Chemical and mineralogical characterization method for tailings deposit

Irene Aracena[1]*, Tania Triviño[2] and Juan D. Rayo[3]

1. *Geosciences Department, JRI Ingeniería, Chile*
2. *Geosciences Department, JRI Ingeniería, Chile*
3. *Technological Development Department, JRI Ingeniería, Chile*

ABSTRACT

Older low-performance and monometallic ore recovery methods make current tailings deposits potentially profitable sources of valuable elements and materials. In Chile, it is estimated that the sum of all tailings could contain the equivalent of 60 million pounds of fine copper if just 80% of these tailings was recovered. Nowadays these elements are not only confined to traditional metals, such as copper, gold, iron, molybdenum, among others, but also in more sophisticated ones like cobalt and rare-earth (REE).

In order to assess the potential economic value of a tailings deposit, it's necessary to first identify the elements, then quantify them, and finally select the best method to extract them.

This paper briefly summarizes a proposed methodology to characterize tailings, starting from low-cost samples and moving toward more specific and expensive analyses. The authors consider the chemical and mineralogical characterization reports on Chilean tailings made by SERNAGEOMIN's (National Chilean Mining and Geology Services Institution) geochemical sampling program. The data from this program were used to study the genetic and geological relations between valuable chemical elements and mineralogic species. This knowledge is extremely important to consider in order to associate valuable hard-to-measure elements with lower-value, easier-to-sample massive mineralogical species. This proposed methodology would allow the tailings owner to have a preliminary idea of the chances of extracting valuable resources before spending on more costly analyses.

This study identifies four main stages to recognize the economic value of a tailings deposit: 1) drilling techniques, 2) sampling techniques, 3) chemical and mineralogical techniques and 4) data analyses. These techniques are different from the ones used for natural ore deposits, but they require the same care and standards as with primary mining. Special technical challenges must be considered if special elements (like REE) are to be extracted profitably. The final product of this study is a public reference book on characterization of valuable elements on tailings deposits.

INTRODUCTION

The fast development of the latest generation of the technological industry has brought growing demand for elements defined by the European Union (EU) as strategic. Studies carried out by JRI Ingeniería (JRI 2015), CAMCHAL-BGR (Mallea 2013) y SERNAGEOMIN (2018) demonstrate the presence of these elements in Chilean copper tailings, including active, inactive, and abandoned tailings. The evidence gathered from these projects has attracted attention to tailings as new potential market niches for our country, which will result in technological innovation and development in both extraction processes and disposal of these environmental liabilities, which in some cases are currently found in substandard conditions.

The growing strictness of environmental regulations - for example, the mine closure law - create a favorable platform for carrying out this type of project, whose objective is recovering valuable elements from massive passive mining, such as tailings. Therefore, recovering strategic valuable elements from tailings, together with freeing up physical space for new waste disposal, generating resources that help finance mine closure, and developing proposals for waste disposal that will be generated by tailings treatment, all represent both an opportunity and a challenge for a sustainable business model in this sector.

A tailings deposit can be defined as a potential secondary deposit from primary mining waste, originated in a geological mineral deposit that has been mined to recover some of the abundant elements in Chile such as: Copper (Cu), Iron (Fe), Silver (Ag), Gold (Au), Lead (Pb), Molybdenum (Mo), and Zinc (Zn), among others.

The study of this type of secondary deposits is somewhat familiar, since secondary deposits have already been mined for their primary elements and are now found in residual waste form, such as Cu, Mo and Fe. However, for those valuable but less abundant elements that have recently grown in value, such as Co and REE, their identification and analysis is more expensive and less apparent. Drilling, sampling, and analysis techniques are slightly different than those for primary deposits, and usually present higher budgetary restrictions. The purpose of this paper is to explain how these tailings can begin to be studied from a more viable economic perspective with appropriate techniques for such deposits, making use of the available information provided by SERNAGEMON.

METHODOLOGY

When evaluating the potential of a tailings, the chemical and mineralogical information from the primary deposit is usually not readily available, if it exists at all. To that end, a methodology is used based on the associations between the major oxides, measured with X-ray fluorescence (XRF), the mineralogical species of the tailings deposits, and the elements of value or trace elements, measured with induction coupled plasma (ICP) method. This information is key to understanding the behavior of the minerals inside the tailings, since the majority of the "bargain minerals" (mostly silicates) can be expressed as compounds associated with the major oxides.

To evaluate the economic potential of a tailings deposit, it is necessary to first determine which potential elements of value it might contain, using reliable and preferably low-cost searching techniques in the exploration stage.

