Pyrite Oxidation Changes in Sulphidic Mine Wastes from the Itos Sn-Ag Deposit, Bolivia

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Abstract Serious ARD effects take place in Oruro, Bolivia. Quite often the pyrite content of the huge tailings and mine waste heaps reaches or exceeds 10 %. In three consecutive years the pyrite oxidation rate was investigated on the same samples by coloumn test. This long-lasting method gave good result suitable to characterize the behaviour of the waste in long-term. Mineralogical and column test analyses show that the changes in the pyrite oxidation rate split the samples into three different stages, where the oxidation rate shows decreasing or increasing tendencies, or the oxidation is maximal.

Key Words pyrite oxidation, pyrite oxidation changes, ARD, column test, SEM, EPMA

Introduction

In the past two decades, the effect of Acid Rock Drainage (ARD) has become the leading environmental problem in metal mining. Weathering starts to degrade sulphidic type ore, which is unstable on the surface environment, resulting low pH and mobilizes heavy metal contamination. The release of ARD to surface- and groundwater deteriorates the water quality and may cause depletion of alkalinity, acidification, bioaccumulation of metals, accumulation of metal in sediments, effects on habitats, elimination of sensitive species and unstable ecosystems.

Following the "nature pays principle", in the Itos mine, a polymetallic vein deposit was mined for silver and tin until 1990, giving one third of the world's silver production in the 19th century (Chance 1948/a and b), leaving behind a great number of huge tailings and mine waste heaps. Quite often the pyrite content of the waste reaches or exceeds 10 %. Oxidizing sulphides produce serious acid rock drainage affects in Oruro, the mining town next to the mine wastes heaps. These processes can be characterized by the pH 1 of the seepage water, which mobilizes heavy metals from the waste itself or the neighbouring rocks (Walder et al 2010).

In three consecutive years the pyrite oxidation rate was investigated on the same seven samples by column test, which was complemented with mineralogical analyses (EPMA, XRPD). Five-to-seven-month pauses were left between the coloumn test periods, which allow mimicking the alternation of wet and dry periods, typical of the climate of Oruro. Thus the results give much more information than the oxidation rate for an individual coloumn test period, showing the changes by time.

The column test show that samples can be split by the changes of the pyrite oxidation rate into three different stages: where the oxidation rate shows increasing (marked type "A") or decreasing tendencies (marked type "C") or where the oxidation is maximal, so stable in the different years (marked type "B").

Theoretical part and the samples

As it was mentioned in the previous part, the problem is caused by the oxidizing iron sulphides – mainly pyrite – when it reacts with water and oxygen at surface conditions as shown in equation (1) (Seal et al 2003).

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

For investigating the oxidation rate of the samples, a special combination of humidity cell and coloumn test methods was used. In the column test, experiments can be used to determine the kinetic behaviour of wastes when exposed to atmospheric weathering (sub-aerial storage), or stored under water cover (sub-aqueous storage). The advantage of the humidity cell test is that, primary reaction products are flushed out by rinsing water (Lapakko 2003).

The main concept for the experiments was that using the column test, continuous airflow was pumped through the samples to maintain the maximal rate of pyrite oxidation. The through flowing air is more than the pyrite could use for its oxidization. In this way the oxidation rate is controllable and maintained as maximal during the column test, so the process works like a "worst case scenario". In cyclic time periods the samples were washed through and the seepage water was analysed for basic chemical parameters, anion and cation content.

Using equation (1), the pyrite oxidation rate could be determined in four different ways, such as 1) from the oxygen consumption, 2) the sulphate or 3) iron content and 4) from the H^+, which defines the pH. In this paper, pyrite oxidation rate was determined by inverse calculation from pH, which could be easily and accurately measured, thus the H^+ content in the seepage could be determined correctly. Based on equation (1), it was shown that the correlation ratio between the pyrite and H^+ is 1:2, because each mole of pyrite results in 2 moles of acid. In the column test 1000 cm^3 destilled water was used for flushing, thus theoretically total oxidation of 59.99 mg pyrite is needed for 1 dm^3 of 1 mmol/l H^+ content seepage.

