

An experimental investigation into the oxidation of four pyritic shales from Western Australia

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ARTICLE INFO

Article history:

Received 18 September 2008

Accepted 10 January 2009

Available online 23 February 2009

Keywords:

Acid rock drainage

Environmental

Sulphide ores

Oxidation

Ore mineralogy

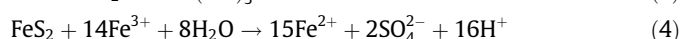
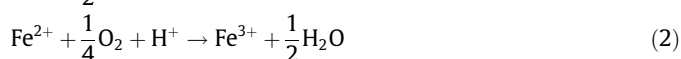
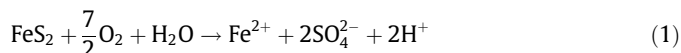
ABSTRACT

The oxidation of pyritic shale under different experimental conditions was studied using an isothermal batch reactor technique. Four pyritic shale samples collected from different areas of an iron ore mine with different stratigraphic compositions in Western Australia were employed in this study. The influence of shale properties on the oxidation of pyritic shale was studied. It was found that the reaction rate constant k ($\text{L kg}^{-1} \text{h}^{-1}$) of the shale oxidation as measured with the present isothermal reactor technique on a per unit pyrite mass basis, was not constant for the different shales and was dependent on their physical properties, where increasing grain size and increasing encapsulation of pyrite grains both result in decreased surface exposure of pyrite to oxidation (per unit mass) which coincides with a decrease in the oxidation rate of pyritic shale (per unit mass). This study demonstrates that pyrite grain size and encapsulation are important parameters for the interpretation and evaluation of acid mine drainage potential associated with individual shales.

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1. Introduction

Large quantities of mining wastes containing sulphide minerals are produced in many mining operations. Pyrite is one of the most abundant sulphide minerals in the earth's crust and occurs in more recent sedimentary deposit (Lowson, 1982; Moses and Herman, 1991). As a dominant sulphide mineral in many ore deposits, pyrite plays a key role in acid mine drainage (Lottermoser, 2003). The weathering of sulphide-rich minerals, principally pyrite, within a wide range of wastes can generate high acidity and concentrations of heavy metals and trace elements. These may contaminate surface and ground water on a large scale in the areas surrounding both operating and spent mines, causing long term environmental damages (Moses et al., 1987; Haan, 1991; Moses and Herman, 1991). This is termed Acid Rock Drainage (ARD), also known as Acid Mine Drainage (AMD), which results from the exposure of sulphide minerals to oxygen and water, and represents one of the greatest environmental problems confronting the mining industry (Lowson, 1982; Parker, 1999; Batterham, 2003). The generally accepted reactions taking place between pyrite, dissolved oxygen and water are as follow (Singer and Stumm, 1970; Lowson, 1982; Moses et al., 1987):



The rate of pyrite oxidation is rather limited before the sulphide minerals were unmined, while the oxidation occurs more rapidly once the sulphide minerals were excavated and exposed to oxygen and water as shown in Eqs. (1)–(4) (USEPA, 1994; Harries, 1997; Brown and Garvie, 2008). The chemical nature of the weathering of pyritic shale is complex and the rate of pyrite oxidation is a function of the mineralogical properties of the pyritic shale, chemical, physical and biological factors such as particle size, temperature of the environment, microbiological activity, oxygen concentration in the gas and water phases (Ritcey, 1989; Lottermoser, 2003). A large pool of literature has studied pyrite oxidation extensively from different scientific views (Singer and Stumm, 1970; Lowson, 1982; Joshi et al., 1983; Moses and Herman, 1991; Nakamura et al., 1994; Evangelou, 1995; Schoonen et al., 2000; Jerz and Rimschidt, 2004). Experimental variables such as sample mass and oxygen concentration were found to affect the oxidation process of sulphides (Dunn, 1997). Borek (1994) investigated pyrite oxidation by employing six pyrite samples under humid environments without reporting a rate law. He reported that the relative humidity affects the products of pyrite oxidation by using Mossbauer spectroscopy to analyse the weathering products, and the humidity control can

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limit pyrite oxidation. Jerz and Rimstidt (2004) developed a rate law for the rate of oxygen consumption by pyrite oxidation in humid air which shows that the rate is a function of oxygen partial pressure and time.

The purpose of this study is to present an experimental system for the investigation of the oxidation of pyritic shales from Western Australia under different experimental conditions, so that the influence of the shale properties on shale oxidation and subsequent acid generation can be evaluated.

2. Experimental

2.1. Materials

Four pyritic shale samples, denoted as shales 1, 2, 3 and 4, which were collected from different areas of an iron ore mine with different stratigraphy compositions in Western Australia were employed in this study. Shale 1 was a pyrite-free waste rock, shale 2 and shale 3 both contained varying amounts of scattered pyrite, and shale 4 was very rich in pyrite in the form of large nodules. The shale samples were dried in the oven at 105 °C overnight to remove the moisture. In order to reproduce the sub sampling of small portions used in experiments, shale samples were homogenised through crushing and pulverising. The samples were subsequently sealed in aluminium bags purged with N₂ for storage until needed. The resulting powders showed BET surface areas of 16.3, 16.6, 2.8 and 5.6 m²/g, respectively, when measured using a Micromeritics TRISTAR 3000 instrument. Geochemical characterisation of the shales, including the total sulphur and forms (sulphate and sulphide), total carbon and forms (carbonate, graphite and organic carbon), soluble iron and forms (ferrous and ferric) and metal assay were conducted (Table 1). The total S and C were analysed using a LECO Carbon–Sulphur Analyser. The water soluble iron and sulphate was analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The sulphide content was calculated as the difference between total S and water soluble sulphate content. The ferrous iron was determined using a spectrophotometer. The ferric iron concentration was calculated as the difference between water soluble iron and ferrous iron. The metal element assay was obtained using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The pH values of the four samples were tested at a solid to distilled water mass ratio at 1:10 after 5 min using an epoxy body combination pH sensor (Ag/AgCl reference, double junction with porous Teflon junction). Before the test, the

