

# Zinc in the flotation tailings pond of Brăteasa Valley (Suceava County, Romania)

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## Abstract

The tailings pond located in Brăteasa Valley, near the former ore-processing plant of Tarnița, shows a particular shape of the beach, given the tailings stockpiles deposited on its northwestern sector. This geometry produced three types of waste: (i) tailings of the stockpiles (A-type); (ii) tailings from the lowlands (B-type), laying underneath the salt crusts; (iii) salt crusts, precipitated from the water puddles accumulated on the beach lowlands. Pyrite oxidation controls the pH of the three environments, so that the pyrite-poor B- and C-type wastes have a little higher pH (above 2.5) than type A. Descriptive statistics revealed that the distribution of Zn in the three types of waste is related to the following minerals: (i) sphalerite (in A-type waste); (ii) sphalerite and secondary minerals, i.e., jarosite, goethite, and ferrihydrite (in B-type waste); (ii) secondary minerals, i.e., rozenite, halotrichite, and kaolinite (in C-type waste). Zn-bearing secondary minerals that may trap Zn in their structure seems to appear at a pH higher than 2.5. The Principal Component Analysis (PCA) confirmed the influence of the nature of minerals (either primary or secondary) on the Zn distribution in the waste. It also showed that the amplitude of water evaporation from either tailings pores or shallows puddles accumulated on the lowlands would play a role in the Zn distribution.

Keywords: zinc, secondary minerals, descriptive statistics, PCA, tailings, Eastern Carpathians.

## 1. Introduction

The tailings ponds represent one of the environmental issues related to mining activities and metal extraction in the oreprocessing plants. This is because, over time, the water film which initially covers the beach of the waste deposit evaporates and the tailings interact with the environment. Consequently, the grain minerals of the waste undergo weathering processes that produce both liquid and

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solid products, which may represent an environmental risk. The weathering of tailings is relatively rapid and intense as long as the waste grains are small, having, therefore, a large surface of interaction with the alteration agents.

The mineralogy of the waste is one of the major factors that control the weathering products with a potentially harmful effect on the environment. The environmental risk is represented by the sulfides lasting within tailings due to incomplete treatment of ore in the processing plants. The process that triggers the environmental issues related to tailings ponds is the oxidation of sulfides in the presence of water. In such circumstances, the oxidation of Fe-sulfides (especially pyrite, but also marcasite and pyrrhotite) produces acidic solutions (Acid Mine Drainage, AMD), charged with potentially toxic elements (Balistrieri et al., 1999; Dold and Fontbote, 2001; Arroyo and Siebe, 2007; Durocher and Schindler, 2011; Ferreira da Silva, 2015; Lindsay et al., 2015). On the other hand, the oxidation of sphalerite, galena, and chalcopyrite may also release metals ions such as Fe, Cu, Pb, and Zn, without generating acidity (Balistrieri et al., 1999).

Through its high acidity, its capacity of leaching potentially toxic elements and susceptibility of spreading into the neighboring areas, AMD has critical consequences on the environment. Moreover, when evaporation occurs, a large range of secondary minerals (Jambor, 1994) may precipitate from these leachates, e.g., jarosite, gypsum, goethite (Romero et al., 2007); copiapite, halotrichite-pickeringite, and alunogen (Gomes and Favas, 2006); apjohnite and slavikite (Hammarstrom et al., 2005); melanterite, rozenite, fibroferrite (Jerz and Rimstidt, 2003) etc. The secondary minerals may appear as efflorescent aggregates (e.g., hexahydrite, alunogen, copiapite, rozenite) (Valente and Gomes, 2009; Valente et al., 2013; Carbone et al., 2013) or crusts (e.g., goethite, jarosite, rozenite, halotrichite) (Valente et al., 2013; Carbone et al., 2013). As most of the secondary minerals are hydrated sulfates, they are highly soluble. As a consequence of dissolution produced during rainfall, some of the secondary minerals may generate acidic leachates: jarosite, alunogen, and römerite (Khorasanipour, 2015); melanterite, rozenite, copiapite, and halotrichite (Jerz and Rimstidt, 2003; Valente and Gomes, 2009). On the contrary, some of the secondary mineral species do not generate acidity through dissolution, i.e., gypsum and hexahydrite (Khorasanipour, 2015).

