

Impact of temperature on weathering rates – a long-term kinetic study on waste rock from Bergslagen, Sweden

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Abstract To assess the impact of different climatic conditions four weathering systems with waste rock from Bergslagen, Sweden, were followed. Secondary weathering products (ferrous and ferric sulphates and (oxy)hydroxides) on pyrite surfaces can slow down oxidation rates. It was investigated if repeated freezing/thawing could have an effect on the stability of the secondary product layer. After 90 weeks of weathering, freezing/thawing had not enhanced weathering rates, not even in combination with warm, humid air. Highest weathering rates were unexpectedly found in a reference system constantly kept at room temperature, and not in the more forceful humidity cell system.

Keywords climate, prediction, acidity, pH, iron, mineralogy

Introduction

Acid rock drainage (ARD) is a large environmental problem, mainly arising from mining of sulphidic ore. When exposed to oxygen, some sulphide minerals, like pyrite (FeS_2), 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. Re-

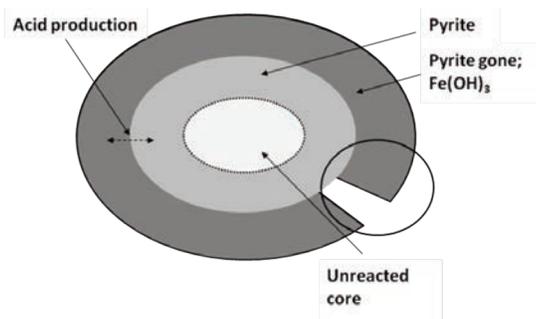


Fig. 1 Schematic illustration of the shrinking-core model and a crack in the product layer, enabling exposure of unoxidized pyrite surfaces and further acid production.

gional climate condition could therefore be a key parameter for ARD prevention and mitigation and in that case, it is important with climate specific test methods for accurate mine water chemistry prediction.

Materials and Methods

Waste rock used in the experiments was sampled at the historical mine site Ljusnarsbergsfältet in Kopparberg, approximately 200 km NW of Stockholm, Sweden. Collected rocks were crushed with a jaw crusher and then screened. A fraction of 1–4 mm were taken out and distributed into eight 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.

Waste rock

An ocular investigation of the material indicated that sulphides (pyrrhotite, pyrite, chalcopyrite and sphalerite) were present in all

rocktypes but with different matrix and that about 60 % of the rocks had a matrix dominated by amphibole skarn, 35 % had a silicified matrix ("ore-quartzite"), 4 % had a biotite-amphibole-skarn matrix and 1 % a biotite-flourite-amphibole skarn matrix. Results from XRD-analysis of the material are shown in Table 1 and elemental composition is shown in Table 2.

All systems were based on the standard protocol for humidity cell testing: weathering for six days followed by leaching with deionized water on the seventh day. Leaching schemes for the systems are shown in fig. 2. System (i) – (iii) started in January 2011, while system (iv) started in March 2012. All systems were run in duplicates

Climate chamber

The humidity chamber was constructed from three 2 L containers which had been cut off and piled on each other. The bottom container

Mineral	Formula	Weight-%
Quartz	SiO ₂	30.7
Pyrite	FeS ₂	12.3
Pyrrhotite	Fe ₇ S ₈	11.3
Magnetite	Fe ₃ O ₄	6.0
Hornblende	NaCa ₂ (Mg,Fe,Al) ₅ [AlSi ₆ O ₂₂](OH) ₂	20.7
Phlogopite	K(Mg,Fe) ₃ [AlSi ₃ O ₁₀](OH,F) ₂	8.9
Spangolite	Cu ₆ Al(SO ₄)(OH) ₁₂ Cl*3H ₂ O	3.0
Sphalerite	ZnS	3.7
Chalcopyrite	CuFeS ₂	3.4

Table 1 Results from XRD analysis on the waste rock (weight- %). The sample was finely ground and examined with XRD with CuK. Concentrations were calculated by Rietveld analysis.

Element	%	Element	mg/kg
Si	35	As	<0.3
Al	4.6	Cd	7.3
Ca	6.8	Co	110
Fe	33	Cr	400
K	0.98	Cu	8000
Mg	3.7	Ni	6.8
Mn	0.12	Pb	310
Na	0.17	S	104000
P	0.02	Zn	3800

Table 2 Elemental composition of the waste rock. Total digestion in microwave oven with nitric acid. Analysis performed with ICP-AES and (ICP-SFMS).

