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Complex geochemical-mineralogical behaviour of sulphidic mine wastes - a case study based on sampling from Bolivian mine sites and Recsk, Hungary

THESES OF THE PHD DISSERTATION

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OBJECTIVES

In the PhD dissertation the different chapters are focusing on the different type of characterization of the oxidizing system from vary point of views. They show much further than the regular characterization of the system, moreover, they can be adaptable and used in other cases and other areas of geochemistry.

The guiding principle of the dissertation was to make new specific theses and calculations, via testing and proving them on Bolivian and Hungarian sulphidic samples in case studies. Moreover to reflect that the sulphidic oxidizing systems can result in serious or even catastrophic environmental impacts or contaminations, which frequently cannot be reversed, stopped or even mitigated.

The first in this to reflect that the acid rock drainage (ARD) effect not always creates acidic condition. In presence of sufficient neutralizing minerals, the acidic condition is buffered, so acidic impacts will be not seen. But even if the system has circumneutral pH, the sulphide oxidation can strongly take place.

A new method was created for the calculation of the exact mineralogical composition of the sample. This is based on the combination of X-ray powder diffraction (XRD) and sequential chemical extraction (SCE). The method could be a geochemical key in the sharp determination of mineralogical composition. The aim was also to describe and show the method in details and to prove the applicability of it on altered sulphidic mine waste materials via case studies. A further aim was to prove the presence of sulphides by calculation even if they are in extremely low concentrations.

The speed and the rate of the oxidation were always one of the main information, which needed to determine for the scientists. Based on the parameters of the seepage – resulted in humidity cell test – four different modes of calculations were made. The pH, the dissolved sulphate and iron content can define the pyrite oxidation, as well as the oxygen consumption of the system. The applicability of these methods, which can be determined the oxidation rate with, show further than the border of this PhD thesis, as they can be applied in laboratories or even in field tests.

Also, an objective was to show, that much more information can be reached out from the humidity cell test if it is used several times on the same sample in consecutive years. The trends point much more forward than the results in the individual years. The comparison of them can give a reliable forecast of the real long term behaviour for the sample, showing the changes in function of long term future. This could help in waste management to characterize the produced material before ARD could take place.

The aim is to show that mineralogical inhomogeneity can be formed in the filling of the humidity cells in case of fine-grained samples. As the porosity and permeability were low, inhomogeneity was created. In the case studies, it is pointed out that not every sample is suitable for humidity cell test. For a consequence, that the grain size is a limiting factor in the application.

I would like to highlight also the possible applicability of these methods, in other areas of geochemistry.

I. ABIOTIC AND BIOTIC TYPE OF PYRITE OXIDATION

The mining activities are as old as the human history, it started with the Stone Age and then by the discovery of metals, which can be strongly linked to ancient mineral exploitation, but the mining-related serious environmental problems are dominantly modern. The manual mining technique produced such a small amount of mining waste material, which can be handled by natural processes. This fragile balance changed as modern mining techniques started to produce a huge amount of waste during a short time.

In the last four decades, the pyrite oxidation caused acid rock drainage (ARD) has become the leading environmental problem in the sulphidic mining industry. In the sulphidic mine wastes, the principal weathering process is the sulphide oxidation, which results in low pH. This acidic environment creates a much more serious effect – than the low pH itself – as the heavy metal mobility increases dramatically. Further, an aggravating circumstance can be if the heavy or toxic metals are in the structure of the oxidizing sulphides, because in this case by the alteration of the sulphides directly lead to quick and high rate of heavy or toxic metal (Pb, Zn, Cd, Cu, As, etc.) mass load on nature.

Ore beneficiation processes selectively extract minerals of commercial value and exclude minerals that cannot be economically recovered. The most abundant sulphide minerals in most tailings impoundments are pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$). Because these minerals are the most abundant, they are the most common source of acidic drainage. (Jambor 1994)

Mill tailings can also contain very large accumulations of these Fe-sulphide minerals, but other sulphide minerals are also present, such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), galena (PbS) and arsenopyrite (FeAsS). (Blowes et al. 2003/a)

The pyrite starts weathering on surface condition in presence of oxygen and water. This quite simple equation (Eq. 1) for abiotic oxidation of pyrite was described by Nordstrom in 1982.

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

The Fe^{2+} can further oxidize to Fe^{3+}, with a redox potential dependent reaction, which is strongly catalysed by Acidobacillus Ferrooxidans. The Fe^{3+} also reacts with pyrite (Eq. 2), moreover, it will be the primer oxidizer agent and not the O_2. This is the biotic oxidation process of the pyrite, as the bacterial activity is needed.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

Whether pyrite oxidation proceeds on abiotic (Eq. 1) or biotic (Eq. 2) depends on the chemical conditions of the oxidizing system. Singer and Stumm (1970) published that Fe^{3+} is the dominant oxidant under low pH (<3) conditions. More studies proved, that if Fe^{3+} is present at low pH, it will be the primary oxidant. (Bonnissel-Gissinger et al. 1998; Singer and Stumm 1970; Blowes et al. 2003/a)

Those sulphides, which have no iron in their structure, like galena, sphalerite, etc., are not acid producers if O_2 is the oxidizer agent, so in case of the abiotic reaction. The situation turns if the Fe^{3+} acts as the oxidizer in biotic reactions. Even the iron non containing sulphides become acid producers (Table 1), thus they will be also responsible for the acidic environment.

	Iron containing sulphides (pyrite, marcasite, arsenopyrite, etc..)	***Iron not containing sulphides*** (galena, sphalerite, etc..)
O_2, as oxidizer agent	acid production	no acid production
Fe^{3+}, as oxidizer agent	acid production	acid production

Table 1: Outcome of the oxidizing reactions in the function of the two different oxidizer agent

In the last almost 40 years, since the first reaction was described by Nordstrom, the knowledge in ARD effect increased largely. There are many parameters, which have an influence on the oxidation reactions. These are the mineralogy and mineral chemistry, the microbial activity, the gas transport, the rain, water and infiltration and the solubility. The combination of these and their interactions determine the working of the oxidizing system. (Singer and Stumm 1970; Scharer et al. 1991; Blowes and Jambor 1990; Blowes et al., 1991; Smith and Beckie 2003; Seal and Hammarstrom 2003; Walder and Stormont 2004)

II. SAMPLES

2.1. Bolivian samples

The 16 samples were collected from the most famous Bolivian mining districts. Some of them, mainly around Oruro, were already mined under the civilization of the Incas, even before the Spanish conquistadors. These mines are located along the NNW oriented metallogenic zone, on the junction of the Central Cordilleras and the Bolivian highland, the Altiplano, called as Bolivian Tin Belt. (Grant et al. 1980). In these deposits of mine wastes and tailings serious ARD effect took place, but the dominant problem is not the acidic environment itself, but the dramatic increase of the heavy metal mobility (such as Pb, As, Cu, Zn, Cd, Sn, Sb, etc....) by the low pH. These parameters indicate that these samples are ideal for the humidity cell test series.

Among the samples, there are mine wastes as well as mechanical enrichment tailings and flotation tailings The samples contain different types of sulphides in varying amount and also they were in varying stage of oxidation. The map (FIG. 1) shows the 5 different sampling sites. 6 samples were collected from Oruro in 2007, 2 samples from Milluni and 1 sample from "Bolsa Negra" in 2008, 5 samples from Morococala and 2 samples from Huanuni in 2009.

The aim of the sampling by using kinetic testing was to determine the “worst case scenario”, thus to reach the maximal oxidation speed, that the sample can produce. With this, the maximal heavy metal pollution and mass load can be calculated, so it can let us know, what can be the maximal pollution which will be produced by the mine waste dumps and different types of tailing deposits.

