# Chemical and mineralogical characterization of cemented arsenic-containing mine wastes

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**Palabras Clave:** Arsenopirita, escorodita, arseniatos de Ca (Fe), (oxihidr)óxidos de Fe, cementación. **Key Words:** Arsenopyrite, scorodite, Ca (Fe)-arsenates, Fe (oxyhydr)oxides, cementation.

## INTRODUCTION

Arsenic is listed as a priority pollutant, being regarded as one of the most toxic elements, causing serious environmental and health impacts. This element, commonly in the form of arsenopyrite (FeAsS), is present in a great variety of ore deposits. The exploitation of these deposits for the economic ore minerals has provoked a large legacy of As in mine wastes. Measures should be adopted to manage these wastes and so to prevent further As spreading to the environment. Cementation can be an affordable technique to deal with this kind of mine wastes. The main objective of this study is to perform the chemical and mineralogical characterization of As-containing mine wastes subjected to cementation processes.

## MATERIALS AND METHODS

The cementation process was carried out using mine waste samples rich in arsenopyrite (As) and scorodite (Es) from the former dumps of the Barruecopardo mine, the most important tungsten deposit in Spain. The chemical and mineralogical characterization was performed on cemented samples using Ordinary Portland cement (OPC) and calcium hydroxide ($Ca(OH)_2$) as binders, a binder:mine waste ratio of 30:70 wt%, and an OPC:$Ca(OH)_2$ ratio of 90:10 wt% in the binder mixture. These samples were selected considering their low leachable As contents (< 2 mg/kg, the limit value for acceptance at non-hazardous waste landfills (Council Decision 2003/33/EC)), as determined previously from the environmental characterization of mine waste samples cemented under different conditions (Brenes Marín et al., 2022). X-ray diffraction powder method, polarized light microscopy (transmitted and reflected light), and electron microprobe were employed for their chemical and mineralogical characterization.

## RESULTS AND DISCUSSION

In the diffractograms of both samples, the minerals of the original mine wastes are present. It is worth noting the abundance of quartz and muscovite. Ettringite and portlandite from the cementing agent (from OPC and $Ca(OH)_2$, respectively) and minor microcline and albite also appear. Higher proportion of arsenopyrite over scorodite is observed in the As sample whereas higher proportion of scorodite over arsenopyrite is found in the Es sample.

The microscopic study of the As sample reveals that arsenopyrite is the main mineral, appearing mostly unaltered, sometimes with scorodite on its edges and fractures and, occasionally, in more altered crystals. The presence of phases of orange and reddish tones, with a laminar habit, that seem isotropic, stands out. These phases appear on the edges and fractures of arsenopyrite, on the edge of phases of intense red color, cracked, close to arsenopyrite, and also forming spherical aggregates with retraction cracks (Fig. 1a). Additionally, thin reddish-orange films are observed on these aggregates, scorodite, quartz, and muscovite. Colorless areas appear in the cementing agent and in contact with the orange and reddish phases. The spot chemical analyses show that the phases with a laminar habit could correspond to Ca arsenates ($As_2O_5$: 22.18-39.37%, CaO: 15.49-38.61%), those that appear in spherical aggregates, to As-Ca-Fe-(K) compositions, and the deep red phases, to Fe (oxyhydr)oxides ($Fe_2O_3$: 51.11-54.34%, $As_2O_5$: 14.58-15.87%, CaO: 10.13-10.68%). In the cementing material, the contents of Ca, Si, Al and Mg stand out, with an $As_2O_5$ content of 0.57%. The colorless areas observed in it correspond to calcium arsenates ($As_2O_5$: 29.19-

