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THE ACID ROCK DRAINAGE AND ITS IMPLICATIONS ON THE ENVIRONMENT. (II) PRODUCTS OF EXPERIMENTAL ALTERATION

DAN STUMBEA

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Introduction

Over the past decade, in our country there has been an increased interest in the acid rock drainage (ARD) of mine wastes, knew as acid mine drainage (AMD) in the scientific publications from abroad. The P-T parameters that rule the AMD processes allow scientific approaches on two directions: a physical and a chemical characterization of natural AMD products and an experimental approach that consists mainly in attempts to simulate processes similar to AMD, in a characterization of artificial products and in a comparison between the natural products and the artificial ones.

The present study deals with an experimental approach that lead to artificial products developed on natural samples (sulfide-poor low-grade metamorphic rocks) and with a short morphological, mineralogical and chemical description of these products.

Ore deposits of Bălan (Harghita County, Romania)

The sulfide mineralization bodies of Bălan – Fagul Cetăţii District are hosted by the geological formations of Tulgheş Group (*lithogroup* – Balintoni, 1996) consisting of low-grade metamorphic rocks. Previous studies in this area revealed two distinct geological sequences – sequence of Bălan and sequence of Sândominic – distinguished by a regional fault. Tulgheş Group is built up of 5 formations (Tg_1-Tg_5); the two geological sequences belong to Tg_3 formation probably.

The mineralization of the district was described as developed at five geological horizons, mostly in the metasediments of Bălan sequence (Berbeleac, 1988):

- *Arama Oltului horizon* built up of sericite-chlorite-quartz schists with pyrite+chalcopyrite disseminations;

- *Sedloca horizon* built up of sericite schists, sericite-quartz-feldspar schists, sericite-chlorite schists, metavolcanic rocks (rhyolites) and white-colored quartzites with pyrite+chalcopyrite disseminations;
- *Fagul Cetății horizon* consisting of sericite-chlorite bands alternating with layers and lenses of disseminated sulfides;
- *Valea Băilor horizon* with pyrite-chalcopyrite disseminations put in place in sericite-chlorite schists;
- *Bălan horizon* consisting of massive and disseminated sulfides (pyrite, chalcopyrite) hosted by chlorite-quartz schists and chlorite-sericite schists.

Ore bodies are 200 to 300m long and 1 to 35m width, and consist mostly of pyrite and chalcopyrite, subsequently sphalerite, galenite, tetrahedrite, bournonite, arsenopyrite and galenobismutite (Berbeleac, 1988); sporadically, gold, silver, magnetite, hematite, ilmenite, cassiterite and rutile have been recorded. Gangue mineral associations consist of quartz, chlorite, sericite, siderite, ankerite, albite, apatite, barite and tourmaline.

Samples and methods

The experimental approach has been carried out using three samples of low-grade metamorphic rocks: PM – quartz-sericite-feldspar schist; B27 – sericite-quartz schist; B12 – chlorite-sericite-quartz schist. The mineralogical composition of the three samples is as follows:

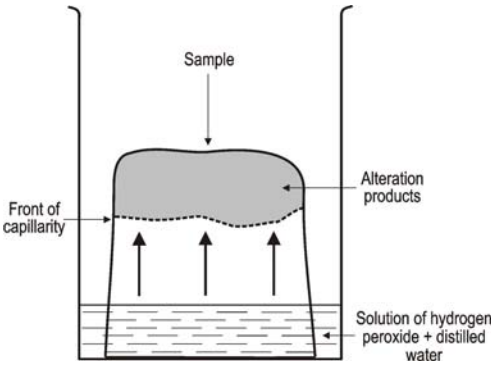

Fig. 1 Sketch of the experiment (partial immersion of sample)

PM – quartz-sericite-feldspar schist. The rock has a foliated and folded texture, subsequently cataclastic, and a greenish color. Microscopically, it appears as a quartz + feldspar mass, crossed by layers of sericite and chlorite; chalcopyrite and disseminated grains of pyrite have been observed too. At the border of metallic minerals, small flakes of biotite develop;

B27 – sericite-quartz schist. The sample has a foliated texture and a white-gray-greenish color. Microscopically, the rock consists of layers of sericite that alternate with layers of anhedral quartz. As metallic minerals, euhedral pyrite crystals have been recorded, often associated with quartz and only accidentally with sericite.

