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High-purity hydrogen gas from the reaction between BOF steel slag and water in the 473–673 K range

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ABSTRACT

A novel method for producing hydrogen with water and BOF steel slag was developed. The steel slag was reacted with water during 2–57 days at 50 MPa for temperatures ranging from 473 to 673 K. The quantitative evolution of the slag and gas compositions indicated that the main H_2 producing reaction is:

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$

At 523 K, approximately 5 NL of H_2 per kg of slag were produced in 3 days. The reaction rate was only 1.5 times faster when the slag was crushed down to an initial particle size below 50 μm. The H_2 production has been also tested on slags carbonated beforehand at 0.142 ± 0.002 kg of CO_2 per kg of slag. The reaction was found to be thermally activated. A high purity hydrogen (99.995%) is produced with non-carbonated steel slag below 573 K whereas CH_4 production was measured in all the other experiments.

1. Introduction

Hydrogen is a promising energy vector for two reasons: 1) after radioactive substances, it is the fuel with the highest specific energy (above 120 MJ/kg); 2) water is the main by-product in hydrogen fuel cell or during combustion. However, nowadays, 98% of the hydrogen is produced by fossil fuel reforming, a high temperature process which is energy consuming and produces greenhouse gases [1]. Consequently, other processes of H_2 production are investigated in order to make hydrogen a renewable energy vector.

The steam–iron process is the oldest route for producing hydrogen [2]. It is a cyclic process in which iron oxide (typically, magnetite, Fe_3O_4) is reduced (stage I) and re-oxidized (stage II) at temperatures ranging from 873 to 1173 K. Iron reduction is achieved with a reducing gas (generally, a gas mixture of H_2 and CO produced by coal gasification) which reacts with magnetite to form wüstite (FeO) and/or iron metal (Fe). This reduced material is then oxidized back with steam to produce high-purity H_2 and magnetite [3,4].

High-tonnage carbon steel production generally consists in a first step of the reduction of the iron ore with a reducing

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agent such as coke, in a blast furnace. In a later step, removal of carbon is achieved in a basic oxygen furnace (BOF) by blowing pure oxygen onto the molten metal (oxidation to CO and CO_2). This process produces slags (BOF slags) as by-products generally used as road ballast or as land filler. BOF steel slags do contain iron as a main constituent, mainly in the form of FeO (wüstite, [5]). Like in stage II of the steam–iron process, it has been shown that H_2 can be directly produced during the steel-making operations by oxidizing the slags at ~1873 K with steam [6–8]. However, compared to the steam iron, this process does not produce hydrogen of high purity since CO, CO_2 and CH_4 gases are also present.

As a possible alternative, we propose here to study experimentally the high-purity H_2-producing potential of BOF steel slags oxidized with water at low temperature (below 750 K). The role of temperature, pH and crushing was investigated; these three parameters are expected to influence the wüstite oxidation kinetics and, thus, the hydrogen production kinetics.

The presence of calcium oxide and hydroxide imposes a high pH to water when contacted with BOF slags [9]. On the other hand, these two calcium-bearing phases are easily carbonated at room temperature. Carbonation allows, at the same time, to reduce the pH [9,10] and to sequester up to 0.270 kg of CO_2 per kg of BOF steel slag [9,11]. Therefore, the effect of pH lowering on H_2 purity and production has been tested here by carbonating the BOF slag beforehand. Obviously, the consecutive use of BOF slag for CO_2 sequestration and hydrogen production is tested by this mean.

2. Materials and methods

2.1. Materials

A Basic Oxygen Furnace (BOF) steel slag was sampled by [5] and used here as a starting material. The BOF steel slag was crushed for 10 min in a mortar grinder (Retsch® RM 100) into a powder with a particle size ranging from below 1 μm to 50 μm, referred to as CBOF in the following. Crushing allows to both increase the reactive surface area and homogenize the starting material. Major and minor element composition and iron speciation were previously determined by ICP-OES, X-ray diffraction, SEM and EXAFS [5,12–14]. The major element composition of the BOF slag is: CaO (44.7 wt.%), FeO (20.58 wt.%), Fe_2O_3 (3.16 wt.%), Fe (2.7 wt.%), SiO_2 (7.6 wt.%), MnO (2.86 wt.%), MgO (4.9 wt.%), Al_2O_3 (1.2 wt.%) and P_2O_5 (1.61 wt.%).