The following were techniques used in this study:

- Drilling in the tailings to obtain samples and ascertain the mineralogy inside the tailings
- Chemical analysis techniques (ICP and XRF) and mineralogical analysis techniques (scanning electron microscopy (SEM) and X-ray diffraction (XRD))
- The expert knowledge of a professional who knows the genetic relationships between the occurrence of a valuable element and the type of mineral it contains.

To perform this analysis, it is necessary to have information about the valuable elements grades regarding the greater oxides (XRF) and trace elements (ICP) from the samples obtained from the deposit. The minerals found in the tailings deposit must also be identified. Mineralogical analysis, specifically traditional XRD, or quantitative evaluation of minerals by SEM (QEMSCAN, TESCAN, or MINSCAN) are suggested.

The methodology used can be summarized in the following steps:

1. Chemical and mineralogical data from the deposit is gathered
2. Distribution of major oxides and their associated minerals is analyzed
3. Correlation analysis (R^2) is carried out, mainly between greater oxides and trace elements, as well as between minerals and trace elements

The occurrence of the aforementioned elements, mainly as sulfides or oxides, stems from the genetic conditions (chemical composition, pressure and temperature, among other factors) at work during their geological formation and is reflected in the chemical and mineralogical composition of the original deposit.

The mineralogy, meaning the original minerals as well as those of the tailings, can be divided into mineral species of high concentration (e.g. silicates, carbonates, iron oxides and aluminum oxides, etc. -- concentrations expressed as percentage) visible at a glance and trace elements (concentrations expressed in ppm and ppb), lodged mainly in crystalline networks of the minerals in the tailings.

In order to provide evidence for the occurrence of minerals, especially on trace elements of value, the chemical and genetic affinity between the minerals and trace elements contained within them must be known. Given that trace or valuable elements are usually found in very low concentrations (at the ppm level) and are generally associated with crystalline networks of the minerals, a sampling method must be designed which might/is be able to detect their presence in the mineral species of which the tailings are composed.

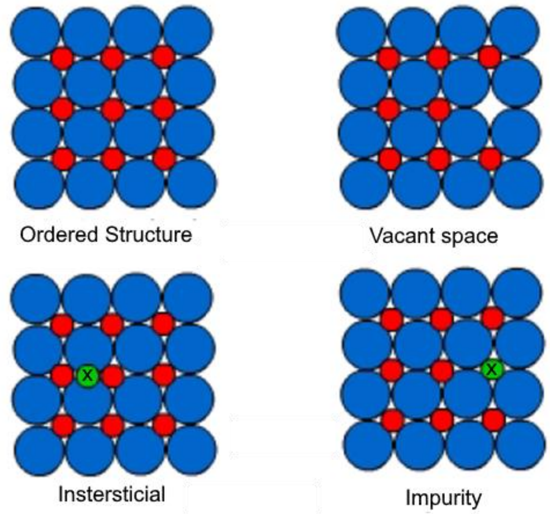

Figure 1. The trace elements are found inserted into the crystalline networks of the mineral species which make up the rocks of a mined deposit.

To this end, a search method was designed for the visible and quantifiable mineral species where valuable trace elements can be found. It's important to note that the identification and quantification techniques (XRF and mineral SEM) of the mineral species is still semi-quantitative, and are used as a guide for searching for trace elements and major oxides that are (mostly) part of the silicate mineral species of a tailings deposit (SiO_2 – Al_2O_3 – TiO_2 – Fe_2O_3 – CaO – MgO – MnO – Na_2O – K_2O – P_2O_5 and S total).

The mineralogical species that make up a tailings deposit can be identified through mineralogical and chemical optical techniques:

Minerology	**Chemical**
Traditional microscope	Traditional chemical analysis
Electron microscope	XRF
SEM Techniques	ICP
XRD	Neutron Activation

Obtaining samples from tailings which allows this search to be performed requires an adequate drilling and sampling method that can guarantee not contaminating them (Aracena 2018 & 2019). This condition was met with two drilling techniques: cone penetration test X-ray fluorescence (CPT – XRF) online analysis (Fugro 2015) and drilling, obtaining the samples with ultrasound (Denken).

The online CPT – XRF analysis allowed for the immediate measuring of grades of Cu – Fe – As – Pb and Zn. Later, a 3D spatial distribution model of Cu and Fe was acquired. These field measurements were compared with ICP techniques from samples taken in the same points where the CPT – XRF probe passed.

It is important to note that CPT – XRF on site technique do not take nor dissolve a sample to measure elements quantity, like ICP technique of which the samples are taken to a lab.

The sampling, chemical analysis, and mineralogical techniques used are in accord with the standards established by the companies responsible for carrying out this activity. The mineralogical characterizations are performed with SEM techniques and the chemical analysis of the samples is performed with XRF for the major oxides, while ICP is used for the trace elements.

