Effect of salinity on the kinetics of pyrite dissolution in oxygenated fluids at 60 °C and implications for hydraulic fracturing

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Abstract

Shale hydraulic fracturing involves the injection of oxygenated acidic fluids which trigger redox driven and acid driven reactions, in particular with pyrite and carbonates. These reactions alter the shale pore and fracture network and mobilize potentially harmful elements. Hence, understanding the kinetics of pyrite oxidation at shale reservoir conditions is critical. Here, we investigate the effect of salinity on the rate of pyrite oxidative dissolution by fluids of pH 1 at 60 °C, and 0 to 3.4 mol L⁻¹ NaCl. We determine a pyrite dissolution rate of about 1.2 x 10⁻⁹ mol m⁻² s⁻¹ in non-saline oxygenated acidic fluids at 60 °C, consistent with previously established rate equations, considering an activation energy of 57 kJ mol⁻¹. Our results suggest the following correlation between the pyrite dissolution rate r (in mol m⁻² s⁻¹) at 60 °C and Eh (0.580 to 0.700 V), $\log(r) = 4.47 \text{ Eh} - 12.03$. This reaction order is lower than that established in previous studies involving pyrite reaction with Fe³⁺ enriched fluids in the presence of dissolved O₂. Furthermore, we calculate that the pyrite oxidation rate varies from 0.8 x 10⁻¹⁰ to 1.3 x 10⁻¹⁰ mol m⁻² s⁻¹ at 25 °C, based on salinity-determined dissolved oxygen content. The mixed flow reactor experimental results suggest a dependence of pyrite oxidation rate on Cl⁻ activity a_{Cl} (in mol kg⁻¹) at 60 °C for fluids with 0.6 to 3.4 mol L⁻¹ NaCl and Eh of 612 ± 8 mV as follows, $\log(r) = -0.58 \log(a_{\text{Cl}}) - 9.42$. The pyrite oxidation rate varies within less than half an order of magnitude for the salinity range tested, and hence, the impact of salinity is less important than the Eh and temperature. The improved understanding of factors controlling pyrite oxidation kinetics may help in predicting environmental and engineering impacts of injection of hydraulic fracturing fluids in shale.

Keywords

Pyrite oxidation; shale hydraulic fracturing; kinetics; heavy metals; ionic strength

1. Introduction

Pyrite is a common mineral in organic-rich shale, from which unconventional hydrocarbons are produced by hydraulic fracturing. Oxidative dissolution of pyrite has been identified as one of the key mechanisms that causes the alteration of the shale pore structure and the mobilization of potentially harmful elements due to the interaction of hydraulic fracturing fluids with shale (Harrison et al., 2017; Jew et al., 2017; Lerat et al., 2018; Wilke et al., 2015). A good understanding of the rate of pyrite oxidation is thus critical. Most previous studies on pyrite oxidation kinetics were conducted with fresh water fluids and at room temperature, conditions relevant to the context of acid mine drainage, a significant environmental issue (Holmes and Crundwell, 2000; Lehner et al., 2007; Liu et al., 2008). However, pyrite oxidation caused by hydraulic fracturing activities involves reactions at reservoir temperature and with saline fluids. Little is known yet about the impact of fluid salinity on the rate of pyrite oxidative dissolution, and this is the focus of our study.

Tackling both challenges of global warming and an increasing demand in energy, cleaner fossil fuels (natural gas) remain of interest while transitioning towards renewable energy (Blazquez et al., 2018). Recent developments in horizontal drilling and hydraulic fracturing technologies have led to a boom in the production of natural gas from unconventional hydrocarbon resources, especially in the US, Canada and China (Rogers, 2011). However, there are environmental concerns with shale gas production, in particular induced microseismicity (Ellsworth, 2013) and potential leakage of hydraulic fracturing fluids or released gases into groundwater aquifers or to the surface (Jackson et al., 2013; Prpich et al., 2016; Westaway, 2016; Wilke et al., 2015). Hydraulic fracturing fluids are composed of water, sand, HCl and other chemical additives (Stringfellow et al., 2014). The chemical compounds may react with the minerals and cause dissolution or form byproducts, sorb to the shale, enhance mobility of potentially harmful elements, return to the surface with the produced water, or leak into groundwater, and it is thus essential to consider their environmental effect.

Injection of oxygenated, acidic hydraulic fracturing fluids into the reducing environment of organic-rich shale triggers acid driven and redox driven chemical reactions. Previous research highlights the rapid dissolution of both pyrite and carbonate minerals in such systems, resulting in the release of contaminants and the generation of porosity (Harrison et al., 2017). Pyrite oxidation leads to the formation of sulfuric acid which can lower the fluid pH to 2-3, depending on the buffering capacity of carbonate content within the shale (Wang et al., 2016; Wilke et al., 2015). The extent and rate of mobilization of elements is influenced by the mineralogy and geochemistry of the shale and the chemistry of the hydraulic fracturing fluids (Wang et al., 2016). Moreover, the rate of pyrite oxidation by dissolved O₂ is enhanced by bitumen in shale, especially at low pH (Dustin et al., 2018). Mobilized trace elements such as As, Cu, Co, Ni, Zn, and Pb from shale hydraulic fracturing activities have been identified to originate from the oxidative dissolution of pyrite (Dustin et al., 2018; Lerat et al., 2018; Xie et al., 2020). Furthermore, pyrite dissolution can enhance the degradation of, for example, dazomet, a commonly-used biocide, resulting in the formation of formaldehyde and methyl isothiocyanate compounds which have potential human health and environmental impacts (Consolazio et al., 2019).

Besides the mobilization of trace elements, pyrite oxidation also alters the shale pore and fracture network, which impacts hydrocarbon production. Pyrite oxidative dissolution initially increases the shale porosity and the connectivity of the nanoscale pore network, improving the imbibition pathway and water retention (You et al., 2018). One of the biggest challenges in shale gas production from hydraulically fractured unconventional reservoirs, though, is that the productivity can drop significantly within several months of the start of production (Bustin and Bustin, 2012; Falk et al., 2015; Patzek et al., 2013). Efforts in modelling have mainly focused

on flow transport with changes to advective flow due to the decreasing subsurface pressure linked to gas extraction (Karra et al., 2015). However, a late-stage decrease in production could also be caused by clogging of pores and fractures due to mineral precipitation (Jew et al., 2017; Pearce et al., 2018). Experiments have indicated that pyrite dissolution can become inhibited over time by the formation of $\text{Fe}(\text{OH})_3$ as a surface coating in particular at higher fluid pH (Harrison et al., 2017; Kamei and Ohmoto, 2000). The formation of these secondary precipitates can attenuate the mobilization of trace contaminants by coprecipitation or adsorption (Harrison et al., 2017; Pearce et al., 2018). In addition to iron secondary precipitates, barite and gypsum have been recognized to form due to chemical alteration of shale, which can decrease shale permeability (Li et al., 2019; Li et al., 2020). Besides the clogging of the pore and fracture network, it has also been suggested that the potential replacement of carbonate by gypsum due to sulfate released from pyrite oxidation could generate reaction-induced microfractures by the gypsum crystallization force (Chen et al., 2018b).

