Release Characteristics of Pb from Zn-Pb Mine Tailings Under Simulation Leaching Conditions

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Abstract

In this paper, the results obtained from various leaching tests to determine the leaching behavior of lead from lead-zinc mine tailing under natural conditions were evaluated. In order to measure the level of toxicity of the tailings, synthetic precipitation leaching procedure (SPLP), toxicity characteristic leaching procedure (TCLP), leachate extraction procedure (LEP), and field leach test (FLT) protocols were used. The effect of liquid to solid ratio, particle size, contact time, and pH on lead release from tailings was also tested. Based on the results, the release of lead from the tailings was entirely affected by pH and amphoteric leaching behavior was observed. According to the results of the TCLP leaching protocol, the tailings categorized as hazardous material. Lead mobility index for S₁ and S₂ samples were 51% and 5.6%, respectively. The release of lead from the tailings was affected by the solubility process. The highest amount of lead release from S₁ and S₂ samples were observed in the particle size range of 0.3-0.5 mm and 0.6-1.0, mm respectively. According to the results, management of tailings and prevention of the release of lead into the environment, requires a special strategy. Controlling the amount of pore water, the size range of tailing particles in order to prevent wind erosion, prevent in situ pH changes, and acidification of tailings, and classification is essential factors in tailing management. In fact, health and diet security, climate change, safe water, accountable production, biodiversity, and ultimately the people must be considered in the planning of the authorities.

Introduction

In the Wall Street report, oil, gas, coal, forest and timber, gold and silver, copper, uranium, lead, crude iron, and phosphate, all of which are important global sources, are considered wealth indicators. With this approach, Russia, the United States, Saudi Arabia, and Canada rank first to fourth in the world, and Iran ranks fifth in the world with \$ 27.3 trillion in natural underground resources. In the foreign trade sector, Iran in the mining and mineral industries sector with exports of \$ 9.2 billion in 2020, has a share of 21% of the total value of the country's exports. Unfortunately, in recent years, due to economic factors, little attention has been paid to the environment and the environmental impact of mining activities has been overshadowed. In this case, it is natural that a very large volume of tailings is produced in different parts of Iran, which will have many environmental effects. The major portion of this wastes is tailings which are the result of metallurgical extraction (Çoruh et al., 2013).

Tailings are usually a by-product of the process of extracting valuable elements in mining. They are different types and usually produced by crushing, grinding, sieving, and chemical processes on the mined ore. After performing these steps, two substances are formed: a valuable concentrate that contains the desired element and a discarded substance that contains different types of pollutants, particles, and chemicals called tailing (Hudson, 2001, Younger and Wolkersdorfer, 2004, Lottermoser, 2010, Zhang et al., 2019). The fast growth of industrial development has created an ever-growing amount of harmful mine tailings. Currently, estimated that the amount of tailings is generated several million tons per year while this volume is exponentially increasing due to high demand and low-grade deposits (Hudson-Edwards and Dold, 2015). Mine tailings are mostly rich in poisonous trace metals, such as As, Pb, Cu, Ni, Mn, Cd, Cr, and etc (Mendez and Maier, 2007, Yang et al., 2013, Uugwanga and Kgabi, 2020). Over the past few decades, pollution of the environment, water, and soil resources have intensified due to mining activities (Al-Jabri et al., 2006).

The existence of heavy-trace metals, especially lead, due to mining activities in the environment, has caused a great deal of concern owing to its toxicity to human life (Moors and Dijkema, 2006, Montanaro et al., 2001, Nurcholis et al., 2017). Leaching of the poisonous metals unavoidably will pose a hazard to the environment and public health worldwide (Ye et al., 2015). Tailings among mine wastes act as the most an important source of environmental contamination (Roussel et al., 2000). Lead and zinc mine tailings have great levels of heavy metals, like Zn, Pb, and low concentration of macronutrients, negligible physical structure, and plenty of salinity (Khan et al., 2019). Solubility and mobility are two important processes in the leaching of heavy metals such as lead from wastes and their entry into water and soil sources. Pollution of soil and water resources to lead causes many diseases for humans and plants. Some scientists reported that the entry of lead into the human food chain can cause various diseases such as the most sensitive brain, abdominal pain symptoms, constipation,

headaches, irritability (Schreck et al., 2012), memory problems, inability to have children, and tingling in the hands and feet (Jaishankar et al., 2014).

Heavy metals (Pb, Zn, Cd) concentrations in lead-zinc mine tailings are naturally greater than the earth's crust (Wani et al., 2015). The maximum permissible concentration of lead in drinking water is $10 \mu\text{g L}^{-1}$ (Organization, 2008) while the average lead concentration in tailings dam seepage water is more than $500 \mu\text{g L}^{-1}$ (Lottermoser, 2010). For example, in some running waters from metal mine sites such as tailings pond water Jumna tin mill; mine site drainage water, Montalbion silver mine and tailings dam seepage water, Mary Kathleen uranium mine, lead concentrations were 607, 36 and $450 \mu\text{g L}^{-1}$, respectively. Tailings contain abundant sulfide minerals and these sulfides are a mixture of sulfide with various metals (zinc, lead, copper). This can lead to acid mine drainage (AMD) and damage to the environment. The behavior and mobility of Pb in lead-zinc mine tailings depend on the physicochemical structure and the properties of tailings (Falagán et al., 2017)

