

Effects of pH on the Arrhenius Paradigm

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Abstract

Kinetic weathering reactions are temperature sensitive, and most industry standard kinetic tests are conducted at room temperature. The temperature effect on sulphide oxidation rates measured in room temperature experiments is generally scaled using the Arrhenius equation. Activation energies are only available for a limited number of mineral phases, therefore, temperature scaling is generally done by assuming metal leaching rates are controlled by oxidation of the dominant sulphide mineral, which is often pyrite. In order to evaluate this approach, 12 humidity cell tests were operated at room temperature until geochemical loading rates stabilized. The tests were then moved to a cold room at 4°C where the tests were continued. This temperature change would theoretically result in pyrite oxidation rates decreasing by a factor of 0.37 to 0.11 based on activation energies available in the literature. The decrease in sulphate loading rates generally fell within this range. However, distinct differences are observed in metal loading rates depending on the pH of the kinetic test. In acidic samples, most metal loading rates decreased to a similar degree as sulphate. Conversely, in pH-neutral tests declines in metal cation loading rates showed little change, or in some instances produced higher loading rates at colder temperatures. While temperature effects on individual elements may vary depending on the activation energy of the host mineral, increases in metal loading rates at lower temperatures is not consistent with the Arrhenius equation. These results demonstrate that under acidic conditions the Arrhenius relationship accurately predicts temperature effects on rates of metal cation release, however, this equation cannot accurately predict metal cation loading behavior in pH-neutral kinetic tests. The inability to accurately predict metal cation behavior in pH-neutral kinetic tests is interpreted to result from metal cation release being more closely tied to pH related solubility constraints than to weathering rates of primary sulphides.

Key words: Scaling Factors, Temperature Effects, Cold Climate

Introduction

A growing proportion of new mines and mineral prospects are located in arctic and sub-arctic environments where mean annual temperatures are near or below 0°C. These cold weather environments present challenges for water quality predictions. Kinetic weathering reactions (e.g., sulphide oxidation) are temperature sensitive, and most industry standard kinetic tests are conducted at room temperature. The temperature effect on sulphide oxidation is generally estimated using the Arrhenius equation of the form:

$$k = Ae^{-Ea/RT}$$

where k is the reaction rate, A is the pre-exponential factor, R is the noble gas constant, T is the temperature in Kelvin, and Ea is the activation energy. The activation energy must be experimentally derived for a mineral phase. Estimates of Ea values for pyrite range from 39 kJ mol⁻¹ to 88.0 kJ mol⁻¹ (Lowson, 1982; Nicholson, 1989; and, Kamai and Ohmoto, 1999). Data for other sulphide minerals is more limited, however, available data indicates activation energies are generally similar to the range observed for pyrite. For instance, activation energies for chalcopyrite, sphalerite and pyrrhotite have been estimated by Ahonen and Tuovinen (1991) as 77 kJ mol⁻¹, 45 kJ mol⁻¹ and 40 kJ mol⁻¹, respectively.

The effect of temperature on sulphide oxidation rates can be estimated with the above equation and the range of Ea values observed for pyrite. The Arrhenius relationship normalized to the temperature of laboratory kinetic experiments is graphed in Figure 1. This relationship shows that pyrite oxidation

rates at concentrations just above the freezing point of water (0.1°C) are 28% to 6 % of loading rates at room temperature (22°C).