Flowback waters from shale hydraulic fracturing have a high salinity. Fluid-shale interaction can increase the salinity of the fluid to some extent; however, the high salinity of flowback water from hydraulic fracturing of shale is more likely caused by fluid-fluid and fluid-salt interactions (Zeng et al., 2020). Mixing of the injected hydraulic fracturing fluid with saline formation water suggests that pyrite oxidation occurs in fluids that may have varying degrees of salinity. Fluid salinity can impact chemical reactions and sorption processes (Dustin et al., 2018). Although the main pyrite oxidation mechanisms have been identified, most previous studies have investigated pyrite oxidation in fresh water and at room temperature conditions (Chandra and Gerson, 2010; McKibben and Barnes, 1986; Moses and Herman, 1991; Moses et al., 1987; Rosso et al., 1999). The main pyrite oxidation reactions are represented by the following two reactions, and the ferrous ions produced in those reactions are oxidized to ferric ions in the third reaction (Moses et al., 1987; Rimstidt and Vaughan, 2003; Williamson and Rimstidt, 1994).

The overall objective of this study is to understand the impact of salinity on the kinetics of pyrite oxidative dissolution by oxygenated fluids at 60 °C, conditions relevant to shale hydraulic fracturing reservoirs. Gaining more insight in pyrite oxidation under those conditions will help our understanding of the geochemical alteration impacting shale gas production and mobilization of trace contaminants. This knowledge can then aid improving wastewater disposal practices, remediation strategies and risk assessments.

2. Material and methods

2.1. Material

The starting material consists of natural pyrite (FeS_2) mineral cubes (with 1 to 1.5 cm sides) sourced from Navajún mine in La Rioja, Spain. Pyrite samples from the same mine have been characterized and used in several other recent physicochemical studies (König et al., 2019; Schaible et al., 2019; Torres et al., 2019) and pyrite oxidation kinetic studies (Li et al., 2016; Osborne et al., 2010; Papangelakis and Demopoulos, 1991). The cubes have metallic gold colour, and some cubes are intertwined. The pyrite looks pure macroscopically. The mineral cubes were ground to a fine powder using an agate mortar and pestle, and the 63-125 μm grain size was separated by dry sieving. Subsequently, the powder was cleaned with acetone in an

ultrasonic bath to remove microparticles, followed by centrifugation (1000 rpm, two minutes) and decanting the supernatant, and this process was repeated a few times. The powder was then dried in a drying oven at 50°C, and was sieved again to collect the 63-125 µm grain size, to remove any particles <63 µm that may have resulted from the ultrasonic cleaning process. The powder was then stored in a dessicator with indicator silica gel for one or two days until its use in the batch and mixed flow reactor experiments. The specific surface area of the pyrite powders in the experiments is $0.21 \pm 0.01 \text{ m}^2 \text{ g}^{-1}$ as determined by N₂ adsorption BET measurements.

2.2. Mixed flow reactor pyrite dissolution experiments

Duplicate series of eight mixed flow reactor experiments were conducted in several batches with four sequential experiments of each 24 hours. In the different experiments, the salinity was varied, namely 0.0, 0.3, 0.6, 0.9, 1.2, 1.5, 2.4 and 3.4 mol L⁻¹ NaCl. This wide range of salinities covers most natural environment settings. The sequential experiments were run with salinity increasing from 0 to 0.9 mol L⁻¹, and the second batch with salinity increasing from 1.2 to 3.4 mol L⁻¹ (Fig. 1). In such batch of four sequential experiments, the pyrite powder (a total of 3 g) was added at the start of the experiment and remained the same within one batch. For each experiment, a total of 3.5 L of the respective solution was prepared by addition of the required amount of NaCl to milliQ water and the pH of the solution was adjusted to 1.0 by addition of a small amount of HCl in order to avoid precipitation of iron (hydr)oxides so that dissolved iron can be used as a measure for pyrite dissolution. The solution was prepared at least 18 hours before use in the experiments to allow equilibration with air and fluid pH stabilization. The reactor was filled with 300 mL of the solution, and the mixed flow system was set up to keep the fluid volume constant in the reactor, with replenishing of fluid at a rate of 2 mL per minute. The flow was driven by a Fisher FH100M multichannel peristaltic pump over a total period of 96 hours for each batch. Both the inlet and the outlet of the flow system were fitted with 2 µm titanium filters. The flow lines were flushed with milliQ water both before and after the experiments; in addition, the lines were conditioned with the first experimental fluid before starting the batch of sequential experiments. The reactors were closed and put on a Stuart hotplate stirrer which kept the temperature of the system constant at 60 ± 1 °C, as continuously controlled by a Teflon temperature probe. A temperature of 60 °C was selected for the experiments, because this is a relevant temperature for formations targeted for shale gas production. For example, the temperature of the Longmaxi shale gas target reservoir is 60 °C (Chen et al., 2018a), and the reservoir temperature of Marcellus shale is 66 °C (Vankeuren et al., 2017). Specifically, this study is part of a project assessing shale gas fracturing of the Bowland shale in the United Kingdom. Burial history modelling of the deposits have indicated an estimated temperature of about 60 °C for the lower Bowland shale layers (Andrews, 2013). The fluid was continuously stirred using a floating magnetic Teflon-coated stirrer bar. The pH, dissolved oxygen (DO) content and redox potential (Eh) were measured in-line using a custom-designed flow cell unit (also kept at 60 °C) between the batch reactor and the outlet using a Fisher accumet pH meter and Mettler Toledo Seven2Go DO meter. Fluids were collected and characterized at multiple time steps to verify the system had reached steady state by 24 hours. The fluids were then also characterized using inductively coupled plasma mass spectrometry (ICP-MS) to determine the iron and sulphur concentrations needed to calculate the pyrite dissolution rate. Also samples of the prepared fluids before interaction with pyrite were collected for ICP-MS analysis as blank samples. Upon finishing the experiments, the reacted pyrite sample was collected, dried at 50 °C and stored in a dessicator until further characterization with powder X-ray diffraction.