The main factor in determining the rate and amount of lead released into the environment by leaching is the concentration and distribution of lead in tailing particles (Ma et al., 2019). Also, the influence of mine tailings on the environment is mainly in relation to the possible concentration of heavy metals in the contacted water with tailings to the total concentration of heavy metals in the tailings. The concentration of heavy metals in a leachate solution affected by the physical-chemical properties of the tailings, such as pH, particle size, water to tailing ratio, heavy metal fractionation, mineralogy, chemical composition, and contact time of the particles with water (Karaca et al., 2016). These factors are the most important key factors affecting the bioavailability of heavy metals and are used to evaluate the toxicity of mineral tailings in various environmental scenarios (Grathwohl and van der Sloot, 2007, Grathwohl and Susset, 2009, Guyonnet, 2010). Leaching and erosion are some of the processes that lead to the transfer of tailing-related contaminants to water and soil resources. Leaching of contaminants from tailings directly affects groundwater sources, especially when the pollutants (like Pb) in the tailing particles are easily transported by acidic rain or any other flowing water and discharged to surface and groundwater sources (Ugwanga and Kgabi, 2020).

A huge amount of Zn-Pb mine tailings are produced in Iran, which has very high concentrations of lead. Environmental impacts of Zn-Pb mine tailings have not been well considered and the mechanism of lead release from these tailings is poorly studied and still unclear. Hence, it is very important to realize the leaching characteristics of lead for better controlling of Zn-Pb mine tailings. However, in a few studies, the effect of liquid to solid ratio, oscillation time, pH, and particle size on the process of lead release from tailings has been published. Therefore, in this paper, lead release behavior from tailings and mechanisms affecting this process was tested. For this purpose, batch leaching tests were carried out to investigate the liquid-solid ratio, pH, contact time, and particle size effect on the release of lead from mine tailings. The toxicity level of tailings was investigated by synthetic precipitation leaching procedure (SPLP), toxicity characteristic leaching procedure (TCLP), field leach test (FLT), and leachate extraction procedure (LEP) and the sequential extraction procedure was also applied to evaluate the mobility behavior of lead in tailings.

Materials And Methods

3.1. Study region

The research samples of tailings were prepared from the lead-zinc mine of Anguran, which is located ($36^{\circ} 37'$ north and $47^{\circ} 24'$ east) in Mahnanshah city, province of Zanjan, Iran. The area has a semi-arid climate and the amount of Angoran mine reserves are 8 million tons in the open field and 4 million tons of Zn in the subterranean section. Angoran lead and zinc mine and Angoran lead and zinc production plant is the largest producer of lead and zinc in Iran and the largest lead and zinc mine in the Middle East with more than 80% of its reserves in the form of carbonate and 20% in the form of sulfide (Borg, 2005). The average annual precipitation, temperature, and humidity in this region is 295 mm, 10.9°C and 54% respectively. Anguran ore is located among the limestone gems and the main geology is composed of Precambrian felsic gneiss.

3.2. Sample collection and preparation

The Anguran Zn-Pb mine was exploited in 1940 and a lots of tailings from this mine stockpiled without proper treatment. A sampling of tailings from Angoran lead-zinc mine was done in May 2019 and two kinds of mineral tailings created in this mine that were generated during different extraction processes were collected. In the lead-zinc plant, during the processing of deposits, two types of tailings were created, which include hot filter cake or cobalt cake (sample S₂) and cold filter cake or nickel cake (sample S₁). High-grade zinc ores are first acidified with sulfuric acid, and chemicals such as manganese dioxide, iron sulfate, and aluminum sulfate are added to the solution. In the continuation of the route, the neutralization process with lime is made on these materials and via filtering the neutralized solution, a leached filter cake (leach cake) is achieved. As regards various impurities are precipitated at this phase, the quantity of some metals like lead and iron, in the leaching filter cake (leach cake) increases. After the mentioned step, the obtained solution is filtered by adding potassium permanganate to precipitate the cobalt metal. The result of this process is the formation of a hot filter cake. The solution obtained from this step is filtered by adding zinc powder and copper sulfate, which leads to the production of a cold filter cake. To conduct this research, sampling of both types of tailings (cold and hot filter cakes) was performed. The samples were air-dried for two weeks after transfer to the laboratory, passed through a 2 mm sieve, and kept in a desiccator throughout the test period.

3.3. Hazard assessment

In this research, the following leaching procedures were used to recognize the hazardous nature of tailing samples.