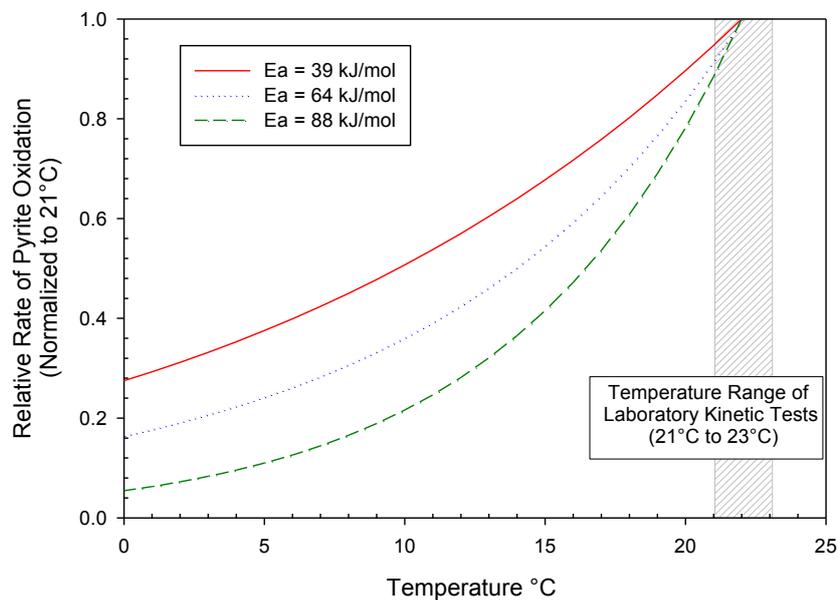


Figure 1: Influence of temperature on pyrite oxidation rate normalized to 22°C.

In scaling kinetic tests to field conditions, it is often assumed that temperature effects of mine waste can be described by an Arrhenius equation using the activation energy of the dominant sulphide mineral. This approach is predicated on the assumption that sulphide mineral oxidation rates are the primary control on metal release. The appropriateness of this assumption likely varies from site to site. In general, metal loading rates can be expected to be more closely linked to the oxidation rate of primary sulphide minerals in acidic mine waste environments where there are few secondary controls on metal mobility. Whereas in neutral pH environments, secondary mineral solubility and carbonate equilibrium will present a significant control on metal release and must also be considered when predicting temperature effects on metal release.

The temperature effects on kinetic test loading rates were investigated as part of a geochemical characterization program conducted to support source term predictions for the Casino project, which is a proposed copper porphyry mine in Yukon, Canada. This was done by operating 12 kinetic tests at room temperature until geochemical loading rates stabilized. The tests were then moved to a cold room at 4°C where the tests were continued. The difference in individual metal loading rates are then compared against predictions produced by the Arrhenius equation using a range of Ea values. The purpose of this comparison is to determine whether an Arrhenius relationship defined by the dominant sulphide mineral can accurately predict temperature affects on laboratory kinetic experiments.

Site Background

The Casino deposit is a gold-copper-molybdenum (Au-Cu-Mo) porphyry deposit that occurs in the Yukon Crystalline Terrane. The Terrane is dominated by the Yukon Group Metamorphics which are intruded by the Dawson Range Batholith. The project site is in a sub-arctic climate where mean monthly temperatures range from -18.1°C in January to 11.1°C in July.

The mineralization zones identified in the core of the Casino deposit include: an oxide cap (CAP) zone where sulphide and carbonate minerals have been leached; a supergene (SUP) zone where copper and sulphates leached from the CAP zone re-precipitated; and, a hypogene (HYP) zone which is unweathered and contains hydrothermal mineralization.

Methods

Kinetic test samples representing waste rock were obtained from drill core and samples representing tailings were obtained from metallurgical testing. The samples were characterized by acid base accounting (ABA) and quantitative X-ray diffraction (XRD) analysis prior to testing. Acid base accounting is used to measure sulphur speciation (total S, sulphate S and sulphide S) and various forms of neutralization potential. Acid base accounting parameters were measured following the procedures described in Price (2009). The mineralogical makeup of kinetic test samples was determined using XRD analysis with a Rietveld refinement as described in Raudsepp and Pani (2003).

Metal loading and acid generation rates were investigated using humidity cell and unsaturated column kinetic tests. Humidity cells consisted of Plexiglas cylinders (10.2 cm inner diameter, 25.5 cm length) filled with 1 kg of sample. Unsaturated columns were constructed using Plexiglas cylinders (21.0 cm inner diameter, 20.5 cm length) and a 5 kg crushed rock sample. Drill core samples of waste rock were crushed to approximately minus 6 mm while the grain size of metallurgical tailings were not modified.

The effect of temperature on metal release rates was evaluated on waste rock and tailings by operating 11 humidity cell and 1 column experiments at room temperature (22°C) until geochemical loading rates had stabilized, which required anywhere from 39 to 215 cycles. The kinetic tests were then moved into a cold room kept at 4°C where the experiments were continued. The temperature effects were then assessed by comparing the loading rates in the five cycles before and after the temperature change.