2.3. Batch reactor pyrite dissolution experiments

Two main series of batch reactor experiments were carried out. Both series consisted of the same range of five NaCl salinities, namely 0.0, 0.3, 0.6, 0.9, 1.2 mol L⁻¹ NaCl. The decision was made to not conduct the three highest salinities (1.5, 2.4 and 3.4 mol L⁻¹) of the mixed flow reactor experiments in the batch reactor experiments due to the negative impact of the high salt concentration fluid measurements on the ICP-OES equipment and the fact that the pyrite dissolution rates from the mixed flow reactor experiments were very similar in these high salt concentration fluids. One series was prepared using just NaCl, as for the mixed flow reactor experiments, whereas in the second series NaClO₄ was added to a concentration of 0.01 mol L⁻¹ NaClO₄. The latter chemical was added to stabilize the Eh over the range of salinities and NaClO₄ was selected because of the stability of the perchlorate ion in aqueous solutions (Dimitrijevic et al., 1996) and to avoid introducing additional elements in solution. Both series of experiments followed the same overall procedure. Two hundred ml of solution was prepared by adding the required amount of NaCl, and for the second series also NaClO₄, to milliQ water in a reactor. The pH of the solution was set to 1 by addition of a small amount of concentrated HCl. The reactors with added NaClO₄ were left for one or two days until the Eh in the series of reactors with different salinities became very similar. At least two hours before adding the pyrite to start the dissolution experiments, the reactors were put in a water bath on a hotplate stirrer which was maintained at 60 °C ± 0.5 °C, as controlled by a temperature probe immersed in the water bath. The solutions were continuously stirred using a Teflon-coated magnetic stirrer bar. To start the experiment, 2 g pyrite powder was added to the reactor, which was then immediately closed. Fluid samples of 1.2 mL were collected every hour by a syringe with needle piercing through the self-healing silicone rubber seal on the reactor. The collected fluid was filtered using a 0.22 µm PES filter, and 1 mL of the filtered solution was diluted 5 times in a 2% HNO₃ matrix in preparation for geochemical elemental analysis using an inductively coupled plasma optical emission spectrometer (ICP-OES) to determine the concentrations of Fe and S in solution. The experiments were run for a total of 11 hours. The Eh, pH and DO were measured both at the start of the experiments (just before adding the pyrite powder), and upon finishing the experiment (just after the last sample was taken at 11 hours). All chemicals mentioned were purchased from Fisher Chemicals.

2.4. Analytical methods

The mineralogy of the starting material was confirmed by powder X-ray diffraction (PXRD) analysis on a PANalytical X'Pert Pro X-ray diffractometer which uses CuKα radiation at a tube voltage of 40kV and current of 40mA. The PXRD technique measures the intensity of diffracted X-rays (resulting from constructive interference of incident X-rays and the sample following Bragg's law) under a range of angles with the powder sample surface. The diffracted pattern depends on the crystal structure of the material, specifically on the distance between atom layers in the crystal. Hence, a mineral has a specific diffraction pattern, which can thus be used for identification of crystalline phases and minerals. The pyrite samples both before and after the experiments were scanned over a sampling range of 5 to 70 °2θ, with a step size of 0.0066° and a scan speed of 0.023 °2θ per second. The pyrite powder specific surface area was determined with triplicate analysis using the Brunauer-Emmett-Teller (BET) gas adsorption method. This technique measures how much nitrogen gas is adsorbed by the sample under a series of different pressures. Based on the BET theory of multilayer adsorption of an inert gas, the specific surface area of the sample can be calculated. The analyses were

conducted on a Micromeritics 3Flex instrument using nitrogen gas. Prior to the measurement, the sample powder was degassed overnight at a temperature of 100 °C.

The geochemical composition of the solutions from the mixed flow pyrite dissolution experiments were determined by ICP-MS analysis using a Thermo-Fisher Scientific iCAP-Q equipped with collision cell technology with energy discrimination. ICP-MS is a type of mass spectrometry that uses inductively coupled plasma which can ionize the atoms in sample fluids, which are then detected. The intensity of the signals can then be converted to concentrations of elements in the sample fluids upon calibration. This technique is commonly used to quantify the concentration of elements occurring in trace amounts in sample fluids. Multi-element analysis is undertaken with a Flatopole collision cell upstream of the analytical quadrupole to reduce polyatomic interferences. Internal standards include Sc, Ge, Rh and Ir in 2% HNO₃ matrix, and also external multi-element calibration standards are used. The concentration of Fe and S in the fluid samples collected during the batch pyrite dissolution experiments were determined by ICP-OES analysis using a Perkin Elmer spectrometer Optima 2000 DV. ICP-OES is an optical emission spectrometer that also uses inductively coupled plasma to ionize the atoms in sample fluids for subsequent measurement by emission spectrometric methods. This technique is commonly used to quantify the concentration of major and minor elements in sample fluids. A standard solution containing 28 elements at 100 mg L⁻¹ (Fisher Chemicals) as well as a separate standard solution for sulphur at 100 mg L⁻¹ (Fisher Chemicals) were used to make several calibration series of 0.1, 1, 3, 5, 7 and 10 mg L⁻¹ solutions with 2% HNO₃ matrix with different NaCl concentrations to match the matrix of the solutions in the different experiments in order to accommodate for matrix effects linked to the relatively high salt concentrations in the fluids.

2.5. Calculation of dissolution rate from mixed flow reactor experiments

In the mixed flow reactor experiments, the pyrite dissolution rate is derived from the difference in concentration of the chemical elements that are part of the mineral (Fe and S) between inlet and outlet of the system, taking account of fluid flow rate, fluid volume in the reactor, the total surface area of the pyrite powder in the reactor, and the stoichiometric factor. The stoichiometric factor for Fe is 1, and for S it is 2 because of the stoichiometry of those elements in pyrite (FeS₂). The total pyrite surface area is calculated by multiplying the total weight of the sample used in the reactor (in g) with the BET specific surface area (in m² g⁻¹). The determination of the pyrite dissolution rate from mixed flow reactor experiments relies on achieving a steady state dissolution rate and homogeneous fluid conditions in the reactor. The rate of pyrite dissolution can then be calculated using the following equation:

$$r = \frac{Q ([Fe]_o - [Fe]_i)}{A}$$

where r refers to the pyrite dissolution rate (in mol m⁻² s⁻¹), Q to flow rate (in L s⁻¹), $[Fe]_o$ and $[Fe]_i$ to the Fe concentration in the fluid outlet and inlet respectively (in mol L⁻¹), and A to the total surface area of the pyrite sample in the reactor (m²).