- **TCLP** (Toxicity Characteristic Leaching Procedure): this protocol is mainly applied to decide whether a waste needs to be disposed of in the form of a landfill and classified as hazardous or not. Since mentioned in the TCLP method, if the tailings have acidic pH, extraction fluid No. 1 with a pH of about 4.93 was used. To make the extraction fluid No. 1, first combine 5.7 mL of glacial CH₃CH₂OOH with 500 mL of deionized water in a one-liter volumetric flask. Then add 64.3 mL of 1N sodium hydroxide and by addition of deionized water bring the container to a volume of one liter. Then add 64.3 mL of a 1N NaOH and bring the solution to a volume of one liter. After this solution was carefully prepared, the final pH of this solution should be 4.93± 0.05. Before starting the extraction process, the tailings samples were passed through a 10 mesh aperture lab standard test sieve stainless steel. The liquid to solid ratio in this experiment was 20:1, and the suspension was stirred using a rotary agitation apparatus for 18 hours at 30 rpm. The mixture is centrifuged and 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). The used extraction fluid in this method is acidified deionized water, which aims to simulate acid rain in natural conditions. Because the SPLP leaching protocol simulates natural rainfall and describes the leaching potential of pollutants from waste, it provides a straight method to evaluate the mobility of metals in the environment. A mixture of 60 to 40 sulfuric acid to nitric acid (by weight) is used to prepare the extraction fluid with a pH of 4.2. In this method, similar to the TCLP procedure, 10 g of the tailings samples were combined with 200 mL of extraction fluid and stirred for 18 hours at 30 rpm. After this section. The samples centrifuged at 4000 rpm for 10 min to separate the liquid from the solid part (USEPA, 1994).
- **FLT** (Field Leach Test) was developed primarily for rapid evaluation, estimation and comparison of leachate geochemistry from mineral tailings accumulation masses.

This method is very fast, high quality, and low-cost and simulates the interaction between water and different materials. There are several examples of different materials such as bio-solids, dust, flood sediments, solid sewage sludge, municipal waste, etc. that have been evaluated by this method (El-Kamash et al., 2005, Hageman, 2007). The procedure for using the FLT method involves weighing 50 grams of the sample and adding one liter of deionized water to it in a one-liter bottle (liquid to solid ratio 20 to 1). Then capped the bottle and shook it vigorously by hand for 5 minutes. After the shake, allowed to settle contents of the bottle for 10 minutes. Then, a part of the leachate filtered with Whatman filter paper grade 42 (Hageman and Briggs, 2000).

- **LEP** (Leachate Extraction Procedure): It is a modern and standard method that is used to classify waste into hazardous and non-hazardous types. It is also designed to simulate the leaching of heavy metals from hazardous materials in

landfills.

Firstly, 50 g of the tailing sample is mixed with 800 mL of deionized water ($\text{pH} = 5 \pm 0.2$ with a 0.5 normal of acetic acid solution) and stirred at 10 rpm for 24 hours. Note that by the end of the test the pH of the solution should be recorded several times and not more than 5. Also, the volume of added 0.5 normal acids acetic should not exceed 200 mL (Çoruh et al., 2013).

3.4. Leaching Behavior

To investigate the effect of 4 factors (contact time, particle size, liquid to solid ratio, pH) on the leaching amount of heavy metals from tailings, the following leaching protocols were implemented (Liu et al., 2017). A: contact time tests b: liquid to solid ratio tests c: particle size tests d: pH-dependent leaching tests.

In the case of pH-dependent experiments, the pH of the deionized water was adjusted by adding HCl (0.1 Molar and 1 Molar) and NaOH (0.1 Molar and 1 Molar) to the desired values of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 and 14. 1g of samples was weighed into polypropylene bottles and Then 10 ml of deionized water with desired pH values were added to the dishes. The samples were stirred for 360 minutes at 25 ° C. 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 are shaken for 0, 10, 30, 60, 100, 150, 210, 280, and 360 minutes at 30 rpm. The amount of lead leaching from lead-zinc mine tailings to solution due to the liquid-solid ratio changes were investigated by the following method. Firstly, 1g of each tailing sample is spilled into a centrifuge tube and a certain amount of deionized water is added to the tubes to obtain ratios of 20:1, 20:2, 20:4, 20:6, 20:8, 20:10, 20:12, 20:14, 20:16 mL g⁻¹. 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). 1g of every lead-zinc mine tailing samples with various particle sizes were set in a 50 mL centrifuge tube and 10 mL of deionized water was added. After this section, the samples were stirred for 360 minutes at 25 ° C on an orbital shaker. The samples were then centrifuged and the obtained extracts were stored in the refrigerator (4 °C) to read the lead concentration.

3.5. Sequential Leaching Procedure

Sequential leaching procedure is an instrument that evaluates and estimates the potential mobility and accessibility of metal contents 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. The six steps are as follows, 1: water-soluble fraction (Wat), 2: exchangeable fraction (Exc), 3: carbonate fraction (Car), 4: Fe/Mn oxide fraction (Fe/Mn), 5: organic fraction (Org), 6: residual fraction (Res). The full schemes are explained below:

F₁, The water-soluble fraction (Wat.): used to measure available metal species in solution. First, one gram of the tailing sample weighed and pour it into the centrifuge tube. Then add 25 mL of deionized water. After 2 h of vibration under the desirable condition (25 °C), solid and liquid components were separated by centrifugation (10 minute in 4000 rpm). The residue saved for the next fraction and keep extract for later analysis in the refrigerator at 4 °C.