FIG. 1: Locations of the collected samples. (Source: after Worldometers 2020)

2.2. Hungarian (Recsk) samples

Sulphidic ore mineralizations can be found also in the Mátra Mountains, in NE Hungary. In 2011, a sulphidic sample was collected from the waste dump of the Recsk -900 deep level. The ore body was a copper porphyry and skarn copper deposit. The sample was taken from the extracted material of the “Western 3” ore exploration adit, which drove the contact of the exoskarn and the carbonates.

For the experiments, fragments of 10-20 cm were selected. After the removal of the secondary mineralization (such as iron oxides) from their surface, they were crushed into five different grain sizes: between 1-2; 2-4; 4-8; 8-16 and 16-32 mm, in amount of 3.0 kg in each sections. The crushing process gave fresh, non-oxidized, thus fresh surface, which is ideal for the kinetic test analysis.

III. MEASURING METHODS

3.1. Humidity cell tests

The humidity cell test is a standardized process which was developed in Canada. It was designed to determine the acid-producing and neutralizing potential and the rate of oxidation. (Grant et al., 1980) With this method, the system can reach the maximal oxidation rate, thus with this geochemical method the “worst case scenario” can be mimicked. This gives us an estimation, what can be the maximal speed of oxidation and what can be the maximal environmental and heavy metal load.

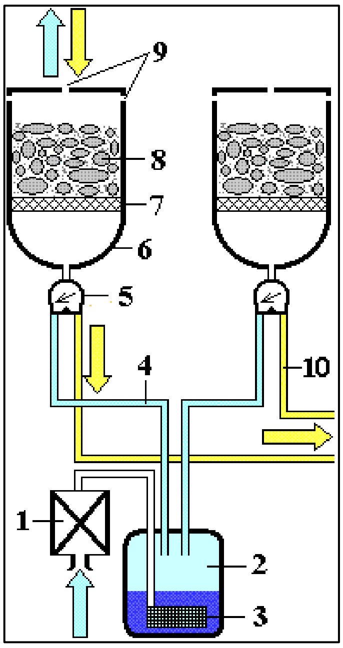


FIG. 2: Humidity cell test

The basic concept is that through the samples, moisture saturated air was pumped and weekly the samples are flushed through with distilled water. The leachate was collected and analysed for pH, conductivity, alkalinity and anion concentrations. The weights of the Bolivian samples were between 1.5 and 2.5. In the Hungarian set, each fraction was 3.00 kg, because the main question was whether the grain size effects on the pyrite oxidation rate or not. On a schematic draw (FIG. 2) the air pump (1) pushes air (light blue arrow) into the water containing tank (2), through a bubbler (3). The humid air via the air pipe (4) and the valve (5) can enter the acrylic sample keeper (6). Then it can go through the filter and the mesh (7) and the sample (8), before it exit (9) on the top of the sample keeper. The humidified air is a perfect tool to give O_2 for the oxidation of the sulphides – to be sure, several magnitude larger amount than it can use up – as well as H_2O for the mineral alteration reactions. Through the drainage collecting pipe (10) the seepage was collected, analysed, filtered and stored in plastic bottles on 4 °C for further analysis.

In 4 consecutive years on the 16 Bolivian and the 5 Hungarian samples humidity cell test was completed. The testing place and the laboratory was assured by KREC (Kjeøy Research and Education Centre) in Northern-Norway, at Kjeøy Island. The earliest collected ones were analysed for 4 years, while the Hungarian samples only for 1 year (Table 2). The samples were analysed for 3-4 months, then a break was kept without air pump for the rest of the year, with opened up sample keeper.

Sample	***2008 summer***	***2009 summer***	***2010 autumn - 2011 spring***	***2011 autumn - 2012 spring***
Year code	1st year	2nd year	3rd year	4th year
Jalpha 1-7, Playa Iroco 1-7	0 - 101 days	0 - 42 days	0 - 115 days	---
Itos Jig 1-7; Itos Jig 2-7	0 - 101 days	0 - 42 days	0 - 121 days	0 - 119 days
Itos Granza 1-7, Itos Granza 2-7	0 - 101 days	0 - 35 days	0 - 121 days	0 - 119 days
BOL 1-8; BOL 2-8; BOL 3-8	---	0 - 42 days	0 - 121 days	0 - 119 days
BOL 1-9; BOL 2-9; BOL 3-9; BOL 4-9; BOL 5-9	---	---	---	0 - 112 days
BOL 6-9; BOL 7-9	---	---	0 - 115 days	0 - 119 days
HU 1-2; HU 2-4; HU 4-8; HU 8-16; HU 16-32	---	---	---	0 - 119 days

Table 2: Length of the humidity cell test period in the four consecutive years

3.2. Mineralogical and chemical measuring methods

For measuring the chemical concentrations of both the main and trace elements of the bulk sample were used a Rigaku® Supermini 200 WDXRF (wave-length X-ray fluorescence spectroscope) measuring equipment. The machine was provided by a 200 W (50kV and 4.0mA) Pd cathode X-ray tube, with LiF, PET and XR25 analyser crystals, which was driven by ZSX programme.

For the mineral phase determination a Bruker D8 Advance X-ray Powder Diffractometer (Cu-Kα source, 40kV 40mA, Bragg-Brentano geometry) equipped with secondary graphite monochromator was used. The measurement was run in the 2Θ = 5 - 65° domain. The evaluation was performed with EVA module of Bruker DiffracPlus data handling software. TOPAS3 software was employed for the quantitative analysis.

Each samples were analysed by an electron microscope, which can give high-resolution images and by microprobe the chemical composition of the tiny grains can be measured. with JEOL JXA-8600 Superprobe EMPA. The measurements were made with an upgraded SAMX software, with 15-20 kV acceleration voltage and 20 nA beam current. PAP correction was used during the measurement.

Each measuring methods were completed at the Department of Mineralogy and Petrology, University of Miskolc, Hungary.

IV. HUMIDITY CELL TEST RESULTS

Important to highlight, that in this dissertation, the results of the humidity cell test are only used as a useful tool for the confirmation of the thesis points in the different topics. The purpose of the PhD dissertation does not directly show the results of the humidity cell test itself, as a reached and final target, but this information is only a kit of tools.

In each sample, in case of each parameter in each year, two figures are plotted. The circle represents the data, which was measured in the effect of “first flush”, while the rectangular represents the stabilized parameter during the test period.

The pH content (FIG 3.) of the seepages vary between wide range. In case of the Bolivian samples, generally, the first rinsing resulted in a unit lower pH – which means ten times higher H^+ concentration – than it was later in the stabilized phase of the samples, where the H^+ was given by the oxidation of the pyrite. The Hungarian samples did not produce such strong first flush effect, as they were fresh samples.

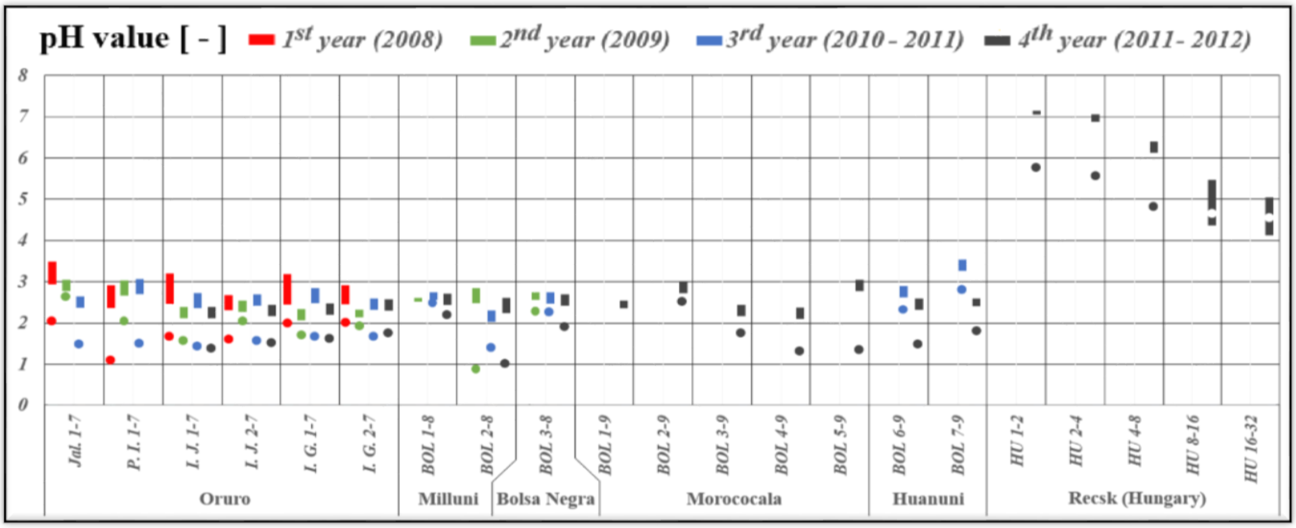


FIG. 3: Changes of the pH values of the seepage during the humidity cell test analysis