2.6. Calculation of dissolution rate from batch reactor experiments

The oxidative dissolution rate of pyrite in fluids of pH 1 and a temperature of 60 °C was determined for fluids of different NaCl salinities based on the iron concentration in the fluids collected every hour from two to 11 hours in the batch experiments. The mineral dissolution rate in batch reactor experiments can be obtained by the change in the concentration of

chemical elements that are components of the mineral over time, taking account of the total mineral surface area, the amount of fluid in the reactor and the stoichiometry of the element in the mineral. The iron content, rather than sulphur content, has been used in this study for the calculation of the pyrite dissolution rate, based on expected behaviour and increase of iron in solution, in contrast to the sulphur increase and subsequent decrease, probably caused by the formation of a secondary, sulphur-containing, mineral phase (which was not abundant enough to be detected using X-ray diffraction analysis) in the batch reactor experiments. The stoichiometric factor for Fe is 1, since 1 mol Fe is released in solution upon dissolution of 1 mol pyrite (FeS_2). The pyrite dissolution rate is thus calculated as follows:

$$r = \frac{d[\text{Fe}]}{dt} \frac{V_f}{A}$$

where r refers to the pyrite dissolution rate (in $\text{mol m}^{-2} \text{s}^{-1}$), $[\text{Fe}]$ to the Fe concentration in the fluid (in mol L^{-1}), t to time (in s), V_f to fluid volume in the batch reactor (in L), and A to the total surface area of the pyrite sample in the reactor (m^2).

3. Results

3.1. Mixed flow reactor experiments

Steady state reactive fluid Fe concentrations were measured in the outlet fluids and used to calculate pyrite dissolution rates. Rates were not calculated by using the S concentrations because the S did not show a consistent increasing trend in the batch reactor experiments, as discussed below. Therefore, the S concentrations may not reflect the pyrite dissolution rate. Mass balance calculations indicate that the pyrite mass did not decrease by more than 1% during our experiments. Hence, this negligible change in mass, and related surface area, was not considered in the calculation of the pyrite dissolution rate.

Steady state rates based on Fe release obtained from the mixed flow reactor experiments show that the pyrite dissolution rate decreases with increasing fluid salinity (Fig. 2A). Despite the clear overall trend, duplicate analysis of the experiments show that several pyrite dissolution rate values are within error of each other. The largest difference in pyrite dissolution rates is observed between those at the lower salinity of 0 and $0.3 \text{ mol L}^{-1} \text{ NaCl}$, with pyrite dissolution rate of $1.1 - 1.4 \times 10^{-9} \text{ mol m}^{-2} \text{s}^{-1}$ and those at higher salinity of 0.5 to $3.4 \text{ mol L}^{-1} \text{ NaCl}$, with pyrite dissolution rate of $2 - 7 \times 10^{-10} \text{ mol m}^{-2} \text{s}^{-1}$.

The fluid pH remained within 0.1 from the initial pH of 1 in all mixed flow reactor experiments. The Eh was influenced by the salt concentration in the fluids, and the Eh in the outlet fluids shows that many values fall within error of each other for most of the experiments (Fig. 2B). As for the pyrite dissolution rates, the main difference is observed between the lower salinity (0 and $0.3 \text{ mol L}^{-1} \text{ NaCl}$) experiments, with Eh of $630 - 645 \text{ mV}$ and the higher salinity (0.5 to $3.4 \text{ mol L}^{-1} \text{ NaCl}$) experiments, with Eh of $595 - 620 \text{ mV}$.

3.2. Batch reactor experiments

Two series of five batch reactor experiments were run to study the pyrite dissolution rate in a series of solutions of different salinity (namely $0.0, 0.3, 0.6, 0.9, 1.2 \text{ mol L}^{-1} \text{ NaCl}$) with pH 1 at 60°C , one series without and another series with $0.01 \text{ mol L}^{-1} \text{ NaClO}_4$.

For the first series, without NaClO_4 , the far from equilibrium Fe concentration in the solution increases linearly with time, whereas the S concentration is much more variable and seems to

increase in the first 7 hours and then decrease during the remaining 4 hours of the experiments (Fig. 3). The stoichiometry of Fe versus S release within the first 7 hours of the experiment is challenging to assess because of the variability of the S measurements, but the general trend seems to follow roughly the expected stoichiometric 1:2 ratio of Fe:S from pyrite dissolution. The pH in the fluids remains stable at 1 ± 0.2 for the duration of the experiments. The measurements show that the rate of change in far from equilibrium Fe concentration in the experiments distinguishes two groups, (i) the two experiments with the lowest salinity (0 and 0.3 mol L⁻¹ NaCl), with a rate of $8.4 \pm 0.3 \mu\text{mol L}^{-1} \text{ hr}^{-1}$ and (ii) the three higher salinity (0.5 to 1.2 mol L⁻¹ NaCl) experiments, with a rate of $4.0 \pm 0.3 \mu\text{mol L}^{-1} \text{ hr}^{-1}$ (Fig. 3). The pyrite dissolution rates derived from the measured Fe concentrations correspond to $1.02 - 1.08 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ for the lowest salinity group and $4.7 - 5.5 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ for the higher salinity group. Similarly, the Eh values can be differentiated in two groups, (i) 660 – 685 mV for the lowest salinity group, and (ii) 605 – 611 mV for the higher salinity group.

For the series of experiments with 0.01 mol L⁻¹ NaClO₄, the Fe and S concentrations show similar behaviour as in the experimental series without NaClO₄, with linear increase in Fe concentrations and variable S concentrations with initial increase followed by a decrease after 7 hours in the experiments (Fig. 4). In these experiments, the S concentrations are a bit higher than expected based on the stoichiometric ratio and Fe release from pyrite. During the course of the experiments, the fluid pH remains within 0.2 of the starting fluid pH of 1. Comparing the experiments with different NaCl salinities, the rate of Fe release in the solution is very similar amongst all experiments. Only the experiment without added NaCl has a slightly higher rate of Fe increase of $8.9 \mu\text{mol L}^{-1} \text{ hr}^{-1}$, in comparison to an Fe increase rate of $8.8 \pm 0.3 \mu\text{mol L}^{-1} \text{ hr}^{-1}$ in the other experiments with salinities of 0.3 to 1.2 mol L⁻¹ NaCl (Fig. 4). Calculated based on these measured Fe concentrations, the pyrite dissolution rate in the fluid without NaCl is $1.2 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$, and the rate is $8.7 - 9.5 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ in the fluids with added NaCl. The Eh values are very similar in the different experiments, which was the aim of this series of experiments; nevertheless, the values are still slightly higher in the experiments with the two lowest salinities, 686 – 694 mV, in comparison to 670 – 671 mV in the experiments with the higher salinities. These Eh values for the higher salinity experiments are significantly higher than those in the experiments without NaClO₄, which will help to separate a potential impact of salinity versus Eh on the pyrite dissolution rate.

