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Geochemical effects of an oxycombustion stream containing SO_2 and O_2 on carbonate rocks in the context of CO_2 storage

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ABSTRACT

This paper describes the effects of the injection of a CO_2-dominated gas mixture into a geologic reservoir rock through experimental work in the context of limiting greenhouse gas emissions into the atmosphere. The injected gas mixture consists of the exhaust fumes from an oxyboiler without desulphurisation with the following mole fraction composition: $CO_2 = 0.82$, $SO_2 = 0.04$, $O_2 = 0.04$, $N_2 = 0.04$ and $Ar = 0.06$. Corresponding experiments using pure CO_2 and N_2 were performed as a benchmark. The rock sample was obtained by drilling to a depth of 4600 m into a low-porosity dolostone reservoir containing micrometric to centimetric fractures in the south-west of France (northern Pyrenees). The fracture network represents the primary volume available for CO_2 storage and is partly filled with dolomite separated from the rock matrix by a thin layer of calcite covering the wall rocks. Experimental reactivity of the rock was tested in 2-cm^3 batch reactors in the presence of saline water (25 g/l NaCl) and a gas phase (pure N_2, pure CO_2 and gas mixture). Chemical analyses of the reacting solutions indicated that the mineralogic assemblage during exposure to pure CO_2 was in equilibrium with the aqueous solution. Raman analyses of the gas phase revealed only the presence of CO_2. Optical and electronic microscopy of the resultant solid phases indicated partial dissolution of carbonates and oxidation of the pyrite surfaces. In the presence of the gas mixture, important mineralogic alteration occurred together with the consumption of half of the O_2 and total consumption of the SO_2. This high reactivity with the gas mixture leads to the complete dissolution of calcite and partial dissolution of dolomite and the precipitation of anhydrite and barite, particularly in the zones where the calcite was initially present. Similarly, pyrite was completely oxidised to hematite. Analyses of the rock samples indicated partial alteration of the clay minerals in the matrix to potassic beidellite in the experiment involving pure CO_2 and solely to vermiculites in the gas mixture experiment. In conclusion, the presence of SO_2 in the injection stream associated with the presence of O_2 results in an early strong acidification of the water, which was buffered by the significant reactivity of the carbonates (dissolution of all of the calcite and 6% of the dolomite) and partial alteration of the clay minerals (87% of illite and 100% of smectite) to vermiculites. Pyrite and aqueous Fe from clays were completely oxidised by O_2, resulting in hematite and Fe^{3+}. The mineralogic alteration and consequent volume changes under experimental conditions led to a slight increase in the porosity of the dolomite matrix and an average pore volume loss of 11% in the fractures caused by the replacement of calcite with anhydrite. Due to its high reactivity with carbonate, SO_2 can react early during the injection phase. The spatial distribution of calcite in the fractures of the reservoir has to be considered as one of the primary parameters controlling the evolution of the reservoir in terms of injectivity and petrophysical properties, particularly in the zone near the injection wellbores. The integrity of the calcite-rich caprock is, however, ensured due to its thickness (more than 1000 m) and its calcite content, which leads to pH buffering and anhydrite precipitation, which, in turn, induces a porosity reduction and a possible coating of the rock formation.

1. Introduction

Anthropogenic emissions of carbon dioxide have accumulated in the atmosphere for decades, thus modifying the atmospheric gas composition. Several options for reducing the amount of CO_2 in the atmosphere involve geological storage of CO_2. This storage consists of CO_2 injection from stationary generators (industrial facilities and coal, gas and other hydrocarbon-fuelled power plants) into deep geologic reservoirs, such as unmineable coal beds, structural traps in deep saline aquifers and depleted oil and gas fields (Holloway, 1997). The option of using depleted oil and gas fields presents several advantages, such as the presence of existing infrastructure (wells) and geological knowledge of the site. However, before any industrial-size injection is considered feasible, the future safety of such a site over several centuries should be