In the redox potential results (FIG. 4) three trends can be observed, such as the Eh was the lowest in time of the first rinsing, than it also can be somewhere within the whole range, that the sample produced during the humidity cell test, or finally it can be the highest in case of the first rinsing, than later in the test period. For each attitude, the mineralogy and its changing can give the reason.

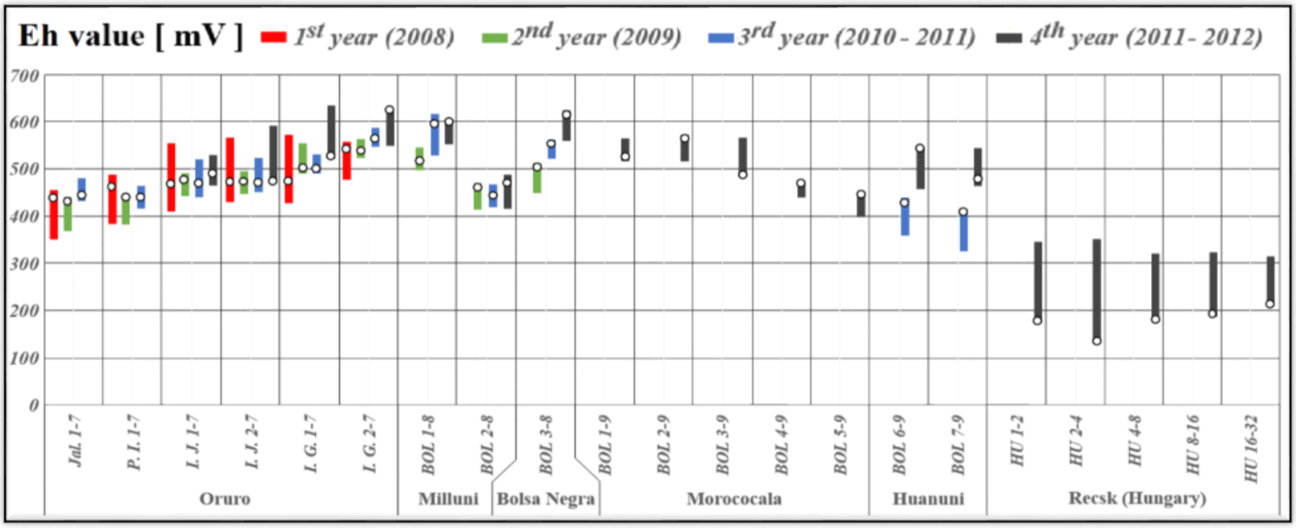


FIG. 4: Changes of the redox potential (Eh) values of the seepage during the humidity cell test analysis

The sulphate content (FIG. 5) behaved more simply. In case of all samples in all years the first rinsing caused significantly higher concentrations than later the system had stabilized. In general, the starting concentration was at least one magnitude, thus 10-times higher than in the stabilized test period.

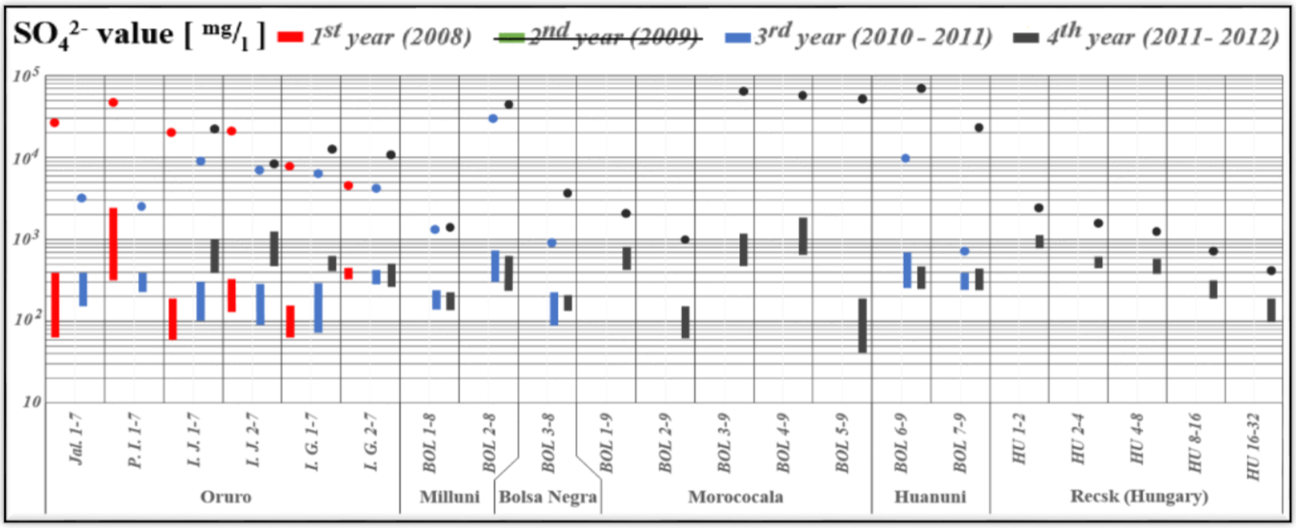


FIG. 5: Changes of the sulphate concentrations of the seepage during the humidity cell test analysis

The original aim with the Hungarian sample set was to determine how the different grain size can modify the pyrite oxidation rate. During the 119 days of analysis of the 4th year, this effect was not determined yet. 17 weeks (119 days) were analysed by me and further 66 weeks were analysed by Rodrigo Embile, who continued the test, which was designed, setup and started only by me. In a common article (Embile et al., 2016) the effect was published. As the result is not only my own property, I do not use it in my dissertation.

V. THESES

1st topic – Pyrite oxidation under circumneutral pH condition

1st thesis: ***By using the results from the humidity cell test of the Hungarian sample HU 1-2 sulphidic mine waste material, can be declared, that significant pyrite oxidation can take place, even if the pH of the seepage stays circumneutral. This means, that even if the pyrite oxidation produces acidity, it will not necessarily appear if neutralizing minerals are present. Nevertheless, the oxidation process of pyrite will happen. This was proved by the sulphate release, the O_2 consumption and CO_2 production and also the secondary mineral coatings, such as gypsum on calcite and iron oxyhydroxide on pyrite grains.***

With different types of analyses of the HU 1-2 sample, is show that serious pyrite oxidation can take place, without the appearing of the caused acidity. If neutralizing mineral is present, the formed acidity can be buffered for an uncertain time. In the above mentioned sample, the calcite played this role, as showed neutral pH. As a hypothesis (Eq. 3), summarized oxidation and neutralizing equation was made.

$$2FeS_2 + 3CaCO_3 + 3H_2O + 6O_2 \rightarrow 2FeOOH + 3CaSO_4 * 2H_2O + 3CO_2 \qquad (3)$$

The key in proving the oxidation process of the pyrite is to find the by-products of the reaction, such as Fe-oxyhydroxide, gypsum and carbon dioxide, moreover to find some remained sulphate and calcium ions in the seepage.