The fluid compositions from the batch reactor experiments, as well as the outlet fluid composition from the mixed flow reactor experiments were used to calculate the saturation state of primary and potential secondary mineral phases using PHREEQC software (Parkhurst, 1995) with the llnl and Pitzer databases. The calculations showed that the fluids from all experiments are undersaturated with respect to pyrite and all potential secondary minerals present in the database. Only the simulation of equilibrium with pyrite using the starting fluids and llnl database indicates that the saturation index for sulphur is getting close to zero, whereas that of all other phases are significantly undersaturated. A representative set of pyrite powders were also analysed before and after reaction by XRD, and no secondary phases were detected.

4. Discussion

4.1. Pyrite dissolution rate and pyrite origin, composition and grain size

Pyrite oxidation studies have been conducted on pyrite samples from a wide range of sources. Most pyrite samples used in previous studies have a hydrothermal origin and are coarse cubic crystals such as those from copper mines in Turkey (Kadioglu et al., 1995), China (Sun et al., 2015), South Africa (Boon and Heijnen, 1998), Serbia (Dimitrijevic et al., 1996), or from the

Huanzala lead-zinc mine in Peru (Caldeira et al., 2010; Jerz and Rimstidt, 2004; Kamei and Ohmoto, 2000; Kocaman et al., 2016). Framboidal pyrite has also been used in oxidation kinetic studies, and it was shown that the oxidation rate of framboidal pyrite was 2.5 times higher than that of euhedral pyrite because of its much higher chemical reactivity (Boon et al., 1999). Impurities in pyrite can slightly accelerate the rate of pyrite oxidation; pyrite with As has higher oxidation rates than pyrite with Ni or Co, and pyrite without impurities has the lowest rates (Lehner and Savage, 2008; Lehner et al., 2007). However, a study on Ag-doped pyrite indicated that a higher Ag content in pyrite decreases the pyrite electrochemical reactivity (Li and Ghahreman, 2018). These studies on impurities were conducted mainly on synthetic impurity-doped and undoped pyrite, which could introduce different findings in comparison with natural pyrite. A comparison of natural pyrite from ten geographical locations has shown that the pyrite dissolution rate amongst those can vary up to one order of magnitude for oxidation under the same conditions (Osborne et al., 2010). The pyrite sample used in this study was also reported in the latter study, and has a mid range pyrite dissolution rate. Hence, the rates derived in our study are considered to be representative for general pyrite oxidation under the conditions tested here.

In many previous papers, the pyrite oxidation rate is often presented per mass of material rather than per surface area. A wide range of pyrite grain size fractions have been used in different pyrite oxidation studies, such as 40-60 μm (Jerz and Rimstidt, 2004), 45-75 μm (Sun et al., 2015), 50-63 μm (Dimitrijevic et al., 1996), 53-75 μm (Boon et al., 1999), 63-75 μm (Fowler et al., 2001), 53-106 μm (Osborne et al., 2010), <150 μm (Lehner et al., 2007), 74-177 μm (Kamei and Ohmoto, 2000), 180-250 μm (Kadioglu et al., 1995). Several studies have shown that pyrite oxidation rates (in $\text{mol h}^{-1} \text{g}^{-1}$) increase with decreasing grain size, and consequently increasing specific surface area (Kadioglu et al., 1995; Nicholson et al., 1988). A linear correlation was established between the pyrite oxidation rate (in $\text{mol h}^{-1} \text{g}^{-1}$) and the inverse of the particle diameter (Nicholson et al., 1988), and between the apparent rate constant and the inverse of the particle diameter (Dimitrijevic et al., 1996). These correlations show that the oxidation rate depends on the total surface area for a certain mass of pyrite, supporting the function of specific surface area which equals $\frac{6}{\rho d}$ with ρ the density and d the diameter, assuming spherical geometry of the particles.

In several pyrite oxidation kinetic studies, the shrinking core model is presented,

$$1 - (1 - X)^{1/3} = kt$$

with X the fraction of pyrite reacted, k the apparent reaction rate constant and t the time, where it is demonstrated that pyrite oxidation is controlled by chemical reaction on the particle surface (Dimitrijevic et al., 1996; Fowler et al., 2001; Papangelakis and Demopoulos, 1991; Sun et al., 2015). In this study, we have taken account of the specific surface area of the pyrite material used in our experiments directly in our calculation of pyrite dissolution rate, expressed in $\text{mol m}^{-2} \text{s}^{-1}$. Direct comparison of the pyrite dissolution rates obtained in our work with those from previous studies is in many cases not possible because of the lack of specific surface area data of the pyrite samples used, or because of the different experimental conditions investigated in the studies, as discussed below.

4.2. Pyrite dissolution rate as a function of temperature

Multiple studies have shown that the pyrite oxidative dissolution rate increases with increasing temperature (Dimitrijevic et al., 1996; Kadioglu et al., 1995; Nicol et al., 2013; Papangelakis and Demopoulos, 1991; Sun et al., 2015), which is generally expected for chemical reactions.

Arrhenius plots of the logarithm of rate constant against the inverse of the temperature for pyrite oxidation by O_2 or Fe^{3+} oxidants have enabled determining an activation energy of 39 to 88 kJ mol^{-1} , suggesting that diffusion is not the rate limiting step (Nicholson et al., 1988). An electrochemical study with Fe^{3+} in solution has established an activation energy for anodic dissolution of pyrite of 80 kJ mol^{-1} , suggesting a reaction controlled process (Holmes and Crundwell, 2000). Kinetic studies on pyrite oxidation in aqueous solution with nitric acid have yielded activation energies between 25 and 52 kJ mol^{-1} with the higher values corresponding to experiments with higher nitric acid concentration (Kadioglu et al., 1995). Also in pyrite dissolution experiments with H_2O_2 and perchloric acid and with H_2O_2 and hydrochloric acid, a similar activation energy of 57 kJ mol^{-1} and 65 kJ mol^{-1} , respectively, was determined, indicating that the chemical reaction at the pyrite surface is the rate controlling step for dissolution of pyrite by H_2O_2 in these acidic solutions (Dimitrijevic et al., 1999; Dimitrijevic et al., 1996). More recent experiments, with controlled redox potential, with H_2O_2 confirmed the activation energy for pyrite oxidation with values of 57, 56 and 52 kJ mol^{-1} for redox potential of 700, 800 and 900 mV, respectively (Sun et al., 2015).

Our study focused on determining the pyrite dissolution rate at a fixed temperature of 60 °C, selected as the most relevant temperature with regards to pyrite dissolution in the context of shale hydraulic fracturing. To enable comparison of our pyrite rate data at 60 °C with other previous studies with the most relevant conditions (O_2 and fluid pH 1) that were conducted at 25 °C, we have assumed an activation energy of 57 kJ mol^{-1} in our calculation using the Arrhenius equation, which is presented below.

