Using Oxygen Consumption Rates as a Guide to Scale Up Laboratory Kinetic Data to Field Conditions

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ABSTRACT

Field and modelling studies of sulfide oxidation in waste rock from the scientific literature indicate that O_2 penetration is typically less than about 50 m and commonly less than 20 to 30 m due to consumption by reactions with sulfide minerals. A compilation of data from a range of field and simulation modelling efforts indicates a consistent trend of increase in the intrinsic oxidation rate (IOR) with temperature over range of 2 to 57°C, yielding an activation energy of 91 kJ/mole. This value is consistent with the value of 92 kJ/mole determined for pyrite oxidation by ferric ion. This activation energy indicates an increase in IOR of about 3.7 times per increase in temperature of 10°C.

The O_2 consumption rate data provide a potential guide to scaling kinetic data collected in laboratory experiments to field conditions. A comparison of the field data to O_2 consumption rates for 594 laboratory tests from the International Kinetic Database (Morin et al. 1995) shows that ratios of the laboratory IOR to field IOR range from 23 at the 25th percentile to 58 at the 50th percentile to 206 at the 75th percentile or about one order of magnitude. If the potential exists for a waste rock to increase in temperature by 20°C due to exothermic oxidation reactions, the potential increase in IOR based on an activation energy of 91 kJ/mole is about 13.7 times. If this factor of temperature increase is considered in the scaling approach, the range in ratios of laboratory IORs to field IORs decreases to 1.7 to 15 at the 25th to 75th percentiles. With this scaling approach, no other scaling factors are needed because the IOR values here are based on field data and therefore include the various effects of particle size, water-rock ratio, and elemental content.

Keywords: oxygen, consumption, kinetics, waste rock

INTRODUCTION

One of the most common and often problematic tasks facing geochemists using predictive models of future water quality for mine wastes is developing approaches to extrapolate or scale up results from laboratory experiments conducted on small sample sizes (typically 0.5 to 1 kg of material) to represent reactivity in storage facilities that will contain tens of millions to billions of tons of material. Making this scale up effort especially difficult in many cases is the fact that the extrapolations for mine permitting are generally carried out prior to the placement of any material in the storage facilities, meaning that direct observations of reactivity are not available at the time of study.

In most cases, estimations of reactivity are focused on the rates of oxidation of sulfide minerals with respect to their potential to cause acid generation and metal leaching and thereby affect water chemistry. Even when leachates do not become acidic, sulfide mineral oxidation will produce some amount of metal leaching. Humidity and column leaching kinetic tests are the most common laboratory tests used to determine reactivity of mine waste materials. Different approaches have been used to scale up the laboratory kinetic tests to field conditions, such as water-to-rock ratios, water contact time duration, reaction kinetics for individual minerals comprising rock types, particle size, and surface area. The surface area approach may make the most technical sense in that reaction kinetics should be a function of surface areas of minerals and their degree of exposure to air and water; however estimating reactive surface areas for different minerals within a larger rock matrix of variable particle size often requires considerable estimation (Morin, 2013).

Scaling factors developed by various procedures indicate that laboratory rates may range anywhere from 2 to 8 times (Drever and Clow, 1995) to 100 to 1,000 times faster (Malmstrom et al., 2000; Smith and Beckie, 2003; Ritchie, 1994) faster than field rates. These ranges are very wide and difficult to apply with confidence to mine wastes containing sulfide minerals due to the many complicating factors of mineralogy, reactive surface area, particle size distribution, secondary mineral formation, and microbial activity. The purpose of this paper is twofold: 1) assess the effect of temperature on sulphide oxidation rate, and 2) provide a summary of oxidation rates interpreted to occur in existing waste rock storage facilities and compare those rates to laboratory rates in an effort to provide a narrower, statistically based range for typical scaling factors. It is important to note that while O_2 consumption rates provide an indication of the reactivity of sulfide minerals and potential for acid production, they are not necessarily a reliable indicator of leaching rates of all solutes that might be released from all mineral forms.

