

PYRITE OXIDATION UNDER CIRCUMNEUTRAL pH CONDITIONS

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1. Introduction

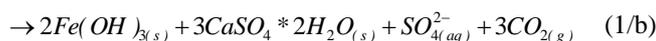
In the last two decades, the effect of Acid Rock Drainage (ARD) has become the leading environmental problem in the mining of sulphidic type ores. In sulphidic mine wastes a principal weathering process is the sulphide oxidation, resulting in low pH and mobilizing heavy metal contamination.

Usually the extracted sulphidic ores consist of different metal sulphides with various oxidation rates. The most common, iron-bearing sulphides – pyrite, pyrrhotite – usually became part of the mining waste and are stored in mine waste facilities where these minerals are exposed to atmospheric water and oxygen that results in quick oxidation processes. However, if neutralizing minerals are available, they can buffer the acid production and hence reduce the heavy metal mobilization.

From a mining waste management point of view, a crucial question is whether there are enough available buffering minerals that can consume acidity. Regulations require that the neutralisation potential should exceed by 3-4 times the acid producing potential to consider the waste material safe from ARD production. However, this does not mean that pyrite oxidation stops even under these conditions. In the porous waste rock material in presence of water and oxygen, pyrite grain surfaces start oxidizing, thus creating an acidic micro-environment. Calcite, as a quick neutralizing mineral, is able to maintain a pH range. The net chemical reaction does not show acid production, but sulphide oxidation with possible metal leaching takes place.

Neutral rock drainage (NRD) was detected at some mining waste facilities (e.g. mines in the Kola Peninsula, Russia (high-F), the Schwaz and Brixlegg Mines, Austria (high-Sb), the Endako Mine, BC, Canada (high-Mo)), where weathering and consequent metal leaching takes place under circumneutral conditions [1].

The focus of the current work is to prove whether the ARD effects and pyrite oxidation could happen in the zone of neutral pH and to estimate the oxidation rate. Moreover, the authors would like to emphasize the importance of proper waste management and planning of mining waste facilities. This research work was completed to prove whether Equation (1) takes place, to demonstrate the presence of the oxidation process, even if the discharging pH is not acidic.



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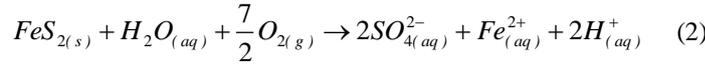
Based on Eq. (1), the sulphide oxidation can be indicated by the following: an iron-hydroxide crust on the surface of the fresh pyrite grains, gypsum coating on the surface of the calcite, detection of the sulphate concentration in the seepage, the appearance of released carbon-dioxide and increasing oxygen gas consumption.

In the experiment, a kinetic test (column test) was done on a sulphidic mine waste sample from Recksk to speed up the sulphide oxidation and therefore mimic the long-term geochemical behaviour of the sulphidic mining waste material.

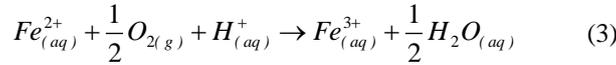
2. Theoretical background

The most abundant sulphide minerals in most sulphidic waste facilities are pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$). Only iron-bearing sulphides produce acid during their oxidation. Iron release itself is not so toxic, but the acidification promotes toxic element release from other sulphides such as sphalerite (ZnS), chalcopyrite ($CuFeS_2$), galena (PbS) and arsenopyrite ($FeAsS$) [2].

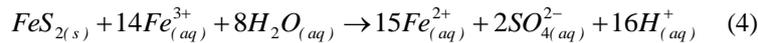
Detailed investigation of the sulphide oxidation began a few decades ago. One of the basic equations for pyrite oxidation, Eq. (2). was created by Nordstrom [3], who assumed the process to be an abiotic system, thus the oxidizer agent is the oxygen:



The Fe^{2+} – released by pyrite oxidation – may be further oxidized (3) to Fe^{3+} , decreasing the acidity by consuming a proton:



The resulting Fe^{3+} is a stronger oxidizer agent than the oxygen itself, thus it can lead to the oxidation of pyrite even in an oxygen free environment (4). Moreover, the transport of the gas is limited by slow diffusion processes, but the Fe^{3+} as a dissolved ion can move easily by seepage or water flows.