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demonstrated. Previous investigations involved natural analogues (Baines et Worden, 2004; Moore et al., 2005), large-scale pilot studies (e.g., in Sleipner, by Korbøl and Kaddour, 1995; or in Lacq, France, by Thibeau et al., 2009; Lescanne et al., 2011), laboratory experiments (e.g., Kaszuba et al., 2003; Pokrovsky et al., 2005; Rosenbauer et al., 2005; Bertier et al., 2006; Sterpenich et al., 2009; Jobard et al., 2013; Sterpenich et al., 2014) and numerical simulations (Gunter et al., 2000; Xu et al., 2004; Gaus et al., 2005; Knauss et al., 2005; Lagneau et al., 2005; Xu et al., 2005, 2006; Zerai et al., 2006,). All of these studies considered only the use of pure CO_2 injection. However, the complete separation of CO_2 from other industrial offgas components involves energy and economic costs. Industrial offgas contains substantial amounts of other components, such as N_2, Ar and O_2, up to a mole fraction of 5 to 10%, and SO_x and NO_x may also be present if desulphurisation and denitrogenation are avoided to limit energy consumption (IEA GHG report, 2005). The potential effects of such components on the host rocks should be analysed because studies devoted to their effect are still limited. A few experimental simulations address the presence of pure SO_2 in the context of sulphur capture by limestone at high temperatures in bed boilers (Lyngfelt and Leckner, 1989; Hansen, 1991; Mattisson and Lyngfelt, 1998) and the reduction of hematite using a CO_2–SO_2 gas mixture in aqueous conditions at 150 °C and 300 bar (Palandri et al., 2005). There have also been experimental studies of the reactivity of pure SO_2 or a CO_2–SO_2 mixture with a mixture of pure mineral phases (Renard et al., 2011a,b; Wilke et al., 2012). A numerical simulation by Xu et al. (2007) involved a geochemical analysis of the injection of CO_2, SO_2 and H_2S into a sandstone formation. Other studies focused on the behaviour of well materials when subjected to co-injected gases such as H_2S under borehole conditions (Jacquemet et al., 2005; Lécolier et al., 2006; Jacquemet et al., 2008, 2012) or the action of H_2S on reservoir rocks (Machel, 2005; Pironon et al., 2007).

The present study examines the specific interaction of a potential co-injected mixture of N_2, Ar, O_2 and SO_2 gas with carbonate rocks by comparing its interaction with experiments using pure CO_2 and pure N_2. The gas mixture consisted primarily of offgas from an oxyboiler lacking desulphurisation. The rocks consisted of core samples obtained from a 4600 m deep carbonate reservoir. These rocks are described in detail by Renard (2010). Raman analyses of the gas and aqueous phases and the optical and electronic microscopy of the minerals allowed for the establishment of mineralogical and chemical budgets.

2. Apparatus and methods

The experiments were performed on a batch of natural samples subjected to a temperature of 150 °C and pressure of 100 bar for one month. These conditions correspond to the expected bottom-hole pressure and temperature, i.e., 30 bar and 150 °C, after two years of steam injection in a deep depleted reservoir at a depth of 4500 m.

To match realistic pressure–temperature conditions, an existing experimental setup was upgraded, consisting of a specific gas line linked to various devices for specific gold batch reactor loading and outlet gas analysis (Fig. 2). The initial device, which was described in detail by Jacquemet et al. (2005), has been routinely used in several experimental studies involving similar pressure and temperature conditions (Landais et al., 1989; Teinturier and Pironon, 2003; Jacquemet et al., 2005) designed to mimic deep geologic environments. The batch reactors consisted of hermetically welded gold capsules. Gold was used because of its chemical inertness and its ability to withstand substantial pressures and temperatures (Seyfried et al., 1987). The internal volume of each capsule was limited to 2 cm^3 (inner diameter of 0.5 cm and length of 10 cm) for safety reasons related to possible leakage of toxic gas, such as SO_2. The gold capsules were then placed into a 100-cm^3 pressure vessel heated by a coating device (Fig. 1). The system was linked to a pressure line filled with water-oil fluid and connected to a pump and pressure gauges to maintain a constant hydraulic pressure.