F₂, The exchangeable fraction (Exc.): is used to extract metal species with poor electrostatic absorption that are easily leached by the ion replacement process. Firstly. 10 mL of 1 mol/L magnesium chloride solution at pH= 7 is combined with the remainder of the previous step and the resulting mixture was shaken for 1 h and centrifuged at 4000 rpm for 15 min to separate the extract from the tailings.

F₃, The carbonate fraction (Car.): this fraction is related to metals bonded to carbonate substances. One molar sodium acetate solution is used to extract lead bound to these components. For this purpose, 10 mL of one molar solution of sodium acetate was added to the remaining component of the previous step. After stirring for 5 hours at 25°C, it was centrifuged at 5000 rpm for 10 minutes. The supernatants were passed through filter paper and the residue was saved for the next fraction.

F₄, The Fe/Mn oxide bound fraction (Fe/Mn)

this component is a very important chemical structure for many heavy metals in various waste materials. The remaining from the carbonate fraction was treated with 20 mL of 0.04 mol L⁻¹ NH₂OH.HCl in 25% (v/v) acetic acid for 6 h in a bain-marie (96°C) and with special stirring. The samples were then centrifuged at 5000 rpm for 10 minutes.

F₅, The organic fraction (Org.)

the remaining from the Fe-Mn oxides fraction was treated with 20 mL of 30% hydrogen peroxide for 5 hour in a bain-marie (85°C). When the centrifuge tubes were cooled, 20 mL of 3.2 mol L⁻¹ NH₄OAc (pH= 2, set-out by HNO₃) was added and the tube shaken continuously for 1 h at 25 ° C. The samples were then centrifuged at 5000 rpm for 10 minutes.

F₆, The residue fraction (Res.): To extract the lead in the structural part (residual), 20 mL of Aqua Regia solution was added to the remaining component of the previous step and placed in a bain-marie (85° C) for 12 hours.

3.6 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).

3.7 Recovery: The efficiency of the sequential extraction procedure was evaluated using the following equation. In this equation, whatever the resulting number is closer to 100, the extraction process is more accurately was performed (Nemati et al., 2011, Lei et al., 2010):

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

3.8 Mobility Index (MI): The mobility and bioavailability of elements mainly depend on their geochemical form (Kabala and Singh, 2001, Olajire et al., 2003). A high percentage of heavy metals in more mobile components causes more leaching and bioavailability of that metals. The mobility index for Pb was calculated by the below equation:

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

3.9. 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 (Kα) radiation (40 kV, 40 mA), specimen length 10mm, start Position (°2θ): 10.0200, end position (°2θ): 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 replicate, and their meanings were used for analyzes and drawing graphs. Concentrations of lead in the eluates were determined using the inductively coupled plasma Emission Spectrometry (ICP-OES) spectrometer (Varian series 700 model 710 Axial). The used plastics, centrifuge tubes and glassware in this test were drown in a 10% nitric acid for 48 h and after this time, washed with deionized water. Concentration of lead in used purified water was 0.0001 mg L⁻¹.

Results And Discussion

4.1. Characteristics of lead-zinc mine tailings

In Table 1 the composition percentage of sample was shown. The major ingredients of the samples were calcium oxide, Silicon dioxide, Sulfur trioxide, ferric oxide and aluminum oxide while oxides of, iron, phosphorus, sodium, titanium, and

magnesium constituted the remaining tailings. The high percentages of SO_3 indicate that the tailing materials have a high ability to produce AMD (Acid Mine Drainage). Consequently, trace-heavy metals in the tailings can be easily released and enter to the environment.

Table 1
The results of chemical composition analysis of lead-zinc mine tailing samples

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	TiO_2	MnO	P_2O_5	LOI	SO_3
	%	%	%	%	%	%	%	%	%	%	%	%
S_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	9.2	2.74	2.52	18.85	0.4	0.86	0.48	0.10	2.2	0.044	32.2	27

The X-ray diffraction (XRD) patterns for the tailing samples illustrated in Figure 1. XRD analyses were conducted to study the mineralogy of tailings. The XRD patterns as well as support the XRF results that the major phases in tailing samples are silicon oxides and calcium sulfate. The present research revealed that the chemical composition of tailing is not constant and differs considerably from one type of tailing to another type depending on the kind of mining process in different stages and mining methods. Chand et al. (2009) also gave similar results. There are, however, no peaks recognized except for quartz and gypsum. Thus, Pb, Al, Mn, S, and Fe would be non-crystalline forms that could not be identified by XRD, and it was impossible to elucidate the chemical forms only by XRD. Therefore, the sequential extraction procedure and risk assessment leaching tests were applied for the characterization of the associated forms of Pb, and the results were discussed below.

