



## Characterization of mining tailings in México for the possible recovery of strategic elements

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### ABSTRACT

The supply of minerals and energy is critical to a global society. Extraction of minerals results in the concurrent production of a significant volume of waste material, including tailings. The volume of tailings is normally far more than the liberated resource, tailings may be reprocessing because they often contain significant amounts of potentially valuable elements. The physicochemical, mineralogical and elemental characterization of nine different samples of mining residues from the exploitation of both iron ores and polymetallic minerals (Pb-Zn-Ag) was done to evaluate the possibility of recovery of strategic elements, like Ga, In, Ge and/or rare earth elements. The mineralogical characterization was carried out by X-ray Diffraction and Scanning Electron Microscopy with Energy Dispersive X-ray analysis. The elemental characterization was performed by total digestion and Inductively Coupled Plasma Atomic Emission Spectrometry with a Mass Spectrometer detector and Instrumental Neutron Activation Analysis. The results indicated that the major elements (> 100 mg/kg) in the samples are Fe, Zn, Pb and Cu. The strategic elements with the greatest recovery potential are Ga, Y, La, Ce, Nd and Sc from iron non-oxidized tailings, indium from a Zn refinery hydrometallurgical waste. While in the old oxidized Pb-Zn-Ag tailings the recovery of Au in particle less than 250 μm is viable.

### 1. Introduction

The mining industry has produced and will continue producing large amounts of mining wastes. An estimated 1150 million tons of heavy metals (copper, lead, iron, zinc, cadmium and chromium) have been mined since the Stone Age with estimates of an actual mine tailings production ranging between 5 and 7 billion tonnes per year worldwide (Edraki et al., 2014). Mine tailings consist of the remaining fine grained (1–600 μm) ground-up rock after minerals of value have been extracted from mined ore, tailings are highly reactive because of their small particle size. The physical and chemical characteristics of mine tailings and wastes vary with ore type and the way the mineral is processed. Mine tailings and wastes may contain metals, such as iron, copper, nickel and zinc, in relatively high concentrations (from 0.5 to 3%), and occasionally precious metals such as gold and silver. Toxic elements, such as arsenic, may also be present in concentrations up to 100 mg/kg (Falagán et al., 2017).

Nowadays, there are projects for reuse, recycling and reprocessing

of tailings to improve the environment by generate alternatives in tailing management. The reuse of mine wastes is the new use of the total mine waste for a specific purpose directly without any reprocessing. Recycling, on the other hand, extracts new valuable resource ingredients, or uses the waste as feedstock and converts the entire mine waste into a new valuable product or application with some reprocessing. In reprocessing the waste material is used as a feedstock for producing a valuable product, such as recovered minerals and metals. Higher metal prices and environmental costs may justify reprocessing of some old tailings (Edraki et al., 2014; Marabini et al., 1998; Geise et al., 2010).

Since mine tailings have already been part-processed, the cost of extracting residual metals from them is often economically more attractive than mining a deep-buried primary ore body. In addition, mine wastes may contain metals (such as gallium, indium or rare earth elements) that were not considered worth extracting when the ores were initially processed, but now have increased in value and use (Falagán et al., 2017; Zhang et al., 2014).

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Research on reprocessing mine waste is not new (Rampacek, 1982), since concentration of some elements (with supply risk) are localized in limited areas. Countries have been looked for alternative sources of these materials, including reusing, recovery and recycling of waste material (Dodson et al., 2012).

The critical raw materials or strategic elements are those necessary in development of new technologies. Strategic elements have a great economic value for aerospace, automotive and electronics industries. The European Union (EU) Commission has issued the first warning about the depleting raw material sources in 2008, declaring that meeting our needs in raw materials is critical for the economic growth. The following elements have been defined as having a high supply risk in the EU: antimony, indium, beryllium, magnesium, cobalt, niobium, platinum group elements (PGE), gallium, rare earth elements (REE), germanium, tantalum, graphite and tungsten (European Commission, 2010).

The demand for these strategic elements has increased and will continue to rise because of strong economic growth, and the realization of an efficient supply could present difficulties due to the need to extract ores at great depths, with lower concentrations and complex mineralisation. These elements are generally recovered as by products or ‘companion metals’ of other metal ores (Mudd et al., 2014). Therefore, it is necessary to consider other alternatives to obtain such elements, which avoids overexploitation of mines.

It has been found that these elements can be recovered from the waste generated by the electronics industry and the mining industry for the benefit of other metals such as Fe, Zn, Pb and Cu (Wood and Samson, 2006). Growing industrial demand for critical elements led to various projects for re-assessment of mining residues as potential source of such raw materials. Mine tailings and wastes often contain residual ore with important amounts of strategic elements, the recovery of valuable minerals and reuse of waste rock materials and tailings are becoming increasingly important. (Afum et al., 2018; Zhang et al., 2014). The tailings dams are currently investigated about the recovery of strategically important raw materials accompanied by reducing environmental problems. Tailings were investigated for the potential exploitation of residual valuable metals e. g. zinc, cobalt, copper or indium by using alternative technologies like bioleaching (Martin et al., 2015; Falagán et al., 2017). A novel hydrometallurgy process was employed for separating and recovering REE from Bayan Obo tailings (Zhang et al., 2014). Based on technological advances in recovery techniques, mine waste are potential resources for reprocessing, for example in the past, gold recovery efficiencies were in the ranges of 35–60%, but in recent times, gold recovery efficiencies are in the ranges of 92–97%. In 2015, AngloGold Ashanti Obuasi Mine completed the remaining of its tailings. Also, a gold and copper mine located in Australia, was being reworked. In 2016, True North Gold Mine of Klondex Canada Limited in Manitoba, Canada, commenced tailings reprocessing project (Afum et al., 2018) A project by the French geological survey identified interesting old mining wastes to assesses the potential metal recovery of these deposits with emphasis in the critical metals for the industrial development compiled by the European Commission in 2010 (Guézennec et al., 2013).