4.3. Pyrite dissolution rate as a function of oxidant concentration

Solution Eh has been identified as the most critical factor that controls the rate of pyrite dissolution (Williamson and Rimstidt, 1994). Oxidation of Fe^{2+} by dissolved oxygen is the rate-limiting step in the pyrite oxidation process (Li et al., 2016), and ferric iron (Fe^{3+}) is confirmed to be a more effective oxidant than O_2 in experiments at all pH values (Sun et al., 2015). Hence, the Fe^{3+} to Fe^{2+} concentration ratio is the determining factor that controls the rate of chemical oxidation of pyrite (Boon and Heijnen, 1998). The reaction order with respect to ferric iron is 0.5 for pyrite oxidation both in the presence and absence of bacteria (Fowler et al., 2001). Electrochemical experiments have indicated that the pyrite mixed potential does not change with total iron content, if the Fe^{3+} to Fe^{2+} concentration ratio remains constant (Holmes and Crundwell, 2000), and thus an increase in the total amount of Fe or Fe^{3+} has no impact on the pyrite dissolution rate (Li et al., 2016). The reaction order with respect to Fe^{3+} and Fe^{2+} for pyrite oxidation is 0.9 and -0.4, respectively, when dissolved oxygen is present in the solution (Williamson and Rimstidt, 1994). In the absence of dissolved iron in solutions containing dissolved oxygen, although a few studies suggested a reaction order of 1 with respect O_2 (Kamei and Ohmoto, 2000), most studies agree that the reaction order with respect to O_2 is 0.5 for pyrite oxidation (Holmes and Crundwell, 2000; Williamson and Rimstidt, 1994). This half order dependence on the dissolved O_2 concentration has been explained by the dissociation of dissolved O_2 during adsorption onto the surface of the pyrite mineral (Johnson et al., 2019). Moreover, modelling of the oxidation reaction at the pyrite surface has indicated that Fe sites mediate as both sites for anodic reaction with dissociation of molecularly sorbed H_2O and sites for cathodic reaction with the dissociative chemisorption of O_2 (Rosso et al., 2000). A few other pyrite oxidation kinetic studies have investigated other oxidants, such as pyrite oxidation by H_2O_2 in perchloric and hydrochloric acid solutions, where a reaction order of 1.3 with respect to H_2O_2 was determined (Dimitrijevic et al., 1999; Dimitrijevic et al., 1996).

In our experiments, the solutions to which pyrite is added to start the reaction did not contain Fe^{3+} , but dissolved oxygen acted as the initial oxidant. Our results indicate a pyrite dissolution rate of about $1.2 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ in fluids without added NaCl at 60 °C. In order to compare this rate to pyrite dissolution rate equations presented in literature for similar conditions at 25 °C, we have used the Arrhenius equation with an activation energy of 57 kJ mol⁻¹. Our pyrite dissolution rate converted for a temperature of 25 °C is then an order of magnitude smaller, namely $1.1 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$. Considering a fluid pH of 1 and dissolved oxygen content of 8.2 mg L⁻¹ mol, a pyrite oxidative dissolution rate of $1.3 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ is predicted by Williamson and Rimstidt (1994), and of $4.2 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ as predicted by Johnson et al. (2019) for a temperature of 25 °C. Thus, our experimental result matches that predicted by Williamson and Rimstidt (1994) very closely, and is almost three times higher than that predicted by Johnson et al. (2019) whose study focused on much lower oxygen pressures.

Given pyrite dissolves during the experiment, Fe^{2+} is released in the solution and is oxidized to Fe^{3+} , which is a more effective oxidant than O_2 for pyrite oxidation. Therefore, it is useful to also compare our data with the pyrite oxidation rate equation that is based on Fe^{3+} and Fe^{2+} concentrations in the presence of dissolved O_2 from Williamson and Rimstidt (1994). In the mixed flow reactor experiments, a steady state condition is achieved from which the iron concentration and Eh have been determined, and thus the Fe^{3+} and Fe^{2+} concentrations can be calculated. For the experiment without salt added, the Eh value of 643 mV and measured total Fe concentration indicate an Fe^{2+} and Fe^{3+} concentration of 2.7×10^{-5} and $3.1 \times 10^{-7} \text{ mol L}^{-1}$, respectively. Using these concentrations, the equation by Williamson and Rimstidt (1994) predicts a pyrite oxidation rate of $5.1 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$, which is an order of magnitude lower than that measured in our experiments with extrapolation for 25 °C. The Williamson and Rimstidt (1994) rate equation was derived using results at higher iron concentrations than those found in our experiments, and hence, it is possible that a deviation from their established relationship occurs at lower concentrations.

Considering our entire dataset for pyrite dissolution rates derived for fluids at a pH 1 at 60°C and for the series of different salinities, we can derive a correlation between the pyrite dissolution rate and Eh as follows

$$\log(r) = 4.47Eh - 12.03$$

with pyrite dissolution rate r expressed in $\text{mol m}^{-2} \text{ s}^{-1}$ and Eh in V (Fig. 5). Considering an Fe^{2+} concentration of $1.0 \times 10^{-4} \text{ mol L}^{-1}$, and a calculated Fe^{3+} concentration based on Eh, we have derived the rate dependence on Eh (for the range 580 to 700 mV) based on Williamson and Rimstidt (1994) for pH 1 and 25 °C, and then extrapolated for 60 °C, as explained above. This leads to the following equation

$$\log(r) = 14.07Eh - 17.99$$

with pyrite dissolution rate r expressed in $\text{mol m}^{-2} \text{ s}^{-1}$ and Eh in V (Fig. 6A). A comparison between those rate equations indicates that the rate dependence on Eh is much lower in our derivation, the absolute rates predicted for Eh values of around 620 mV are very similar, and the rates predicted by our equation are lower at higher Eh values than those predicted by Williamson and Rimstidt (1994), but remain within one order of magnitude for the range of Eh values used in our experiments (Fig. 6B). Overall, we can conclude that the pyrite oxidation rate data from our salt-free experiments are in good agreement with that predicted from previously published rate equations.