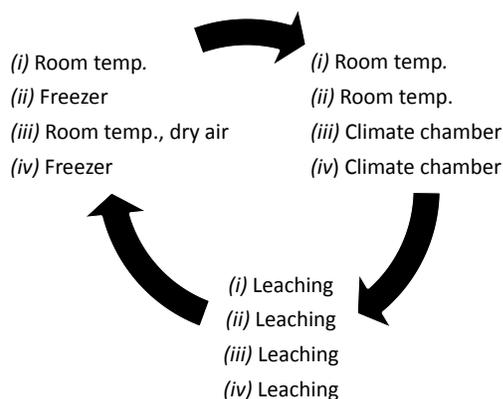


Fig. 2 Leaching scheme for the four systems. All systems were run in duplicates. (i) weathering in room temperature (6 days), (ii) weathering in room temperature (3 days) alternated with freezing conditions, -20°C (3 days), (iii) weathering in room temperature (3 days) alternated with humid air, 25°C (3 days; standard humidity cell) and (iv) weathering at freezing conditions, -20°C (3 days) alternated with humid air, 25°C (3 days).

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.

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. System (iii) was exposed for dry air at room temperature for 3 days, thereafter the climate chamber for 3 days followed by leaching (following the standard protocol for humidity cell testing; fig. 2)

Freezing/thawing

Samples were frozen for 3 days at -20°C and were then brought to room temperature (16°C) or climate chamber for system (ii) and (iv), respectively, where they thawed and then stayed for 3 days, followed by leaching (fig. 2).

Reference system

Two reference containers were also rinsed and sampled weekly, system (i). In the reference test, the same kind of containers was used as in the previously described systems. The reference samples stayed at room temperature (16°C) throughout the whole cycle, followed by leaching (fig. 2).

Leaching and Analytical

Samples were leached with 500 mL deionized water and the samples stayed immersed in the

System	Until week 36			Until week 90		
	pH	El. Cond. ($\mu\text{S}/\text{cm}$)	Acidity (meq/L)	pH	El. Cond. ($\mu\text{S}/\text{cm}$)	Acidity (meq/L)
(i)-a	4.28	109	0.18	4.30	95.0	0.15
(i)-b	4.18	117	0.18	4.19	109	0.16
(ii)-a	5.04	31.7	0.04	4.87	52.0	0.04
(ii)-b	5.02	29.2	0.03	4.85	52.6	0.05
(iii)-a	4.61	76.9	0.11	4.56	80.5	0.11
(iii)-b	4.44	90.9	0.14	4.44	78.3	0.12
(iv)-a	3.38	81.1	0.06	-	-	-
(iv)-b	4.62	54.8	0.05	-	-	-

Table 3 Average values for pH, electrical conductivity ($\mu\text{S}/\text{cm}$) and acidity (meq/L) for the different systems. Until week 90 for systems (i)-(iii) and until week 36 for all systems.

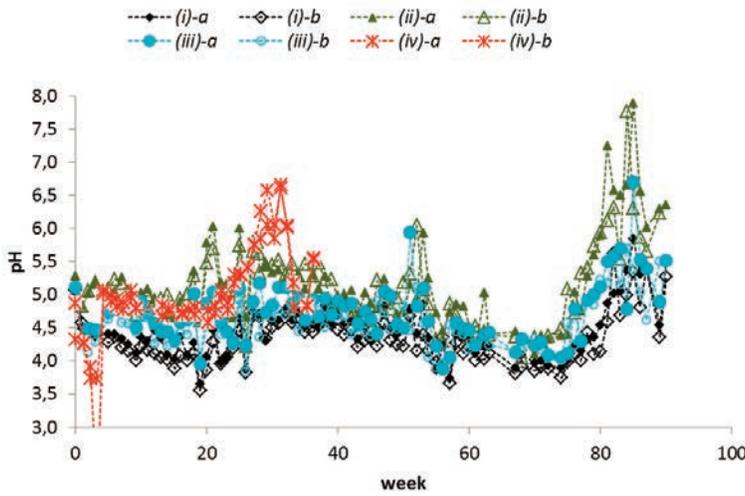


Fig. 3 pH in systems (i)-(iv) plotted against weeks of weathering, a and b denote replicates of each system.

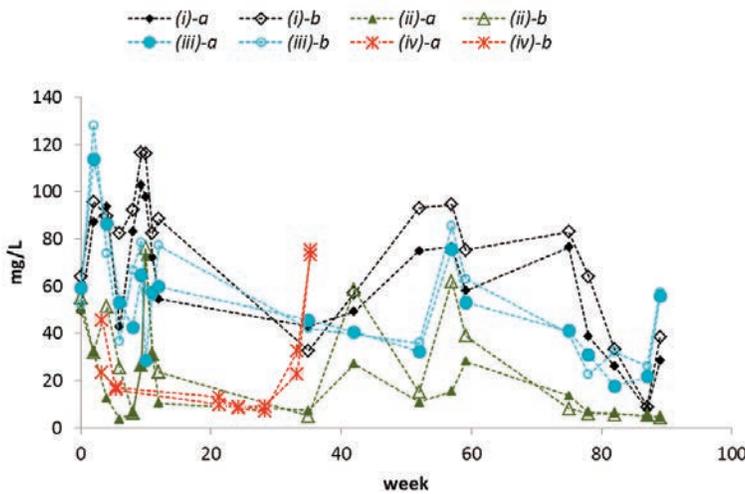


Fig. 4 Sulphate concentrations (mg/L) in systems (i)-(iv) plotted against weeks of weathering, a and b denote replicates of each system.