In México, both iron and zinc-lead-silver mining industry has produced and will continue producing large amounts of mining residues, which may have great potential for economic gain if certain elements of industrial interest are obtained. Some strategic elements such as gallium and germanium can be found associated with iron and zinc ores (Dutrizac and Chen, 2000), tailings and mining wastes can serve as future resources in times of scarcity, technological advancement and, improvements in mining and processing techniques. Therefore, in the present paper we characterized mining tailings from iron or Zn-Pb-Ag ores as well as a hydrometallurgical iron rich waste from a zinc smelting refinery with emphasis on the identification and quantification of strategic elements and rare earth elements for its recovery with the aim of proposed a characterization methodology that can be

**Table 1**  
Type and color of mining waste composite samples.

Sample	Type	Oxidized/Non-oxidized	Color
J01	Polymetallic tailing	Oxidized	Brown
J02	Polymetallic tailing.	Oxidized	Yellow
J04	Polymetallic tailing	Oxidized	Yellow
J05	Polymetallic tailing.	Oxidized	Brown
J03	Ferric tailing.	Non-oxidized	Gray
J06	Ferric tailing.	Non-oxidized	Gray
J07	Ferric tailing.	Non-oxidized	Gray
J08	Ferric tailing	Non-oxidized	Gray
R01	Hydrometallurgical waste	Oxidized	Yellow

extrapolated to other sites.

## 2. Materials and methods

### 2.1. Samples

Nine composite samples of mining wastes were obtained, four of them from polymetallic Zn-Pb-Ag mining areas, four more from different ferric mining areas and the last one is an hydrometallurgical waste from a zinc plant (Table 1). To ensure the representativeness of the composite sample from each waste dam, a systematic sampling was carried out collecting 12 simple samples that were mixed to form a composite sample.

Composite samples were air dried for 48 h, followed by their homogenized and stored in plastic bags.

### 2.2. Characterization of composite samples

#### 2.2.1. pH and electrical conductivity measurement

For these analyses, ultrapure deionized (Nanopure) water was used throughout. All reagents were of analytical reagent grade or higher purity. A rigorous quality control program was implemented including reagent blanks, duplicate samples, and certified reference materials. pH and electrical conductivity analyses were performed in the *Laboratorio de Biogeoquímica Ambiental, Facultad de Química*, UNAM.

The EPA 9045D method was used for the determination of pH in wastes (EPA 9045D, 2004).

20 g of each sample were weighed and 60 mL of deionized water was added and stirred for 5 min at 240 rpm. They were then allowed to stand for one hour and the pH was measured with a Thermo Scientific OrionStar A211 potentiometer. Then the electrical conductivity was measured with a Corning 441 conductivity meter calibrated with KCl standard solutions.

#### 2.2.2. Mineralogical characterization

The mineralogical characterization was carried out by X-ray Diffraction (XRD), the apparatus used is an Advance Davinvi D8 Model with theta-theta Bruker AXS that belongs to *Unidad de Servicios de Apoyo a la Investigación y la Industria (USAI)*, *Facultad de Química*, UNAM. All samples were analysed at angular interval  $2\theta$  from  $4^\circ$  to  $70^\circ$  and a speed of  $2^\circ/\text{min}$ , with Cu K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ) and Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM-EDS) in a Table Top Hitachi TM-1000, from *Laboratorio de Biogeoquímica Ambiental, Facultad de Química*, UNAM.

#### 2.2.3. Elemental characterization

For the elemental characterization the samples were sieved and separated into three particle sizes: a)  $> 150 \mu\text{m}$ ; b) between  $150$  and  $75 \mu\text{m}$  and c)  $< 75 \mu\text{m}$ . The chemical analyses of the different particle sizes for each sample were performed by Activation Laboratories Ltd., by means of a total digestion with 4 high purity acids:  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$  and HF for analysis by ICP-MS (TD-ICP-MS), digested samples

**Table 2**  
pH an Electrical conductivity for the mining waste samples.

Sample	pH	Electrical conductivity ( $\mu\text{S}/\text{cm}$ )
J01	7.8	368
J02	7.9	332
J04	2.8	2210
J05	8.2	51
J03	7.8	676
J06	8.7	300
J07	7.9	1812
J08	8.3	1221
R01	4.3	14225

are diluted and analysed using a Perkin Elmer Sciex ELAN or by Instrumental Neutron Activation Analysis (INAA), the sample is encapsulated in a polyethylene vial and irradiated with flux wires and an internal standard (1 for 11 samples) at a thermal neutron flux of  $7 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . After a 7-day decay to allow Na-24 to decay the samples are counted on a high purity Ge detector with resolution of better than 1.7 KeV for the 1332 KeV Co-60 photopeak. Using the flux wires, the decay-corrected activities are compared to a calibration developed from multiple certified international reference materials. (Hoffman, 1992). For quality control they used blanks, digested standards and duplicate samples.

### 3. Results and discussion

#### 3.1. pH and electrical conductivity measurement

For the pH and electrical conductivity measurements (Table 2), the samples presented slightly alkaline pH values (7.8–8.7), unlike one of the polymetallic tailings (sample J04) has a pH value of 2.83, and the hydrometallurgical waste (sample R01) present a pH value of 4.28. This means that the samples with alkaline pH values have more minerals with neutralization capacity (carbonates, hydroxides), instead of acidic minerals (sulphides) (Romero et al., 2008).

It was also found that the same samples with the lowest pH values (J04 and R01) were those that presented the highest conductivity values (2210 and 14 225  $\mu\text{S}/\text{cm}$  respectively). The pH is the most influential factor in the mobilization of metals due to the hydrolysis reactions of the cations, so that at neutral and basic pH values are found minerals that are poorly soluble with relatively low electrical conductivities (Ramos-Gómez et al., 2012), sample R01 has the greatest conductivity because is an oxidized hydrometallurgical waste rich in sulphates.