4.2. Leaching hazard assessment

SPLP, TCLP, LEP, and FLT methods were carried out to specify the leachability of lead from lead-zinc mine tailings in various situations and also to specify whether the lead-zinc mine tailings can be classified as toxic to the biota. Figure 2 shows the extracted lead concentration after each leaching extraction method. The amount of leached lead varied in leaching protocols. Particle size range, type, and composition of leachant, and contact time of particles with leaching agent are among the factors that cause differences in the concentration of leached lead from tailings. The TCLP procedure, a diluted acetic acid extraction of waste, was expanded to evaluate the potential of a contaminant to release from a waste. If the extract obtained from the TCLP method contains a concentration greater than or equal to the permissible toxicity limits specified in accordance with U. S. EPA protocols, the waste material shall have toxicity characteristics and should be classified as hazardous waste (Boyer, 1990). In each of the four leaching tests, more lead was released from sample S_1 than sample S_2 , which could be due to the structural difference between samples. The highest amount of leached lead was in the TCLP test and sample S_1 . TCLP-extractable Pb for S_1 and S_2 samples ranged from 145.2 to 50.39 mg kg^{-1} , respectively (Figure 2). Released lead concentration from sample S_1 was higher due to different processes of tailing operations. The concentrations of leached lead in the S_1 and S_2 samples were higher than based on the U.S. EPA TCLP limits (EPA, 2004, Liu et al., 2017). U.S. EPA regulatory limit for Pb is 5.0 mg L^{-1} . Then each of the two samples qualifies as hazardous materials. This must be considered that the term hazardous describes consciousness to the reality of hazard due to the humans and the environments, on condition that necessary operations for transport, storage, and organization are not taken.

The leached lead concentration in the SPLP test was shown in Figure 2. The extractant liquid used in this method simulates acid rain. In contradiction to the high TCLP leachability for Pb, the simulated acid rain extracted less than 24.6 and 19.8 mg kg^{-1} of Pb from the S_1 and S_2 samples which are equal to 1.23 and 0.99 mg L^{-1} , respectively. According to TCLP, in the SPLP extraction test, the concentration of lead released from sample S_1 was greater than sample S_2 . The result from the SPLP experiment, performed on the lead-zinc mine tailings show that the concentration of lead is above the MCLs (Maximum Contaminant Levels) or recommended concentration under the National Primary and Secondary Drinking Water Regulations (NPDW and NSDW). The primary and Secondary Drinking Water standard for lead is 0.015 mg L^{-1} . Therefore, the entry of

rainwater into the tailings and the formation of leachate or the formation of fluid flow can lead to great concentrations of lead into the environment and cause high contamination in periods of time.

In Figure 2 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 valuable method for geochemical classification of the active, easily soluble, and possibly bioavailable elements that are movable after these constituents are leached by means of 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⁻¹, respectively) 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 S_1 . However, a lower concentration of Pb was released, due to the low acidity of the leaching solution. The advantage of the FLT method in comparison with other methods is that in the short term, the waste material can be checked and provides almost acceptable results.

The Leachate Extraction Procedure (LEP) was developed to investigate the waste material in Ontario, Canada. This method was eventually adopted by Canadian General Standards Board (CGSB, 1987) and accepted to be used to identify wastes that are highly toxic to the environment. Pb was extracted from the lead-zinc mineral tailings at a concentration of 106.4 and 50.6 mg kg⁻¹ for samples S_1 and S_2 respectively in LEP test. Similar to previous tests, a greater amount of Pb was released from sample S_1 than sample S_2 . The differences in the amount of lead release from the samples is due to the various procedures of metallurgical extraction in the processing of minerals.

All of these methods operate on a different basis. The TCLP test provides buffered conditions in which the extraction of heavy metals can take place. Instead, in the LEP method, the tailings are subject to fluctuations in pH, a condition that is more representative of the actual environment. Hence, there is the increased possibility that there is an entrance of oxygen into the extraction tube, which could affect the pH of the extracting and also the oxidation state of the dissolved metals. The purpose of the SPLP extraction procedure (solutions are unbuffered) is to simulate the states of acidic precipitation that may be present in the environment where rainwater may cross through the tailings and travel toward the groundwater bearing the soluble materials with it. In other words, the experiments mentioned in the previous sections are generally expensive, time-consuming, and complex, and require a lot of equipment to perform. But FLT is a very low-cost, practical, and fast method that can simulate possible reactions between leachant and tailings in a short time.

In this study, all of these methods were studied and the differences in the amount of lead leaching from the lead-zinc mine tailings were due to the difference in leaching solutions, the time and the rate of shaking. All batch leach tests indicate the potential for contaminant release from tailings to the environment.

4.3. Partitioning of lead in samples: sequential extraction method

The sequential extraction procedure was carried out to assess the fractionation of lead within the tailing samples. The purpose of the sequential extraction procedure is to simulate the process of releasing heavy metals into solution under different environmental conditions (Jones and Hao, 1993). The chemical fractions of heavy metals in tailings determine their mobility, bioavailability, and stability in the environment, so are more important from an environmental perspective than the total concentration of the heavy metals (Peng et al., 2017). Pb concentrations in each chemical fraction, considered as percentages of total Pb, are shown in Figure 3. The recovery rates for the lead in the lead-zinc mine tailing samples (S_1 and S_2) were reasonably good (106.6% – 107.1%). The different distribution fractions of Pb, are observed in both lead-zinc mine tailing samples. Among the studied six fractions, the percentages of water-soluble fractions of Pb, associated with F_1 in both tailing samples are the smallest and the dominant levels of lead observed in residual fraction. The order of lead concentration in various factions of sample S_1 and sample S_2 as below, respectively: Residual > Carbonate > Exchangeable > Organic > Fe/Mn Oxide > Water soluble; Residual > Organic > Exchangeable > Carbonate > Fe/Mn Oxide > Water soluble. The distribution trend of lead concentration was different in the studied fractions. In sample S_1 , more than 50% of lead is in the first three components (mobile), whereas this value for sample S_2 is less than 7%. Based on the binding energy of heavy elements with different