The masses of the samples were premeasured, so for better comparison the results were calculated back to mass unit of oxidized pyrite for each kilogram of samples. For pyrite oxidation rate we use equation (2), to be determined from the measured pH of the rinse.

$$R_{pyox} = \frac{10^{(-pH)} \times \frac{py_{mw}}{2} \times V_l \times \frac{7}{N_d}}{M_s} \qquad (2)$$

where R_{pyox} is the pyrite oxidation rate (in unit of g pyrite / week / kg of sample), py_{mw} is the molecular weight of pyrite (119.98 g/mol), V_l is the volume (in dm^3) of the rinse, N_d is time (in days) between rinsing the samples and M_s is the mass (in kg) of the sample.

The aim in the column test is to reach a steady state in the oxidizing system, which could mean stability in sulphate release rate, pH or other seepage water parameters. Previous studies and practice showed that in the case of fresh pyritic samples a year (easily even more time) is needed in the column to reach a steady state, while in the case of already oxidized samples this time is shorter, covering only some months (approximately 2—4 months).

Seven samples were collected by Ingar Walder in 2007 and 2008 in Itos mining district, Bolivia from the surface vadose-zone from approximately 10–30 cm depth of the waste heaps side walls, on which the column tests were completed. The samples represent different geotechnical and mineralogical scenarios, which are shown in Table 1 (Moricz et al 2010). From the point of geotechnical parameters and pyrite content, the sample Bol 1 and Bol 3 were similar. They were collected from the same waste heap, but from different parts.

The maturation state of the sample, i.e. the residence time under field conditions will affect on the time that is required to reach the steady state oxidation during the column test. Fresh sample needs more time to start oxidizing as well as longer column test investigation to reach a steady state pyrite oxidation rate compared to the already oxidized samples.

In Oruro there were no strict mining regulations, thus the composition and the size of the waste dumps and tailing heaps are not known. The age is also uncertain, so we have no exact information about the residence time of these samples, except Bol 2, which is relatively fresh sample, because it stayed only 1—2 years as tailing. From visual, macroscopic and stereo microscopic observation we have an assumption, that the samples were stored about 15—25 years, but this is only a rough estimation.

In the three-year test period, the length of the column test was different for the individual years. The two Itos jig samples together with the Itos Granza samples underwent 3 years of analysis that means 101 days in the first one, 42 days in the second and 114 days in the third one. Whereas the three Bol samples had no column test analysis in the first year, so they underwent analysis only in the second (42 days) and third (114 days) years.

Analytical part and results

Column tests provide information to characterize the pyrite oxidation rate. Additionally analytical methods were used for determination of the individual mineral phases and mineral alterations,

Table 1 *Physical parameters and pyrite content of the 7 samples analysed*

Sample	*Residence time*	*Character*	*Grain size / main fraction*	*Pyrite content (from XRPD)*
Bol 1	15–25 years	shaking table tailing	2-15 mm / 3-5 mm	2-3 %
Bol 2	1–2 years	flotation tailing	0.1-1 mm / 0.3-0.5 mm	10-12 %
Bol 3	15–25 years	shaking table tailing	2-15 mm / 3-5 mm	2-3 %
Itos jig 1	15–25 years	jig tailing	0.5-25 mm / 2-5 mm	6 %
Itos jig 2	15–25 years	jig tailing	0.5-25 mm / 2-5 mm	4 %
Itos Granza 1	15–25 years	waste rock	0.5-40 mm / 4-7 mm	5 %
Itos Granza 2	15–25 years	waste rock	0.5-40 mm / 4-7 mm	4 %

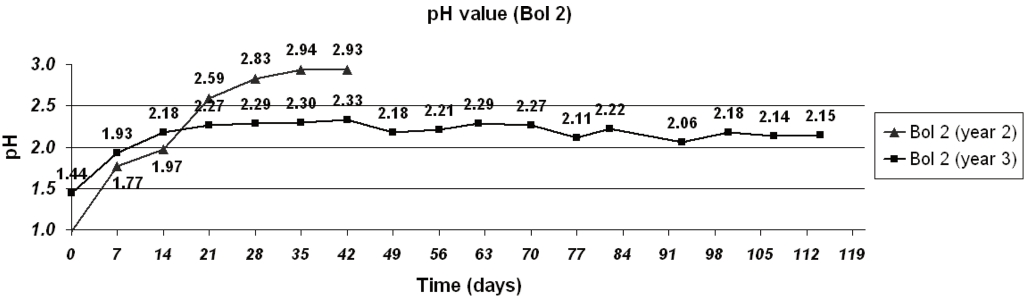

Figure 1 *The pH changes of the sample Bol 2 during the investigation period*

such as XRPD was used for pyrite content analysis and SEM + EPMA for the definition of mineralogical composition and texture properties.