OXYGEN CONSUMPTION RATES IN WASTE ROCK

Intrinsic Oxidation Rate

A review of the literature shows a number of field-scale studies focused on deriving O_2 consumption rates in sulfidic waste rock (Table 1). The list in Table 1 is not meant to be exhaustive of all the geochemical literature, but is reflective of those found in peer-reviewed journals or easily found sources. Most of the studies in Table 1 involved the development of simulation models of complex air-water-mineral processes in waste rock where the rate of O_2 consumption is a key component for understanding reaction rates and in situ temperature. The rate of O_2 consumption is often referred to as the intrinsic oxidation rate (IOR) with units of kg O_2/m^3-yr where the m^3 term indicates a cubic meter of waste rock. The IOR can be converted to an all mass set of units by dividing by the bulk density (kg/m^3).

In the simulation modelling studies cited in Table 1, the IOR is typically a parameter determined either through a calibration process by comparison of model results to temperature profiles, O_2 depth profiles, and/or rates of SO_4 production. Hence, in all cases, the IOR values in Table 1 are essentially empirical values that are indicative of sulfide mineral oxidation primarily in the outer portions of waste rock piles where sufficient O_2 is available to cause oxidation. For waste rock with high contents of reactive sulfides, O_2 penetration may produce heating and convective air flow, which may speed air transport into the pile, but the reactive nature also more rapidly consumes the O_2, limiting penetration depth. For waste rock with low sulfide content, O_2 may penetrate much farther before it is consumed. In addition, the method of dumping will affect O_2 penetration with end dumping more favourable to promoting air circulation than paddock dumping. For the most part, the results from the simulation models suggest that the depth of O_2 penetration will typically range from 5 to 50 m. This outer rim is the portion of the waste rock pile where oxidation occurs.

Table 1 Summary of waste rock studies focused on O_2 consumption rates

Source	IOR (kg O_2/ m^3-yr)	T* (°C)	Mean Pyrite (%)	O_2 Depth (m)	Max Air Velocity (m/s)	Notes
Molson et al. (2005)	0.04	10	6	NA	NA	Long term rate (20 years); simulation model (Doyon, Quebec)
Molson et al. (2005)	0.40	10	6	NA	NA	Initial rate (1 year); simulation model (Doyon, Quebec)
Linklater et al. (2006)	4.73	2	1.9	10-20	NA	Simulation model (Svartliden, Sweden)
Linklater et al. (2006)	1.58	2	0.6	5-20	NA	Simulation model (Svartliden, Sweden)
Linklater et al. (2006)	0.32	2	0.09	5-20	NA	Simulation model (Svartliden, Sweden)
Wels et al (Infomine)	0.06	16	1.5	~50	0.2	Simulation model (max temperature at 15 m) (Doyon, Quebec; Nordhalde, Germany; Questa, USA)
Wels et al (Infomine)	2.60	45	7	~50	50	Simulation model (max temperature at 12 m)
Wels et al (Infomine)	0.33	40	3.5	~30	100	Simulation model (max temperature at 20 m)
Sracek et al. (2006)	6.86	45	6.6	~30	NA	Interpretation of field depth profiles (Doyon, Quebec)
Sracek et al. (2006)	135.2	57	8.4	~30	NA	Interpretation of field depth profiles (Doyon, Quebec)
Harris & Ritchie (1985); Ritchie (1994)	1.44	45	2	5-15	NA	Interpretation of field depth profiles (Rum Jungle, Australia)
Lefebvre & Gelina (1995)	7.30	30	7	35-40	20	Simulation model (Doyon, Quebec)
Lefebvre et al. (2001a,b)	23.65	46	7	>20	50	Simulation model (Doyon, Quebec)
Lefebvre et al. (2001a,b)	0.32	16	3.1	~30	0.3	Simulation model (Doyon, Quebec)
Stromberg & Banwart (1998)	0.013	5	0.57	NA	NA	Simulation model; O_2 throughout entire 15-m height of waste rock (Aitik, Sweden)
Andrina et al. (2012)	2.27	45	2	NA	NA	Field measurements at trial dump (100 kt) (Grassberg, Indonesia)
Andrina et al. (2012)	2.58	45	4.6	NA	NA	Field measurements at trial dump (100 kt) (Grassberg, Indonesia)

