Weathering of waste rock in different climatic conditions – a kinetic freeze/thaw and humidity cell experiment

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Abstract Ferrous and ferric sulphates and (oxy)hydroxides can grow on pyrite surfaces and slow oxidation rates. However, in northern climates, repeated freeze/thaw cycles can cause cracks, channeling and exposure of new surfaces. In the present study, weathering in a repeated freeze/thaw experiment was compared to a regular humidity cell experiment. Introductory results (after 17 weeks) show very small changes in pH for the freeze/thaw system (pH around 5), while pH in reference and humidity cell systems decreased rapidly the first weeks (to around 4). An increase in electrical conductivity, sulphate and major ions was noticed in the two latter systems.

Key Words Frost, pH, leaching, trace elements

Introduction

Acid rock drainage (ARD) is a large environmental problem, mainly arising from mining of sulphidic ore. When some sulphide minerals, like pyrite (FeS_2), are exposed to oxygen they produce acid. Low pHs then promotes leaching of primarily iron and cationic trace elements like copper, zinc and lead and hence affects the surrounding environment by bringing these metals in solution (Chandra and Gerson 2010).

The shrinking-core model is widely used to describe reactions at a particle's surface. According to the model, a product layer forms around the core and the unreacted core shrinks while the product layer grows (Safari *et al.* 2009; Szubert *et al.* 2006). In the case of pyrite oxidation, a product layer consisting of ferrous and ferric sulphates and (oxy)hydroxides forms on the surface of the pyrite particle (fig. 1) and as the oxidation reaction proceeds, oxygen transport to the pyrite surface is retarded and hence slows oxidation rates (Jerz and Rimstidt 2004).
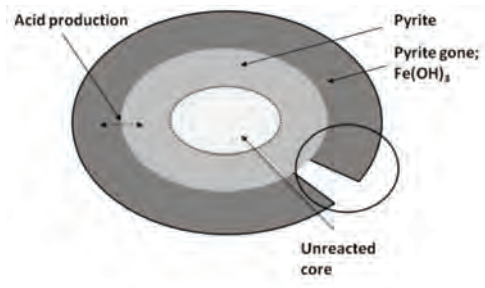
The aim of this study was to investigate effects from freezing and thawing on oxidation rates and more specifically: if the product layer formed is affected by physical weathering caused by repeated freezing/thawing cycles. A scenario of a crack in the product layer is illustrated in fig. 1, enabling exposure of unoxidized pyrite surfaces and accordingly further acid production. If the product layer is susceptible to break from the physical stress, more effects from freezing/thawing would be expected in regions with no permafrost but many freeze/thaw cycles in the spring. Regional climate condition could therefore be a key parameter for ARD prevention and mitigation and in that case, climate specific test methods for ARD generation are crucial.

Materials and Methods
Waste rock

Waste rock was sampled at the historical mine site Ljusnarsbergsfältet in Kopparberg, approximately 200 km NW of Stockholm, Sweden. Sulphides (pyrrhotite, pyrite, chalcopyrite and sphalerite) were present in all rocktypes but with different matrix. About 60 % of the rocks had a matrix dominated by amphibole skarn, 35 % had a silicified matrix ("ore-quartize"), 4 % had a biotite-amphibole-skarn matrix and 1 % a biotite-flourite-amphibole skarn matrix.

Kopparberg is located in a mining region called Bergslagen with many abandoned mines, three operating and three to five planned mines. Bergslagen is situated in the "subarctic" climate zone, along with e.g. Whitehorse and Yellowknife, Canada. Contrary to the more northern parts of Sweden, there is no permafrost in Bergslagen. Ground frost and repeated freezing and thawing is however normal for the region.

Figure 1 Schematic illustration of the shrinking-core model and a crack in the product layer, enabling exposure of unoxidized pyrite surfaces and further acid production.

Experimental

Experiments started February 2011. The collected rocks were crushed with a jaw crusher and then screened. A fraction of 1—4 mm were taken out and distributed into six 250 g samples. Each 250 g sample was put in a 2 L plastic container, and was thereafter treated according to a weekly leaching scheme. Leaching schemes for the systems are shown in fig. 2. Two samples were treated according to the humidity system, two according to the freeze/thaw system and two according to the reference system (fig. 2).

Climate chamber – Humidity system

The humidity chamber was constructed from three 2 L containers which had been cut off and piled on each other. The bottom container collected the fluid and had a hole that was fitted with a 4 mm hose to release air. The sample was placed in the middle container. For air /water to pass through the sample 20 4 mm holes were drilled in the bottom of the container. Under the sample in the bottom of the container was a filter that prevented the smaller particles from leaving the sample. The top container was used as a lid and air inlet.

For the first 3 days the sample was treated with dry air and after that it was treated 3 days with humid air. This left one day for leaching and testing. The humid air was obtained by deionized water heated by an immersion heater to 25 °C in a 10 L container. Air was pumped into the container, where it was divided into small bubbles. The humid air was led through a tube that went into the upper container of the humidity chamber and out through the hole in the lower container.