4.4. Pyrite dissolution rate as a function of acid concentration

The pyrite oxidation rate dependence on pH remains a matter of debate, which may be linked to several mechanisms that can either increase or decrease the pyrite oxidation rate (Johnson et al., 2019) or to the type of acid used in the experiments. Most studies have reported a negative value for the reaction order with respect to H^+ concentration for pyrite oxidation (Caldeira et al., 2010), namely -0.5 (Fowler et al., 2001; Holmes and Crundwell, 2000), -0.25 (Johnson et al., 2019), -0.11 (Williamson and Rimstidt, 1994). Dimitrijevic et al. (1999) suggested that the measured lower pyrite oxidation rate with higher HCl acid concentration was probably caused by the chloride ions rather than H^+ because chloride ions adsorb onto the pyrite surface and therefore diminish the contact surface between pyrite and the oxidant. Another study suggested a zero order with respect to H^+ concentration for pyrite oxidation (Liu et al., 2008), and also Nicol et al. (2018) found that the pyrite dissolution rate is independent of the acid concentration. A small positive reaction order with respect to H^+ concentration was proposed for pyrite oxidation in a study with HNO_3 (Kadioglu et al., 1995) and a study with perchloric acid (Dimitrijevic et al., 1996). Overall, it is thus thought that the pyrite oxidation rate dependence on pH is fairly small. Moreover, it is possible that the reaction order with respect to H^+ concentration is influenced by the potential formation of complexes or secondary phases, such as elemental sulfur, ferrous sulfate, Fe^{3+} oxyhydroxides or chloride complexes which may form on the pyrite surface, and in some cases remove Fe^{3+} oxidant from solution (Andersen et al., 2001; Dimitrijevic et al., 1999; Jerz and Rimstidt, 2004). However, Holmes and Crundwell (2000) suggested that the accumulation of surface products, such as polysulphides, does not affect the rate of pyrite oxidative dissolution in ferric sulfate solutions in their electrochemical experiments. Our experiments were conducted at the low pH of 1.0 to limit as much as possible any potential formation of secondary phases, such as iron (hydr)oxides, on the surface. The decrease in the dissolved sulfur content observed after 7 hours reaction time in the batch reactor experiments could indicate the formation of elemental S or S-containing secondary phases, but the concentration is negligible in comparison to the total amount of pyrite in the reactors so that this would not significantly impact the pyrite dissolution rate derived in our study. Moreover, PHREEQC modelling did not indicate any (over)saturation with respect to secondary phases using the actual elemental concentrations of the experiments, so changes in the bulk fluid sulfur concentration are probably caused by very local precipitation of secondary phases (not in equilibrium with the bulk fluid) on the pyrite surface.

4.5. Pyrite dissolution rate and the effect of sulfate, chloride and ionic strength

Most pyrite oxidation kinetic studies focused on the effect of the oxidant and acid concentration, but few researchers investigated the potential effect of anions in solution. However, several studies did evaluate the impact of sulfate concentration, given this is a main oxidation product of pyrite oxidation. These studies found that the pyrite oxidation rate decreases with higher sulfate ion concentration, which could be caused by adsorption of sulfate ions on the pyrite surface (Dimitrijevic et al., 1996; Nicol et al., 2013). Similarly, Williamson and Rimstidt (1994) found that pyrite oxidation is slower in sulfate rich solutions than in chloride rich solutions. In contrast to sulfate ions, bicarbonate and carbonate ions in solution have been shown to enhance pyrite oxidation (Caldeira et al., 2010). The impact of NaCl concentration on the pyrite oxidation rate has not been studied in great detail. In pyrite oxidation experiments with H_2O_2 , Dimitrijevic et al. (1999) found that a higher NaCl concentration decreases the pyrite oxidation rate, and a reaction order of -0.51 and -1.25 with respect to Cl^- concentration was determined for lower Cl^- concentrations (0.2 to 1.1 mol L^{-1}) and higher Cl^- concentrations (1.1 to 3.1 mol L^{-1}), respectively. This inhibiting effect was interpreted to be caused by adsorption of chloride ions onto the pyrite surface, preventing reaction with the oxidant. In contrast to those findings,

a recent electrochemical study on pyrite oxidation in acidic chloride solutions with Fe^{3+} oxidant reported that in solutions of up to 2 mol L^{-1} NaCl, the Cl^{-} concentration does not impact the pyrite oxidation rate (Nicol et al., 2018). Similarly, Williamson and Rimstidt (1994) reported that the pyrite oxidation rate by Fe^{3+} in the presence of dissolved oxygen is independent of the Cl^{-} concentration and ionic strength.

Here, we evaluate how the pyrite dissolution rate may be impacted by the amount of dissolved oxygen content in solution that depends on the fluid salinity. The correlation of higher fluid salinity with lower dissolved oxygen content was established in previous studies (Benson and Krause, 1984; Garcia and Gordon, 1992). Considering standard conditions, the dissolved oxygen content decreases from 8.3 mg L^{-1} in 0 mol L^{-1} NaCl fluid down to 5.7 mg L^{-1} in 1.2 mol L^{-1} NaCl, and further to 3.0 mg L^{-1} in 3.4 mol L^{-1} NaCl, using the equations by Benson and Krause (1984) and Garcia and Gordon (1992), which are within 2% error of each other (Fig. 7). The pyrite dissolution rates corresponding to those predicted dissolved oxygen contents vary from $1.3 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ in 0 mol L^{-1} NaCl fluid to $1.1 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ in 1.2 mol L^{-1} NaCl, and to $8.1 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$ in 3.4 mol L^{-1} NaCl, considering dissolved oxygen as the main oxidant in pyrite oxidation at pH 1 and 25°C (Williamson and Rimstidt, 1994) (Fig. 7). These results show that from a salinity impacted dissolved oxygen content perspective, the pyrite oxidation rate changes only to a minor extent (from 0.9 to $1.5 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ for pyrite oxidation at 60°C), and may not entirely explain the wider range of rates observed in our study, from 0.2 to $1.4 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ (Fig. 8). The general trend of decreasing pyrite oxidation rates correlating with higher salinity is consistent, though.

As discussed above, although dissolved O_2 is the initial oxidant, Fe^{3+} most likely plays a role in pyrite oxidation once some iron is released in the solution, and a correlation between the pyrite oxidation rate and Eh has been established. These findings further confirm that Eh is dominated by the $\text{Fe}^{3+}/\text{Fe}^{2+}$ system rather than dissolved O_2 . Selecting the data from the mixed flow reactor experiments for the fluids with 0.6 to 3.4 mol L^{-1} NaCl, given all of these have similar Eh values ($612 \pm 8 \text{ mV}$) lacking an Eh-salinity correlation, the pyrite oxidation rate dependence on Cl^{-} activity at 60°C is determined as follows,

$$\log(r) = -0.58 \log(a_{\text{Cl}}) - 9.42$$

with pyrite dissolution rate r expressed in $\text{mol m}^{-2} \text{ s}^{-1}$ and Cl^{-} activity a_{Cl} in mol kg^{-1} (Fig. 9). The activities were calculated using the Pitzer model in PHREEQC (Parkhurst, 1995). This derived reaction order of -0.58 is very similar to that determined by Dimitrijevic et al. (1999) for Cl^{-} concentrations of 0.2 to 1.1 mol L^{-1} . Although a correlation can be established, it is clear that for the wide range of salinities tested, covering most natural environment settings, the pyrite dissolution rates vary within less than half an order of magnitude, and the impact of salinity is thus much less important than the impact of Eh and temperature.

