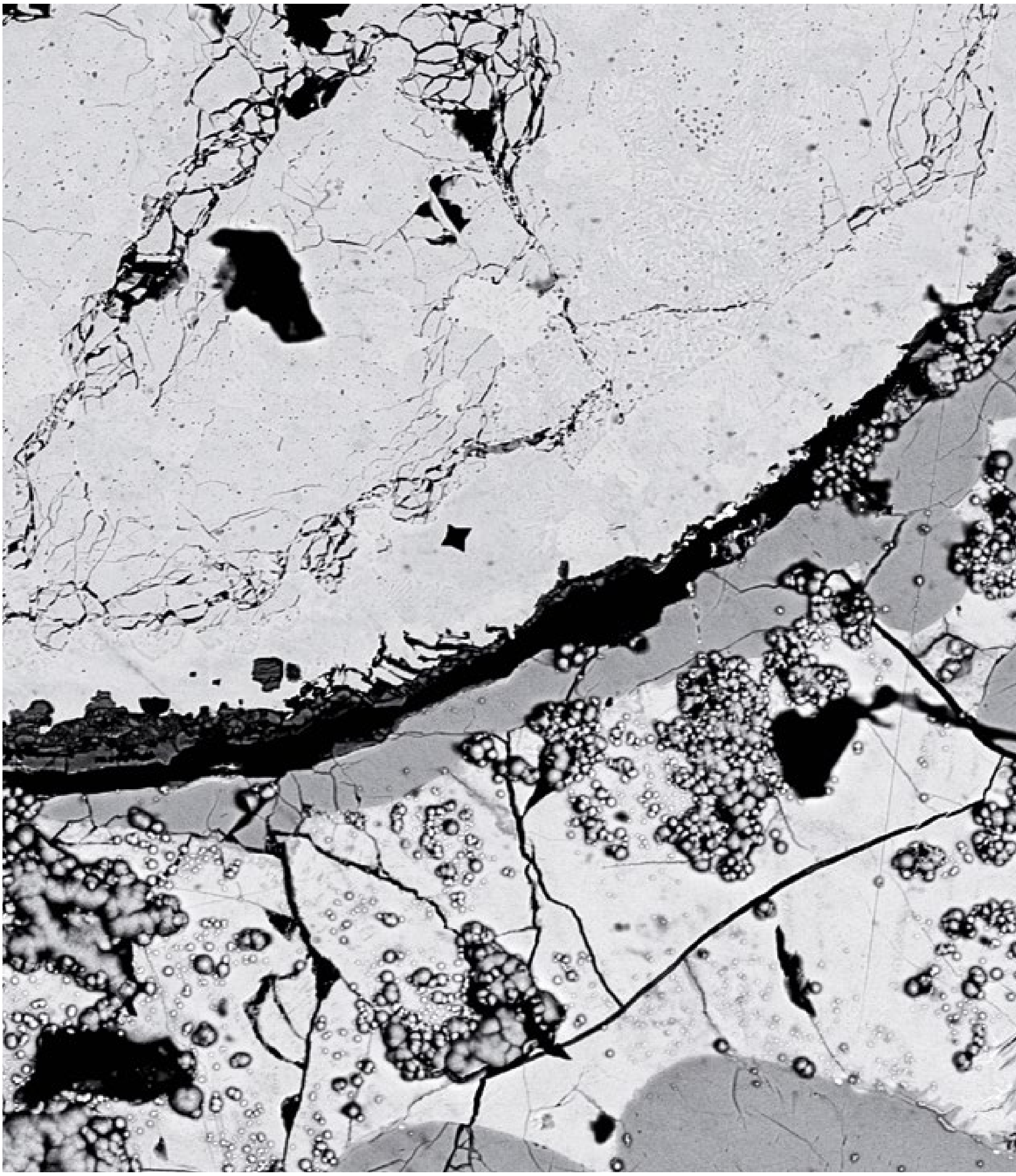
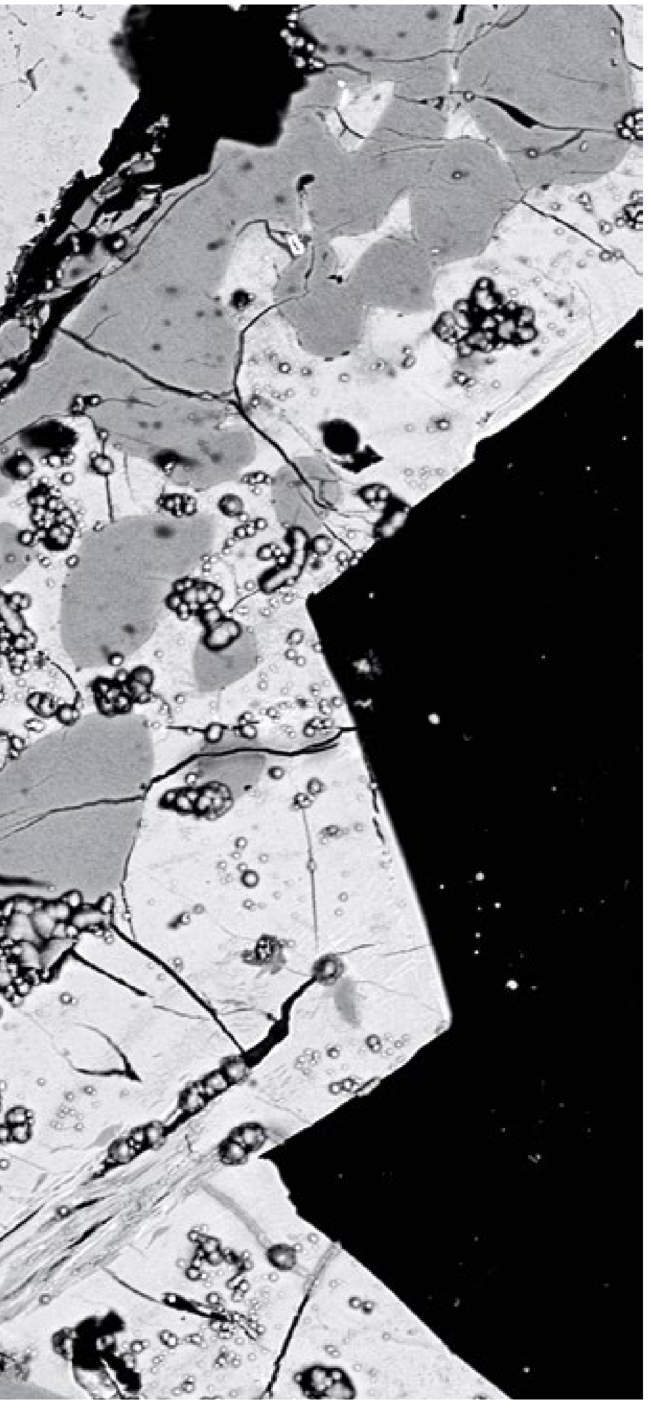
Katarzyna Kądziołka, MSc
is an archaeologist and geologist, a graduate of the University of Wroclaw. Since 2017 she has been writing a doctoral dissertation on the impact of historical metallurgical slags on the environment, at the Department of Experimental Petrology, Faculty of Earth Sciences and Environmental Management, University of Wrocław. A winner of a Diamond Grant. Her other scientific interests include petroarcheology – the study of rock artefacts and ancient ceramics using petrographic methods.
katarzyna.kadziolka2@uwr.edu.pl