The physical and chemical characteristics of tailings vary with ore type, J01, J02, J04 and J05 were Zn-Ag tailings and the principal mineral exploited was sphalerite (ZnS). The four tailings were in oxidized dams. It is important to noticed that J04 is an acid mine drainage

**Table 3**  
Mineralogical compositions of tailings and hydrometallurgical waste by X-ray Diffraction.

Sample	Mineralogy
J01	Quartz: $\text{SiO}_2$ ; Brushite: $\text{CaPO}_3(\text{OH}) \cdot 2\text{H}_2\text{O}$ ; Calcite: $\text{Ca}(\text{CO}_3)$ ; Pyrite: $\text{FeS}_2$ ; Clinocllore: $(\text{Mg,Fe,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ ; Hidroniumjarosite: $\text{K}_{0.35}(\text{H}_3\text{O})_{0.65}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
J02	Calcite: $\text{CaCO}_3$ ; Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; Ferro-actinolite: $\text{Na}_{0.04}\text{Ca}_{1.8}\text{Mg}_{1.9}\text{Mn}_{0.1}\text{Fe}_{3.2}\text{Al}_{0.03}\text{Si}_8\text{O}_{22}(\text{OH})_{1.9}$ ; Hidroniumjarosite: $\text{K}_{0.35}(\text{H}_3\text{O})_{0.65}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
J04	Quartz: $\text{SiO}_2$ ; Gypsum: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; Hidroniumjarosite: $\text{K}_{0.35}(\text{H}_3\text{O})_{0.65}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$
J05	Quartz: $\text{SiO}_2$ ; Calcite: $\text{CaCO}_3$ ; Dolomite: $(\text{Ca,Mg})(\text{CO}_3)_2$ ; Smithsonite: $\text{ZnCO}_3$ ; Mikasaite: $\text{Fe}_2(\text{SO}_4)_3$ ; Goetite stannous: $(\text{Fe}_{0.979}\text{Sn}_{0.021})\text{O}(\text{OH})$ ; Nontronite: $(\text{Na,Ca})_{0.3}\text{Fe}_2(\text{Si,Al})_4\text{O}_{10}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ ; Tenorite: $\text{CuO}$ ; Strontium, Samarium, Cobalt, Manganese Oxide: $\text{Sr}_{1.4}\text{Sm}_{1.6}\text{CoMnO}_7$
J03	Quartz: $\text{SiO}_2$ ; Clinocllore: $(\text{Mg,Fe,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ ; Calcite: $\text{CaCO}_3$ ; Pyrite: $\text{FeS}_2$ ; Actinolite: $\text{Na}_{0.04}\text{Ca}_{1.8}\text{Mg}_{1.9}\text{Mn}_{0.1}\text{Fe}_{3.2}\text{Al}_{0.03}\text{Si}_8\text{O}_{22}(\text{OH})_{1.9}$ ; Albite: $(\text{Na,Al})\text{Si}_3\text{O}_8$
J06	Quartz: $\text{SiO}_2$ ; Calcite: $\text{CaCO}_3$ ; Dolomite: $(\text{Ca,Mg})(\text{CO}_3)_2$ ; Pyrite: $\text{FeS}_2$ ; Magnetite $\text{Fe}^{2+}, \text{Fe}_3^{2+} \text{O}_4$ ; Titanomagnetite $(\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4)$ ; Augite $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Al,Si})_2\text{O}_6$ ; Chamosite $(\text{Fe}^{2+}, \text{Mg})_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ ; Labradorite $(\text{Ca,Na})\text{Al}_{1-2}\text{Si}_{3-2}\text{O}_8$
J07	Calcite: $\text{CaCO}_3$ ; Dolomite: $(\text{Ca,Mg})(\text{CO}_3)_2$ ; Pyrite: $\text{FeS}_2$ ; Magnetite $\text{Fe}^{2+}, \text{Fe}_3^{2+} \text{O}_4$ ; Titanomagnetite $(\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4)$ ; Augite $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Al,Si})_2\text{O}_6$ ; Chamosite $(\text{Fe}^{2+}, \text{Mg})_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ ; Labradorite $(\text{Ca,Na})\text{Al}_{1-2}\text{Si}_{3-2}\text{O}_8$
J08	Calcite: $\text{CaCO}_3$ ; Dolomite: $(\text{Ca,Mg})(\text{CO}_3)_2$ ; Pyrite: $\text{FeS}_2$ ; Magnetite $\text{Fe}^{2+}, \text{Fe}_3^{2+} \text{O}_4$ ; Titanomagnetite $(\text{Fe}^{2+}(\text{Fe}^{3+}, \text{Ti})_2\text{O}_4)$ ; Augite $(\text{Ca,Na})(\text{Mg,Fe,Al})(\text{Al,Si})_2\text{O}_6$ ; Chamosite $(\text{Fe}^{2+}, \text{Mg})_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$ ; Labradorite $(\text{Ca,Na})\text{Al}_{1-2}\text{Si}_{3-2}\text{O}_8$
R01	Quartz: $\text{SiO}_2$ ; Jarosite: $\text{KFe}_3^{3+}(\text{OH})_6(\text{SO}_4)_2$ ; Bianchite: $\text{Zn}_{0.75}\text{Fe}_{0.25}^{2+}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$ ; Zinc melanterite $\text{Zn}_{0.6}\text{Cu}_{0.3}\text{Fe}_{0.1}^{2+}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$ ; Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

(AMD) generator and it is well known that effluents may contain metals. J03 was from a hematite-magnetite tailing dam, that does not produced AMD, however J06, J07 and J08 were non-oxidized samples from magnetite tailings dams but there are potential acid mine drainage generators. Sample R01 is as mentioned from a sphalerite hydro-metallurgical process.

The origin of the tailings indicates the possible presence of strategic elements like Ga, In and Ge, since it is reported that they are associated with iron and zinc ores, such as magnetite  $\text{Fe}_3\text{O}_4$  and sphalerite  $\text{ZnS}$  (Dutrizac and Chen, 2000). Mudd et al., 2014 reported a list of companion metals and their typical hosts. They indicated that in Zn-Ag minerals the companion metals are Ge, Cd, In and Tl, as well as in Fe ores they reported V, Sc, La, Ce, Pr and Nd as companion metals.

#### 3.2. Mineralogical characterization

The composition of the tailings is a function of the mineralogy of the site from which they come. In Mexico, the main deposits are copper, iron, silver and zinc. The mineralogical characterization in the wastes mining samples was done and the results of the X-ray Diffraction (Table 3) showed in the eight tailings samples (J01, J02, J03, J04, J05, J06, J07 and J08) quartz and clays as gangue minerals. Additionally, in samples J01, J02, J04 and J05 among others were sulphates (hydroniumjarosite and gypsum) and carbonates (calcite and dolomite) indicating oxidation process (Fig. 1). In sample J05 smithsonite ( $\text{ZnCO}_3$ ), sulphates and oxides of Fe and Cu were identified, this sample is from the oldest dam studied, where Ag was the mineral of interest.