The aim of this study was to identify the mineralogical control on the distribution of zinc in the waste of a tailings pond located in the vicinity of the former ore-preparation plant of Tarniţa, in Brăteasa Valley. In this respect, a detailed analysis of waste mineralogy was correlated with the results provided by descriptive and multivariate statistic analyses (PCA). The latter has also given information on other factors that may control the distribution of zinc in the study waste.

## 2. Study area

#### 2.1 Geological setting

The ore-processing plant of Tarnița was extracting copper, zinc and led from the polymetallic ores of the Metallogenic field of Leşu Ursului, which is a subdivision of the Polymetallic Belt of Eastern Carpathians. This metallogenic belt develops on 200 km along the Eastern Carpathians and is divided into three metallogenic districts (Berbeleac, 1988), namely (i) Borşa-Vişeu (the northernmost), (ii) Fundu Moldovei-Leşu Ursului, and (iii) Bălan-Fagu Cetății (the southernmost).

The ores of the Polymetallic Belt of Eastern Carpathians are associated with the schists of the low-grade metamorphic Group of Tulghes. More specifically, the polymetallic ores are hosted by the formation Tg<sub>3</sub> of the Tulghes Group, which is one of its five subdivisions. The lithology of the Tg<sub>3</sub> formation consists of schists. quartz-chlorite sericite-quartz schists, and sericite-chlorite schists; they sericite-graphite may alternate with schists and rhyolitic metatuffs.

In the Metallogenic field of Leşu Ursului (Fig. 1), the polymetallic ore is hosted by sericite-chlorite schists, chlorite-quartz schists, and sericite-quartz schists, interbedding with rhyolitic metatuffs. The ores of the Leşu Ursului perimeter occur as either massive or disseminated beds and lens-like beds, concordant with the metamorphic formations. Massive ore lenses develop on several hundreds of meters and a thickness of up to 10 m. The disseminated ore bodies are much larger; they develop on lengths of more than one kilometer and thickness of about 30 m. The polymetallic ore is fine-grained and consists of pyrite, chalcopyrite, sphalerite, and galena. As accessory minerals, arsenopyrite, pyrrhotite, tetrahedrite, bournonite, rutile, and ilmenite were also identified (Chicos et al., 2016; Chicos, 2016).

#### 2.2 Description of the waste deposit

The study tailings pond is located on the right bank of the Brăteasa valley (Fig. 2), in the immediate vicinity of the orepreparation plant of Tarniţa, at around 6 km upstream from Ostra village. It is a



Fig. 1 Geological setting of the Metallogenic field of Leşu Ursului and surrounding areas (modified from Balintoni, 2010).

nowadays dried impoundment of sidehill-type, which was accumulating the waste resulted from the ore-preparation facilities. In the area, the exploitation of polymetallic ore and metal extraction (especially Cu, but also Zn and Pb) started in 1967. From a waste disposal perspective, these activities resulted in five tailings ponds of which that of Brăteasa Valley is the smallest. The waste deposit is NE-SW oriented and has a length of 200 m: the maximum width is around 90 m (Fig. 2). After the cease of the mining and ore-processing activities in the mid-2000s, the waste deposit of Brăteasa Valley was subject of some unfinished rehabilitation works. This activity produced a particular geometry of the tailings pond, consisting in around 4 m high stockpiles of tailings disposed over the northwestern part of the waste deposit beach, contrasting with the lowlands of the southern areas.

The waste has a sandy appearance and a generally greyish color, due to a large abundance of metallic minerals (especially pyrite, but also sphalerite). The slopes of the tailings stockpiles are crossed by 30-40 cm deep gullies (Fig. 3) which were dug by the runoff waters, during heavy rains. At the bottom of stockpiles, traces of redeposited tailings can also be noticed. The lowlands of the tailings pond are covered with commonly whitish salt crusts. In some areas, shallow puddles of dark brown leachates were observed (Fig. 4). The flanks of the waste deposit show no indication of AMD discharge into the Brätreasa river. However, downstream tailings pond, the rock fragments in the river bed display reddish coates that suggest successive discharges of Fe-rich leachates from the waste.



Fig. 2 Sketch of the study tailings pond, showing the collection areas of the three types of samples.