Reaction (2) can occur both abiotically or biotically. Reaction (3) is a slow reaction that requires biotic catalysis, but reaction (4) occurs quickly [4]. Reactions (2) and (3) can occur only in low pH, because the Fe^{2+} - Fe^{3+} oxidation is effective only under pH 2, catalyzed by *Acidobacillus ferrooxidans*, which can maintain such a condition.

If the pH is above 4, the Fe^{3+} can be hydrolyzed and precipitate (5) as Fe^{3+} -hydrite, decreasing the amount of the oxidizer agent in the aqueous solution. Although ferrihydrite is commonly assumed to be the product of sulphide oxidation, goethite (6) is much more commonly observed and is abundant in sulphidic wastes [5].



On the other hand, the reverse of the equation (5) and (6) can be occur as well, if the acidity goes under a limit (approximately pH 3.5) which is acidic enough to dissolve back the

already precipitated solid mineral phases. The leading oxidizer agent - oxygen or Fe^{3+} - depends on the pH value. Singer and Stumm suggested that Fe^{3+} is the dominant oxidant under low pH conditions [6].

If there are neutralizing minerals in the system, they consume the acidity directly, slowing the oxidation rate and stopping the metal release by precipitation. The neutralizing reaction is written in Equation (7), which shows how calcite can dissolve back, and thus can neutralize the acidity. Figure 1 summarizes the above-listed reactions.

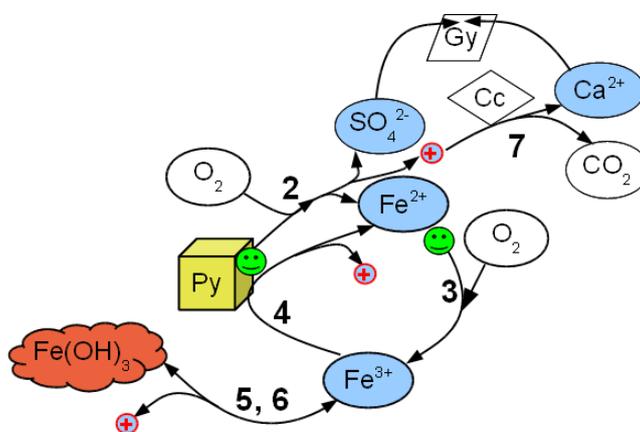
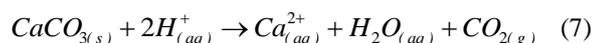


Figure 1. Schematic representation of reactions 2, 3, 4, 5, 6 and 7. Abbreviations and symbols: Py: pyrite, Cc: calcite, Gy: gypsum, ☺: bacteria, +: H^+ ion.

3. Analysis and results

A sulphidic sample was collected from the waste dump of the Recsk deep level (East Mátra Mts., NE Hungary) from the level -900. The ore body is a copper porphyry and skarn copper deposit. The sample was taken from the extracted material of the “Western 3” ore exploration adit, from the contact of the exoskarn and the carbonates. The waste dump on the surface – approximately 300-350 tonnes – makes up only a small part of the original amount, because most of it has already been transported to other waste dumps. For the experiments boulders of 10-20 cm diameter were selected from the waste material. After the removal of the secondary mineralization from the boulders, they were crushed to under 2 mm. This crushing gave us a fresh, non-oxidized surface for the kinetic test analysis.

The major minerals of the investigated sample are about 40% quartz, 40% pyrite, 12% calcite, and 3% chalcopyrite. There is some galena, sphalerite and dolomite, as well.

