoir in this case. This model describes the desorption of metals that are more strongly bonded to tailing constituents (such as Co, Cr, Cu, and Pb) or the slow liquidation of solid forms like Fe-oxides. The release was sometimes linear as a function of time or could be characterized by a single exponential equation. Type 4: some elements represent reabsorption (P, As, which happens as anions in soil) or precipitation behavior (e.g. Ba precipitates as BaSO_4). Differences in the pattern of release of elements from tailings due to mineralogical differences of tailings, as well as various processes of metallurgical extraction have been applied. Some of the patterns mentioned in the previous section were also observed in our research (Figure 9).

CONCLUSION

Several chemical and physical factors determine how much constituents can leach from a material. These factors can vary from site to site and are unlikely to remain constant because the environment, including local conditions and solid materials, changes over time. The followings are some examples of key factors: As a result of increased precipitation, the L/S shifts from solubility-limited to available content-limited leaching; Acid precipitation, atmospheric carbon dioxide influx, oxidation of reduced minerals, or biological activity can alter the pH, thereby altering the solubility of a constituent in water; Redox conditions are altered (e.g., the oxidation state of a constituent is altered (for instance, Cr(III) becomes Cr(IV) after biological activity). Degradation from internal stress (e.g., freezing/thawing cycles, mechanical erosion, resulting in increased surface area/volume); Changes in the material's chemical composition (e.g., from co-disposal with other materials).

By batch leaching and sequential extraction methods, the lead release behavior from lead-zinc tailings was studied in the arid and semi-arid regions (Zanjan province in Iran). The following conclusions and recommendations are made from the findings of this study:

- 1- Calcium oxide and Silicon dioxide were found to be the main components of the samples,

which caused a potential buffering capacity.

2- As a result, of the TCLP tests: The two tested samples are hazardous materials and have a high environmental impact. In addition, the concentration of lead released into the solution was much higher than the levels set by the Primary and Secondary Drinking Water Standards when artificial rain was simulated on the tailings using the SPLP method.

3- During sequential extraction, it was apparent that the water-soluble fraction of lead was much lower than the others in both samples, and the residual fraction accounted for the majority.

4- The mobility index calculation revealed a clear difference between samples in terms of lead distribution in different sections. Sample S₁ had a lead mobility index of 51%, while sample S₂ had a lead mobility index of 6.5 %. This parameter revealed that, despite the fact that both samples are tailings from the same mine, the level of risk they pose to the ecosystem is vastly different.

5- The amphoteric (V-shaped) pH-dependent leaching behavior of lead was observed, with the maximum release rate in alkaline and acidic conditions. The results of a laboratory leaching test demonstrated that the release behavior associated with the liquid to solid ratio has a significant impact on lead leaching, and that when the L/S ratio decreased, the leached concentration of lead from the tailings decreased rapidly due to increased viscosity.

6- Particles with a diameter of 0.3-0.5 mm released the highest concentrations of lead, and their time-dependent leaching behaviour was radically different.

7- The findings clearly demonstrated that the leaching behavior of lead corresponding to various parameters differed, and that heaps of tailings in the environment require special attention.

From the practical point of view, the release of pollutants from tailings is also affected by various other conditions: including dry-wet, freeze-thaw, and oxidation-reduction cycles. This condition was not investigated in the present study. However, it can be a source for further research on other solid materials. The data from this study can be used for inoculations of geochemical modeling and speciation, as well as informing government decision-makers that they must modify the tailings so that the environment suffers less damage. Modification of tailings with biochar, manganese nanoparticles and zeolites, and even the formation of Ecopiling can be appropriate solutions to reduce the environmental impact of tailings.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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