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.

Results and Discussion

Average values for general parameters (pH, electrical conductivity and acidity) are shown in Table 3 and pH against week of weathering is shown in fig. 3. All three systems were run in duplicates and gave almost identical results After 36 weeks of weathering average pH in the different systems were 5.0; 4.0; 4.5 and 4.2 for systems (ii), (iv), (iii) and (i), respectively. After 90 weeks of weathering for systems (i) – (iii), average pH:s were generally the same as after 36 weeks.

Sulphate concentrations plotted against week of leaching is shown in fig. 4. It is obvious that the systems with highest pH (freeze treated systems, (ii) and (iv)) have the lowest

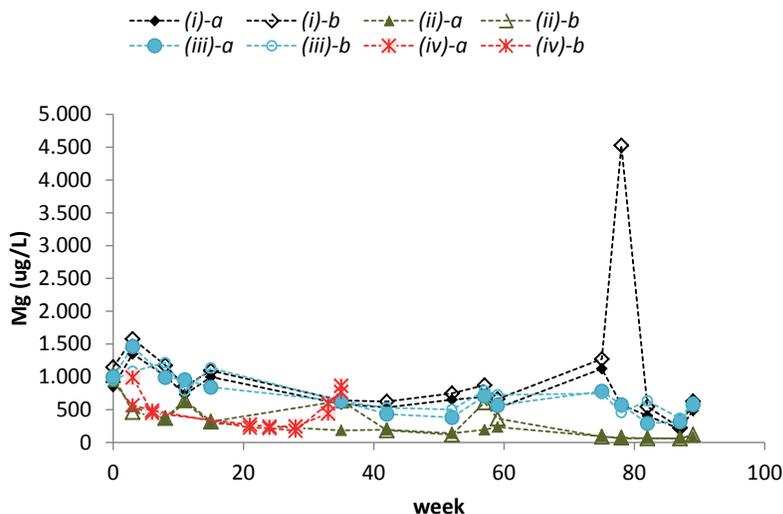
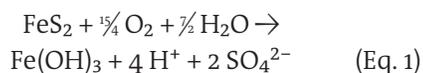


Fig. 5 Magnesium concentrations ($\mu\text{g/L}$) in systems (i)–(iv) plotted against weeks of weathering, a and b denote replicates of each system.

sulphate concentrations. Interesting to note is that the so called reference system (i) has lower pH (fig. 3, Table 3) and higher sulphate concentration than the humidity cell system (iii).

Molar ratios between sulphate and iron ($\text{SO}_4^{2-}/\text{Fe}$) were very close to two for systems (i) and (iii), *i.e.* in agreement with the stoichiometry for pyrite oxidation (Eq. 1; Li *et al.* 2007). This was not seen in the freeze treated systems ((ii) and (iv)), where $\text{SO}_4^{2-}/\text{Fe}$ was > 2 .



Calcium and magnesium are good indicators of weathering, through dissolution of buffering minerals like *e.g.* magnesite, calcite or magnesium silicates. Fig. 5 shows concentration of magnesium plotted against weeks of weathering. It again becomes apparent that the freeze treatments ((ii) and (iv)) has a lower degree of weathering than the two other systems. At this point of the experiment the results, somewhat surprisingly, point to higher degree of weathering in the reference system, *i.e.* the system standing on the bench at 16 °C, than in the humidity cell system.

Conclusions

It was suspected that the growth of secondary weathering products (ferrous and ferric sul-

phates and (oxy)hydroxides) on pyrite surfaces might slow down oxidation rates, but also that repeated freezing and thawing could have an effect on the stability of the secondary product layer (cracks, channeling and exposure of new pyrite surfaces). The 0.25 pH-unit difference between systems (iii) and (i) could be explained by formation of weathering products (more in system (iii) than (i)) in the initial stages of the experiment. Freeze treatment, however, did not have the suspected effect, not even in combination with humid, warm air (system iv). The experiments are nevertheless still running, giving information on the importance of climate specific test methods for mine water chemistry prediction.

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