phases, soluble, exchangeable, and carbonate components are generally created by anthropogenic activities and are rapidly leached (Saleem et al., 2018). The leaching of heavy and toxic metals poses a great danger and infliction to plant and animal organisms. Unlike the previous state, in sample S2, nearly 85% of lead in the residual fraction has been observed, indicating a low toxicity level of sample S2 than that of sample S1. The lead in the residual phase is generally associated with geological and historical resources and human manipulation does not play a big role in that (Islam et al., 2015). Moreover, the Fe/Mn oxide and organic fractions of lead-zinc mine tailings were low (<10% of total). The formation of oxide conditions can lead to the dissolution of iron and manganese oxides and organic fractions (Karbassi and Shankar, 2005; Sundaray et al., 2011).

Potential mobilization of lead was assessed by mobility index (MI). The calculated results of MI are represented in Table 2. A more trustworthy indicator is the MI which considers the weakly adsorbed fractions alone, following a fractionation method. The computed mobility index illustrated that Pb has high mobility (MI= 51%) in sample S₁, which was more consistent with the concentration of lead in this sample which represents a very high risk to the environment (Table 3). However, in sample S₂, the mobility index was low (6.5%), and this difference in the mobility index of the studied samples could be due to the structural differences in the tailings and the difference in the processes of metallurgical extraction (Lei et al., 2010). The lead mobility index in the S₁ sample was very high, which means that lead can easily move and enter water and soil resources under optimal environmental conditions. (Table 3). Whatever the amount of MI in tailings was higher, show that this substance creates a more serious environmental hazard. According to the Russian general toxicological standard, lead is a highly hazardous element (Vodyanitskii, 2016). Therefore, it is necessary to manage the entrance of excessive lead into the environment. The mobility of elements in the environment depends on several factors: level of mobility, the concentration of elements in tailing particles, and their solubility. Although prevailing oxide conditions can cause the mobility of heavy metals attached to organic parts, metals attached to organic parts are not dangerous to the environment because they are extracted slowly under favorable environmental conditions. However, they can mobile when the environmental conditions become severely oxidized or severely reducing. In some modes, prolonged flooding created by microclimate alteration (e.g., rain surge) might because of the mobilization of trace metals and pesticides saved in the soil and tailings or the mobilization of metals adsorbed on the solid matrix (Liang et al., 2014).

Table 2
Pb concentrations (mg kg⁻¹) 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 3
Assortment of mobility index and risk them for environment

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

4.4. Bath leaching experiments

The process of leaching elements from waste materials affected by various physicochemical properties and happens if a leachant permeates through (e.g soil matrix) or passes the particles. As a result, organic and inorganic pollutants are leached away and enter to the environment (Houben et al., 2013). One of the most important methods for determining the leaching of elements from tailings is the batch leaching test. Batch tests are approximately rapid and simpler than to the column leaching tests. A batch leaching test is a fast and low-priced way to evaluate the toxicity of a hazardous material disposed to land (Cote and Constable, 1982). The results are more reproducible than those from column leaching because conditions can be almost controlled over a relatively little course of time (Colombani et al., 2015). Very important physical parameters are the shape, size, percentage of particle porosity in waste materials and the most important chemical factors include temperature, contact time, liquid to solid ratio, amount of leaching agent, and pH. Different aspects of batch leaching experiments should be performed to simulate the effect of different ecological conditions on the release of pollutants from tailings. In this study some of the more important aspects of these test conditions are examined:

4.4.1. pH dependent release

The amount of acidity of the aqueous solution (concentration of hydrogen ions) has a very important effect on the dissolution of mineral phases and also the speciation of lead in the solution. The adsorption ability of cations or the cation exchange process on active surfaces with adsorption-desorption power is directly affected by the acidity (pH) of the environment. The aim of this section is to evaluate the influence of pH on the leaching behavior of lead. The leaching procedure described in Section 2.4 was performed and the obtained eluates were applied to evaluate the lead concentration. The process of releasing lead into solution from the tailings due to pH changes was completely different. As shown in Figure 4, the final pH of the extracts changed significantly compared to the initial pH. At the initial pH range of 3-12, the final pH in sample S₁ and sample S₂ remained at around 5.6 and 4.9 respectively. This is due to the buffering capacity of the tailing samples. This is probably related to oxyhydroxide compounds, salts containing weak bases, and the process of dissolution-precipitation. In fact, the acidity of the leaching agent that comes in contact with the tailings can lead to very large changes in the quantities of pollutants that may be discharged to the environment as reported by many authors (Król et al., 2020). However, in highly acidic (pH= 1 and 2) and very alkaline (pH=13 and 14) conditions, the tailings buffering capacity could not overcome and the pH of solution had sharp changes. pH changes directly affect the solubility of the compounds.