3.1 Column test

Three kg of this freshly crushed sample was investigated by column test at Kjeøy Research and Education Centre, Norway, to mimic the long-term behaviour of the sulphidic mine wastes. The column test was done for 119 days (17 weeks). On 3 kg of the sample, with a grain size of 1-2 mm, continuously humid air was pumped through to provide the oxygen and humidity that speeds up and maintains the pyrite oxidation. Once a week the sample was rinsed through with 1000 ml distilled water and the seepage was analyzed for basic chemical parameters (pH, alkalinity), anion and cation content.

The pH curve (Figure 2) clearly indicates that after 2 weeks the system has already stabilized. The circumneutral pH (around 7.2) shows that the presenting calcite buffers the acidity and can balance the system. The instability of the first 2 weeks and the initial lower pH was caused by the effect of the “first flush”: some easily soluble secondary sulphates remained on the grain surfaces, which dissolve back, resulting in lower pH.

The same effect is visible in the sulphate concentration curve (Figure 2). The gradually decreasing sulphate release after the first 2 weeks shows that there was some available fine-grained – therefore quickly oxidizing – pyrite in the sample. As the fine-grained pyrite is consumed, the sulphate release gradually stabilizes.

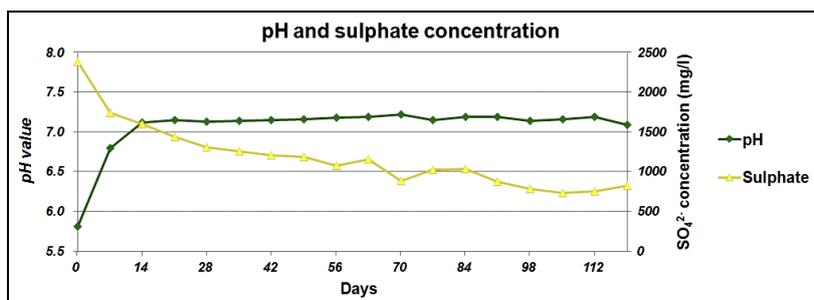


Figure 2. pH value and sulphate content in the seepage of the column test

At the end of the test period, the column was sealed to air for a week to measure the oxygen consumption and carbon dioxide release by the oxidation (Eq. (2)) and neutralizing (Eq. (7)) process. Figure 3 shows clearly that carbon dioxide content increased continuously, which shows the dissolution and efficient neutralizing effect of calcite, while the decreasing oxygen content shows the presence of the oxidation process.

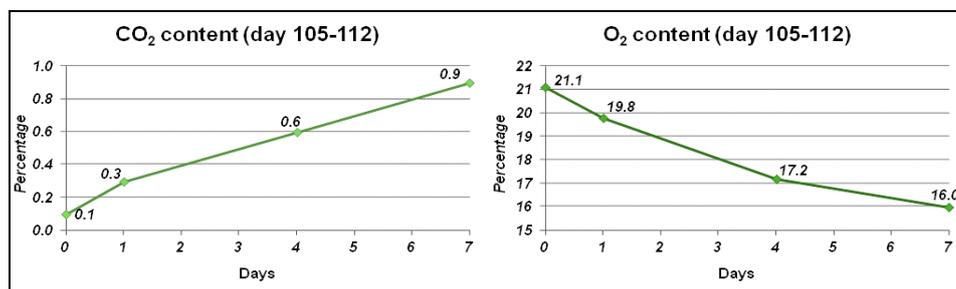


Figure 3. CO₂ release and O₂ consumption in the column

3.2 Mineralogical changes

Equation (1) tells us that if pyrite is oxidizing and calcite is present, a secondary iron mineral crust should form on the surface of the pyrite grains. Moreover, taking into consideration Eqs. (4) or (5), gypsum coating needs to appear on the surface of the calcite. Backscattered SEM images were taken from the sample surface. Figure 4 shows the non-altered pyrite surface with brighter colour and the secondary iron phases – caused by alteration of pyrite – with darker grey colour. The iron oxide phases appear as tiny plates and cover the pyrite surface.