*In-situ waste rock temperature not external air temperature

Effects of Temperature

The studies given in Table 1 show a wide range of IOR but they include both young and old waste rock located in a variety of climates some of which have sufficient sulfide mineral oxidation to produce exothermic heating and elevated temperatures. The range of IOR from these various studies allows examination of the effect of temperature (Figure 1). The data in Figure 1 show a clear trend of increased rate with increased temperature with the exception of the rates derived from Linklater et al. (2006), which deviate significantly from other data for low temperature. The slope of the regression line implies an increase in IOR of 3.7 times per increase of 10°C, not including the IORs from Linklater et al. (2006).

If the same data are re-cast in an Arrhenius type plot, then it becomes possible to calculate an apparent activation energy. Figure 2 shows an Arrhenius plot of the logarithm of IOR as a function of the inverse of temperature. A regression of the data in Figure 2 results in a slope of –4,914.7 and an R^2 of 0.71, which yields an activation energy of 94 kJ/mol.

It should be noted that the regression analysis did not include three IOR values from Linklater et al. (2006) for 2°C because they appeared to deviate significantly from the trend established by the other data. The Linklater et al. (2006) IORs show there can be significant differences in rates, depending on conditions and mineralogy.

It seems reasonable to expect that IOR should be a function of the sulfide mineral content; hence, Figure 3 shows another Arrhenius plot but with IOR divided by the average pyrite content reported in the studies listed in Table 1. Linear regression of the data in Figure 3 produces an activation energy of 80 kJ/mole and a R^2 of 0.74, indicating that normalizing the IOR to pyrite content yields only a minimal improvement in the regression statistics.

The average of the two regression curves gives an activation energy of 87 kJ/mol. This average value is at the higher end of most of the values reported in experimental studies (Table 1). It is consistent with the activation energy of 92 kJ/mol determined by Wiersma and Rimstidt (1984) for pyrite oxidation by ferric ion, which is not surprising given the generally accepted concept that ferric ion is the primary oxidant in acidic systems with rapid enough sulfide mineral oxidation to produce an increase in temperature.

Table 2 Activation energies for sulfide mineral oxidation from various studies.

Source	Activation Energy (kJ/mole)	Notes
This study	87 (80-94)	Extrapolation of field-derived IORs
Linklater et al. (2006)	20	Estimate for field waste rock facility
Lowson (1982)	39-88	Experimental with pyrite
Schoonen et al. (2000)	48-86	Experimental with pyrite
Belzile et al. (2004)	34-100	Review of experimental pyrrhotite oxidation kinetics
Nicholson & Scharer (1994)	50 (pH 2-4) 100 (pH 6)	Experimental with pyrrhotite
McKibben & Barnes (1986)	56.9(±7.5)	Experimental with pyrite
Lu et al. (2005)	64.5(±8.1)	Experimental with pyrite
Rinker et al. (1997)	66-71	Experimental with marcasite
Nicholson et al. (1988)	88	Experimental with pyrite
Wiersma & Rimstidt (1984)	92	Experimental with pyrite; oxidation by ferric ion