Results and Discussion

Sample Characterization

The results for sulphur speciation and inorganic carbon (i.e., carbonate) content for kinetic test samples are provided in Table 1 below. This analysis shows that sulphide-S is the dominant form of sulphur in HYP and SUP samples, while sulphate-S is dominant in the single CAP sample (Col 2A). X-ray diffraction results identified pyrite in all HYP and SUP samples, with the only other sulphide mineral identified being molybdenite in HC5. Other sulphur bearing minerals identified by XRD are K-jarosite in Col2A and gypsum in HC5 and T4. Inorganic carbon content is present in most HYP and SUP samples, the dominant carbonate mineral being calcite which is identified by XRD in all samples where inorganic carbon is detected. Calcite is also detected at a low concentration (0.3%) in HC9 by XRD where ABA analysis found inorganic C to be below detection limits. Samples lacking carbonate mineralization had a circumneutral to mildly acidic paste pH, indicating that non-carbonate buffering minerals are generally ineffective at maintaining a neutral pH.

Table 1 Select Acid Base Accounting Results of Kinetic Test Sample

Test ID	Mineralization Zone	Sample Type	Paste pH s.u.	Inorganic-C wt. %	Total-S wt. %	Sulphide-S wt. %	Sulphate-S wt. %
Col 2A	CAP	Waste Rock	5.3	<0.01	0.32	0.02	0.31
HC3	HYP	Waste Rock	8.4	0.27	4.23	2.04	0.03
HC4	HYP	Waste Rock	8.3	0.69	4.29	4.22	0.03
HC5	HYP	Waste Rock	8.1	0.21	2.21	1.07	0.07
HC6	HYP	Waste Rock	8.1	0.19	1.81	1.65	0.02
HC7	HYP	Waste Rock	7.1	0.29	3.26	3.16	0.08
HC8	HYP	Waste Rock	5.1	<0.01	4.28	4.13	0.03
HC9	HYP	Waste Rock	7.9	<0.01	0.92	0.86	0.02
HC10	HYP	Waste Rock	5.1	<0.01	3.56	2.97	0.05
HC11	SUP	Waste Rock	8.2	0.22	2.27	1.95	0.03
HC12	SUP	Waste Rock	5.4	<0.01	3.11	2.94	0.04
T1	HYP/SUP	Tailings	8.7	0.27	1.18	1.13	0.05
T4	HYP/SUP	Tailings	8.6	0.19	1.49	1.36	0.04

Temperature Effects on Acid Generation and pH

The change in pH and sulphate loading rates measured in the 12 kinetic tests in the 5 cycles before and after the temperature change are presented in Table 2. The decline in acid generation rates, as measured by sulphate, is used to calculate activation energies by assuming an Arrhenius relationship. These activation energy calculations are not produced with the intention of confirming or replacing literature values, rather, they are brought forward in the context of determining the effectiveness of using the Arrhenius equation to scale kinetic test results to colder temperatures.

Most of the derived activation energies in samples where pyrite is the dominant form of sulphur fall within the range of literature values (39 kJ mol⁻¹ to 88 kJ mol⁻¹ from Lawson, 1982; Nicholson, 1989; and, Kamai and Ohmoto, 1999). Two tests (HC6 and HC11) have calculated activation energies that are notably lower than this range. It appears that HC6 and HC11 had not reached steady-state sulphate loading rates before the temperature was decreased.

The unsaturated column Col2A, where K-jarosite is the dominant sulphate mineral, produced a relatively low activation energy for sulphate (21 kJ mol⁻¹). This calculated value is notably lower than literature values of activation energy for K-Jarosite which range from 51.6 kJ mol⁻¹ to 63.8 kJ mol⁻¹ (Zahria et al., 2010; Mireles et al., 2016). The cause of this discrepancy may be related to the relatively large increase in pH that occurred in this sample when moved to the cold room (+0.39 pH units). The rate of K-jarosite dissolution increases with pH (Elwood Madden, et al., 2012), hence, the increase in pH would have counteracted the temperature effects, leading to an underestimation of activation energy. These results indicate that the Arrhenius relationship provides a reasonably good approximation of the effects on sulphide oxidation in neutral and acidic pH kinetic tests where pyrite is the dominant sulphur mineral, but may not accurately describe dissolution rates of sulphate minerals such as K-jarosite if a decline in temperature is accompanied by a change in pH.

The effect of temperature on pH is variable. Kinetic test samples containing calcite mineralization showed only a small change in pH, ranging from -0.08 to +0.06 pH units. This is somewhat surprising, as the solubility of calcite increases at lower temperatures, which is expected to lead to an increase in pH. Samples that lacked carbonate content all produced acidic leachate and showed a more significant shift in pH, ranging from +0.21 to +0.65 pH units when moved from 22°C to 4°C conditions. This result indicates that the pH of carbonate buffered kinetic tests is relatively insensitive to temperature, while the pH of acidic samples is more responsive to changes in the rate of acid generation.