The leaching behavior of lead corresponding to the different pH values is represented in Figure 5. Approximately v-shaped (amphoteric) leaching behavior was observed in both samples especially in sample S₁. This means that the highest amount of solubility occurred in the low and high pH values. As can be seen the amount of leached lead in highly acidic and highly alkaline conditions was high. In both samples, the leaching of lead increased with decreasing pH, although in sample S₂ a non-negligible amount (37.5 mg kg⁻¹, almost equal to water-soluble fraction) of this element was also leached in the alkaline pH range. But in sample S₁, more lead was leached, which was even more than the acidic condition. This condition because of the different mineralogical compositions of the tailing samples (Figure 1). The critical limit of Pb in waste samples for disposal in hazardous waste landfills set by Portuguese legislation is 20 mg kg⁻¹. In acidic conditions leached Pb concentration was largely exceeded the legal limit and because the tailings contain sulfide, its oxidation creates acidic conditions that liberate high levels of lead to the environment. Thus the tailings should be considered a hazardous material. It should be noted that, although in the acidic condition, a higher concentration of lead is released to the solution, even in this condition, the amount of released lead into the solution is less (1%) than the total concentration of Pb in samples (Table 1). In the present project, a significant part of the total lead concentration was observed in the structural part which matches with sequential extraction results. Heavy and toxic metal lead is one of the most challenging toxic and hazardous metals in relation to potential environmental impacts on wastes. Similar results for pH dependent leaching behavior of Pb was indicated by other researchers (Van Herck et al., 2000; Van der Sloot et al., 2001; Bożym, 2017, Król et al., 2020). Analysis of the obtained data proved that the release of lead is affected by the solubility process because the amount of concentration of lead in the liquid phase is controlled by various minerals whose solubility is affected by pH. 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: Pb(OH)₂(aq) for acidic

condition forming > 50%, while PbOH^+ forms 27%. Under the neutral conditions, carbonates ($\text{Pb}(\text{CO}_3)_2^{2-}$, $\text{PbCO}_3(\text{aq})$ and PbHCO_3^+) and chloride (PbCl^+ , $\text{PbCl}_2(\text{aq})$, ZnCl_3 and PbCl_4^{2-}) lead compound overcome the solution at 41% and 45% respectively. In alkaline conditions, about 80% of total solvable lead existed as $\text{Pb}(\text{OH})_2$. Another compound that can play a role in lead solubility is Cerrusite (PbCO_3). The research values obtained for lead in the experiments are in accordance with other residues conducted in this field (Chandler et al., 1997; Zhang et al., 2008; Fernández-Olmo et al., 2009; Kogbara, 2011).

4.4.2. Liquid to solid ratio

To examine the influence of the liquid-solid ratio on the concentrations of lead released into the water, different liquid to solid ratios were applied. The liquid to solid ratio employed in this study varies from 20:1 to 20:16. Figure 6 shows the results of liquid to solid ratio tests on tailing samples. With a decreasing L/S ratio, the leached concentration of lead from the tailings reduced rapidly due to an increase in viscosity. At low liquid to solid ratios, the solution thickens and the viscosity increases, which causes mass transfer resistance around the tailings particles (Liu et al., 2006). The leachability discipline for certain elements is independent of the liquid to solid ratio and for the others, the leaching rate is a function of L/S (Zandi and Russell, 2007). In this study, the leaching behavior of lead from tailings was dependent on the liquid to solid ratio. In general, there are several factors that can control the release of a specific component of tailings samples into the aquatic environment. Extremely soluble metals available on the surface of tailings typically fall into the group of available controlled leaching if the concentration leached into the extract is limited just by the quantity of the metals in the tailings. It is expected that these elements in the aquatic environment will be highly available and leached as soon as in high concentration. Leachability of some other metals may be solubility controlled where leachability of metals in tailings can be described through dissolution and deposition processes. Therefore, according to the definitions, the process of release of lead from the tailings is solubility controlled leaching (Figure 6).

4.4.3. Particle size results

One of the main causes contributing to the wrong extrapolation of metal release from tailings is the size of particles (Janusa et al., 1998; Karius and Hamer, 2001). Particle size distribution in the amount of adsorption and storage capacity of heavy metals on tailings plays a very important role. Figure 7 offer the leached concentrations of the lead with different particle size for tailing samples (S_1 and S_2). As shown in Figure 7 the tailings showed a completely different leaching behavior in relation to various particle sizes. In sample S_1 with decreasing the particle size of tailings, the leached concentrations of lead first increased and afterward decreased. Lead concentrations in various particle sizes of sample S_1 were similar to the normal distribution model and the highest concentrations (13.9 mg kg^{-1}) were observed in sizes of 0.3- 0.5mm and particles that were courser or finer than this size had lower leached lead concentrations. Li and Chen (2017) reported the same leaching behavior for Waste printed circuit boards. It is well-founded that whatever the particle size is smaller, the metal leaching rate is higher because the surface area of particles increases by the decrease of particle size, which is useful for metal leaching (Guo et al., 2020). However, particle size below a critical value will result in particle-particle agglomerations, hindering the leaching liquid permeate through fine powders (Yang et al., 2011). Unlike Sample S_1 , sample S_2 had a completely different leaching behavior and reduced the amount of lead released to the solution by decreasing the particle size. As shown in Figure 7, when particle size decreases from 1.8- 2mm to 0.10–0.6 mm, lead leaching ratio increase from 11.5 to 12.5 mg kg^{-1} . With the further reduction of tailing particle size, lead leaching rates reduced and reach 9.5 mg kg^{-1} in particles with diameter of >0.045 mm. The differences in metallurgical extraction treatments and the particles crushing method cause such different behaviors in the form of leaching of elements from the tailings.