The pH graph (FIG. 6; left axis) clearly indicates that after 2 weeks the system has already stabilized. The circumneutral pH (between 7.1 and 7.3) shows that the calcite buffers the acidity perfectly. The gradually decreasing sulphate (FIG. 6; right axis) release after the first 2 weeks shows relative stability.

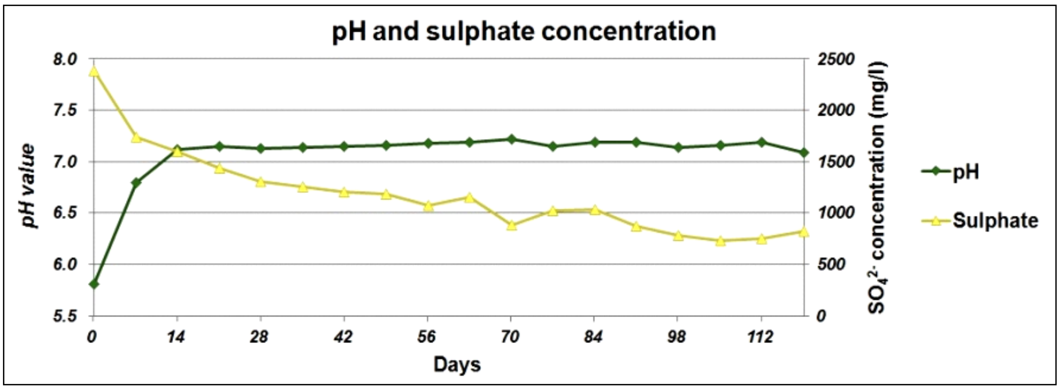


FIG. 6: pH value and sulphate content in the seepage of the humidity cell test

At the end of the test period, the column was sealed hermetically for a week to measure the oxygen consumption and carbon dioxide release. FIG. 7 shows clearly that carbon dioxide content increased continuously, which shows the dissolution (Eq. 3) of calcite, while the decreasing oxygen content shows the presence of the oxidation process.

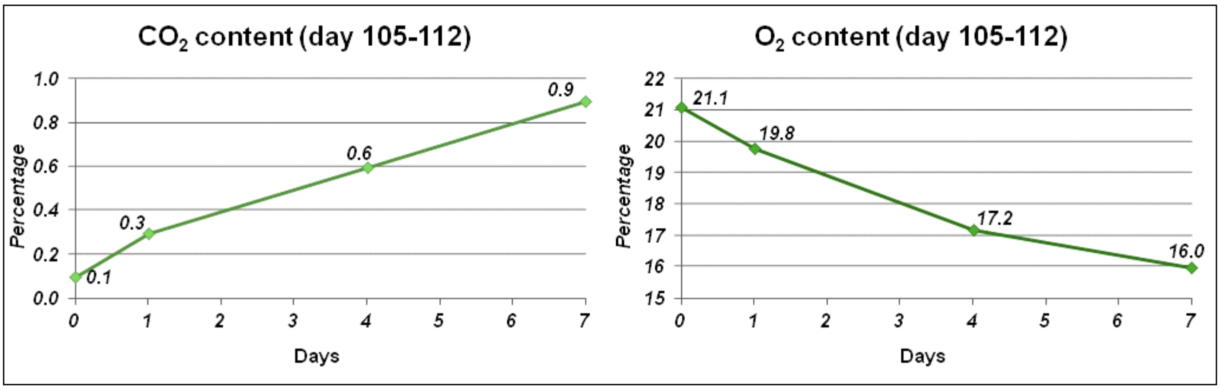


FIG. 7: CO_2 release and O_2 consumption in the column

The combined equation (Eq. 3) tells that if pyrite is oxidizing and calcite is present, secondary iron mineral and gypsum should be formed. Backscattered SEM images were taken, where clearly visible, that on the surface calcite gypsum coating (FIG. 8) was formed, while on the surface of the pyrite grains (lighter colour) secondary iron mineral (darker colour) was appeared (FIG. 9/a and b).

FIG. 8: Gypsum needles on calcite

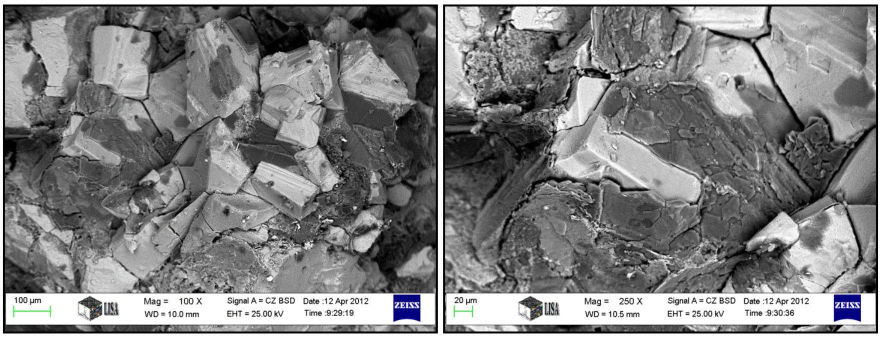


FIG. 9/a and b: Secondary Fe mineral coating on pyrite (a:100x;b:250x)

As a conclusion, the pyrite oxidation in the sample was detected and proved by the sulphate concentration (FIG. 6) from the seepage, the appearance of CO_2 and decreasing of O_2 in the hermetically closed sample holder (FIG. 7), as well as with the gypsum coating on the surface of the calcite (FIG. 8) and secondary iron mineral crust on the surface of the pyrite grains (FIG. 9/a and b).

On the other hand, important to highlight, that it would be necessary to change the thinking in the waste management, because most commonly only the pH value is monitored. This can lead to severe environmental damage that could have been prevented if the situation handled more carefully.

2nd topic – X-ray powder diffraction (XRD) versus sequential chemical extraction (SCE) – A new combined method for exacting mineralogical speciation of sulphidic mine wastes

2nd thesis: ***With the using of the combined method of the X-ray powder diffraction (XRD) and the sequential chemical extraction (SCE), exact mineral phases with sharp amounts can be calculated. Moreover, the calculation method perfectly works on such strongly altered sulphidic materials, where the byproducts are amorphous, so the XRD method is not able to determine them. With an electron microscope and microprobe, the presence of such minerals were proved in the samples, which were calculated even as low amount as 0.002 or 0.005 %.***

Determination of the exact mineralogical composition of an oxidizing sample has always been a big challenge for scientists, although it is essential to understand more precisely those reactions which could take place during weathering. The X-ray diffraction (XRD) is an efficient method for this purpose, but in case of altered and not well-crystallized rocks, the efficiency of this method is already not acceptable, as the produced secondary minerals are poorly crystallized or even quite often are amorphous.

It is shown, how the X-ray powder diffraction (XRD) and the sequential chemical extraction (SCE) can complement each other. Using them as a combined method, the efficiency of determination of the mineralogical composition can be dramatically increased. A further aim is to show the applicability of the combined method for altered sulphidic mine waste materials, where the mineral(s) with extremely low concentration could be calculated out.

Among the SCE procedure, the Dold type 7-step method was used, which has the highest variety for the separation of the mineral phases. (Dold 2003)

In the calculation (FIG. 10) only one data set is used at a certain time, so just calculating step by step, started with the water-soluble phase and finishing with the silicates. In the next step, the molecular weights of both the mineral and the element itself were defined in order to calculate the weight ratio of the mineral compared to the element. Finally, the starting concentrations of those elements were decreased, which were used in the calculated mineral.