B12 – chlorite-sericite-quartz schist. The texture of the sample is foliated and the color is dark green. The observations under microscope show layers of chlorite that alternate with layers of quartz; sericite crystals parallel to chlorite crystals have been recorded. The metallic minerals appear as euhedral crystals of pyrite and galenite or as bands parallel to layered chlorite-sericite grains.

The purpose of the experiment was to simulate the leaching of rock debris from the lower part of the mine wastes by solutions which already have a low pH as a result of the acid mine drainage processes.

The experiment consists of a partial immersion of each of the three samples in solutions of hydrogen peroxide (distilled water + hydrogen peroxide), at different concentrations: 10%, 15% and 20% H_2O_2 (fig. 1). In this purpose, each sample we shortly described above has been cut in three fragments (PM, B27) or in two fragments (B12). A short description of samples and solutions involved in the experiment is presented in table 1.

Table 1 Samples and solutions involved in the experiment

Sample	Solutions		
	10% (pH = 2.951)	15% (pH = 2.666)	20% (pH = 2.454)
	V = 25ml	V = 25ml	V = 25ml
PM m = 87g	●	●	●
B27 m = 91g	●	●	●
B12 m = 45g	●	-	●

V = volume of the solution; m = mass of the sample

The process on which the experiment lies is the rise of solution in the sample, throughout the foliation of the schist; thus, in the upper part of the sample, a front of capillarity arises (the limit between the dry part and the wet part of the sample). Moreover, after 4 days, on the top of the samples green-bluish (PM sample) and yellow-brown-reddish (B27 sample) solid products developed; as about sample B12, orange products have been recorded after 5 days.

At the same time, the solutions get a slight color as follows: greenish-olive color (PM) and green-yellowish color (B27); B12 solution remains colorless. On the bottom of the Berzelius vessel in which the samples have been immersed, brown-greenish (PM) or white (B27) precipitates have been observed after the first 4 days of experiment. After seven days, solutions of the same concentration have been added in the vessel, in order to reach back the starting volume of 25ml.

The experiment was carried out on a two weeks span of time and it involved pH measurements on solutions every 2 hours, using a MeterLab PHM Ion Analyzer (Radiometer Copenhagen). On the other hand, at the end of the experiment, XRD analysis (Philips PW 1730 diffractometer) have been performed on the solid products developed at the up most part of the samples.

Results

Solutions. As stressed above, the studies carried out on solutions involved the measurement of pH variation in a two weeks span of time.

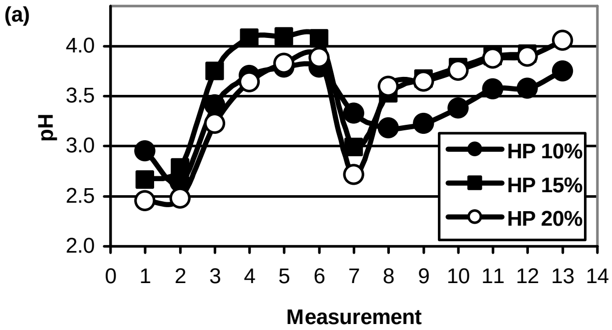

Fig. 2 Solution pH vs. Number of measurement (time) – sample PM. Measurement 2 performed after 72 hours; HP-hydrogen peroxide.