Freeze/thaw system

In the freeze / thaw test, the same kind of containers and the same amount of sample was used as in the climate chamber test. The samples were frozen for 3 days at -20 °C and were then brought to room temperature (16 °C) where they thawed and then stayed for 3 days, followed by leaching.

Reference system

Two reference containers were also rinsed and sampled weekly. In the reference test, the same kind of containers and the same amount of sample was used as in the previously described systems. The reference samples stayed at room temperature (16 °C) throughout the whole cycle, followed by leaching.

Leaching and Analytical

Samples were leached with 500 ml deionized water and the samples stayed immersed in the water for one hour. Samples were collected for analysis of pH, Eh, electrical conductivity, alkalinity/acidity, inorganic anions and major and trace elements.

Electrical conductivity, pH and redox potential were determined immediately after sampling using relevant electrodes. Alkalinity (end-point pH 5.4) and acidity were determined through titration with HCl and NaOH, respectively. Inorganic anions (chloride, fluoride and sulphate) were analysed with ion chromatography. Elemental analysis was performed using ICP-MS. Photographs were taken weekly in order to study the evolution of the secondary precipitates. Also, the time it took for the leach solution (deionized water) to pass the material was noted, as a proxy for permeability.
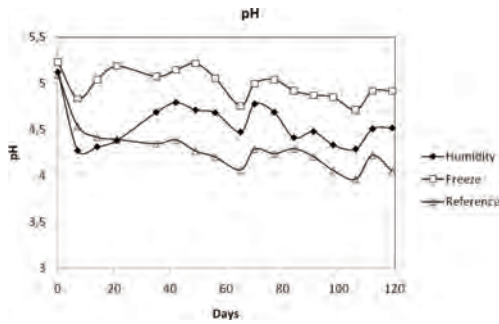
Results and Discussion

General parameters (pH, electrical conductivity, acidity and sulphate) are shown in fig. 3—5. All three systems were run in duplicates and gave almost identical results. For the reader's convenience, all values given in the figures are mean values of the duplicates.

pH started around 5.1 in all systems where after it immediately dropped in the humidity system (down to pH 4.3) and in the reference system (down to pH 4.5) (fig. 3). pH in the freeze system has been fairly stable around 5 since the beginning of the experiment (fig. 3). Between the third and fourth week (day 25), there was a shift between the humidity and reference system in both pH (fig. 3), electrical conductivity (fig. 4, left) and
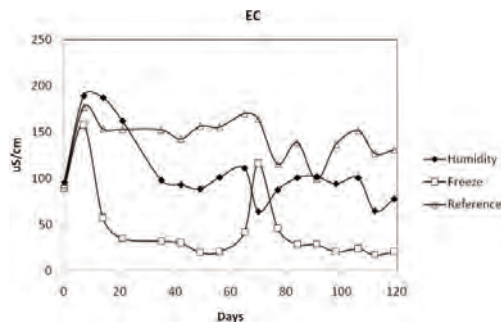

Figure 2 Leaching scheme for the three systems. All systems were run in duplicates.

Figure 3 *pH in humidity, freeze and reference systems since the start of the experiments in February 2011 (day 0) to June 2011 (day 120).*
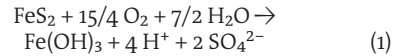
and trace elements (copper) are shown in fig. 6—8. Iron concentrations were around 15 mg/L at the start, where after it rapidly increased to around 25 mg/L in the humidity and reference systems (fig. 6). In the freeze system, iron concentration instead decreased to around 2 mg/L (fig. 6).

Molar ratios between sulphate and iron (SO_4^{2-}/Fe) were very close to two for the reference and humidity systems. This was in agreement with the stoichiometry for pyrite oxidation (Eq. 1) (Li *et al.* 2007). For the freeze system, this ratio was varying between two and six.

acidity (fig. 4, right). This shift indicated a more rapid wash out of surface weathering products in the humidity system than in the reference system. As the loosely attached weathering products had been washed out, pH increased (fig. 3) and electrical conductivity and acidity decreased (fig. 4) in the humidity system.

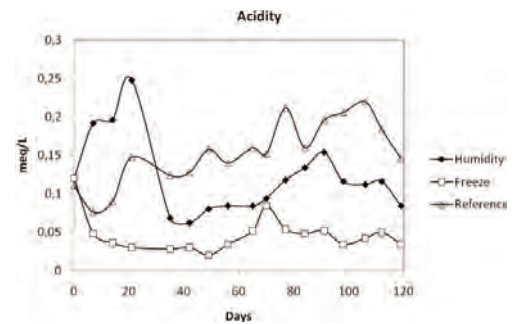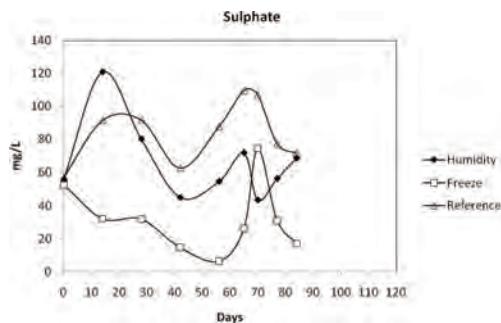Selected major (iron, magnesium and calcium)