4.6. Consequences for hydraulic fracturing activities

This study shows that fluid salinity has only a secondary impact on pyrite dissolution rates. The shale reservoir temperature and fluid Eh are more important factors that determine the rate of pyrite oxidation. Moreover, the shale rock composition largely determines the fluid composition by fluid-rock interaction. Shale with a higher pyrite content causes more acidic fluids due to the generation of sulfuric acid. Acidic fluids in addition to high salinity of the fluids are more corrosive for drilling equipment than acidic fluids with low salinity, and could thus form greater risks to shale fracturing operations such as long term damage to infrastructure. Saline acidic fluids present also greater environmental hazards in terms of potential

contamination of potable waters in case of leakage. The generation of acidic fluids by pyrite oxidation triggers additional fluid-rock interactions, such as dissolution of carbonates present in the shale. Pyrite oxidation and carbonate dissolution result in the formation of pores, which act as nucleation points for fractures during hydraulic fracturing activities. Nevertheless, if secondary phases are locally formed on pyrite surfaces, then these could potentially also lead to clogging of pore throats. In particular, carbonate in the shale rock could neutralize the acidity generated by pyrite oxidation, and then favour the formation of secondary phases (more than under acidic conditions). Finally, if the pyrite in specific shale formations contains impurities, such as heavy metals, in relatively high concentrations, then pyrite oxidation could mobilize these elements in solution, which could form potential hazards.

5. Conclusions

Injection of oxygenated acidic hydraulic fracturing fluids into subsurface anoxic shale formations triggers acid driven and redox driven chemical reactions, resulting in the dissolution of pyrite and carbonates, and the mobilization of trace elements. In this study, we have investigated the impact of fluid salinity on the rate of pyrite oxidation at conditions relevant to shale hydraulic fracturing, with fluids of pH 1 and at a temperature of 60 °C. Our main findings are the following.

- Our results indicate a pyrite dissolution rate of about $1.2 \times 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1}$ in non-saline oxygenated fluids of pH 1 at 60 °C. This value matches the rate predicted by Williamson and Rimstidt (1994) for pyrite oxidation by dissolved oxygen, considering an activation energy of 57 kJ mol⁻¹ to convert between different temperature conditions.
- The dissolution of pyrite releases Fe²⁺ in solution, which is subsequently oxidized by O₂ to Fe³⁺, which is considered a more effective oxidant for pyrite oxidation than O₂. The dependence of the pyrite oxidation rate on Eh, controlled by the Fe²⁺/Fe³⁺ system, in our experiments for the Eh range of 580 to 700 mV is lower (with a reaction order of 4.47) than that established in previous studies (with a reaction order of 14.07 for reaction at 60 °C) where experiments involved reaction of pyrite with Fe³⁺ enriched fluids in the presence of dissolved O₂.
- Fluid salinity impacts the amount of O₂ that dissolves in solution. Using the equation by Williamson and Rimstidt (1994), we have shown that the pyrite oxidation rate is predicted to vary within the small range of 0.8×10^{-10} to $1.3 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1}$ for pyrite oxidation at 25 °C, considering only the salinity impacted dissolved oxygen content effect on rate.
- The mixed flow reactor experimental results suggest a dependence of pyrite oxidation rate on Cl⁻ activity at 60 °C with a reaction order of -0.58 for fluids with 0.6 to 3.4 mol L⁻¹ NaCl and Eh of $612 \pm 8 \text{ mV}$. The pyrite oxidation rate varies within less than half an order of magnitude for the wide range of salinities tested, and hence, the impact of salinity is considered less important than the effect of Eh and temperature on the rate.

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The authors declare that they have no competing interests.

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Figures and figure captions

Fig. 1. Scheme of the sequential mixed flow reactor experiments.

Fig. 2. Results of mixed flow reactor experiments with a series of fluids of different NaCl concentrations, and all with fluid pH 1 and at 60 °C. (A) Pyrite dissolution rate, derived from Fe concentrations in outlet fluids, versus NaCl concentration. (B) Outlet fluid Eh versus NaCl concentration.

Fig. 3. Results of batch reactor experiments with a series of different NaCl concentrations, and all with fluid pH 1 and at 60 °C. (A) Far from equilibrium data of Fe concentration against time, used for pyrite dissolution rate calculations, and (B) far from equilibrium data of S concentration against time.

Fig. 4. Results of batch reactor experiments with 0.01 M NaClO₄ and a series of different NaCl concentrations, and all with fluid pH 1 and at 60 °C. (A) Far from equilibrium data of Fe concentration against time, used for pyrite dissolution rate calculations, and (B) far from equilibrium data of S concentration against time.

Fig. 5. Pyrite dissolution rates derived from our two types of batch reactor experiments and mixed flow reactor experiments against Eh for fluid pH 1 and 60 °C. The thin red trendline is the best fit curve taking account of only the batch experimental results indicated by the red dot symbol, whereas the thicker black trend line is the best fit curve taking account of all batch and mixed flow reactor experimental pyrite dissolution rate data and corresponding Eh values.

Fig. 6. (A) Plot of the log of the pyrite dissolution rate against Eh, with the rates calculated based on Williamson and Rimstidt (1994) for a set concentration of 10⁻⁴ M Fe²⁺ and an Eh-

determined Fe^{3+} concentration (assuming Eh is controlled by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ system) for 25 °C. These rates expected at 60 °C are also presented by applying the Arrhenius equation with an activation energy of 57 kJ mol⁻¹. (B) Plot of the difference between the log of the pyrite dissolution rate based on the relation with Eh derived from the measurements in our study (as presented in Fig. 4) and the log of the calculated rate for the same Eh value (as presented in A) against Eh for a temperature of 60 °C.

Fig. 7. Plot of the pyrite dissolution rate (left axis) and the dissolved oxygen content (right axis) against NaCl concentration. The pyrite dissolution rate is calculated based on dissolved oxygen content, pH 1, and 25 °C in the equation by Williamson and Rimstidt (1994). The content of dissolved oxygen decreases with increasing salinity, and is calculated using the equation by Benson and Krause (1984) and Garcia and Gordon (1992).

Fig. 8. Pyrite dissolution rates derived from our two types of batch reactor experiments and mixed flow reactor experiments against NaCl concentration for fluid pH 1 and 60 °C.

Fig. 9. Plot of the log of the pyrite dissolution rate against the log of Cl^- activity for the mixed flow experimental data with similar Eh (612 ± 8 mV) and fluid pH 1 and a temperature of 60 °C.