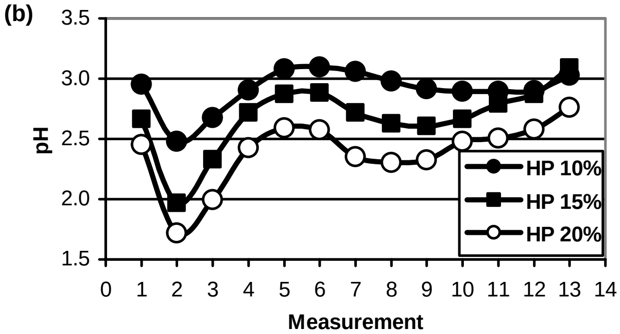

Fig. 3 Solution pH vs. Number of measurement (time) – sample B27. Measurement 2 performed after 72 hours; HP-hydrogen peroxide.

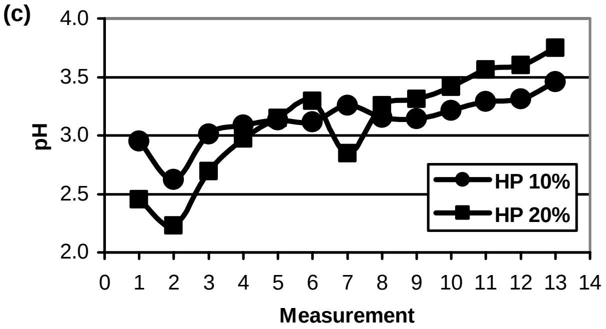

Fig. 4 Solution pH vs. Number of measurement (time) – sample B12. Measurement 2 performed after 72 hours; HP-hydrogen peroxide.

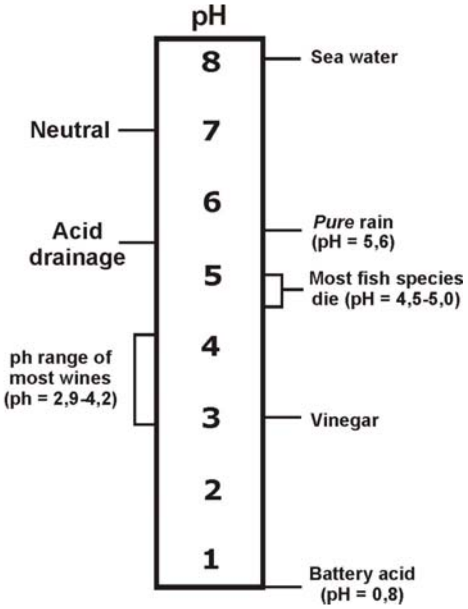

Fig. 5 The pH limit of acid rock drainage, after Jambor (2000)

Data from table 1 show that the starting pH values of immersion solutions are below pH = 3, that means far under the upper limit proposed by Jambor (2000) (fig. 5) for the acid drainage.

However, diagrams of pH variations in respect of time for all three samples (figures 2, 3 and 4) reveal a common pattern: during the first 3 days, the pH decreases dramatically (sometimes more than 0.50 units of pH) no matter the sample or the concentration of solution is. After the first 3 days, the pH of solutions starts to increase and seems to stabilize at higher values (even 1.00 unit of pH) than the initial pH of the solution.

The behavior of pH values shows also a more (PM) or less (B27) dramatic decrease in the seventh day of experiment; the explanation consists in the addition of hydrogen peroxide solutions in the Berzelius vessels, in order to reach back the starting volume of 25ml. As the diagrams of figures 2 and 3 reveal, after the addition of the acid solution, the pH values start to increase and tend to reach the values at which it was stabilizing in the first week of experiment (table 2).

Table 2 Some pH values of (hydrogen peroxide + distilled water) solutions during the experiment

Sample	Concentration of solutions*	Solution pH			
		Initially	After 3 days	After 7 days (constant)	End of experiment
PM	10%	2.951	2.638	3.787	3.625
	15%	2.666	2.785	4.075	4.014
	20%	2.454	2.480	3.884	3.909
B27	10%	2.951	2.479	3.096	2.976
	15%	2.666	1.968	2.885	2.983
	20%	2.454	1.716	2.573	2.670
B12	10%	2.951	2.624	3.117	3.377
	20%	2.454	2.228	3.294	3.639