The waste deposit is situated in a region of a low-altitude mountain (elevation around 800 m) with climate conditions specific to temperate zones. The average air temperature is  $15-16^{\circ}$ C, during the summer and the humidity is about 80%. The rainfall regime is over 100 mm/year, while the average wind speed is up to 4 m/s.

#### 3. Sampling and analytical techniques

#### 3.1 Sampling

The samples were collected during a late-summer field survey, following a two-weeks of dry weather. The sampling strategy was compelled by the peculiar geometry of the tailings pond beach, which yield three types of waste, namely (i) waste collected from the tailings stockpiles (type A); (ii) tailings collected from the beach lowlands (type B), immediately underneath the salt crusts;



Fig. 3 Gullies produced by the runoff waters on the flanks of the tailings stockpiles. Example of sampling point for A-type waste.

(iii) salt crusts (type C), resulted through precipitation during the evaporation of the stagnant pools' water. The sampling was also conducted relative to a quasirectangular grid of  $25 \times 30$  m. Consequently, 55 samples of detritus and salts were collected, of which 19 are of A-type waste and 36 of B- and C-type. The tailings and salt crusts samples were collected using a plastic paddle, from the surface of waste, considering that this is the most exposed layer to the weathering agents. Afterward, the samples were stored within sealed plastic bags.

#### 3.2 Grain size analyses

The grain size of the tailings was determined using the dry sieving method. For this purpose, the samples were previously dried for 6 hours in an electric oven, at 40°C. Then they were passed through a set of three sieves (i.e., 1 mm, 0.25 mm and 0.063 mm), to determine the grain size classes corresponding to coarse sand, medium and fine grain sand, very fine sand, and silt + clayey fraction (Folk, 1974).



Fig. 4 Partially evaporated reddish leachate in a stagnant pool. Example of sampling point for B- and C-type waste.

## 3.3 Mineralogical observations and analyses

The preliminary information on the mineralogy of waste was given by the observations made with help of a stereomicroscope Stereo Optika SZM2; this resulted in the identification of most of the primary minerals exclusively. For more detailed mineralogical information, the waste samples were ground, then XRD analyses were performed with a Philips PW 1050/25 X-ray diffractometer, equipped with monochromatic CuKa  $(\lambda=1.54056$  Å). In order to make a subsequent Rietveld refinement of data, the scan settings were the following: step size of  $0.05^{\circ} 2\theta$  and step time of 2 s. The Rietveld refinement was carried out using the Rietica 1.77 software. The identification of low-crystalline ferrihydrite was made through the differential X-ray diffraction, using the procedure described by Dold (2003).

#### 3.4 X-ray fluorescence

Prior to XRF procedures, the samples were dried in an electric oven, then

ground with the help of an agate mortar. Afterward, the sample powder was mixed with Hoechst® wax and pressed to pellets at 20 t/cm<sup>2</sup>. The X-ray fluorescence analyses were performed with an energy dispersive EDXRF-spectrometer (Epsylon 5). To calibrate the spectrometer, river and lake sediments, as well as soil samples, were used as reference materials.

## 3.5 Leaching tests

To determine the pH of waste, the samples were placed within a beaker and immersed in distilled water, at a ratio of 1:5 (solid/liquid). The resulted slurry was then stirred and let to settle for 1 hour. After that, the pH was measured using a MeterLab ion-pH meter Corning 555. The sample preparation for the measurement of the soluble fraction consisted in mixing up 10 g of waste with 100 mL deionized water in a beaker. After that, the slurry was stirred for 20 minutes and then filtered through a 0.2 µm cellulose filter. The insoluble fraction remained on the cellulose filter was dried and weight afterward, to eventually calculate the mass percentage of the soluble fraction.

## 3.6 Statistical analyses

The assessment of the distribution of each geochemical variable was conducted through univariate statistical methods. In this regard, the central tendency (mean, median) and dispersion (range and coefficient of variation) were determined. The relation among different geochemical was evaluated variables using the Principal Component Analysis. To fulfill the demands of this method, all variables were log-transformed and standardized by calculating the standard score (Güler et al., 2002). Both data of descriptive and

multivariate statistics were obtained using XL Stat Pro 7.5 software.