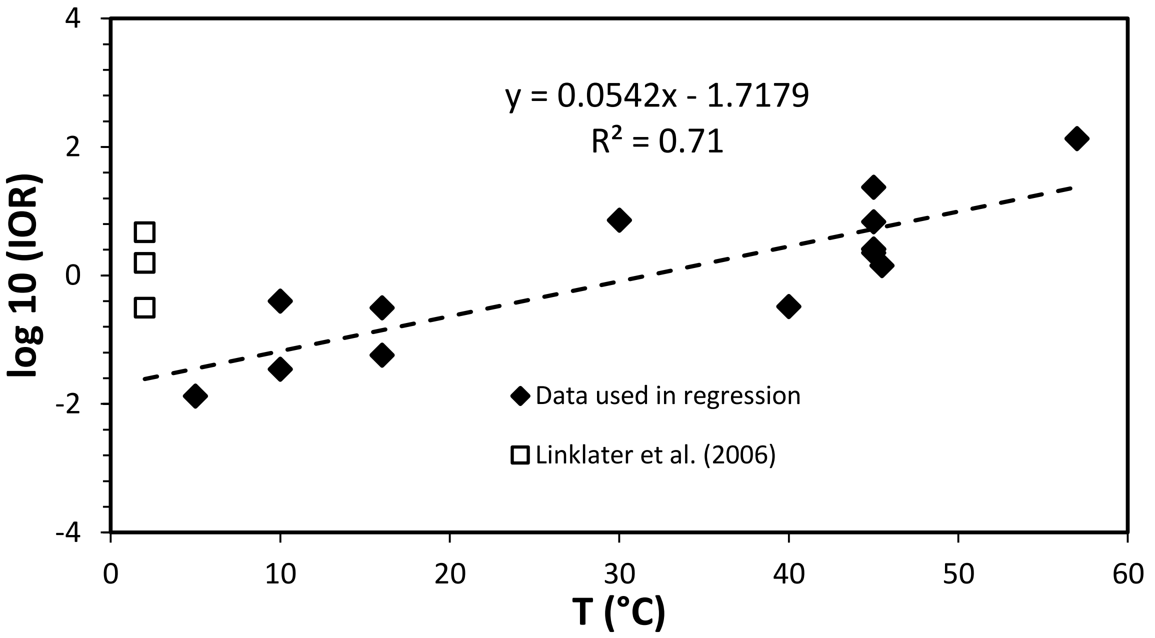

Figure 1 Effect of temperature on IOR

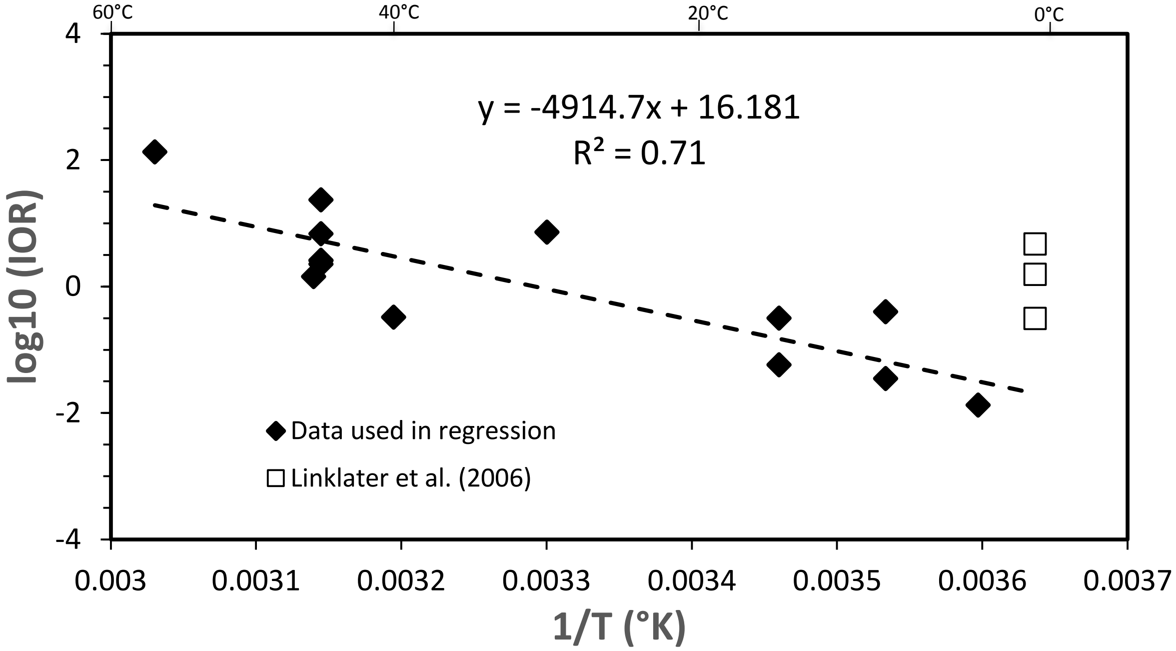

Figure 2 Arrhenius plot for IOR

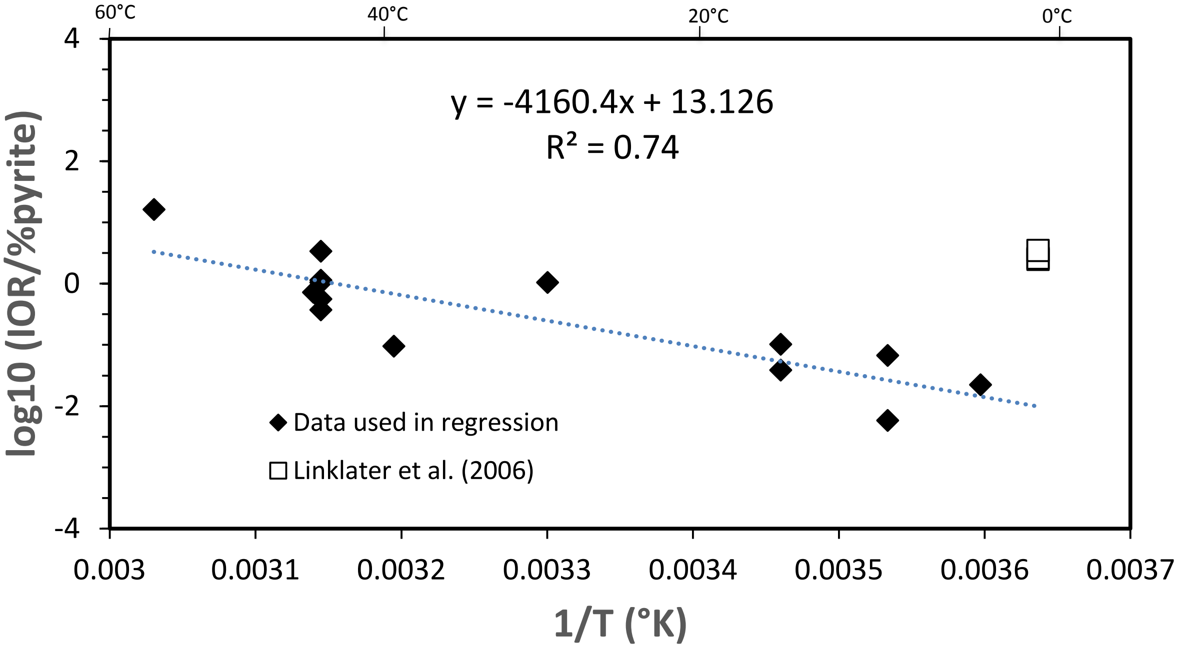

Figure 3 Arrhenius plot for IOR divided by percent pyrite

Comparison of Field and Laboratory IOR

The International Kinetic Database (IKD) from MDAG Publishing (Morin et al. 1995) contains a compilation of a kinetic leaching data from a large number of laboratory studies over a range of rock types and sulfide mineral contents. Figure 4 shows the distribution of IORs from the IKD where the IOR values were calculated from the rate of SO_4 production (mg/m^3-week), assuming a bulk density of 2000 kg/m^3, all sulfide-sulfur is FeS_2, and the following reaction stoichiometry:

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

The distribution of IORs from the IKD data set range from 0.03 at the 5th percentile to 2.21 at the 95th percentile and median of 0.95 kg O_2/m^3-year/%Pyrite (Figure 4). The range of percentile values from the IKD is shown in Figure 5 relative to the field-derived rates from Table 1, assuming a laboratory temperature of 25°C. The ratios of the IKD laboratory IORs to field IORs range from 11 at the 5th percentile to 58 at the 50th percentile to 660 at the 95th percentile. The range in ratios from the 25th to 75th percentiles is 23 to 206 or about one order of magnitude. This range is greater than that observed in a series of laboratory to field scale tests conducted by Andrina et al. (2012), who found laboratory rates ranging from about 2 to 10 times field-scale measurements.