As it was already mentioned in the Theoretical part, the pyrite oxidation rate was determined by the pH value, based on equation (1) and (2). As a simple example, Figure 1 shows the pH values of the seepage water from the column test in the case of Bol 2 flotation tailing sample. Each year column test started with an up-running part, caused by the effect of the first flushes, where the secondary minerals, accumulated during the dry period were dissolved and washed out. After this quickly changing period, the pH has been stabilized, the stable pH refers to the pyrite oxidation. For the calculation these stable periods were used, such as year 3 from day 21st till day 114th (Fig. 1).

In year 2, when only 42 days (6 weeks) were available for running the tests, for the pyrite oxidation rate calculation, the pH values from the last 2—3 weeks were used. Figure 1 shows that even during this short time the pH became stable enough to do the oxidation rate calculations.

The following three figures show the changes in oxidation rate in the consecutive years. Figure 2 introduces the three samples called Bol 1, 2 and 3, Figure 3 shows the two Itos Granza waste rock samples while Figure 4 presents the two Itos jig tailing samples.

To investigate the mineral alteration and pyrite oxidation, scanning electron microscope analyses were completed on samples before the column test, at Department of Mineralogy and Petrology at the University of Miskolc. The SEM analysis also proved that the samples have already been strongly corroded. In addition to the primary minerals – such as quartz, pyrite, galena and cassiterite –, secondary sulphates (various types from the jarosite subgroup and gypsum), different iron oxi-hydroxides and oxides were found.

Intensive pyrite corrosion was detected both in tailings (Itos jig 1 and 2) and waste rock samples (Itos Granza 1 and 2) where the pyrite oxidation was usually complemented by formation of secondary iron sulphates. In Figure 5, a corroded pyrite (Py) crystal with cassiterite grains is shown from the sample Itos Granza 2. Strongly corroded pyrite (Py) particles with secondary iron sulphates