## 4. Results and discussions

## 4.1 Particle size

The particle size analyses of waste were correlated with the granulometric classes used to study the detrital sedimentary deposits. As stated in section 3.2, the grain size classes identified in this study are coarse sand, medium and fine sand, very fine sand, and silt + clayey fraction. Almost 80% of the waste samples have a grain size similar to sand. According to Folk's (1974) classification, the texture of the detritus varies between silty sand and clayey sand. The waste of the lowlands displays a higher abundance of the silt+clay fraction, which can reach 30%. This may be explained by the larger capacity of runoff waters to transport fine grains from the waste stockpiles toward lowlands.

## 4.2 Mineralogy of waste

The observations with help of the stereomicroscope revealed two group of minerals in the waste, i.e., (i) primary minerals that originate from the meta-morphic rocks (quartz, sericite, chlorite) and associated metallic ores (pyrite, and much less abundant sphalerite and galena), and (ii) secondary minerals, which appear as fibrous, bladed or earthy, generally whitish, crystals.

The X-ray diffraction data showed that the group of secondary minerals consists of a large variety of hydrated sulfates (apjohnite, alunogen, hexahydrite, halotrichite-pickeringite, rozenite, jarosite, coquimbite, and ferricopiapite) and some oxyhydroxides (goethite and ferrihydrite), along with few clay minerals (kaolinite and illite-montmorillonite). Among these mineral species, only a part is susceptible to trap Zn in their structure. Table 1 shows the potentially Zn-bearing minerals identified by XRD and their relative abundance in the three types of waste.

Mineral		Type of waste			
		А	В	С	
Primary minerals					
Sphalerite	ZnS	٠	•	-	
Secondary minerals					
Kaolinite <sup>1</sup>	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH)	(●)	•	••	
Halotrichite <sup>2</sup>	$Fe^{2+}Al_2(SO_4)_4 \cdot 22(H_2O)$	-	•	••	
Rozenite <sup>3</sup>	$Fe^{2+}SO_4 \cdot 4(H_2O)$	-	-	••	
Jarosite <sup>4</sup>	KFe <sup>3+</sup> <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	•	••	(●)	
Ferrihydrite <sup>5</sup>	$Fe^{3+}_{2}O_{3} \cdot 0.5(H_{2}O)$	(●)	••	•	
Goethite <sup>5</sup>	Fe <sup>3+</sup> O(OH)	(●)	••	(●)	

Tab. 1 Minerals that may trap Zn in their structure (identified by XRD)

Abundance estimations (Rietveld refinement):  $\bullet \bullet$  major (> 10%);  $\bullet$  minor (< 10%); ( $\bullet$ ) trace (doubtful); \* Minerals reported to trap Zn in their structure by previous works: <sup>1</sup> (Ferreira da Silva et al., 2009); <sup>2</sup> Hammarstrom et al. (2005), Jamieson et al. (2005); <sup>3</sup> Sheriff et al. (2011), Sracek et al. (2010); <sup>4</sup> Hammarstrom et al. (2005), Romero et al. (2007), Smuda et al. (2014); <sup>5</sup> Graupner et al. (2007), Root et al. (2015) (ferrihydrite and goethite).

Tab. 2 The pH variation, the average of soluble fraction abundance and the source of Zn in the three types of waste, based on descriptive statistics

		Types of waste	
	A-type ( <i>n</i> = 19)	B-type ( <i>n</i> = 18)	C-type ( <i>n</i> = 18)
pH	2.3–2.5	2.6–3.0	2.7–3.3
Soluble fraction (%) Zn in sphalerite	13	6	85
Zn in secondary minerals	-	•	•

## 4.3 Geochemistry of the waste 4.3.1 Soluble fraction and pH

The abundance of the soluble fraction and pH are summarized in Table 2. The soluble fraction is strictly related to highly soluble secondary minerals, i.e., hydrated sulfates. The C-type waste, which consists exclusively of salts, shows the highest abundance of soluble fraction. Being buried underneath C-type waste, the waste of type B has the lowest percentage of soluble fraction. This is because C-type waste prevents air circulation and the precipitation of salts through the evaporation of pore-leachates does not occur. The soluble fraction in samples of type A also appears due to pore-leachate evaporation, but its abundance depends on the elapsed time from the last leaching produced by rainfall.