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow$$
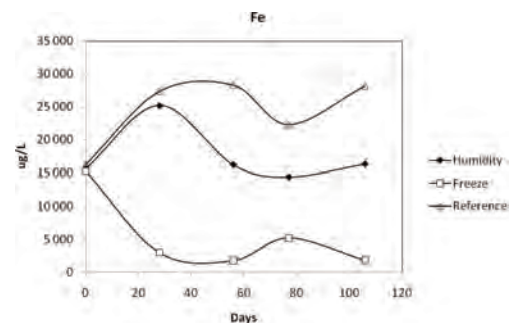$$Fe(OH)_3 + 4\ H^+ + 2\ SO_4^{2-} \quad\quad (1)$$

Calcium and magnesium are good indicators of weathering, through dissolution of buffering minerals like e.g. magnesite, calcite and/or magnesium silicates. Concentration of especially calcium was higher in the reference system than in the humidity system already from the beginning, while magnesium concentrations were almost the same for these two systems (fig. 7). Both calcium and magnesium concentrations in the freeze sys-

Figure 4 *Electrical conductivity (EC) and acidity in humidity, freeze and reference systems since the start of the experiments in February 2011 (day 0) to June 2011 (day 120).*

Figure 5 *Sulphate concentrations in humidity, freeze and reference systems since the start of the experiments in February 2011 (day 0) to May 2011 (day 90).*

Figure 6 *Iron concentrations in humidity, freeze and reference systems since the start of the experiments in February 2011 (day 0) to June 2011 (day 120).*
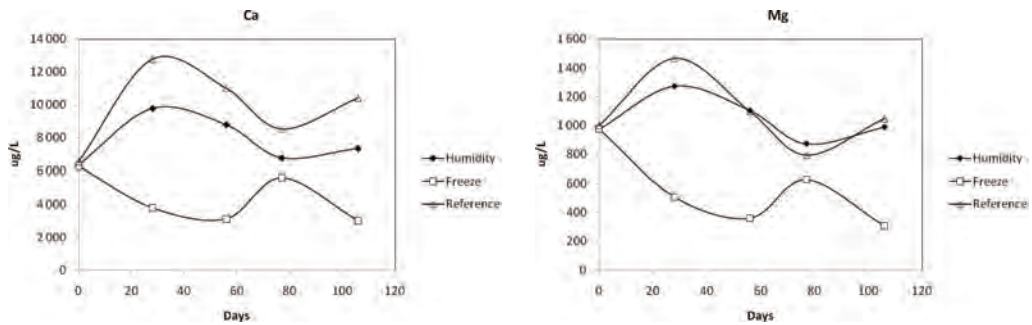
Figure 7 Calcium and magnesium concentrations in humidity, freeze and reference systems since the start of the experiments in February 2011 (day 0) to June 2011 (day 120).
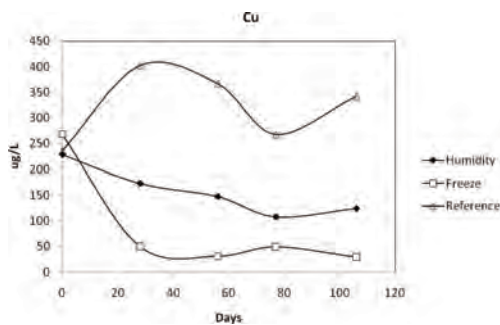

Figure 8 Cu concentrations in humidity, freeze and reference systems since the start of the experiments in February 2011 (day 0) to June 2011 (day 120).

tem were low, indicating that no particular weathering/buffering process has been initiated (fig. 7).

The degree of trace element leaching in the different systems was mainly dependent on pH. Variations in copper concentrations during the first 120 days are shown in fig. 8. Obviously, the system with the lowest pH (reference) also had the highest concentrations of copper (fig. 8). Other trace elements, e.g. lead, zinc and cadmium, followed the same trend.

No distinct color changes have been noticed from the photographs so far. However, the time it takes for the leach solution (deionized water) to percolate through the material seem to be a good indicator of secondary mineral formation. In the freeze system the leach water passed through rapidly, average time for the water to pass the material was one minute. For the reference and humidity systems the same parameter was ten and eighteen minutes, respectively.

Conclusions

At the moment, highest weathering rates are observed in the reference system, kept constantly at room temperature and leached once a week. The humidity system had a rapid initial wash out with low pH (4.3) and high acidity. Formation of secondary weathering products, preventing further pyrite oxidation, is probably the reason for the ceased weathering rate in the humidity system.

The time it takes for the leach solution to percolate through the material may be a good indicator on the degree of secondary precipitates formation (weathering products).

At this point, no conclusions regarding the effect of freezing/thawing can be made. The freeze treatment more or less seems to conserve the material rather than increase weathering rates. The experiment is however continuing and once oxidation reactions starts in the freeze/thaw system, it may be possible to see some effects from freezing/thawing on the stability of the secondary product layer.

Acknowledgements

References

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