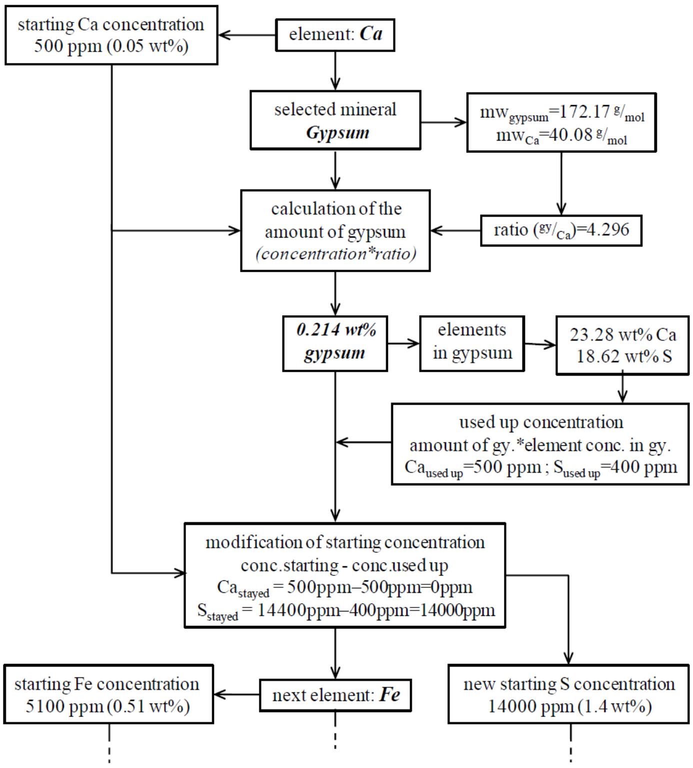
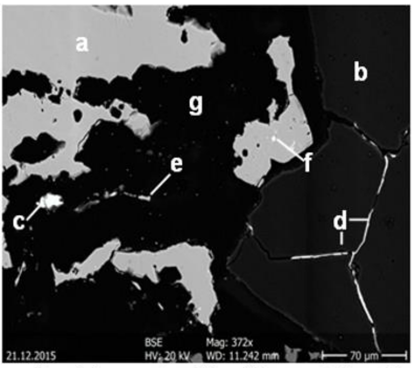


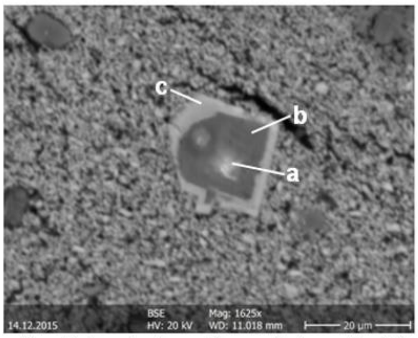
FIG. 10: Recalculation flow sheet of the gypsum (the 1st step in Jalpha 1-7)

Without showing the steps of the calculations, the result of it is listed on the left side of FIG. 11. The aim was to find those mineral phases, which have lower concentration than 0.1% (marked with red rectangles). By using an electron microscope and microprobe, verification was completed. Although these concentrations are extremely low, the grey arrow marked phases were found. With the phases of the names are visible at the left side of FIG. 11.

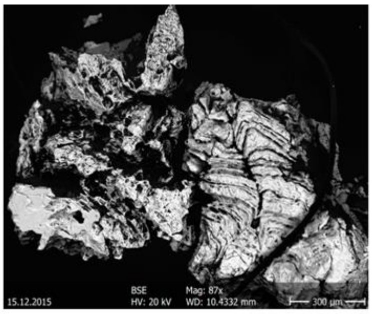
Mineral	Wt%	Formula	
Alunogen	*0.71*	$Al_2(SO_4)_3*17\ H_2O$	
Alum-(K)	*0.36*	$KAl(SO_4)*12H_2O$	
Melanterite	*1.10*	$FeSO_4*7\ H_2O$	
Anglesite	*0.09*	$PbSO_4$ ⇦	
Ferrihydrite	*0.14*	$Fe(OH)_3$	
Hydroniumjarosite	*0.14*	$H_3OFe_3(SO_4)_2(OH)_6$	
Jarosite	*0.79*	$KFe_3(SO_4)_2(OH)_6$	
Plumbojarosite	*0.42*	$PbFe_6(SO_4)_4(OH)_{12}$	
Alunite	*0.51*	$KAl_3(SO_4)_2(OH)_6$	
Magnetite	*0.17*	Fe_3O_4	
Pyrite	*3.87*	FeS_2	
Arsenopyrite	*0.04*	$FeAsS$ ⇦	
Wurtzite	*0.002*	$Zn_{0.9}Fe_{0.1}S$ ⇦	
Chalcopyrite	*0.003*	$CuFeS_2$	
Galena	*0.005*	PbS ⇦	
Stibnite	*0.009*	Sb_2S_3 ⇦	
Herzenbergite or Berndtite	*0.008*	SnS *or* SnS_2	
Cassiterite	*0.009*	SnO_2 ⇦	
Valentinite	*0.025*	Sb_2O_3	
Dravite	*7.92*	$NaMg_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$	
Illite	*38.1*	$K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe_{0.1}Si_{3.5}O_{10}(OH)_2*(H_2O)$	
Biotite (XRD)	*0.9*	$K(Mg,Fe)_3[AlSi_3O_{10}(OH)_2$	*0.9*
Quartz (XRD)	*39.9*	SiO_2	*39.9*



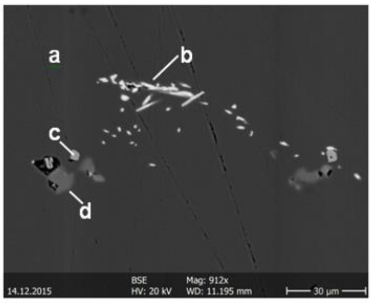
pyrite (a), quartz (b), chlorargirite (c), anglesite (d), mix of cassiterite and arsenopyrite (e), galena (f), APS (g)



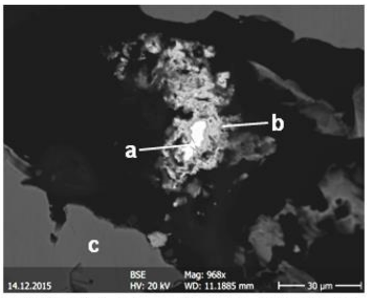
mix of plumbojarosite and jarosite (a), mix of alum-(K) and alunogen (b), jarosite (c)



sphalerite (wurtzite)



pyrite (a), stibnite (b), cassiterite (c), sphalerite (d)



galena (a), anglesite (b), pyrite (c)

FIG. 11: Recalculated mineralogical composition and electron microscope images with the determined phases

Of course the other phases were also found – such as alunogen or alum-(K) – but they are shown in pictures below, only focusing on the extremely low concentration minerals. As a conclusion, such calculated minerals were found, like 0.002% of wurtzite, 0.005% of galena or 0.009% of stibnite and cassiterite. These results confirm the correct working in the calculation, furthermore that this combined method could stand its place among geochemical methods.

Important to mention that the calculation method requires a strong chemical, geochemical and mineralogical background, with some additional information from the ore geological origin of the sample. Nevertheless, its result can be very valuable.

3rd topic – Calculations of bulk pyrite oxidation rate from humidity cell test results

3rd thesis: ***Four different new formulas were established for the determination of the bulk pyrite oxidation rate, which are applicable both for abiotic or biotic oxidation systems, or even for the mixture of them. The using of these formulas is not limited for laboratory experiments, they can be used in larger scale also, even in field tests. The formulas for the oxidation rate determination are based on the four main parameters of the oxidation process, such as:***

3rd/a. pH value of the seepage

3 rd/b. sulphate concentration in the seepage

3 rd/c. iron concentration in the seepage

3 rd/d. O_2 consumption of the oxidizing system

In long term thinking for the ARD characterization, one of the most important parameter is the oxidation speed of the sulphides, especially the pyrite. Thus the determination of the oxidation speed became one of the most important – as well as the most searchest – parameter in the oxidizing system. The aim is to determine calculations for the oxidation rate, based on the different parameters which are measured during the kinetic tests, either in humidity cell or column one.