The waste of type A has the lowest pH among the three types of waste (Tab. 2), due to the intense oxidation of pyrite. The latter is abundant in this type of waste and is known to generate acidity (Balistrieri et al., 1999; Dold and Fontbote, 2001). The pyrite oxidation is much less intense in the environments of B-type waste, because of the lack of oxygen. The C-type waste precipitates from diluted leachates transported by runoff during rainfall and accumulated as puddles in the lowlands. The dilution of leachates results in a higher pH, while the continuous evaporation indicates transient conditions. This explains the higher range of pH variation in the waste of type C.

## **4.3.2** Chemical composition *Descriptive statistics*

Table 3 shows some univariate statistic parameters of Zn contents. Among these, the coefficient of variation (CV) and results of normality tests were used to identify the minerals that control the distribution of Zn in the study tailings pond.

Tab. 3 Parameters of descriptive statistics estimated for the abundance of Zn (mg·kg	of Zn (mg·kg <sup>-1</sup> )
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Waste type	Min.	Max.	Mean	Median	CV	NT
А	782	9691	3677	2190	0.79	n
В	129	2190	681	271	1.04	n-n
С	85	4757	1226	834	1.18	n-n

CV - coefficient of variation; NT - normality test; n - normal distribution; n-n - non-normal distribution.

The chemical dataset on Zn in the Atype waste follows a normal distribution. suggesting a single origin of zinc, i.e., sphalerite (Tab. 4). The explanation for the relatively high coefficient of variation (0.91) may be the frequent substitution of Zn by Fe in the structure of sphalerite, which may generate outliers. In the waste of type B, zinc seems to originate from both primary sphalerite and secondary minerals (Tab. 4), a fact that is confirmed by the non-normal distribution of dataset and the high coefficient of variation (1.01). The secondary minerals, in B-type waste, susceptible to trap zinc in their structure, are jarosite (Hammarstrom et al., 2005; Romero et al., 2007; Smuda et 2014), goethite and ferrihydrite al.,

(Graupner et al., 2007; Root et al., 2015). The content of zinc in the waste of type C is presumed to be related exclusively to the secondary minerals (Tab. 4) reported by previous works to collect this element, i.e., halotrichite (Hammarstrom et al., 2005; Jamieson et al., 2005), rozenite (Sherriff et al., 2011; Sracek et al., 2010) and kaolinite (Ferreira da Silva et al., 2009). The coefficient of variation of 1.27 may be explained by the highly transient conditions of precipitation, specific to leachates in the stagnant pools of the waste deposit.

In order to perform Principal Component Analysis (PCA) on Zn data, the samples were separated into two categories, as follows: samples that consist of both primary and secondary minerals (Aand B-type) and salt crusts that contain secondary minerals exclusively (C-type). The PCA approach yielded two dimensions, which explain 51.38 % and 28.02% of the total inertia, respectively (Fig. 5).

The F1 axis seems to be a measure of

evaporation intensity within the environments where the secondary minerals precipitate. Thus, the negative values may refer to environments with a constant abundance of water because of little or no evaporation; this is in agreement with the conditions under which B-type waste

		Types of waste	
	A-type	B-type	C-type
P.m.	Sphalerite	Sphalerite	-
S.m.	-	Jarosite Goethite Ferrihydrite	Halotrichite Rozenite Kaolinite

Tab. 4 Zn-bearing minerals in the study waste, identified using descriptive statistic data

P.m. - primary minerals; S.m. - secondary minerals.



Fig. 5 Principal Component Analysis of Zn contents, using the loadings of the 55 sampling points.

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evolved. The less intense evaporation is due to the position of B-type waste underneath the water body of leachate puddles that subsequently produce the salt crusts (C-type waste). Either water bodies or salts block the pore-water evaporation from the B-type waste below. Positive F1 axis defines the environments initially rich in water, which subsequently underwent intense evaporation. These are the stagnant pools formed over the lowlands of the waste deposit (in waste of type C), but also the tailing pores of the waste stockpiles (in A-type waste).

The axis F2 reflects the origin of minerals presumed to contain Zn as either major or minor element. Relying on the results of descriptive statistics (Tab. 3), it may be assumed that the negative values refer to zinc trapped within the secondary minerals. These are jarosite, goethite, and ferrihydrite (in the waste of type B) and halotrichite, rozenite, and kaolinite (in C-type waste). The positive F2 axis reflects the zinc distribution given by the primary sulfide, sphalerite.