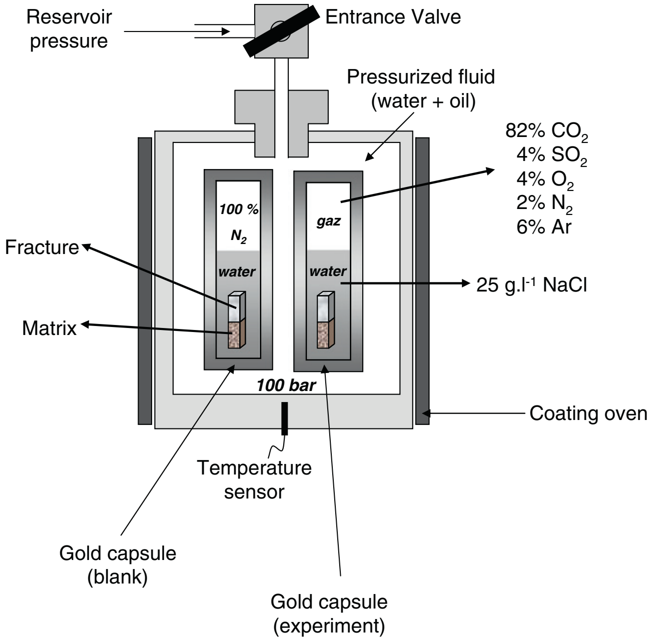

Fig. 1. Schematic diagram of the pressurised autoclave. Gold capsules are filled with rock samples, saline water and a gaseous phase and placed in the autoclave. The pressure is controlled using a fluid linked to a pump and a manometer. The heating device surrounds the autoclave to ensure even heating. The percentages of gases are expressed in mol%. The blank is a capsule in which the reacting gas consists of N_2.

The gold capsules were first filled with the rock sample material and an aqueous solution before injecting the gas phase. The synthetic aqueous solution consisted of a 25 $g\cdot l^{-1}$ solution of NaCl, which was designed to replicate the interstitial saline water within a typical rock formation.

Three separate gases were selected for the experiments: pure N_2, pure CO_2 and a gas mixture with the following mole fraction composition: $CO_2 = 0.82$, $SO_2 = 0.04$, $O_2 = 0.04$, $N_2 = 0.04$ and $Ar = 0.06$. This mixture was selected to approximate the composition of the offgas from an oxyboiler operating in the Lacq area (southern France) in the case of the theoretical absence of desulphurisation (a process that consumes an inordinate amount of energy). For each experiment, the gas was replaced by N_2 – known for its inertness in such systems – in a blank capsule containing the same aqueous and solid phases.

The gold capsules were filled with gas using a modified gas-loading device based on that described by Jacquemet et al. (2005, Fig. 2) and made of stainless steel to avoid reactivity with the dry gases. The gas evolution, loading and release protocols were those described in detail by Renard (2010). After the capsule was hermetically fixed to the capsule connector, it was partially plunged into liquid nitrogen to freeze any water and avoid its partial vaporisation. A vacuum was thus formed throughout the gas line. The desired gas or gas mixture was injected through the gas input valves, and the desired quantity was reached by successive incremental openings and closings of valves and cold traps while the line pressure was monitored.

After the experiment, the gold capsule was mounted in a piercing device under vacuum pressure (less than 0.1 mbar) and then pierced. The gas phase was collected using the nitrogen cold trap before being redirected to the Raman cell for Raman spectra recording.

The rock samples used in this study were obtained from drill cores collected from a fractured Portlandian dolomite, specifically the "Dolomie de Mano". The Dolomie de Mano is a dolostone matrix crosscut by fractures filled with carbonates. The mineralogy and crystal chemistry were determined using XRD (X-ray diffraction), bulk chemical analysis (inductively coupled plasma mass spectrometry and atomic emission spectroscopy: ICP-MS and ICP-OES), SEM (scanning electron microscopy), EPMA (electron probe micro-analysis) and TEM