In sample J03 there were identified clays, calcite and pyrite which agrees with an iron ore tailing. Samples J06, J07 and J08 had the same mineralogy (Fig. 2), in the three cases the iron mineral deposit is magnetite that was identified as well as titanomagnetite and pyrite.

In sample R01 there were identified jarosite and two Zn minerals: bianchite and zinc melanterite (Fig. 3).

The gypsum, the calcite and the hidroniumjarosite are indicators of oxidation of the tailings, since these are secondary minerals from the oxidation of primary minerals.

The four iron solid tailings (J03, J06, J07 and J08) have some sulphide mineralisation remaining after processing and can constitute a potential environmental problem because sulphide minerals, like pyrite, can oxidise.

The particle size determination indicated that solid samples are generally composed of particles larger than or equal to  $100 \mu\text{m}$ . In the SEM-EDS analyses it was observed that in both the smaller and larger particles showed the predominant elements are Si, Al, Ca, K and Fe (Fig. 4).

These elements are typical of clays and quartz, which are generally present in the tailings and wastes, these results agree with those of XRD.

XRD and SEM-EDS methods did not allow the identification of the strategic elements, possibly due to the concentration in which they

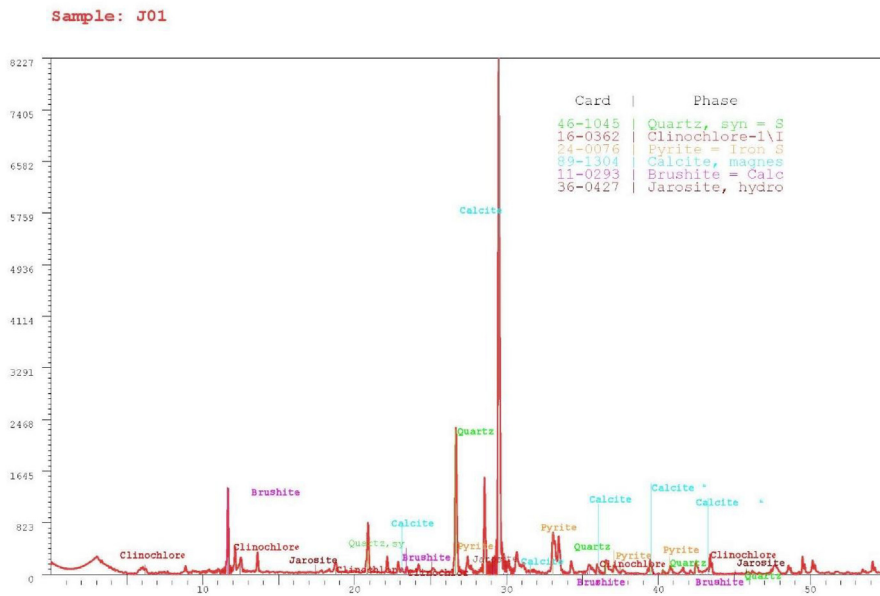


Fig. 1. XRD pattern of sample J01 (polymetallic tailing).

occur or the low crystallinity of their minerals. Sample R01 has the highest electrical conductivity and low pH which agrees with the results of the mineralogy, since it contents sulphate minerals. Samples J01, J02, J03, J05, J06, J07 and J08 with pH between 7.8 and 8.7 agree with the presence of neutralizing carbonate minerals like calcite and/or dolomite.

3.3. Elemental characterization

In general, tailings have the characteristic of having particle sizes from 2 μm to 0.2 mm, however, it is reported that there are certain elements that are distributed according to the particle size, concentrating more on the smaller particles (Roussel et al., 2000), so we quantified elements in different particles size. The results for host metals Zn, Fe and Cu, and companion metals such as Ni, Pb and Au by INAA or TD-ICP-MS analyses are presented in Table 4.

The polymetallic tailings from Zn-Ag ores (J01, J02, J04 and J05)

had an important content of Zn; for example, J01 had an average of 5200 mg/kg and sample J05 had 58 200 mg/kg and was clearly concentrated in smaller size particles (Fig. 5). The Pb content in the four Zn-Ag tailings dam is substantial and may implicated environmental problems. In the case of polymetallic tailings and the hydro-metallurgical waste (J01, J02, J04, J05 and R01), Au concentration increases as the particle size decreases, it is generally admitted that the smaller fraction contains more clay minerals than other fractions (Roussel et al., 2000) so maybe Au could be at least partially sorbed onto clay particles. In samples J02 and J04 in particles smaller than 75 μm, Au concentrations of 2150 and 1230 μg/kg were found (Fig. 6). These Zn-Ag tailings can be reused for the recovery of Au maybe using alternatives cleaner production (Hilson and Monhemius, 2006).

In general, in sample J03 Fe, Cu and Ni concentrations were higher than for the Zn-Ag ore tailings, Fe concentration was 15.16% in average for the three particle sizes. In this sample we did not noticed changes in concentrations of metals with particle size. Additionally, in samples

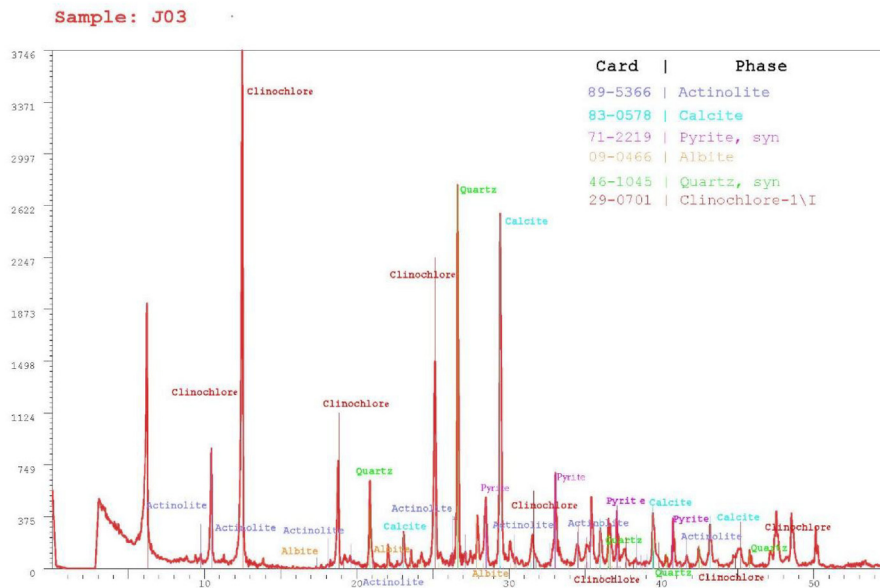


Fig. 2. XRD pattern of sample J03 (iron tailing).