4.4.4. Leaching time results

It has been found that the leaching of heavy metals from materials to water resources is a very slow process, and the balance between the solid and liquid phase cannot be achieved even in long leaching times. For this purpose, time-dependent leaching experiments are carried out to determine the equilibrium time and the amount of leaching of lead at different leaching times.

On the other hand, over time, reactions occur between the leaching solution and the host phase, which reduces or increases the amount of leaching. In this study, two different types of leaching behavior were observed.

An initial rapid release then a reduction in the release amount (100 minutes) and a slow concentration until a stable state is achieved (Figure 8- S_1). In sample S_1 the rapid and incremental entry of lead into the solution can be due to soluble and labile lead (corresponding with sequential extraction) but the researchers generally determined that the decrease of lead in solution by an increase of time as a result of the strong binding of this metal through adsorption processes, sedimentation, complex formation with organic matter and cation exchange (Raskin and Ensley, 2000). In sample S_2 the leaching pattern entirely was different from sample S_1 . Actually, a slow concentration of lead increase until a stable mood is achieved. 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). The common point in both graphs is that almost after 280 minutes of leaching, the amount of lead released into the solution reached a steady state. In steady-state, equilibrium condition between tailings and leachant has been achieved.

Four different patterns of leaching as a function of time could be distinguished (Cappuyns et al., 2003): Type 1: metals are immediately leached at the beginning of the experiment (e.g. Na, Mg, K); the labile reservoir is by far dominant and may be related to cation exchange reactions. Type 2: some metals present an originally fast release, followed by a moderate but fundamental release in the final step of the experiment. The labile reservoir is more momentous than the slowly labile reservoir. This pattern is generally for the more mobile elements in the wastes that are simply desorbed on acidification or illustrate the dissolution of poorly firm solid forms (e.g. carbonates). Type 3: Metals that are easily released. About this type, the steadily labile reservoir is more important than the labile reservoir. This release model refers to the desorption of metals that are more forcefully bound to tailing ingredients (e.g. Co, Cr, Cu, and Pb) or to the slow liquidation of solid forms similar Fe-oxides. Occasionally, the release was linear as a function of time or could be defined with just one exponential equation. Type 4: some elements represent readsorption (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 8).

Conclusion

Leaching experiments are essential methods for the evaluation of the long-term effect of polluted waste matters like tailings on the environment, biota, and soil-groundwater pathway. Release behavior of lead from lead-zinc tailings in the arid and semi-arid regions (Zanjan province, a city in Iran) by batch leaching and sequential extraction method was investigated. The main components of the samples were calcium oxide and Silicon dioxide which cause a potential buffering capacity. According to the TCLP test, each of the two studied samples has a high environmental impact and qualifies as hazardous materials. Also, in simulating artificial rain on the tailings with the SPLP method, it was found that the concentration of lead released into the solution was much higher than the Primary and Secondary Drinking Water Standard. The sequential extraction results indicated that the water-soluble fraction of lead is much lower than the other fractions in both samples and the residual fraction accounts for the highest percentage. The calculation of the mobility index clearly revealed the apparent difference between samples in the distribution of lead in different parts. The lead mobility index in sample S_1 was 51% and sample S_2 was 6.5%. This parameter showed that although both samples are mine tailing from on mine, but their level of risk is very different for the environment. The pH-dependent leaching behavior of lead was amphoteric (V-shape) and the highest release rate was observed in alkaline and acidic conditions. The results of laboratory leaching test revealed that release behavior corresponding to the liquid to solid ratio has a great effect on lead leaching and with a decreasing L/S ratio, the leached concentration of lead from the tailings reduced rapidly due to an increase of viscosity. The maximum release concentration of lead was from particles with a diameter of 0.3- 0.5mm and the time-dependent leaching behavior was completely different from each other. The results have shown clearly that the leaching behavior of lead corresponding to various parameters was different and extraordinary consideration should be paid to the heaps of tailings in the environment.

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Figures

Figure 1

The XRD pattern of the mine tailings

Figure 2

The leaching of lead from tailing samples (S₁ and S₂) in leaching protocols (column mg kg⁻¹, smooth line mg L⁻¹)

Figure 3

Lead distribution in tailing samples(log scale)

Figure 4

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

Figure 5

Effect of pH on leaching behavior of lead from tailings

Figure 6

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

Figure 7

Release of lead from tailings due to changes of particle sizes

Figure 8

The effect of contact time on release of lead.