Based on the abiotic (Eq. 1) and biotic (Eq. 2) pyrite oxidation the following alteration reactions take place by using a simplification of deleting the water and the oxygen, only used mole ratios between pyrite and its byproducts, both in abiotic (Eq. 1/b) and in biotic (Eq. 2/b) case.

$$1M\ pyrite \rightarrow 2M\ SO_4^{2-} + 1M\ Fe^{2+} + 2M\ H^+ \qquad (1/b)$$

$$1M\ pyrite + 14M\ Fe^{3+} \rightarrow 2M\ SO_4^{2-} + 15M\ Fe^{2+} + 16M\ H^+ \qquad (2/b)$$

If the fact is taken into consideration, that for the production of 14M Fe^{3+} used up 14M Fe^{2+} as well as 14M H^+, the net reaction both for abiotic and biotic reactions means, that 1M pyrite produces 2M SO_4^{2-}, 1M Fe^{3+} and 2M H^+. This effects, that there is no difference in calculation between them.

Without showing the whole derivation of the equation, the pyrite oxidation rate can be calculated from the main parameters of the seepage, such as the pH value (Eq. 4), the dissolved sulphate (Eq. 5) or iron (Eq. 6) concentration. The 4th version (Eq. 7) uses the oxygen consumption by the oxidation process. In each case, the unit is given as *grams of pyrite / week / kg of sample*.

$$R^{pH} = \frac{\left(10^{-pH_{sp}^{avg.}} - 10^{-pH_{rs}^{avg.}}\right) * H_{mw}^{+} * \frac{py_{mw}}{2 * H_{mw}^{+}} * V_{rs}^{tot.} * \frac{7}{N_d}}{M_s} \qquad (4)$$

$$R^{SO_4^{2-}} = \frac{C_{SO_4^{2-}}^{avg.} * \frac{py_{mw}}{2 * SO_{4\,mw}^{2-}} * V_{rs}^{tot.} * \frac{7}{N_d}}{M_s} \qquad (5)$$

$$R^{Fe} = \frac{C_{Fe}^{avg.} * \frac{py_{mw}}{Fe_{mw}} * V_{rs}^{tot.} * \frac{7}{N_d}}{M_s} \qquad (6)$$

$$R^{O_2} = \frac{\frac{V_{free} * \left(O_{2\,conc.}^{to} - O_{2\,conc.}^{tx}\right) * P_{tx}}{R * T_{tx}} * O_{2mw} * \frac{py_{mw}}{3.5 O_{2\,mw}} * \frac{7}{N_d}}{M_s} \qquad (7)$$

4th topic – Temporal changes of pyrite oxidation rate in sulphidic mining wastes

4th thesis: ***A classification system was defined for the state of maturity of the sulphidic samples, which were analyzed in humidity cell test for consecutive years. The classification shows much forward than the results of the humidity cell test in the individual years in themselves. The classification can mimick the long-term geochemical behaviour of the analyzed material.***

If on the same material several times the humidity cell test was completed, the results of the changes in the oxidation rate show much forward than in the individual years it does. The comparison of changes in the rates can give a real long term behaviour for the sample. In 3 or 4 consecutive years humidity test was investigated on the same 7 samples (Table 2/b). 5-7 months pauses were left between the test periods, which allow mimicking the alternation of wet and dry periods.

Sample / Year code	1st year	2nd year	3rd year	4th year
Itos Jig 1-7; Itos Jig 2-7 Itos Granza 1-7; Itos Granza 2-7	0 - 101 days	0 - 42 days	0 - 121 days	0 - 119 days
BOL 1-8; BOL 2-8; BOL 3-8	---	0 - 42 days	0 - 121 days	0 - 119 days

Table 2/b: Length of the humidity cell test period for the selected samples in the consecutive years

The result of the humidity cell test shows (FIG. 12) that the samples can be split by the changes of the pyrite oxidation rate into three different stages: the first is when the oxidation rate is ***increasing (type "A")***, which is typical for the fresh or relatively fresh samples, where the surface of the grains are free of secondary minerals, so quick and acute oxidation takes place. By moving forward in time, the oxidation rate becomes ***maximal and stable (type "B")***, so it is not changing (significantly) in time, while the last class, when the oxidation rate starts ***decreasing (type "C")*** in time, as the pyrite starts to be consumed and also, its surface started to be covered by relatively chemically resistant iron oxides.

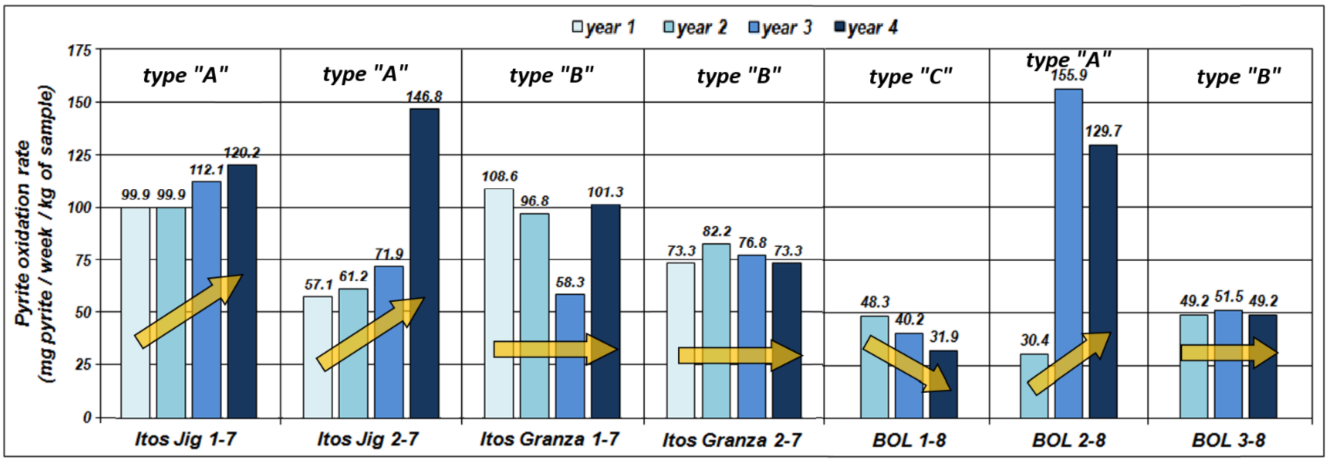


FIG. 12: Changes of the pyrite oxidation rates of the samples in the consecutive years of analyses

In the ***weakly oxidized stage*** (type “A”) the pyrite oxidation rate is increasing in the consecutive years. Samples Itos Jig 1-7, Itos Jig 2-7 and BOL 2-8 (FIG. 12) are good representations of this type of behaviour. The increase in pyrite oxidation rate means that in the future the reactions will become faster. Because of the low pH and speeding up of the reactions, the heavy metal mobility increases.

Partly oxidized stage (type "B") covers the samples Itos Granza 1-7, Itos Granza 2-7 and BOL 3-8 (FIG. 12), where the pyrite oxidation is maximal, thus stable in the different years. The maximal pyrite oxidation rate also means that this stage has the lowest pH, which keeps for a longer time.

Strongly oxidized stage (type "C") includes only the sample BOL 1-8 (FIG. 12), where the pyrite oxidation rate is decreasing in consecutive years. The reaction rate slows down, thus the pH continuously increasing, but not as steep as the decreasing was in the first stage. The slow increase of pH in this phase is due to pyrite being excused. Bulk oxidation rate becomes lower due to less pyrite available.