The parameters of descriptive statistics and PCA indicate that Zn is exclusively related to primary minerals (sphalerite), in the A-type waste (Tabs. 2 and 4). The lack of Zn-bearing secondary minerals may result from the swift removal of pore-waters during intense evaporation before an interaction with sphalerite would occur. It is also possible that the interaction of pore-water with sphalerite has occurred, but the resulted poreleachates were removed by runoff waters before precipitation would take place. In this case, the Zn-charged leachates were transported from the waste stockpiles to lowlands of the tailings pond, where they accumulated as shallow, stagnant puddles.

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Additionally, the mobility of Zn is given by the detrital transport of primary minerals (among which sphalerite) towards the lowlands, during heavy rains.

The A-type waste has the lowest pH among the three types of waste (Tab. 2; Fig. 5), being almost entirely devoid of Zn-bearing secondary minerals. This may suggest that the environments with a pH lower than 2.5 are not suited to the occurrence of Zn-bearing secondary minerals. Nevertheless, the acidity is not generated by sphalerite, which only releases metal ions, without producing acidity (Balistrieri et al., 1999; Romero et al., 2007). Under these circumstances, it can be assumed that the only source of acidity in A-type waste is the oxidation of pyrite.

According to the descriptive statistics, Zn in B-type waste is related to both sphalerite and some hydrated sulfates and Fe-oxyhydroxides (Tab. 2). Figure 5 certifies this assumption, showing the presence of B-type samples in the field of positive F2 (Zn in sphalerite), but also in the field of F2 negative loadings (Zn collected by the secondary minerals). The presence of the three secondary minerals presumed to trap Zn (i.e., jarosite, goethite, ferrihydrite) can be related to their documented persistence either (Romero et al., 2007; Valente and Gomes, 2009; Kossoff et al., 2011) or a pH higher than 2.6 (Tab. 2; Fig. 5). This slightly higher pH is justified by the extremely reduced oxidation of pyrite in the tailings situated underneath the water puddles of the lowlands.

The C-type waste consists almost exclusively of secondary minerals, some of which are capable of trapping Zn within their structure (i.e., halotrichite, rozenite, kaolinite) (Tab. 4). PCA as well shows that nearly all C-type samples are present in the field of F2 negative loadings, assigned to Zn related to secondary minerals. The concentration of Zn in their structure is due to a longlasting evaporation of a larger volume of leachate, compared to pore-leachate. The higher pH seems to be favorable to the precipitation of Zn-bearing salts. The transient pH (2.7-3.3) may be explained by the trap of acidic cations (Fe, Al, Mg) within the early salts (rozenite, halotrichite-pickeringite), which lead to a decrease of the acidity in the residual leachate.

#### 5. Conclusions

The peculiar morphology of the tailings pond beach produces three types of waste, of which two have a detrital texture (A- and B-type), while the third consists of filiform and earthy secondary minerals (Fe-oxyhydroxides and hydrated sulfates) (C-type). The waste of type B has the lowest abundance of soluble fraction, because of the lack of oxygen, specific to its environments. The A-type waste shows the lowest pH, due to intense oxidation of pyrite.

The distribution of Zn in the waste is controlled by specific mineralogical species which, in turn, occur in response to the geochemical characteristics of the distinct environments; thus:

(i) in the waste of type A, collected from the stockpiles tailings, Zn is exclusively related to sphalerite, which is a primary mineral that originates from the polymetallic ore;

(ii) the Zn abundance in the B-type waste, collected from the lowlands, underneath the salt crusts, is in relation with both primary minerals (sphalerite) and some secondary minerals (jarosite, goethite, ferrihydrite);

(iii) in the C-type waste (salt crusts developed on the lowlands), the only minerals that trap Zn in their structure are of secondary nature (rozenite, halotrichite, kaolinite).

Along with the mineral species, another factor that determines the distribution of Zn in the waste seems to be the extent of the water evaporation from the tailings pores (A- and B-type waste) or leachate puddles accumulated on the lowland areas of the waste deposit (Ctype waste). When the evaporation is intense, the pore-leachates produce less or no Zn-bearing secondary minerals. The latter only appears through precipitation from larger bodies of leachates (puddles), accumulated on the lowlands.

The acidity produced by the oxidation of pyrite seems to prevent the appearance of Zn-bearing secondary minerals. It appears like the most favorable environments to develop Zn-bearing secondary minerals are those having a pH higher than 2.5.

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