Solutions to Slag

It looks as if it was frozen lava, but it is a by-product of metal smelting. If left piled up, it may have a strong negative impact on the environment. But when reused in a smart way, it can actually bring many benefits.



A weathering metallic phase, with a chemical composition of three different minerals. The lightest shade is related to pyrrhotite ($Fe_{(1-x)}S$), the darkest to bornite (Cu_5FeS_4), the intermediate to metallic iron (Fe). The weathering and release of metals display as clusters of round incrustations (bulges on a flat surface). The width of the image is 300 μm.

Katarzyna Kądziołka, MSc

University of Wroclaw

A rock containing precious metals is known as ore. After it is mined , it is crushed, separated in water, roasted and then melted in a metallurgical furnace with appropriate additives. At high temperatures, the liquefied metal separates from other ore components such as rock-forming minerals, giving rise to two different products: metal concentrate (matte) and waste. The latter is known as metallurgical slag.

In chemical and mineralogical terms, metallurgical slags are anthropological equivalents of volcanic rocks, which is why they are studied by geologists. Igneous rocks are classified into two basic types: plutonic rocks, which cooled down more slowly in the depths of the Earth, and volcanic rocks, which cooled after erupting to the surface. Different cooling regimes result in changes in the appearance of rocks. The main difference is in the size of the crystals that form in rocks. In the case of deep-crystallizing (plutonic) rocks, such as granite, the temperature dropped slowly, and so the crystals are large and visible macroscopically. But in eruptive (volcanic) rocks, such as basalt, one cannot see much without a microscope. In the case of slags, the situation is even more complicated: magma-like melted ore gets heated to a temperature higher than magma, and also gets cooled much faster. For this reason, most slag samples do not have an ordered crystalline structure and they resemble glass. These amorphous wastes contain only micrometer-sized nuclei of mineral crystallization, impossible to recognize under an optical microscope. That is why sample classification is quite complicated and requires the use of advanced equipment capable of large magnifications (even above 4000x).

Waste to be stockpiled

Scientific interest in metallurgical slags has been growing since the 1990s, due to the extremely large annual increase in quantities of the material at the global scale and the need for its disposal. There is also a growing awareness of the environmental threats associated with uncontrolled storage of this type of substance. The threat is particularly high in the case of slags produced before the nineteenth century as the technological advancement of metallurgical processes was then lower than today, meaning that the separation of metal from the slag was less effective. For this reason, high metal content has been recognized in some, especially older waste. If slags are improperly stored, potentially toxic elements can be released into the environment, subsequently ending up in human bodies – via meat, plants or contaminated surface or underground waters.