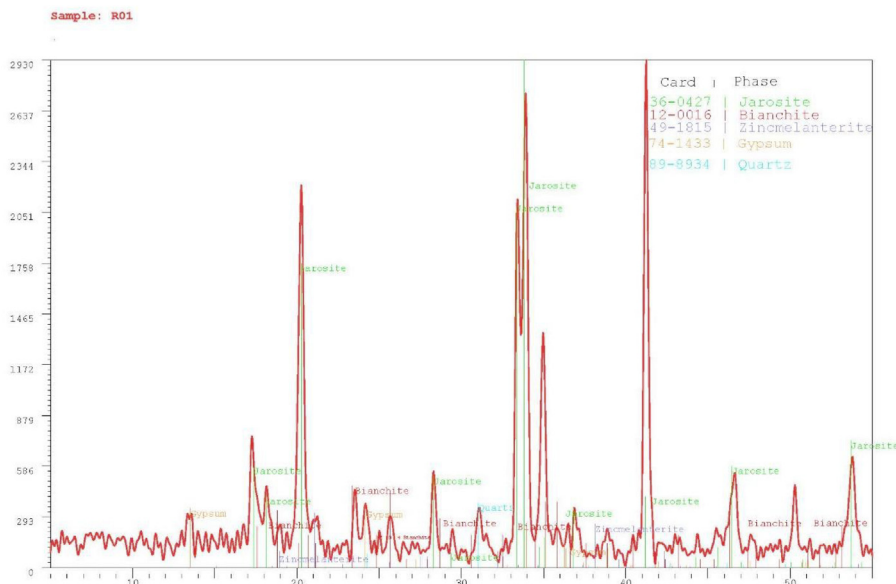


Fig. 3. XRD pattern of sample R01 (hydrometallurgical waste).

J06, J07 and J08 Cu, Ni, Zn and Pb concentrations were similar to J03 and did not depend on particle size.

Finally, sample R01 had the highest content of Zn, Fe, Cu and Pb, its mineralogy characterization indicates Zn minerals as well as jarosite and total concentrations of these elements did not depend on particle size.

The results showed that the total concentrations of Ga, Ge and In do not depend importantly on the particle size (Table 5), this result indicates that a previous concentration is not necessary for their recovery. Ga is the element with the highest concentration, specifically in the iron deposit residues (J03, J06, J07 and J08) and the jarosite residue (R01). The highest concentration is in sample J03 with a value of 12.3 mg/kg in particles > 150 μm.

It was reported that Ga is produced mainly during the processing of bauxite, where it is recovered by electrolysis of Al hydroxide solution. A secondary Ga source is recovered by leaching of iron residue produced during Zn extraction from sphalerite concentrates (Yellishetty et al., 2017). However, there was not previously reported that Ga could be recover from a non-oxidized iron tailing.

The Zn-Ag tailings studied did not content Ga, Ge or In as we expected from a sphalerite ore deposit tailings (Table 5). One possibility for this result is that in the oxidized tailings the strategic elements were leached previously.

In addition, a statistical analysis of the total concentrations, pH and EC was carried out to investigate if there is any significant correlation between them (Table 6). The results indicate that only Ge and In are

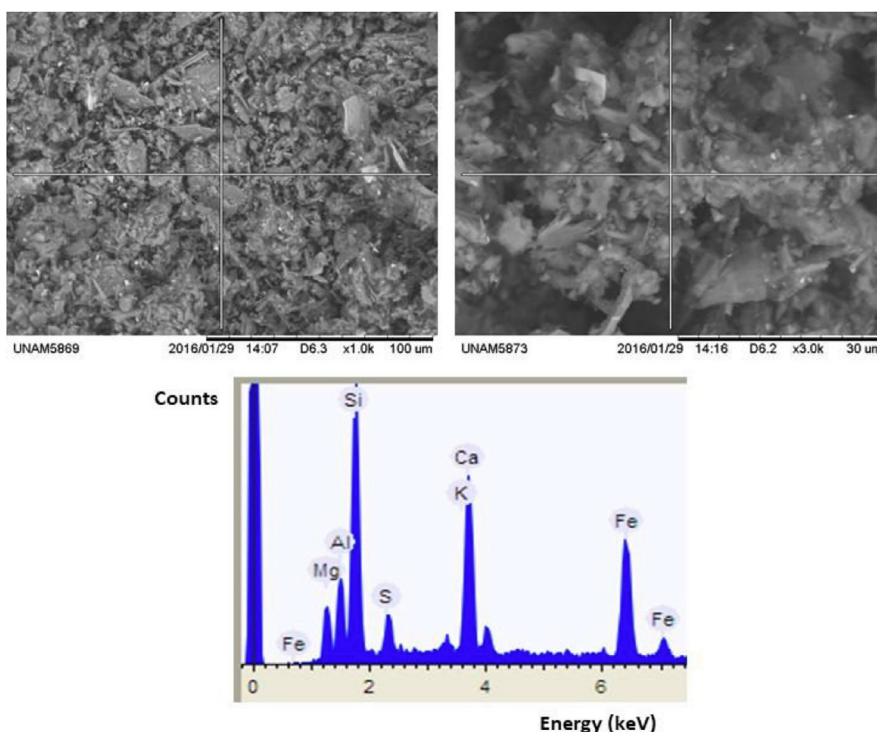
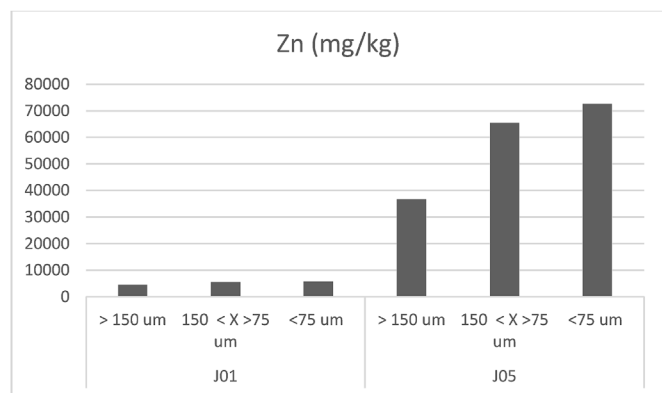


Fig. 4. SEM images and SEM-EDS analysis in sample J03.