38.27%, CaO: 34.48-37.36%). In the Es sample, the arsenopyrite appears partially and totally altered to scorodite on edges, fractures and following certain crystallographic directions. The scorodite and the aggregates of quartz and muscovite are covered by discontinuous films of orange and reddish tones. The presence of reddish-brown grains with cracks due to hydraulic shrinkage stands out, with relicts of arsenopyrite inside, which correspond to scorodite covered by films of the aforementioned color (Fig.1b); around them, colorless zones are observed in the cementing agent. There are also smaller reddish grains finely dispersed in the cementing agent. The chemical analyses carried out on the grains with cracks correspond to mixtures of scorodite and films of Fe (oxyhydr)oxides and cementing material ($As_2O_5$: 42.68-50.72%, $Fe_2O_3$: 33.48-36.98%, CaO: <dl-3.35%, $K_2O$: <dl-2.36%). Liu et al. (2007) revealed the effectiveness of $Ca^{2+}$ to increase the precipitation of Fe (oxyhydr)oxides and the subsequent effects on the coprecipitation of arsenic with them. In contact with the cementing agent, possible calcium arsenates have been identified (CaO: 31.54%, $As_2O_5$: 30.09%). The colorless areas in the cementing agent present compositions rich in calcium (CaO: 26.82-46.49%) with variable arsenic contents ($As_2O_5$: 0.42-38.7%). Orange, reddish and reddish-brown phases have not been detected by X-ray diffraction, probably because of their low amounts (< 5%) or their amorphous character.

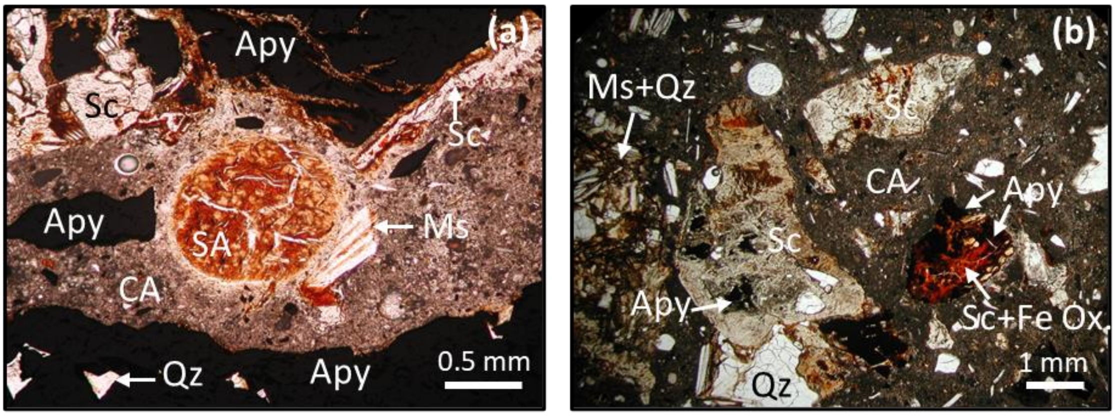

***Fig 1****. Microscopy images in transmitted light (one polarizer) of As (a) and Es (b) cemented samples. Apy: arsenopyrite, Sc: scorodite, Qz: quartz, Ms: muscovite, SA: spherical aggregates, Fe Ox.: Fe (oxyhydr)oxides, CA: cementing agent.*

## CONCLUSIONS

The scorodite as well as the phases mostly containing Fe, As, and Ca (possible Fe+Ca arsenates), Fe (oxyhydr)oxides, and calcium arsenates seem to be the responsible for the arsenic leaching decrease from the studied cemented mine wastes. The formation of these phases is linked to the cementation process. The incorporation of calcium (as hydrated lime) to the chemical formulation of cementing agent promotes the immobilization of arsenic through the aforementioned phases, thus boosting the arsenic leaching decrease.

## ACKNOWLEDGMENTS

The present study was carried out under the project TERMET (Grant number: RTI2018-095433-B-I00) funded by Ministerio de Ciencia e Innovacion (MCIN), Spain/Agencia Estatal de Investigacion (AEI), Spain/Fondo Europeo de Desarrollo Regional (FEDER), EU, and the project "CLU-2019-05 – IRNASA/CSIC Unit of Excellence", funded by the Junta de Castilla y León (Spain) and cofinanced by the EU (European Regional Development Fund (ERDF) "Europe drives our growth").

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