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SELECTIVE NEUTRALIZATION OF ACID MINE DRAINAGE FROM ROBULE LAKE AND SLUDGE CHARACTERIZATION OF THE pH 4 PHASE VIA SEM-EDS ANALYSIS

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Abstract

A century of copper mining in Bor, Serbia, formed Robule Lake, an extreme acid mine drainage reservoir (pH 2.67). This study demonstrates the first stage of a multi-stage neutralization process using $Ca(OH)_2$ up to pH 4. SEM-EDS analysis of the resulting sludge at pH4 evaluates its microstructure and elemental composition. Results show highly selective precipitation of trivalent iron (locally up to 50.35% Fe) alongside a crystalline gypsum matrix. Conversely, copper remains stable in solution, with losses restricted to just 0.60%, enabling its unhindered recovery in subsequent stages.

***Keywords**: Acid mine drainage, Neutralization, SEM-EDS, Iron precipitation, Environmental remediation.*

1. INTRODUCTION

Long-term copper mining activities in the Bor region have generated highly heterogeneous waste dumps. Exposure of these sulfide and oxide minerals to atmospheric oxygen and precipitation triggers autoxidation, leading to the generation of Acid Mine Drainage (AMD) [1]. Robule Lake represents a characteristic AMD reservoir, defined by its low pH values, high residual sulfuric acid, and elevated heavy metal loads, where iron concentrations exceed 500 mg/L and copper levels surpass 50 mg/L [2]. The unmitigated discharge of these untreated effluents severely threatens local river basins all the way to the Danube River. Utilizing calcium hydroxide $Ca(OH)_2$ is widely recognized as the most cost-effective path for chemical neutralization, but conventional single-stage treatment yields an amorphous, inseparable, and hazardous mixed sludge. To overcome this limitation, a multi-stage neutralization process is implemented. The first and most critical step in this operational loop is the phase at pH 4, which aims to quantitatively remove iron from the liquid phase before copper precipitation begins. This study utilizes advanced SEM-EDS analysis to verify the efficiency and selectivity of this primary precipitation stage [3].

2. EXPERIMENTAL

2.1 Materials and methods

Raw acid mine drainage water from Robule Lake (pH 2.67) was treated with a prepared lime milk slurry until reaching exactly pH 4. Under this specific kinetic window, trivalent

iron (Fe^{3+}) undergoes accelerated hydrolysis, while divalent copper (Cu^{2+}) remains highly soluble. The resulting neutralization sludge (pH4) was filtered, washed, and prepared for electron microanalysis (EMA). For the SEM-EDS configuration, a representative split of the powder sludge was embedded into a medium-viscosity epoxy resin mount (~10 cm^2), flat-ground using silicon carbide papers (30, 20, and 15 μm), and polished with diamond paste suspensions (6, 3, and finished at 1 μm). Due to the non-conductive dielectric nature of the phases, the polished section was coated with an ultra-thin carbon layer inside an automated AGAR Automatic Carbon Coater AGB7367A vacuum chamber. Imaging and point-by-point analyses were performed on a JEOL-IT 300 Scanning Electron Microscope linked to an Aztec (version 3.1) EDX analyzer at an accelerating voltage of 20 kV. Very light elements (H to C) were not measured, and the lower limit of analytical detection (LOD) was approximately 0.1 wt.%.

3. RESULTS AND DISCUSSION

Initial analytical sessions on the microscope focused on field mapping to assess the phase distribution of the precipitates. The composite EDS layered image (Figure 1.1) reveals a highly heterogeneous and porous microstructure within the sludge matrix at a magnification of 500×.

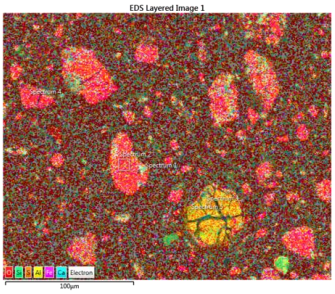


Figure 1. *EDS image with elemental distribution map in sample (magnification 500×)*

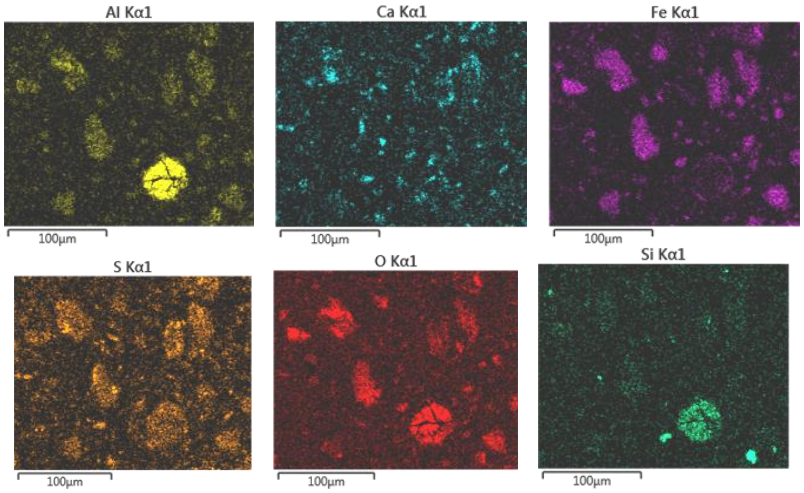


Figure 2. *Element distribution maps in the EDS image*

The composite EDS layered image (Figure 1) reveals a highly heterogeneous microstructural matrix at 500× magnification. Corresponding single-element distribution maps (Figure 2) yield the following spatial data:

- **Iron (Fe Kα1) and Aluminum (Al Kα1) Maps:** Display a strong spatial correlation, highlighting irregular, amorphous, and dense clusters where iron and aluminum are co-localized.
- **Calcium (Ca Kα1) and Sulfur (S Kα1) Maps:** Reveal a distinct crystalline phase separate from the iron clusters, indicating calcium sulfate precipitation.

To achieve precise chemical quantification, targeted point microanalyses were performed at five specific spots marked on Figure 3, yielding explicit answers regarding the precipitation chemistry at pH 4.

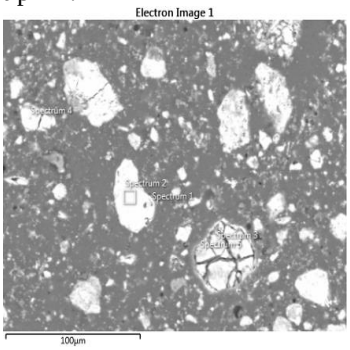


Figure 3. *EDS image with marked places where EDS analysis was performed (magnification 500×)*

Table 1.1. *Chemical composition of the analyzed spectra by EDS analysis*

Element	O	Al	Si	S	Ca	Mn	Fe	Cu	Total
Spectrum 1	26,53	0,97		27,62	39,53		5,35		100
Spectrum 2	44,61	8,31	1,21	6,62	0,38		38,86		100
Spectrum 3	58,95	24,15	7,35	5,14		1,48	2,30	0,63	100
Spectrum 4	51,95	6,63	1,03	5,32	0,19	4,01	30,87		100
Spectrum 5	55,17	25,32	8,55	6,52		1,13	2,71	0,60	100

Gypsum Matrix Formation: At the location marked as *Spectrum 1*, a distinct crystalline phase was identified, dominated by calcium (39.53%) and sulfur (27.62%), alongside oxygen at 26.53%. This structural stoichiometry conclusively confirms the development of gypsum ($CaSO_4 \cdot 2H_2O$), which forms as a direct product of the neutralization of free sulfuric acid by the lime slurry. A minor iron signal of 5.35% at this spot indicates that rapidly growing gypsum crystals mechanically trap fine, colloidal iron oxyhydroxide particles from the surrounding fluid. Replicate analysis on a secondary field of view (*Spectrum 8*) verified an even purer gypsum configuration containing 50.93% Ca and 31.55% S.

Selective Iron Precipitation: Micro-domains analyzed at *Spectrum 2* and *Spectrum 4* provide the definitive proof of the efficiency of the pH 4 phase. Exceptionally high iron values were recorded: 38.86% in Spectrum 2 and 30.87% in Spectrum 4. At pH 4, ferric iron selectively hydrolyzes into insoluble amorphous iron(III) hydroxide $Fe(OH)_3$ or basic hydroxysulfates like schwertmannite, which is supported by the companion

values of aluminum (up to 8.31%) and sulfur (up to 6.62%). On the duplicate control field (*Spectrum 10*), the iron concentration within these hydrolysate phases reached up to 50.35%. The most critical scientific finding is that copper is completely undetected (0% Cu) within these primary iron matrices, validating the absolute selectivity of the separation stage. Spectrum 4 also records a manganese level of 4.01% due to minor early co-precipitation.

Residual Tailings Gangue: In pockets indexed as *Spectrum 3* and *Spectrum 5*, the analysis detected zones rich in aluminum (24.15% and 25.32%) and silicon (7.35% and 8.55%), matching the signature of aluminosilicate clay minerals from the fine flotation tailings suspended in the lake. These clay structures reveal negligible copper peaks of just 0.63% and 0.60%, marking a minor and technologically acceptable metal loss via weak surface physical adsorption.

CONCLUSION

Advanced SEM-EDS characterization of sample at pH4 confirms the validity of the multi-stage neutralization circuit for the remediation of Robule Lake. At pH 4 the added lime slurry efficiently neutralizes free acidity and traps sulfates into a stable gypsum matrix, while iron undergoes massive, isolated precipitation, reaching spot concentrations above 50% in the sludge. Because copper does not transition into the solid phases of iron and gypsum, the remaining liquid filtrate stays clean and enriched, making it ideal for the next stage (raising the pH to 8) where a high-grade copper concentrate can be recovered.

Furthermore, this primary iron-and-gypsum-rich sludge can be safely stabilized and valorized as a raw additive in the Portland cement industry. This establishes the first stage of the multi-stage neutralization process as an eco-friendly and highly efficient method for transforming legacy mining liabilities into secondary raw materials.

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