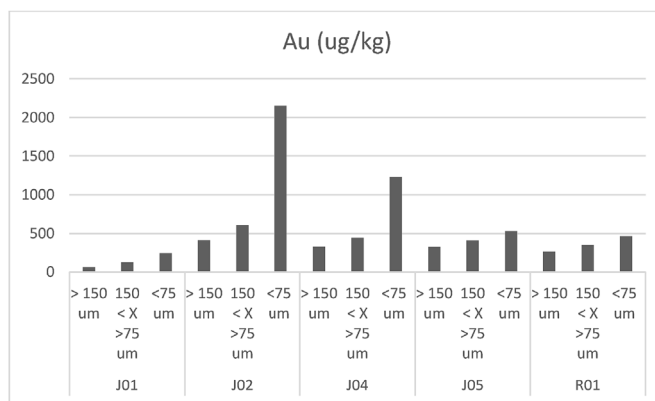
**Table 4**  
Elemental Analyses of the host metals Fe, Zn, Cu and companion metals Ni, Pb and Au in samples with different particle size.

Analyte	Fe	Zn	Cu	Ni	Pb	Au	
Unit	%	mg/kg				µg/kg	
Detection Limit	0.01	0.5	0.2	0.5	0.5	2.0	
Analysis Method	INAA	INAA/ TD-ICP- MS	TD- ICP- MS	INAA/ TD-ICP- MS	TD-ICP-MS	INAA	
Sample	Particle size						
J01	> 150 µm	12.2	4440	106	5.8	766	61
	150 < X < 75 µm	24.8	5480	111	9.1	1020	123
	< 75 µm	27.4	5690	164	14.6	1680	246
J02	> 150 µm	3.42	1010	53	1.4	2930	415
	150 < X < 75 µm	4.92	1190	62.8	0.7	4680	608
	< 75 µm	8.1	1770	136	1.8	5000	2150
J04	> 150 µm	6.49	1400	91.5	2.5	2150	329
	150 < X < 75 µm	10	1850	119	2.2	3380	443
	< 75 µm	18	3180	208	4.5	5000	1230
J05	> 150 µm	9.6	36600	575	1.8	5000	328
	150 < X < 75 µm	13.6	65400	862	2.8	5000	412
	< 75 µm	14.2	72600	939	2.7	5000	530
J03	> 150 µm	14.1	55.2	1480	36.2	5.5	20
	150 < X < 75 µm	15	54.3	1600	40	4.9	14
	< 75 µm	16.4	64.3	1760	38.2	5.4	25
J06	> 150 µm	10.8	78.1	204	34.8	7.3	< 2
	150 < X < 75 µm	11.9	76.3	384	41.8	8.1	< 2
	< 75 µm	16.1	98.3	449	46.2	10.7	< 2
J07	> 150 µm	9.09	89.5	241	23.8	5.1	< 2
	150 < X < 75 µm	8.98	69.4	283	24.1	5.6	< 2
	< 75 µm	9.98	71.9	252	22.6	5.1	3
J08	> 150 µm	5.9	65	169	15.7	4.8	< 2
	150 < X < 75 µm	6.91	58.4	286	23.7	4.8	< 2
	< 75 µm	11.4	70.3	302	28	7.8	< 2
R01	> 150 µm	16.9	60200	7580	12.9	> 5000	268
	150 < X < 75 µm	18.2	62200	7830	14.9	> 5000	351
	< 75 µm	22.1	53900	8090	14.3	> 5000	467

Analyses methods: TD-ICP-MS: total digestion- Inductively Coupled Plasma Atomic Emission Spectrometry with a Mass Spectrometer detector; INAA Instrumental Neutron Activation Analysis.



**Fig. 5.** Zn concentration in tailings samples J01 and J05 with respect to particle size.



**Fig. 6.** Au concentration in tailings samples J01, J02, J04, J05 and R01 with respect to particle size.

**Table 5**  
Elemental Analyses by total digestion and ICP-MS of strategic elements Ga, Ge and In (mg/kg) in samples with different particle size.

Sample	Particle size	Analyte		
		Ga	Ge	In
J01	> 150 µm	2.4	< 0.1	1.1
	150 < X < 75 µm	2.5	< 0.1	1.9
	< 75 µm	2.6	0.2	1.9
J02	> 150 µm	3.6	< 0.1	0.2
	150 < X < 75 µm	2.6	< 0.1	0.3
	< 75 µm	3.5	< 0.1	0.5
J04	> 150 µm	3.4	< 0.1	0.4
	150 < X < 75 µm	3	< 0.1	0.5
	< 75 µm	4.7	0.1	1
J05	> 150 µm	< 0.1	< 0.1	< 0.1
	150 < X < 75 µm	< 0.1	< 0.1	0.1
	< 75 µm	< 0.1	< 0.1	0.1
J03	> 150 µm	12.3	< 0.1	0.2
	150 < X < 75 µm	12	< 0.1	0.3
	< 75 µm	13	< 0.1	0.2
J06	> 150 µm	8.3	< 0.1	0.1
	150 < X < 75 µm	8	< 0.1	0.2
	< 75 µm	7.1	< 0.1	0.2
J07	> 150 µm	7.1	0.2	0.2
	150 < X < 75 µm	6.7	< 0.1	0.2
	< 75 µm	6.3	< 0.1	0.2
J08	> 150 µm	6.6	< 0.1	0.1
	150 < X < 75 µm	7.7	< 0.1	0.1
	< 75 µm	7.3	0.8	0.2
R01	> 150 µm	10.1	0.4	14.3
	150 < X < 75 µm	10.2	0.3	13.9
	< 75 µm	12.5	0.4	17.3

**Table 6**  
Correlation coefficients between the total concentrations of the strategic elements Ga, In, Ge and Au against pH, EC and the total concentrations of the hosts elements Zn, Fe and Pb.

	pH	CE	Zn	Fe	Pb	Ga	Ge	In	Au
pH	1								
CE	-0.60	1							
Zn	-0.36	0.79	1						
Fe	-0.14	0.58	0.57	1					
Pb	-0.42	0.52	0.84	0.14	1				
Ga	-0.03	0.41	0.01	0.54	-0.37	1			
Ge	-0.41	0.91	0.70	0.56	0.39	0.42	1		
In	-0.52	0.98	0.83	0.64	0.56	0.37	0.88	1	
Au	-0.48	0.22	0.43	-0.29	0.83	-0.51	0.06	0.23	1

**Table 7**  
Elemental Analyses (mg/kg) by Total Digestion and ICP-MS of rare earth elements in samples with different particle size.