2.2. Experiments

2.2.1. Carbonation procedure

The steel slag was reacted with CO_2 following the procedure described in [10]. Twenty grams of the crushed steel slag (CBOF) were loaded in a 2 L hastelloy PARR® autoclave together with 1 L of de-ionized water (resistivity of 18.2 MΩ cm). The experiment was conducted at room temperature (296 ± 1 K) for 6 days under constant stirring. After dispersion of the BOF steel slag into water, CO_2 was injected in the reactor to reach an initial pressure of 20 bar. The pressure drop (P_{drop}) associated with both CO_2 dissolution in water and CO_2 sequestration in carbonate minerals was recorded as a function of time until pressure stabilized [10] have shown that the Ca concentration in water has little impact on the measured pressure drop associated with CO_2 dissolution (P_{diss}). Consequently, P_{diss} was measured with the same set-up but without the slag sample, i.e. pumping CO_2 in a vessel only filled with de-ionized water. The pressure drop associated with CO_2 sequestration (P_{seq}) was estimated by subtracting P_{diss} to P_{drop}. CO_2 sequestration was also quantified by thermogravimetric analyses (TGA) using a TGA/SDTA 851^e Mettler Toledo instrument. About 10 mg of powder (±0.1 μg) were heated from 303 to 1473 K (±0.25 K) at a rate of 10 K/min in N_2.

At the end of the carbonation experiments, the solid fraction was separated by centrifugation (15 min at 13,000 rpm) and then dried during 48 h at 353 K. The carbonation product, referred to as CARBOF in the following, was used in further hydrogen production experiments.

The native pH of CBOF and CARBOF powders was determined at 298 K at the end of the carbonation stage for CARBOF and after its stabilization in water with a water to rock ratio of 50 (identical to the one of the carbonation experiment) for CBOF.

2.2.2. Hydrogen production experiments

A total of 32 experiments was carried out (see Table 1 for details). BOF, CBOF or CARBOF powders were loaded in 2–3 cm length gold tube (4.0 mm outer diameter and 3.6 mm inner diameter) with de-ionized water (resistivity of 18.2 MΩ cm) in a water to solid mass ratio ranging from 0.15 to 5.6. The capsules were welded shut and placed in horizontal cold-seal pressure vessels. Run temperatures, ranging from 473 to 673 K, were measured with a Ni–NiCr thermocouple and regulated to within 1 K (see Ref. [15]). A pressure of 50 MPa was applied to all experiments by pumping either argon or water into the vessel. The experiments were finally quenched and both gas and solid analyzed.

2.2.3. Strategy to evaluate the H_2 permeability of the gold sample container

Gas production can be dramatically underestimated if the gold capsule is permeable to hydrogen at the run conditions. Therefore, the permeability of the gold sample container to hydrogen was evaluated by conducting similar hydrothermal experiments but with oxalic acid ($C_2O_4H_2$) as starting material. At temperature above 443 K, oxalic acid decomposes as follows [16]:

$$C_2O_4H_2 \rightarrow CO_2 + H_2O + CO \quad (1)$$

The components produced by this reaction can then react together to various extents depending on run duration and temperature according to the two following reactions:

$$H_2O + CO = H_2 + CO_2 \quad (2)$$

and

$$2H_2 + 2CO = CH_4 + CO_2\,. \quad (3)$$

Following (1), (2) and (3), the number of moles of hydrogen produced during the decomposition of oxalic acid can be deduced from the measurement of the other gas components as follows:

$$n_{H_2C} = \left(n_{CO_2} - n_{CO} - 5n_{CH_4}/2\right) \quad (4)$$

where n_{H_2C} is the calculated number H_2 moles and n_{CO_2}, n_{CO} and n_{CH_4} are the measured number of moles of CO_2, CO and CH_4, respectively.