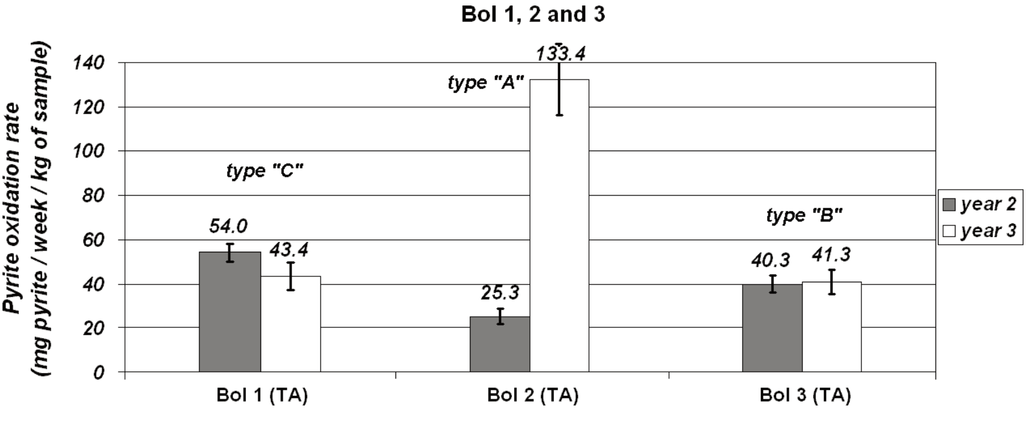

Figure 2 *Changes of the pyrite oxidation rate in samples Bol 1, 2 and 3.*

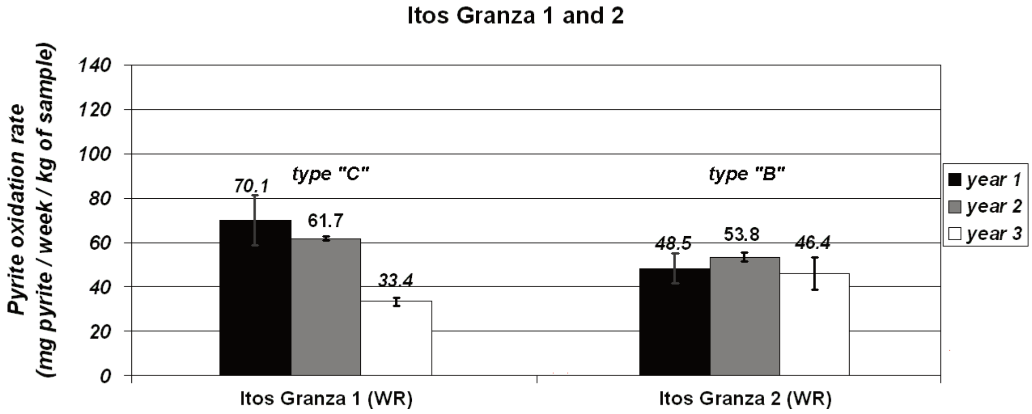

Figure 3 *Changes of the pyrite oxidation rate in samples Itos Granza 1 and 2.*

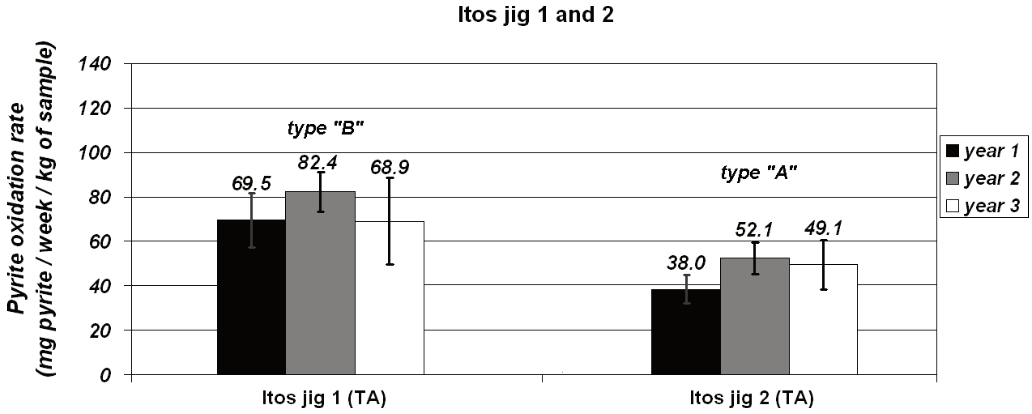

Figure 4 *Changes of the pyrite oxidation rate in samples Itos jig 1 and 2.*

are in Figure 6 from sample Itos Granza 1.The image of Figure 7 shows secondary gypsum formation on galena and pyrite crystals in samples Itos jig tailing 1 (Moricz et al. 2009).

Discussion

Comparing the stabilized pH values, thus the pyrite oxidation rates for the consecutive test periods, the maturity of the samples could be assessed. The samples can be split into three different stages: fresh / weakly oxidized, premature / partly oxidized and mature / strongly oxidized. Other important indicators are the corrosion textures of pyrite and the appearing different secondary mineral groups.

The following stages are determined:

In the *weakly oxidized stage* (marked type “A”) the pyrite oxidation rate is increasing in the consecutive years. Samples Bol 2 (Figure 2) and Itos jig 2 (Figure 4) are good representations of this type of behaviour. In the beginning oxi-hydroxide minerals appear as alteration products after the sulphides. Then the pH goes below 2—2.5, so the oxi-hydroxide minerals dissolve back and under such a low pH only sulphate minerals are formed, such as jarosite, melanterite or gypsum. 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 (marked type “B”) covers the samples Bol 3 (Figure 2), Itos Granza 2 (Figure 3) and Itos jig 1 (Figure 4), where the pyrite oxidation is maximal, thus stable – changes only within a few percentage – in the different years. The maximal pyrite oxidation rate also means that this stage has the lowest pH, which keeps for longer time. In the beginning of this stage still the sulphate minerals will be the dominant secondary