Validating the occurrence of strategic valuable elements present in the mineral species of tailings deposits requires previous knowledge of some of the genetic antecedents of the tailings deposit, such as formation, geology of the primary deposit, i.e., the type of rock, element mined, alteration and mineralization processes associated with the primary deposit. With this knowledge, which is not always available when studying the mineralogy of a tailings, the existence of valuable or trace elements may be suspected.

Another important factor is the availability of reliable chemical analysis and mineralogical techniques in the market. It is known that the more samplings that are taken in a tailings deposit, the greater the knowledge and reliability regarding the existence of valuable elements will be. Before appraising a tailings deposit, companies must clearly ascertain the occurrence of the valuable element being searched, e.g. if the element exists as a mineral species, or if it is found in the crystalline networks of another mineral.

In general, the valuable or trace elements like those that are being searched for in this project are found in the crystalline networks (Figure 1) of other minerals in tailings and are more easily recognizable, such as clay, phosphates, iron oxides, titanium oxides, some silicates, etc.

The chemical and mineralization characterization of a tailings which allows valuable elements to be recognized consists in statistically analyzing (R^2) the relationships between the mineral species and the valuable elements, according to the genesis of the elements and the minerals containing them.

RESULTS AND DISCUSSION

The coordinated application of chemical characterization techniques like ICP, XRF, and mineral SEM to characterize phases made it possible to generate important information about the existence of trace elements of value located within or associated with visible and easily identifiable mineralogic species.

Just as it was possible to identify the existence of Ce in phyllosilicates, such as muscovite/sericite, and Co in oxides and hidroxides of iron in tailings in Region III of Chile.

It was possible to establish a guide to find trace elements or valuable elements associated with minerals from tailings through the identification of the most abundant mineral species that the tailings deposit is made of. According to the analysis of chemical information of the tailings in Chile, performed by SERNAGEOMIN, some positive correlations were established among valuable (trace) elements and more common oxides (including copper, iron, silver, gold, lead, molybdenum, and zinc).

In this study, interesting relationships were found between La and Ce and sericite/muscovite, between Co and iron oxides and hidroxides, and between some rare-earth (La, Ce, Nd) and rutile and/or apatite. Once these relationships are established, the next stage of the evaluation may begin.

Specific results in studied tailings

Based on the information generated by SERNAGEOMIN, statistical correlation (R^2) analyses were performed relating the chemical analyses between major oxides (XRF) and trace elements (ICP). Some results of these correlations are presented in this study:

In Region II, the following positive correlations were found:

- LREE (light Rare Earth Elements) with TiO_2 and Al_2O_3
- HREE (Heavy Rare Earth Elements) with TiO_2
- Sb with As,
- Co with Fe_2O_3,
- Zr with SiO_2
- V with TiO_2.

In Region III, the following positive correlations were found:

- LREE with P_2O_5,
- Co with Fe_2O_3,
- Zr with SiO_2,
- V with TiO_2 y
- Ni with MgO.

In Region IV, the following positive correlations were found:

- LREE with P_2O_5 and TiO_2,
- HREE with TiO_2 and Al_2O_3,
- Co with Fe_2O_3,
- Zr with SiO_2,
- V with TiO_2 and Al_2O_3.

In the Metropolitan Region, the following positive correlations were established:

- LREE with Fe_2O_3, Na_2O and P_2O_5,
- HREE with TiO_2, Na_2O and Al_2O_3.

On this occasion, the positive correlations between the trace elements and major oxides/minerals were especially emphasized, because the genetic affinity between them, in some cases, is better documented at a national and international level. The negative correlations found in this study indicate that there is an inverse relationship between the trace element and the major oxide/mineral.

The development of this investigation has demonstrated that our first working hypothesis regarding the existence of trace elements of value is correct. It must be noted that not all tailings contain trace elements in concentrations that would be above the minimum level that we had self-imposed (100 ppm) in order to consider them in our analysis. The most frequent elements discovered were Ce and La.