* hydrogen peroxide + distilled water solution

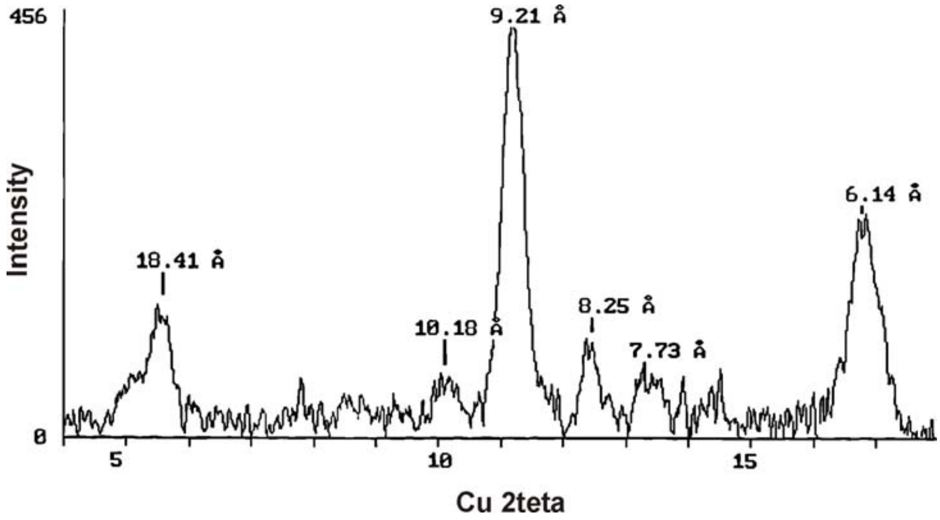

Fig. 6 XRD spectrum of a yellow-brown-reddish solid product developed on a sericite-quartz schist (B27)

Solids. As stressed in the previous paragraphs, the solid products have different colors in respect of the mineralogical composition of the sample. However, sample B27 shows a distribution of solid products into zones, as follows: in the vicinity of the major foliation planes, white, powdery products occur, while beyond this zone brown-reddish solid products develop.

The studies carried out under a stereomicroscope showed that greenish solid products (sample PM) assume crystal forms; the yellow-brown-reddish (sample B27) and the orange products (sample B12) reveal a gel-like appearance. No matter what the color of solid products of alteration is, all products are highly soluble in distilled water; the dissolution of 0.25mg of solid product in 5ml of distilled water (pH = 6.90) lead to an acid solution having a pH of about 3.00.

XRD analysis on yellow-brown-reddish solid products (fig. 6) identified these products as Al, Mg, Na, K-hydrated sulphates as follows:

$MgAlFe(SO_4)(OH) \cdot H_2O$

$(Na,K)_5Fe_3(SO_4)_6(OH)_2 \cdot 9H_2O$

Given the small quantity of solid product developed on the rock samples, a more precise identification of mineralogical terms could not be approached.

Conclusions

The experimental approach and the analytical results we have got during the study lead to the following conclusions:

- excepting time parameter, the experimental approach simulates quite satisfactory the natural processes and products;
- the samples that involve pyrite in the mineralogical composition develop yellow-brown-reddish solid products, while the samples that involve chalcopyrite develop green-bluish solid products;
- the chemical reactions between solid sample and the solution of hydrogen peroxide is proved by the slight coloring of solution: greenish-olive color (samples involving pyrite) and green-yellowish color (samples involving chalcopyrite);
- the pH of solutions decreases in the first three days after the immersion of solid sample in the hydrogen peroxide solution, possibly as a results of a higher reactivity of metallic minerals with the liquid component of the system;
- after the first three days, the solution pH starts to increase at values higher than the initial ones and seems to remain constant; the explanation could be the initiation of chemical reaction between the liquid components of the system and the gangue minerals from the rock;
- the solid products that occur as a result of simulated alteration can assume crystal forms or not (gels);
- the action of capillarity front induces a zonal disposition of solid products: in the neighborhood of the major foliation planes, white, powdery products occur, while beyond this zone brown-reddish solid products develop.

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