pH meter was calibrated using standard buffer solutions with a pH of 4.00 and 7.00, respectively. It can be seen that shale 4 representing the highest pyrite concentration has the lowest pH value.

Pyrite, muscovite, quartz, chlorite and hematite are the major mineral phases in the shale samples, and pyrite is the major sulphur component (Fig. 1 and Table 2), as confirmed by the qualitative and quantitative X-ray diffraction (XRD) using a Siemens D500 X-ray diffraction equipped with a Bragg-Brentano optical system. The analysis was carried out using Cu K α radiation over 2 θ angular ranges of 5–80° with 2 s per 0.02° steps at 40 kV and 30 mA. Quantitative phase analysis was performed using Rietica which employs the Rietveld method for quantitative phase analysis.

2.2. Experimental techniques

The oxidation behaviour of the shales under different experimental conditions was studied using an isothermal batch reactor system. A schematic of the experimental system is illustrated in Fig. 2. The reactor had an empty volume capacity of 2.5 L, and was separated into two compartments by a porous sintered quartz disc. Water (50 mL) was added to the bottom compartment if required, to study the effect of water on shale oxidation. The shale sample was loaded and spread above the sintered disc. The reactor was placed in a water bath maintained at a preset temperature at 48, 57, 66 or 76 °C. The reactor was then purged at room temperature with a N₂ and O₂ mixture (“synthetic air” as noted below) at 4 L min⁻¹ for approximately 4 min and then sealed. Mixtures of N₂ and O₂ of different O₂ concentrations were prepared using different proportions of analytical grade N₂ and O₂ and a “synthetic air” containing 20.6% O₂ and 79.4% N₂. Pressure and vacuum leakage tests were performed on the reactor system before and after each experiment, based on manometer readings to check the integrity of the seal. Over the course of an experiment, water evaporates from the reservoir and passes the porous disc and the shale into the upper chamber where it condenses on the reactor surfaces at the top of the upper chamber and drip back to the shale. The shale becomes wet and water leaches back to the reservoir which becomes discoloured over the duration of the experiment.

The reactor was also connected via a valve and narrow bore tubing to a flexible aluminium foil lined bag (which acted as a reservoir) that was filled with N₂. Upon reaching stable conditions in the reactor, the valve connecting it to the N₂ reservoir bag was opened. The purpose of the narrow bore tubing (length 2 m and ID 0.8 mm) connecting the reactor and N₂ reservoir bag was to allow N₂ to flow from the bag to the reactor to maintain an atmospheric pressure within the reactor as the O₂ was consumed while avoiding significant “back diffusion” of O₂ into the reservoir bag.

Analysis of the gas composition in the reactor was conducted using a gas chromatograph (GC) equipped with a molecular sieve column and a thermal conductivity detector. Two primary standard gases were employed; the first containing 12.04% O₂, 79.29% N₂, 8.63% CO₂ and 0.0443% CO and the second 2.27% O₂, 0.85% CO₂ and 134 ppm CO in nitrogen balance. The GC was calibrated using these two standard gases (as well as air, with allowance for the Ar content) and produced a linear calibration curve with an *r*² (coefficient of determination) value of 0.9966 for O₂, which confirmed the accuracy of the GC measurements.

During the course of each experiment, gas samples of 1 mL were taken from the reactor at suitable intervals until the O₂ concentration reached a sufficiently low level (nominally, below 2.5%). Removal of 1 mL gas samples from the reactor volume did not significantly alter the progress of the reaction. The 1 mL gas samples were withdrawn from the reactor using a syringe and subsequently diluted with 9 mL of He prior to injecting into the GC for analysis. This sampling method was verified using a simulated ver-

Table 1
Characterisation of the four pyritic shale samples (shales 1, 2, 3 and 4).

Elements	Units ^a	Concentration			
		Shale 1	Shale 2	Shale 3	Shale 4
Al	%	8.9	6.5	5.4	4.4
Ca	ppm	2413	467	340	154
K	%	0.8	2.8	2.14	2.7
Mg	%	5.95	0.9	1.14	0.61
Mn	ppm	2095	222	252	82
Fe	%	27.8	9.3	11	17.4
Total soluble Fe	ppm	0	0	67	1700
Water soluble Fe ²⁺	ppm	0	0	62	1180
Water soluble Fe ³⁺	ppm	0	0	5	520
Total S	%	0.005	0.69	2.97	18.5
S-sulphate	ppm	6.6	427	1600	2220
S-sulphide	%	0.0043	0.644	2.81	18.3
Total C	%	0.03	5.98	3.23	3.8
C-graphite	%	0.02	0.05	0.06	0.04
C-organic	%	0	5.8	3.2	3.7
C-carbonate	%	0.01	0.14	0	0.05
pH		8.39	3.38	3.90	2.27

^a Mass base unit.

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