The three stages are members of a natural progression for weathering of iron sulphide containing tailings and waste rocks. This is the theoretical pyrite oxidation curve (FIG. 13). The fresh material starts oxidizing with increasing rate, then with time the reaction rate becomes stable, and finally decreases. As time moves forward, the slopes of the graph continuously changing.

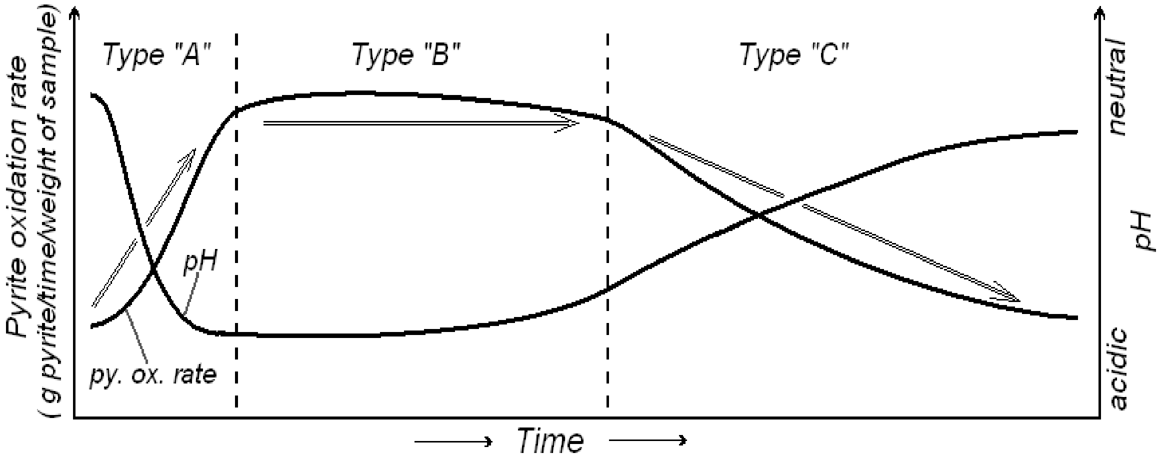


FIG. 13: Pyrite oxidation changes in the function of a long term process (after Ritchie 1994)

This three or four-year-long investigation indicated the maturity of the tailings and waste materials. Table 3 gives an overview of the different oxidation rate stages of the samples. The three stages define also the rates of emitted pollution and heavy metal mobility.

Sample	*Maturity*	*Behaviour in the future*
Itos Jig 1-7 ***Itos Jig 2-7*** ***BOL 2-8***	weakly	increasing in pollution and heavy metal mobility, decreasing pH; pollution peak in the future, further problems; the situation calls for management, monitoring is essential
Itos Granza 1-7 ***Itos Granza 2-7*** ***BOL 3-8***	partly	stable low pH, maximal pollution and heavy metal mobility; pollution peak at present, problems will not increase, but stays for an uncertain time; monitoring is strongly required
BOL 1-8	strongly	decreasing pollution and heavy metal mobility, increasing pH; pollution peak already in the past, no further increasing problems; monitoring is not required

Table 3: Overview for the future from the point of the behaviour of pyrite oxidation changes

5th topic – Chemical and mineralogical analysis of “non homogeneous” mineral alteration in the material of the column filling during the humidity cell test (1st part)

<u>5th thesis:</u> ***<u>A new, flat sample keeper was designed and developed for fine or even clayish structured sample</u>. This new innovation proved with humidity cell test, that it can work perfectly, as the chemical properties of the seepage became much less variable, so the evaluation of the humidity cell test can be more accurate and easier.***

There is a hypothesis, that the material which is used for analysis is mineralogically homogeneous. This hypothetical idea can be true if the grain size is fine. But this small grain size means significantly decreased porosity and permeability, compared with the coarser materials. These decays in the hydraulic and air ventilation parameters result, that the system of the column or humidity cell will not work properly. As the rinsing water is not able to flow through the sample, the result of the humidity cell test will be wrong. The clayish Jalpha 1-7 sample showed this during the humidity cell test in the 1st and 2nd year (FIG. 14). Both the pH and the Eh in both years (yellow and orange line) show fluctuation.

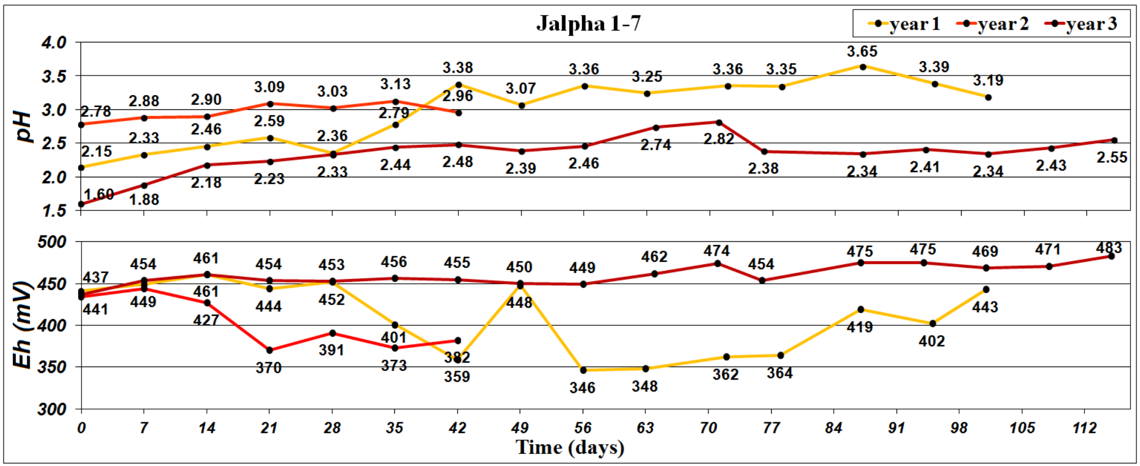


FIG. 14: pH and Eh changes in sample Jalpha 1-7 during the 1st, 2nd and 3rd year of the test period

It seemed that the regular sample keeper can not be applied for such fine samples, like Jalpha 1-7. To solve this problem, a new flat sample keeper was investigated (FIG. 15), which is the author's innovation, both in design and in the investigation. It is made from acryl in a square shape with inside dimension of 250x250 mm and height of 50 mm, with a well-sealed cap, to be able to complete the oxygen consumption test with it. On its side, air inlet (blue arrow) and outlet (orange arrow) pipes are. Horizontal air ventilation is used, so air touches only the surface of the sample, in contrast with the "regular" cylindrical sample keeper. In the weekly rinsing, the seepage was collected from the surface of the sample.

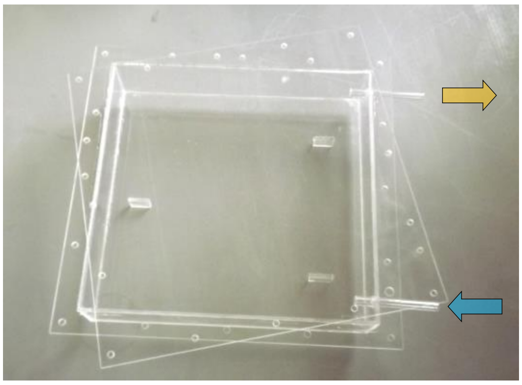


FIG. 15: Newly developed flat sample

The success, as well as the applicability of the new designed sample keeper, were not questionable, as it worked for clayish samples with low permeability and porosity. The proper working is shown by the results of the kinetic test (dark red line on FIG. 14) in the 3rd year, where both the pH value and the redox potential become stable after a few week.

5th topic – Chemical and mineralogical analysis of “non homogeneous” mineral alteration in the material of the column filling during the humidity cell test (2nd part)

6th thesis: ***By analysis of lateral mineralogical changes of the column filling of fine-grained samples, it can be stated that there is a lower limit for the particle size below which the applicability and result of the humidity cell test in the regular sample keeper becomes strongly questionable.***

As the hydraulic and air ventilation parameters are not appropriate in the humidity cell test, the circle of oxidation – secondary mineral formation – dissolution, brake and inhomogeneities take place. From the remained seepage secondary minerals can be formed, so differences have already appeared.