Sample	Analyte Symbol	Y	La	Ce	Nd	Sc <sup>a</sup>	Pr	Sm	Gd	Dy	Tb	Er	Yb	Th <sup>a</sup>	Eu	Ho	Tm	Lu
	Detection Limit	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.05	0.1	0.1	0.1
	Particle size																	
J01	> 150 µm	5	4.6	9.9	4.3	2.7	1.1	0.9	0.9	0.8	0.1	0.5	0.4	1	0.5	0.2	< 0.1	< 0.1
	150 < X > 75 µm	4.9	6.1	13.6	5.5	2.3	1.4	1	1	0.8	0.1	0.4	0.3	0.8	0.58	0.1	< 0.1	< 0.1
	< 75 µm	4.9	4.2	9.4	4.1	2.8	1	0.9	0.9	0.8	0.1	0.4	0.4	0.8	0.49	0.2	< 0.1	< 0.1
J02	> 150 µm	3.8	3.6	7	2.9	3.4	0.8	0.6	0.5	0.6	< 0.1	0.4	0.5	0.9	0.16	0.1	< 0.1	< 0.1
	150 < X > 75 µm	2.8	3.9	8.3	3.2	2.6	0.8	0.6	0.4	0.4	< 0.1	0.3	0.3	0.5	0.19	< 0.1	< 0.1	< 0.1
	< 75 µm	4.2	6.5	13	5.1	5.2	1.4	0.9	0.7	0.7	0.1	0.4	0.4	0.8	0.26	0.2	< 0.1	< 0.1
J04	> 150 µm	3.8	3	6.1	3.1	3.2	0.8	0.8	0.7	0.6	0.1	0.4	0.5	0.8	0.2	0.1	0.1	0.1
	150 < X > 75 µm	3.3	4.3	8.6	4.3	3.2	1	1.1	0.8	0.6	0.1	0.4	0.3	0.7	0.3	0.1	0.1	< 0.1
	< 75 µm	4.2	4.9	9.1	4.3	4.8	1.1	1.1	0.9	0.7	0.1	0.4	0.4	1.1	0.3	0.2	0.1	0.1
J05	> 150 µm	8.4	4.2	7.3	5.1	0.8	1.1	1.7	1.9	1.2	0.2	0.5	0.3	0.2	1.9	0.2	0.1	< 0.1
	150 < X > 75 µm	12.2	5.9	10.5	7.5	1.3	1.5	2.2	2.7	1.7	0.3	0.7	0.5	0.3	2.7	0.3	0.1	< 0.1
	< 75 µm	13.1	7.1	12	8.5	1.6	1.8	2.6	2.9	1.9	0.4	0.8	0.5	0.4	2.8	0.3	0.1	0.1
J03	> 150 µm	11.8	15.2	31.2	11.1	7.9	3.1	1.9	1.8	1.8	0.3	1.1	1.1	1.4	0.82	0.4	0.2	0.2
	150 < X > 75 µm	11.8	15.1	32.2	11.1	7.8	3.1	2	1.8	1.8	0.3	1.1	1.1	1.3	0.82	0.4	0.2	0.2
	< 75 µm	11.9	14.6	29.7	10.8	8.7	3	1.9	1.7	1.8	0.3	1.2	1.2	1.4	0.8	0.4	0.2	0.2
J06	> 150 µm	17.2	15	30.3	17.9	11.4	4.1	3.6	3.8	3.3	0.6	1.8	1.7	1.5	0.79	0.7	0.3	0.2
	150 < X > 75 µm	18.5	17.5	34.8	20	10.2	4.6	4	4.2	3.5	0.6	2	1.9	1.6	0.88	0.8	0.3	0.3
	< 75 µm	26.1	24.7	47.8	27.1	12.9	6.2	5.5	5.8	4.9	0.8	2.9	2.8	2.3	0.97	1.1	0.4	0.4
J07	> 150 µm	20.1	17.3	33	19.3	13.1	4.4	4.1	4.3	3.9	0.6	2.3	2.3	1.8	0.73	0.9	0.3	0.3
	150 < X > 75 µm	21.8	19	36.8	22.3	12.1	5	4.7	4.9	4.3	0.7	2.4	2.4	1.8	0.86	1	0.3	0.3
	< 75 µm	31.4	25.8	48.7	29	15.2	6.5	6.6	7	6.1	1	3.5	3.2	2.4	0.96	1.4	0.5	0.4
J08	> 150 µm	17	14.9	29	17	11.6	3.9	3.8	3.9	3.4	0.6	2	1.8	1.5	0.69	0.8	0.3	0.2
	150 < X > 75 µm	19.9	18.7	35.9	21	10.3	4.7	4.4	4.8	4	0.7	2.2	2	1.7	0.88	0.9	0.3	0.3
	< 75 µm	31.8	28	52.7	30.4	14.1	6.8	6.7	7.3	6.1	1.1	3.5	3.1	2.5	1.03	1.4	0.5	0.4
R01	> 150 µm	2.6	1.1	2.1	1.6	0.7	0.3	0.4	0.4	0.4	< 0.1	0.2	0.2	0.6	0.07	< 0.1	< 0.1	< 0.1
	150 < X > 75 µm	2.3	1	1.8	1.7	1	0.3	0.4	0.5	0.4	< 0.1	0.2	0.2	0.7	0.08	< 0.1	< 0.1	< 0.1
	< 75 µm	1.7	0.9	1.5	1	1.3	0.2	0.3	0.3	0.3	< 0.1	0.2	0.1	0.7	< 0.05	< 0.1	< 0.1	< 0.1

<sup>a</sup> INNA analyses.

related to each other ( $r=0.88$ ) and with EC ( $r=0.91$  with Ge and  $r=0.98$  with In), nevertheless Ga, Ge and In are not related with Fe or Zn as was reported by Dutrizac and Chen (2000). Maybe there are few data to make a conclusive statistical analysis.