Generally, it is the intent and expectation that rates derived from laboratory tests should be significantly faster than field rates. The laboratory to field ratios discussed here based solely on IOR indicate that factors for extrapolating laboratory-derived oxidation rates to field scale can typically range from one to one and half orders of magnitude. However, it should be noted that if this approach is used for scaling up from laboratory to the field, then no other scaling factors are needed because the IOR values here are based on field data and therefore include the various effects of particle size, water-rock ratio, crystallinity, and elemental content.

Another consideration is for cases where kinetic testing data and numerical modelling predict that sulfide oxidation will be rapid enough to result in exothermic heating, then scaling factors should be reduced. For example, if the potential exists for a waste rock to increase in temperature by 20°C more than the temperatures of relevant laboratory tests, such as from 25°C to 45°C, the potential increase in IOR based on an activation energy of 91 kJ/mol is about 13.7 times. If this temperature effect is considered, the range in ratios of laboratory IOR to field IOR is reduced substantially from 1.7 (=23/13.7) to 15 (=206/13.7) at the 25th to 75th percentiles. The converse is also true for field conditions substantially colder than the relevant laboratory testing conditions, such as would be appropriate for northern or high altitude locations where average field temperatures are less than standard laboratory temperatures of 20 to 25°C.

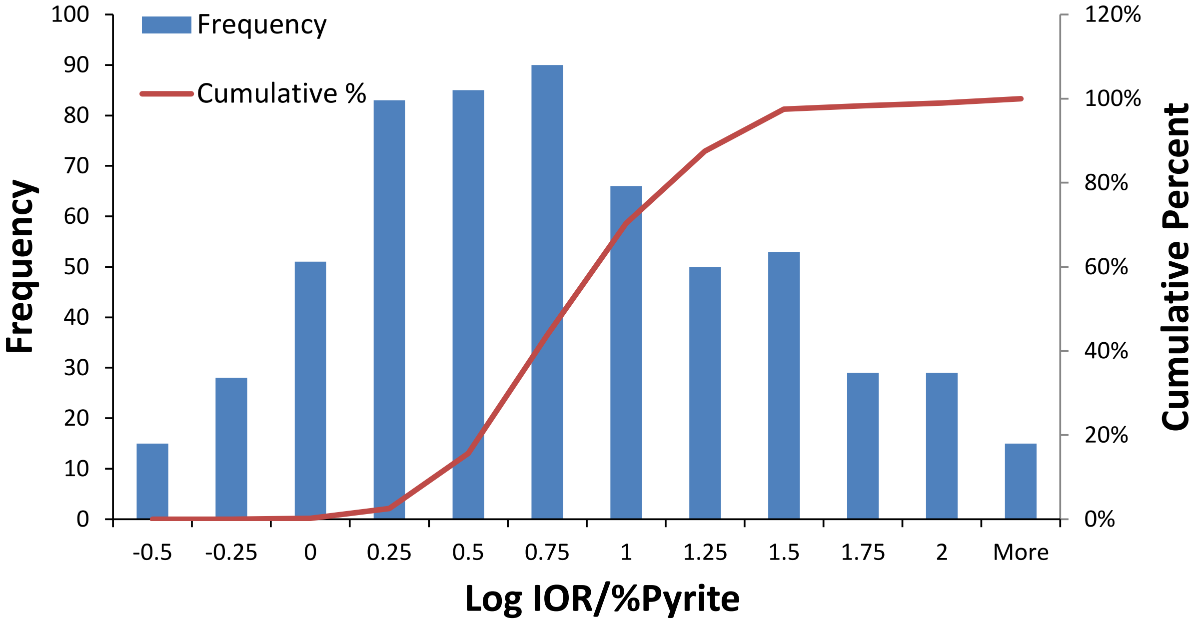

Figure 4 Frequency-cumulative probability for IOR/%Pyrite from the IKD (MDAG Publishing)