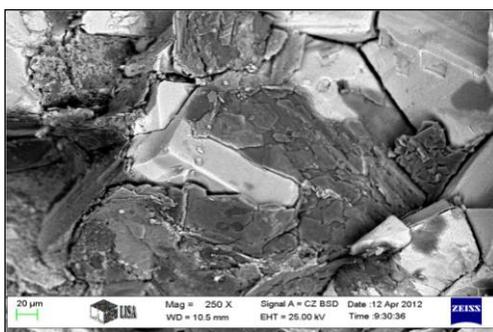


Figure 4. Secondary iron oxide / hydroxide mineral coating on pyrite surface.

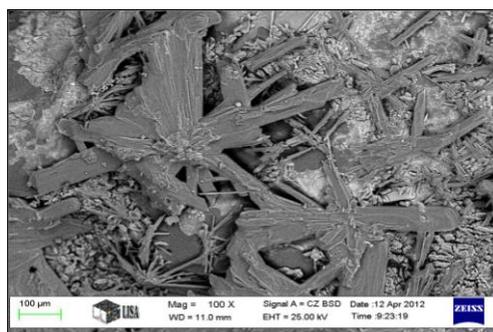


Figure 5. Gypsum needles on calcite grains. Backscattered SEM images

Close to the appearance of secondary iron minerals, tabular crystals of gypsum were also found as a stable end-product after the alteration of pyrite. Figure 5 shows that on the eroded surface of the calcite – appearing with bright colour – tiny, darker gypsum needles are present. This feature means also that the gypsum has already started to cover, thus encapsulate the calcite grains. This phenomena shows that the still effective neutralizing capacity will decrease in the future, due to the decreasing free reactive surface of calcite.

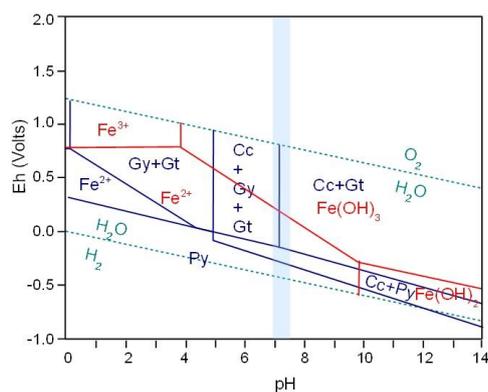


Figure 6. Eh-pH diagrams of C-Ca-Fe-S-H₂O (blue) and Fe-O₂-H₂O (red) systems at standard conditions (calculated by HSC Chemistry). Vertical blue strip: measured stable pH range of the seepage water.

4. Conclusion

Pyrite oxidation of the copper-porphyry and skarn mining waste material was detected in experiments by the sulphate concentration (Figure 2) in the seepage, the appearance of carbon-dioxide and decrease of oxygen gas in the air-tightly closed sample holder (Figure 3) and by the detected secondary iron mineral crust on the surface of the fresh pyrite grains (Figure 4), as well as by a gypsum coating on the surface of the calcite (Figure 5). Conversely, no acidity appears, because of efficient neutralization by the calcite (Eq. (7)).

Although the Eh-pH diagram in Figure 6 shows standard conditions, it shows that the Eh-independent stability: calcite + goethite \leftrightarrow calcite + gypsum + goethite occurs at pH 7.2 – 7.3. The measured and rather constant pH of the seepage was around 7.3, which indicates that the system is upper-limited at this pH by the calcite dissolution. The diagram indicates that in less oxidative micro-environments, dissolved Fe²⁺ can appear within the porous waste rock, which is favourable for pyrite oxidation.

As the amount of the pyrite in the sample is over double the amount of calcite, ARD can be predicted ahead in an uncertain time. Kinetic test results show that the rate of oxidation in the pyritic system is continuous and stable, until the point where the neutralizing capacity is higher than or at least equal to the acid production. After that the oxidation will increase exponentially, because the pyrite oxidation works as a chain reaction, and there will be no available buffering silicates in the waste rock. Without appropriate waste management the increased pyrite oxidation will lead to acidification accompanied by toxic element mobilization from other presenting sulphides such as calcopyrite or galena, although the waste rock heap currently does not show any sign of environmental risk.

Acknowledgement

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