In case of BOL 6-9 tailings, which had an average grain size between 1 and 2 mm, visible mineralogical changes happened in the sample keeper. The sample was analysed in the 3rd (115 days) and 4th (121 days) year. In both years, it reached a stable and continuous system very quickly (FIG. 16). The original material was fine, with reddish-brown colour, as secondary Fe oxyhydroxide (e.g. goethite) or oxide minerals covered the surface of each grain. These secondary minerals were dissolved slowly during the humidity cell test and the colour of the sample slowly become dominantly greyish.

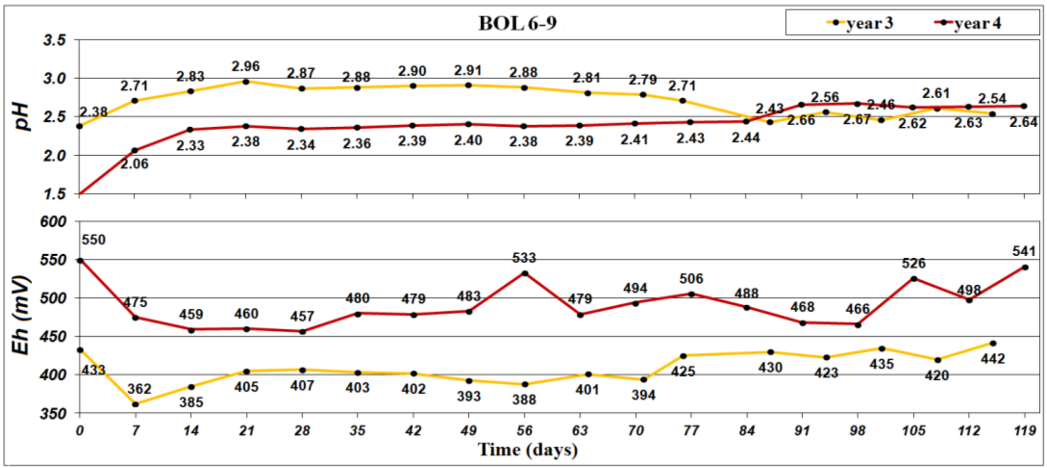


FIG. 16: pH and Eh changes in sample BOL 6-9 during the 3rd and 4th year of the test period

At the last 5-6 weeks of the 4th year, the pH increased from stable 2.4 to 2.6, which means that the concentration of H^+ in the seepage decreased from 4.0 to 2.5 $^{mmol}/_{l}$, which is almost 40 % dropping (FIG 16). Near the pH change, the redox potential becomes more volatile and starting to increase. Also visible mineral alterations (FIG. 17) took place, as a hard, a reddish lateral layer appeared 3 cm below the top in the thickness of 2-3 mm. Moreover the sample above this layer become reddish-brown again, as same as the original sample colour had before the test.

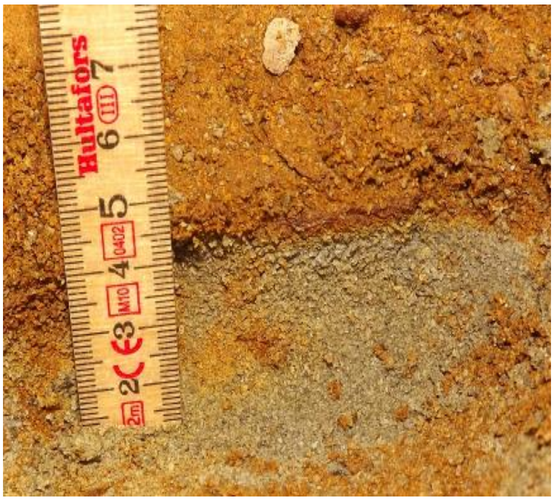


FIG. 17: The three well separateable zone

From the bottom, the middle and the surface zone of the column filling sampling was done, as well as from the solid zone. XRD and XRF analysis were done on these samples, to define the mineralogical changes. The XRD result of the hard layer did not determine the changes, as iron oxyhydroxide or oxide phase was not found, but the analysis measured 7.0% of amorphous amount. As it was visible on the pH and Eh data (FIG. 16) the changes were quick, so the secondary mineral formation also. This indicated, that the formed mineral phase with high probability has to be amorphous, which non-crystallized phase was proved by the XRD measuring.

The XRF results gave the key. As the main iron containing phase was the pyrite, the Fe and S concentration in the zones has to be in the same ratio, so has to be parallel. This is visible in the XRF measuring (FIG. 18). Only the searched solid layer produced a different ratio. As the Fe content is calculated from the S content with the Fe:S ratio – which is constant in the other part of the filling material, less amount of Fe should be in the solid layer, marked with yellow intermitted line and dot. This difference proves, that other Fe content mineral has to be in that zone and not only the pyrite. It has to be in oxyhydroxide or oxide phase and amorphous form.

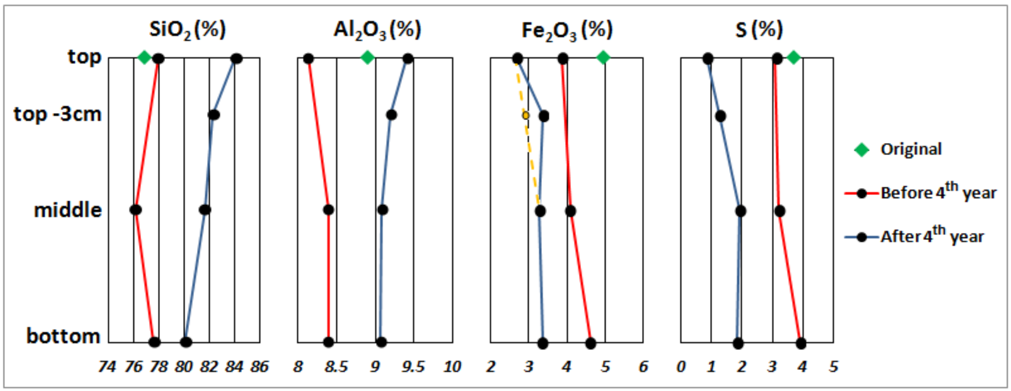


FIG. 18: Si, Al, Fe and S content of the original, before and after the 4th year sample

From the solid layer polished section was made. Electron microscope and microprobe analysis were done on it. The high brightness contrast on the BSE image (FIG. 19) shows difference in average atomic weight. This image represents well the strongly oxidizing pyrite (a), which is covered or even encapsulated into secondary iron oxyhydroxides – like goethite (b) – in the solid lateral layer in sample BOL 6-9. The reddish-brown colour of this 2-3 mm thick hard layer also confirms this measuring.

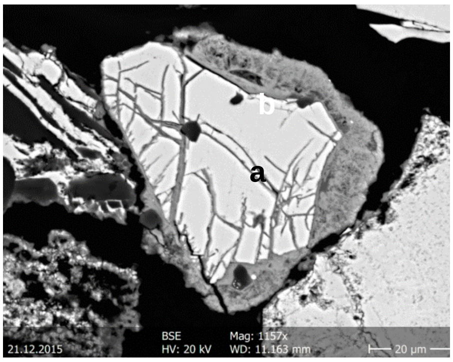


FIG. 19: Oxidation rim on pyrite

As a conclusion can be declared, that under grain size of 1mm the outcome of the humidity cell test can be questionable. A tiny changes in the chemical parameters can start a self-excitation process, thus stronger and stronger changes can take place. This can result the failure of the whole test. In case of sample BOL 6-9 this happened at the end of the 2nd year, was a luck. The humidity cell test run down successfully, as the worst case scenario was reached and even a failure of the test was also shown.

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