

## **SELF-PURIFICATION OF Zn AND OTHER HEAVY METALS IN MINING EFFLUENTS: A NATURAL PHENOMENON**

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The lead-zinc vein and skarn-replacement deposits of the Madan ore district in South Bulgaria, embedded in the high-crystalline gneissic rocks of the Rhodope massif, are one of the greatest ore concentrations in Europe, intensively exploited during the last 50 years. Descending waters actively interact with ore sulphides in the set of underground mining works and become enriched in heavy metals. Going out on the surface of the high mountain terrain they usually infuse into fresh running river waters. Specific reactions occur at their infusing points. Such a case of spontaneous precipitation has been studied in the upper parts of the Erma River in the southern part of the district.

The outflowing mining waters gathered from the higher levels of the exhausted Stratiev Kamuk Mine are of calcium sulphate composition with high contents of Zn ( $93.1 \text{ mg/dm}^3$ ) and Mn ( $48.63 \text{ mg/dm}^3$ ) and high TDS ( $1739 \text{ mg/l}$ ). Pb is rather low ( $< 0.02 \text{ mg/dm}^3$ ). The main stream waters are of Ca Mg sulphate hydrocarbonate composition with only a small content of Zn ( $1.75 \text{ mg/dm}^3$ ), Mn ( $0.14 \text{ mg/dm}^3$ ), Fe ( $0.05 \text{ mg/dm}^3$ ), and lower TDS ( $642 \text{ mg/l}$ ).

In the discharge zone where the mining effluents run into the fresh water stream, spontaneous mineral precipitation has been observed. The newly deposited and weakly lithified mineral mass consists mainly of amorphous zinc hydroxides with high contents of Fe, Al and Mn. The Zn:Al:Fe atomic ratio is about 4:2:1. Small contents of clay material (illite + kaolinite) and minor detrital quartz are also observed.

Interesting organic constituents of the new sediment are two types of algae – *Sargassophitae* and *Diatoms*. Characteristic are the  $\mu\text{m}$ -sized spindle-like diatom frustules of the genus *Achnanthes*. The microanalyses of these frustules show that Zn plays an important role in their composition, too. Si, which normally forms the skeletons of these *Diatoms*, is too low here. Their Zn:Al:Fe ratio is about 4:2:1 again. The probable presence of bacteria is suspected to cause the observed intensive gas bubble formation.

The mineral precipitates have a peculiar cellular texture with some circular micro-atoll forms. It is suggested that they have been formed around adhered gas bubbles. Due to their high porosity and included bubbles, some of these light mineral crusts are floating on the water surface.

The observed phenomenon results in a significant diminishing of the heavy metal concentration (esp. of Zn) in the river area after the discharge point, which is a specific kind of self-purification of the mining effluents. A detailed understanding of this process can contribute to the creation of an effective and sustainable remediation technology applicable in active or abandoned mining areas.