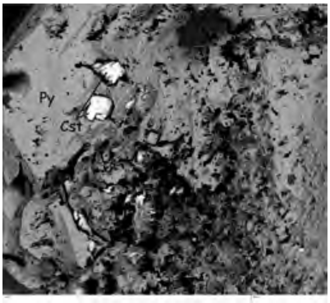

Figure 5 *Corroded pyrite with cassiterite in Itos Granza 2*

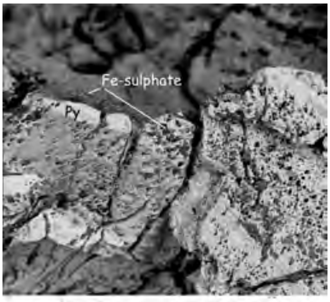

Figure 6 *Altered pyrite surface with iron sulphates in Itos Granza 1*

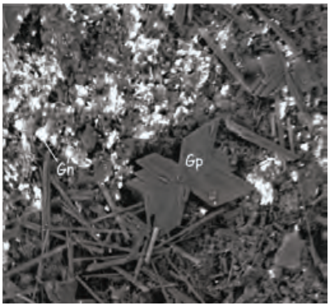

Figure 7 *Well-developed twin gypsum crystal in Itos jig 1*

phases, but in the end of the stage as the pyrite oxidation rate starts decreasing and the pH increasing, beside the sulphates, some oxi-hydroxide minerals can appear.

Strongly oxidized stage (marked type "C") includes the samples Bol 1 (Figure 2) and Itos Granza 1 (Figure 3), 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.

Conclusion

The three stages shown above are members of a natural progression for weathering of iron sulphide containing tailings and waste rocks. The fresh material starts oxidizing with increasing rate, then with time the reaction rate becomes stable, and finally decreases. The complete process looks like a bell shaped curve as it is shown on Figure 8, where a theoretical pyrite oxidation curve is present. The graph is illustrating waste rocks were there is no or little neutralising / buffering reactions, such as massive sulphide deposits and polymetallic veins like the Itos deposit.

This three-year-long investigation indicated the maturity of the tailings and waste materials. Table 2 gives an overview of the different oxidation rate stages of the samples. The three stages define also the rates of the emitted pollution and heavy metal mobility.

In the first – type "A" – stage the pollution and heavy metal content will increase with time. If the material is in the middle stage, the oxidation and the heavy metal mobility are at the maximum, as the pH is the lowest in this stage. The third, the strongly oxidized stage means that the tailing or waste rocks are already after the peak pollution. The slowing down reactions ensure that the heavy metal mobility decreases as the pH increases. The normalizing pH controls mineral alteration, as iron oxi-hydroxides and oxides are produced. Finally a gossan type mineralization could be formed as a cover on the waste.

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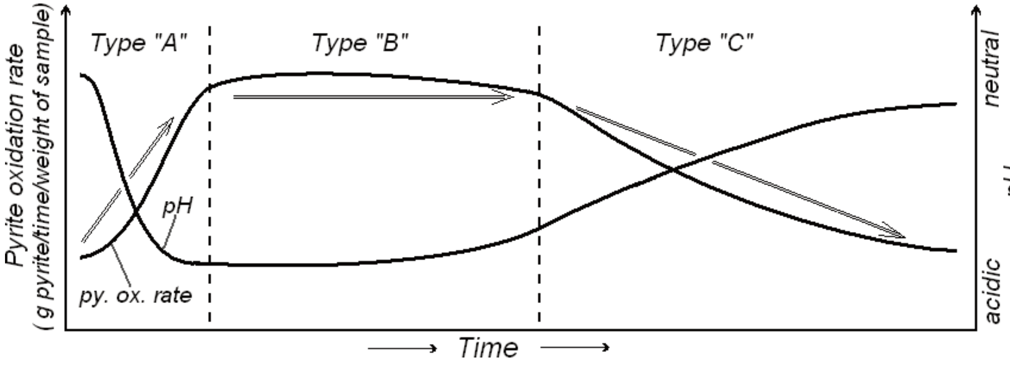

Figure 8 *Pyrite oxidation changes in function of a long term process (after Ritchie1994)*

Table 2 *Overview of the behaviour in the future*

Sample	***Oxidizing stage***	***Behaviour in the future***
Bol 2 ***Itos jig 2***	weakly	increasing in pollution and heavy metal mobility, decreasing pH; pollution peak in the future, further problems; the situation calls for management
Bol 3 ***Itos jig 1*** ***Itos Granza 2***	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 required
Bol 1 ***Itos Granza 1***	strongly	decreasing pollution and heavy metal mobility, increasing pH; pollution peak in the past, no further increasing problems; monitoring is not required

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