Our second working hypothesis was related to the question, "Trace elements are found together with which mineralogical species"

Some results are present in graphs below:

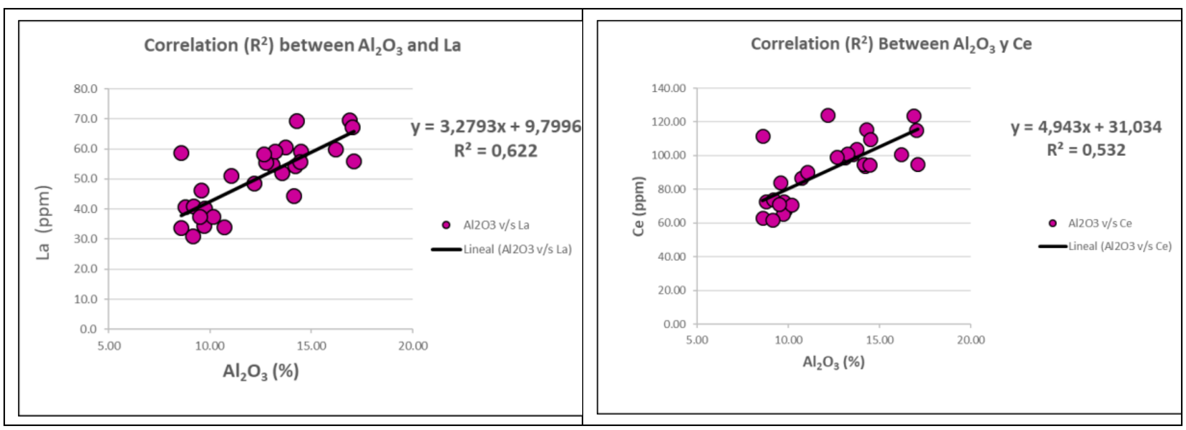

Figure 2 Correlation relationships (R^2) between trace elements (REE) and major oxides

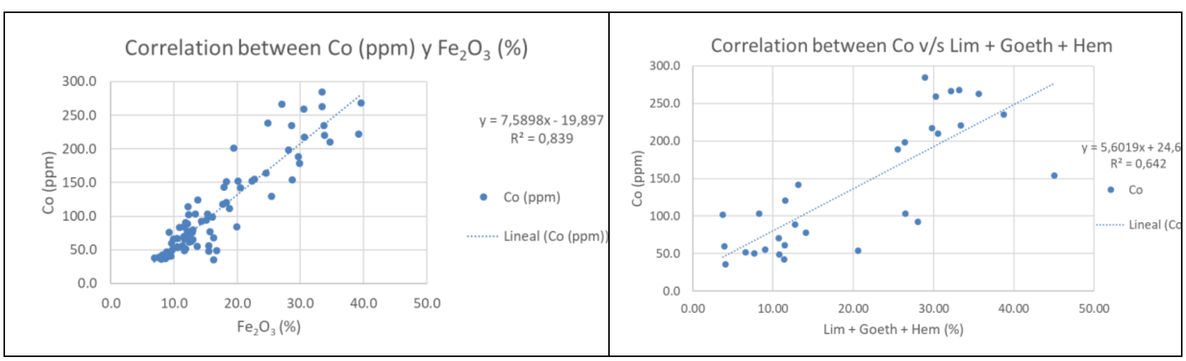

Figure 3 Correlation relationships (R^2) between trace elements (Co) and major Fe oxides

CONCLUSION

The chemical analysis of the major oxides (XRF and ICP) and the minerology are a good search tool for strategic or trace elements, at the exploratory level. Nevertheless, the search through the occurrence of the mineral species requires an expert knowledge of the genesis of the elements and minerals, according to the mineralogy of the primary deposit.

The mineralogy and chemical analysis of major oxides in samplings from a tailings deposit are very closely related variables which allow a company to predict the presence of minor or trace elements included in the mineralogical species typically found in a tailings deposit.

A new technique (CTP - FRX) was tested to measure element quantities on site. A comparison between the results of CTP - FRX and ICP in elements such as Cu, Fe, As, Pb and Zn was made. This comparison correlated in all the tested elements, with Cu having the strongest correlation of all. Most importantly, the tendencies of the measurements were the same using both techniques, which makes them complementary in terms of characterizing a whole deposit area.

The ICP chemical analysis is a very good exploratory tool to detect the presence of valuable trace elements and relate them to the occurrence of major oxides. CPT – XRF is a good tool to make 3D maps of valuable elements within the deposit. Both techniques are complementary

At the same time, the mineralogy identified with specialized high-resolution equipment like mineral SEM is also a powerful tool which makes it possible to quantify the mineralogical species with greater precision. The precision obtained in these analyses allows for a better estimate of the occurrence and concentration of minor or trace elements.

The relationships found between trace elements and major oxides in tailings from different regions of the country can affirm that this study's objective has been achieved. It can be said that current limitations of the chemical and mineralogical analysis techniques to quantify the presence of trace elements were sufficient to do exploratory studies. To quantify and evaluate reserves of valuable elements found in tailings deposits, sampling methods with defined scopes must be designed, specialized chemical analysis that assures the reliability of the grades.

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