Table 2 Sulphate loading and pH at 21°C and 4°C and calculated activation energies (Ea).

Test ID	21°C		4°C		Ea kJ mol ⁻¹
	pH	SO ₄	pH	SO ₄	
Col 2A	5.92	0.41	6.31	0.25	21
HC3	7.58	7.40	7.56	2.82	38
HC4	7.55	10.23	7.57	2.91	50
HC5	7.56	6.08	7.58	2.94	29
HC6	7.51	2.73	7.45	1.88	15
HC7	7.4	11.70	7.3	4.75	36
HC8	2.91	80.84	3.56	12.48	74
HC10	3.21	73.14	3.56	12.48	70
HC11	6.81	4.50	6.87	2.45	24
HC12	3.29	18.68	3.49	7.13	38
T1	7.75	18.05	7.69	5.53	47
T4	7.76	25.20	7.68	4.70	72

Notes: Sulphate loadings in mg/kg/week; pH in s.u.

Temperature Effects on Metal Loading Rates

The temperature effect on metal loading rates are examined by comparing loading rates observed in kinetic tests immediately before and after the tests were moved from room temperature (22°C) to a cold room (4°C). The factors by which loading rates change are presented in Table 3.

The contrasting behavior of oxyanions with divalent metal cations can be related to solubility constraints that effect mobility. Under pH neutral conditions metal cation solubility is limited by sorption and/or secondary mineral precipitation, while oxyanion forming metals are relatively soluble. Conversely, under acidic conditions the solubility of metal cations increases while sorption of metal oxyanions becomes more significant. The contrasting behavior of the oxyanions with divalent metal cations shows that aqueous speciation and related solubility constraints may play a role in determining temperature effects on metal loading rates.

The change in temperature that the kinetic tests experienced would theoretically result in a decline in pyrite oxidation rate by a factor of 0.11 to 0.37 assuming an Arrhenius relationship and the range of activation energies available in the literature for pyrite (39 kJ mol⁻¹ to 88 kJ mol⁻¹ from Lowson, 1982; Nicholson, 1989; and, Kamai and Ohmoto, 1999). Temperature effects on sulphate loading rates typically fall within this range (Table 3). Conversely, there is considerable variability in the temperature effects on metal loading rates which can be attributed to the additional influences of pH and the chemistry of individual elements.

Temperature effects on metal cation loading rates show a strong dependence on pH. For example, the measured loading rates of Cu, Mn, Ni and Zn change by a factor ranging from 0.15 to 0.41 in acidic kinetic tests (HC8, HC10, HC12), which is consistent with the theoretical range of 0.11 to 0.37. However, pH-neutral carbonate buffered kinetic tests (HC3, HC4, HC5, HC6, HC7, T1 and T4) loading rates change by a factor of 0.52 to 1.7, which consistently fall outside the theoretical range. In fact, the metal cations Co, Mn, Ni and Zn produce higher loading rates at cold temperatures in a number of the pH-neutral kinetic tests as shown by ratios > 1.0. Although this result is inconsistent with behaviour predicted by the Arrhenius equation that assumes reaction rates decline with temperature, previous studies have reported increases in Zn loading rates by factors of 1.4 to 2.1 where pH-neutral kinetic tests were moved from room temperature to a refrigerated environment (SRK, 2006).

Table 3 Ratio of humidity cell loading rates observed before and after temperature change.