In my research, I focus primarily on the environmental impact associated with the long-term storage of slags in forest environments. The mobility of elements, i.e. their susceptibility to being released from waste and displaced into soil or water, depends on the form in which they were originally bound. The metals embedded in the structure of oxides and silicate phases are less susceptible to weathering than


P. DERKOWSKI

A wall made of cast slag blocks.

the metals embedded in sulfides, not separated from the slag during melting. Unfortunately, the problem must be approached with caution. Slags and the phases (artificial mineral equivalents) occurring in them are synthetic materials and may show greater variability compared to what can be observed in nature. For this reason, observations obtained by petrographic methods are later verified in the laboratory.

Various types of slags differ from one another; moreover, as it has been shown, variability occurs even in the case of slags produced at a similar time and from the same ore. Therefore, separate environmental simulations for different sites are extremely important. While simulating atmospheric precipitation with low pH (acid rain, acid mine drainage), we saw that the slags tested strongly neutralize the acid and are not easily susceptible to it. This is an important observation because it is in low pH conditions that toxic elements, mainly copper, arsenic, barium and cadmium, are most effectively leached out. However, the low susceptibility to acid does not mean that weathering processes do not occur. Secondary phases crystallizing on the slag surface – tiny green crystals (the color is associated with increased copper content) – and high levels of contamination of soils in the area of slags storage confirm the introduction of metals into the natural environment. Therefore our task is to discover what is still conducive to the leaching of metals from slags and how advanced the pollution is, as it has been going on for over a hundred years. In my further research, I also intend to propose remediation methods that can be initiated in a former smelting area. Appropriate plants, called bio-accumulators, which have the ability to accumulate toxic elements in their tissues, may help clean up the studied area.

Heritage to be scrutinized

Research on metallurgical slags does not address only environmental issues. In the case of historical wastes, there are numerous possibilities related to the reconstruction of the former technology of metal smelting. Demand for such findings is high, especially among historians and archaeologists. And the stakes are high: during smelting carried out 200 years ago, certain parameters simply could not be measured. Some more recent smelters kept books recording details of the smelting process, but – provided these documents have been preserved at all – the information they contain is therein incomplete and/or inaccurate. Such uncertainties may be dispelled through the correct interpretation of indications preserved in the chemical composition of the slags. During chemical reactions related to the oxidation of iron and sulfur residue in the metallurgical furnace, all unnecessary (non-metallic) components are discharged to the slag, namely melted ore contaminants, fuel and flux residues. These impurities leave traces that we can then interpret. For example, high sulfur content in waste is probably due to the fact that the ore in the initial treatment process was not properly roasted. In consequence, the sulfur – originally bounded in ore minerals (sulfides) – was not discharged from the system in gaseous form (SO_2). Interestingly, smelted metal itself is not suitable for this type of analysis, simply because it is a concentrate of the metallic elements (copper, zinc, lead, iron etc.) purified of other components.

Raw material for reuse

Given that modern industry generates hundreds of thousands of tons of slag each year, their possible reuse is an important issue. Such material can be successfully used as a cement additive, fertilizer, road aggregate, and even as a construction material if it is previously appropriately "cleansed" and neutralized. This cleansing consists in removing valuable – though often simultaneously harmful – elements from the slag. For instance, even today relatively high amounts of rare earth elements (REE), or even the smelted element itself, remain in the waste. The problem is to design an optimal recovery process so that companies do not have to incur overly high costs associated with preparing slag for alternative use. After a solution is found, this type of waste will not have to be stored in landfills. We will be able to operate a closed system: the smelting waste-product will become a secondary raw material and thus restrain the exploitation of rock resources, which are after all limited.

Katarzyna Kądziołka

The research described above is financed from budgetary funds for science in 2016–2018 as a research project under the Diamond Grant program, decision: 0233/DIA/2016/45.

Further reading:

Stolarczyk T., Kobylańska M., Kierczak J., Madziarz M., Garbacz-Klempka A. (2015). *Leszczyna. Monografia ośrodka górnictwa i metalurgii rud miedzi* [Lesczyna: Monograph of Mining Center and Copper Ore Metallurgy]. Fundacja Archeologiczna Archeo: Radziechów.

Potysz A., Van Hullebusch E.D., Kierczak J., Grybos M., Lens P.N.L. & Guibaud G. (2015). Copper Metallurgical Slags – Current Knowledge and Fate: A Review. *Critical Reviews in Environmental Science and Technology* 45, 2424–2488.

Kierczak J., Neel C., Aleksander-Kwaterczak U., Helios-Rybicka E., Bril H., Puziewicz J. (2008). Solid speciation and mobility of potentially toxic elements from natural and contaminated soils: A combined approach. *Chemosphere* 73 (5), 776–784.


SMOG
special edition
ACADEMIA
www.naukaonline.pl