The higher Ge concentration was for R01 with 0.4 mg/kg, lower that was expected because Yellishetty et al. (2017), reported that the Ge principal source is the leaching of iron residue produced during Zn recovery from sphalerite concentrates. Also, in the Zn smelting residue In concentration was 14.3 mg/kg in particles > 150µm. It is reported that indium is often associated with zinc deposits and typically departs to Zn concentrates (Mudd et al., 2017). In the world both Ge and In are found at low concentrations in Zn ores, and consequently it is difficult to achieve directly economically feasible production (Mudd et al., 2017).

Finally, the rare earth elements (REE) in the samples were analysed, we also concluded as was seen for Ga, Ge and In that their content did not depend importantly on the particle size (Table 7).

The REE are in concentrations lower than 8.4 mg/kg in the poly-metallic tailings (J01, J02, J04 and J05) and for the metallurgical waste lower than 2.6 mg/kg. However, in the iron tailings the concentrations of Y, La, Ce, Nd and Sc are greater than 10 mg/kg. The element with the highest concentration is Ce with a concentration from 29 to 33 mg/kg in particles < 150 m.

The total concentrations of the REE do not correlated with pH and electrical conductivity, but REE are all correlated between them and with Y with coefficients greater than 0.89, except for Th (example; Y vs Th  $r$ : 0.80). Eu does not correlate with Y ( $r$ : 0.379), nor with the rest of the REE (Table 8).

### 3.4. Perspectives on the recovery of strategic elements from Mexican mine tailings and wastes

There is not much information worldwide about the recovery of

strategic elements from mining waste. In México we found that Ga could be recovered from iron non-oxidized tailings and its extraction and separation from other elements is relatively easy using simple hydrometallurgical methods (Mihaylov and Distin, 1992; Macías-Macías, 2017).

Indium could be recovered only from the iron rich hydro-metallurgical waste from the zinc refinery. The most widely used techniques for the separation and pre-concentration of In traces include ion exchange, solid-liquid separation and liquid-liquid extraction (Lupi and Pilone, 2014).

From the two oldest polymetallic Zn-Ag tailings Au could be recovered in particles size less than 75 µm, we propose use green extraction leaching processes like KSCN or NaS<sub>2</sub>O<sub>3</sub> (Hilson and Monhemius, 2006).

Recycling of REE has been widely studied in recent years (Binnemans et al., 2013). The REE could be recovered from the non-oxidized iron tailings with emphasis in Y, La, Ce, Nd and Sc. The element with the highest concentration is Ce with a concentration from 29 to 33 mg/kg.

## 4. Conclusions

Tailings and wastes studied contain heavy metals and sulphides and cause serious pollution of the environment. To eliminate the environmental risk of the tailings and wastes, re-processing research could be conducted on the recovery of strategic elements such as Au from old polymetallic Zn-Ag tailings in particles size less than 75 µm. Ga could be recovered from non-oxidized iron tailings and from sphalerite smelting waste by different processes that could include leaching and solvent extraction. In could be recovered only from the iron rich hydro-metallurgical waste from the zinc refinery by solid-liquid extraction. We concluded that the appropriate techniques for the identification and quantification of the strategic elements in mining wastes are ICP-MS

**Table 8**

Correlation coefficients between pH and electric conductivity and the total concentrations of the REE and Y.

	pH	EC	Y	La	Ce	Nd	Sc	Pr	Sm	Gd	Dy	Tb	Er	Yb	Th	Eu	Ho	Tm	Lu
pH	1																		
EC	-0.60	1																	
Y	0.59	-0.38	1																
La	0.58	-0.40	0.95	1															
Ce	0.57	-0.41	0.93	1.00	1														
Nd	0.56	-0.36	0.99	0.96	0.95	1													
Sc	0.48	-0.35	0.94	0.95	0.95	0.97	1												
Pr	0.57	-0.39	0.98	0.98	0.98	0.99	0.98	1											
Sm	0.56	-0.36	0.99	0.91	0.89	0.98	0.93	0.96	1										
Gd	0.57	-0.35	0.99	0.89	0.86	0.97	0.91	0.95	1.00	1									
Dy	0.55	-0.33	0.99	0.93	0.91	0.99	0.95	0.97	0.99	0.99	1								
Tb	0.53	-0.37	0.98	0.92	0.91	0.99	0.94	0.97	0.99	0.99	0.99	1							
Er	0.53	-0.33	0.98	0.94	0.92	0.99	0.98	0.98	0.98	0.97	0.99	0.97	1						
Yb	0.46	-0.32	0.96	0.94	0.92	0.98	0.99	0.97	0.95	0.94	0.97	0.94	0.99	1					
Th	0.40	-0.29	0.80	0.89	0.89	0.86	0.94	0.88	0.76	0.73	0.82	0.78	0.87	0.91	1				
Eu	0.54	-0.46	0.38	0.25	0.23	0.27	0.07	0.26	0.37	0.40	0.29	0.35	0.21	0.12	-0.18	1			
Ho	0.56	-0.38	0.98	0.94	0.92	0.99	0.96	0.98	0.99	0.98	0.99	0.98	1.00	0.98	0.85	0.26	1		
Tm	0.42	-0.35	0.96	0.93	0.92	0.96	0.93	0.96	0.96	0.95	0.95	0.97	0.94	0.93	0.77	0.32	0.94	1	
Lu	0.27	-0.27	0.89	0.93	0.93	0.91	0.94	0.93	0.86	0.84	0.89	0.88	0.91	0.94	0.88	0.09	0.89	0.93	1

and INAA. There are both challenges and opportunities for identifying secondary resource for strategic elements like mining wastes for their possible recovery.

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### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jsames.2018.08.013>.

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