Element	HC3	HC4	HC5	HC6	HC7	T1	T4	HC11	HC8	HC10	HC12	Col 2A
pH	7.58	7.55	7.56	7.51	7.4	7.75	7.76	6.81	2.91	3.21	3.29	5.92
Alkalinity	0.89	1.26	1.13	1.08	0.95	0.94	0.94	0.92	NS	NS	NS	1.82
Sulphate	0.38	0.28	0.48	0.69	0.41	0.31	0.19	0.54	0.17	0.17	0.38	0.59
As	NS	NS	NS	NS	0.55	0.64	0.66	0.40	0.28	0.28	NS	NS
Ba	0.72	0.97	0.80	0.91	0.85	1.01	0.94	1.44	1.07	1.07	1.42	0.67
Cd	0.35	NS	NS	NS	1.23	0.64	NS	NS	0.14	0.14	0.21	0.56
Ca	0.57	0.84	0.91	0.94	0.62	0.71	0.48	0.82	0.39	0.39	0.23	0.66
Co	1.15	1.09	1.46	1.10	1.16	1.01	0.49	0.21	0.16	0.16	0.33	0.62
Cu	0.87	0.98	NS	0.42	0.98	0.90	0.52	0.26	0.18	0.18	0.29	0.72
Mg	0.56	0.86	0.81	0.79	0.56	0.69	0.50	0.75	0.13	0.13	0.15	0.63
Mn	0.98	1.35	1.77	1.47	1.01	0.89	0.99	2.42	0.20	0.20	0.41	0.61
Mo	0.34	0.19	0.43	0.35	0.32	0.37	0.26	0.14	0.65	0.65	NS	0.81
Ni	1.06	NS	NS	NS	1.08	0.73	1.13	NS	0.15	0.15	0.22	0.59
K	0.52	0.67	0.51	0.72	0.53	0.52	0.50	0.60	0.48	0.48	0.26	0.48
Se	NS	0.41	NS	NS	0.38	0.31	0.33	0.46	0.31	0.31	0.34	0.68
Si	0.45	0.72	0.57	0.57	0.63	0.69	0.55	0.59	0.41	0.41	0.39	0.50
Na	0.43	0.58	0.37	0.86	0.42	0.42	NS	0.53	0.65	0.65	0.54	0.54
Sr	0.59	0.76	0.82	0.89	0.68	0.70	0.52	0.78	0.72	0.72	0.41	0.75
U	0.88	1.44	0.73	1.92	1.08	0.20	0.24	1.44	0.13	0.13	0.21	0.38
Zn	NS	NS	NS	NS	NS	0.68	1.06	1.07	0.15	0.15	0.27	0.64

Note: "NS" means difference is Not Significant because median values at reporting limit. Ratios reported as loading rate at 4°C divided by loading rate at 22°C.

A different pH dependent trend is observed for other elements when temperature is decreased. Unlike metal cations, temperature effects on Se and Mo in pH-neutral kinetic tests show a decline in loading rates by a factor of 0.19 to 0.41. This decline is similar to behavior predicted by the Arrhenius relationship for pyrite of 0.11 to 0.37. Selenium and Mo speciate as negatively charged oxyanions that are relatively soluble at a neutral pH but are affected by sorption to mineral surfaces under acidic conditions. Molybdenum exhibits a smaller decline in acidic samples (0.65 in HC8 and HC10) than in pH-neutral samples, which is the opposite behavior exhibited by metal cations such as Cu, Co, Mn, Ni and Zn.

These results show that the temperature effects on metal loading rates are determined, in part, by solubility constraints specific to the element in question. The mobility of metal cations in neutral pH environments is often limited by pH related solubility constraints, such as sorption and secondary mineral precipitation. In acidic samples secondary mineral formation and sorption of metal cations is less effective at controlling metal cation solubility than in neutral pH samples. The Arrhenius equation can provide a reasonable prediction of temperature effects on loading rates when metal release is governed by the primary mineral weathering rates. However, the Arrhenius equation generally over predicts temperature effects on metal loading rates when secondary solubility constraints are present.

Conclusions

This investigation examined the temperature effects on geochemical loading rates of 12 laboratory kinetic tests representing mine waste rock and tailings. The results were compared against the Arrhenius equation using the activation energy of the dominant sulphur mineral. The primary observations are as follows:

- Pyrite oxidation as measured by sulphate follows behaviour predicted by the Arrhenius equation;
- K-jarosite dissolution does not follow the Arrhenius relationship due to a rise in pH at colder temperatures;
- Metal cations follow the Arrhenius relationship at acidic pH but not at neutral pH; and
- Metal oxyanions follow the Arrhenius relationship at neutral pH but not at acidic pH.

This study shows that an Arrhenius equation can accurately predict sulphide oxidation rates while loading rates of other elements do not always conform to expected behaviour. The ability of the Arrhenius equation to predict temperature effects on laboratory kinetic test can be related to the pH and aqueous speciation of the element in question. That is, elements that are relatively soluble (*e.g.*, metal cations at acidic pH) generally conform to predicted behavior while elements affected by solubility constraints do not. These results show that an Arrhenius equation can provide a reasonable prediction of temperature effects on loading rates when metal release is governed by the primary mineral weathering rates. However, the Arrhenius equation provides a poor prediction of temperature effects when geochemical loading rates are affected by secondary solubility constraints.

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