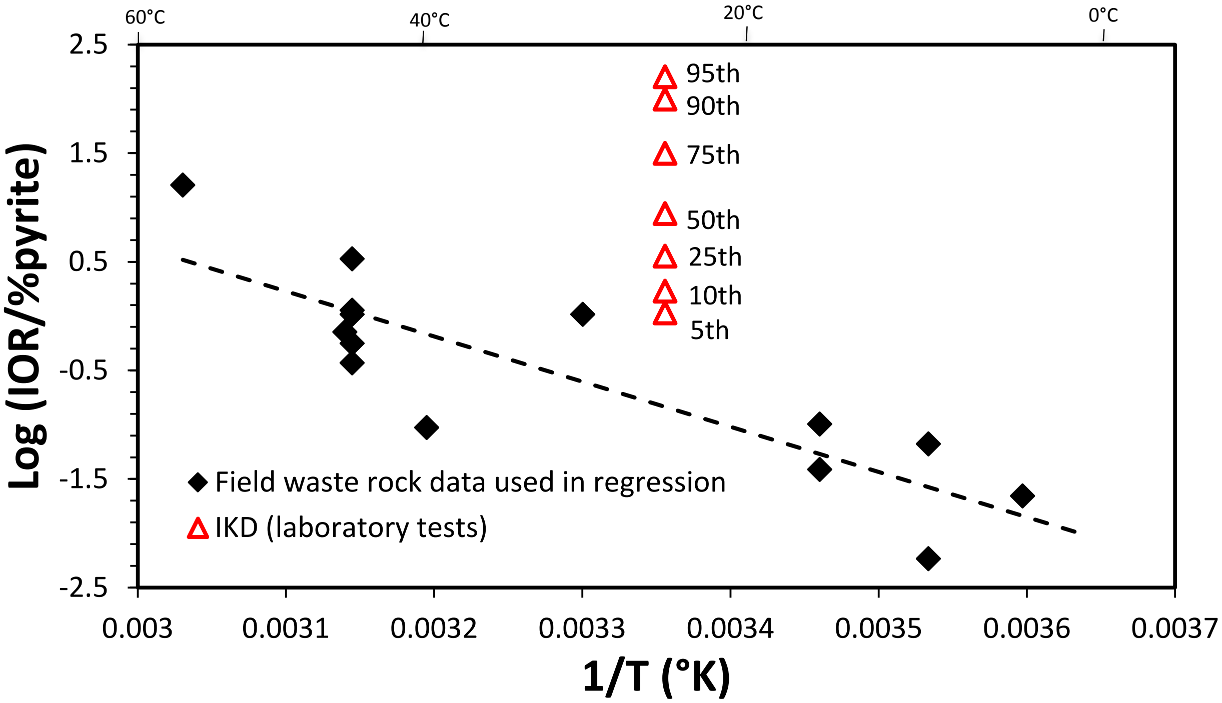

Figure 5 Comparison of IORs from laboratory tests (IKD) to field-derived IORs divided by percent pyrite

CONCLUSIONS

The validity of including temperature effects in approaches for scaling up results from laboratory tests to field scale for modelling oxidation processes in waste rock dumps has never been well established. The IOR data compiled here from a range of field and simulation studies show a consistent and significant effect of temperature, indicating temperature is a significant factor that should be included in scale up estimations. If field temperatures are expected to be substantially different than laboratory temperatures, perhaps greater than 10°, including a temperature factor in scale-up calculations is a reasonable approach. However, if a temperature factor is included as described in this paper, there is no need to add additional scaling factors because the temperature effects on IOR examined here inherently include many other water-rock reaction factors because they are based on observations and interpretations of field-scale systems,

NOMENCLATURE

IOR	intrinsic oxidation rate
kJ	kilojoule
m	meter
s	second
T	Temperature (°C or °K)
yr	year

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