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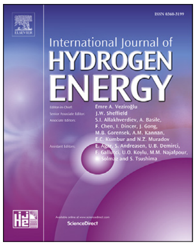

A unified phase equilibrium model for hydrogen solubility and solution density

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ABSTRACT

For the transition to a clean and sustainable energy production from renewable sources like solar or wind power, large and secure storage of energy is required to compensate for the intermittent nature of these sources. Hydrogen could be a suitable energy carrier and hydrogen geological storage could provide the large capacities required. During storage hydrogen will be brought in contact with the formation fluids present, resulting in dissolution and possibly inducing geochemical reactions. Therefore in this work an accurate, consistent and reliable hydrogen solubility model is established, which allows to calculate the hydrogen solubility in the formation fluid and the corresponding variation of fluid density. The model accounts for system pressure, temperature and formation fluid salinity as well as the molar fraction, fugacity coefficient, Henry's constant, Poynting factor and activity coefficient of hydrogen. In the range of typical hydrogen geological storage conditions of 273–373 K, 1–50 MPa and 0–5 mol/kg NaCl this model can reproduce all available experimental data and predict hydrogen solubility in the formation fluid and the formation fluid density accurately. The model can predict hydrogen solubility within a maximum relative error of 5% for pure water and 15% for brines within the salinity range considered, which is in the range of uncertainty of measurement data. For realistic hydrogen gas geological storage, the model is extended to represent also H_2-N_2 or H_2-CH_4 mixed gas systems as well as mixed electrolyte solutions containing Na, K, Ca, Mg, Cl or SO_4 and combinations of those. Model derivation, model calculations and implementation as well as an application example are presented to demonstrate the applicability of the developed methods and the model.

Introduction

Transition of the energy supply from carbon rich fossil fuels like oil, gas or coal to renewable energy sources like wind or solar power is pursued by many countries in the world as a means of reducing greenhouse gas emissions and mitigating climate change effects [1,2]. This transition, termed the "Energiewende" (energy transition) in Germany, causes the share of renewable energy in Germany's energy supply to reach 27.8% in 2014 and to increase to more than 40% in 2025 [3] and even to reach up to 100% of electrical energy by 2050 [4]. Similar trends are seen in countries like Denmark, the UK or the US [1,2]. In China, the fraction of renewable power production is about 20% in 2013, and is rising quickly in subsequent years (www.iea.org). The major renewable energy

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sources are electric power generation by wind or solar power plants, which causes strong temporal fluctuations of the generated power due to the short term weather conditions. In order to stabilize the power grid, compensate for these temporal fluctuations and meet the energy demand in times of low renewable power production, energy storage will be required on the grid scale [4]. Subsurface geological storage has the potential of large storage capacities on a range of time scales [5,6]. Storage options [7] include underground storage of natural gas e.g. Ref. [8], which can be synthesised in times of high power supply, geological gas storage of hydrogen produced from surplus electric power via electrolysis [9–12], compressed air energy storage [13], or subsurface storage of heat. Gas storage in Germany currently accounts for about 20% of yearly demand in both salt cavern and porous medium storage [14], providing a decade-long basis for practical experience.

Hydrogen gas may play an important role in the environmentally friendly production of energy and power from renewable sources [15], as combustion of H_2 leaves H_2O as the only reaction product and - in contrast to fossil fuels - does not result in an emission of greenhouse gases with long residence times in the atmosphere. H_2 has a high combustion heat of about 140 MJ/kg, as compared to 15–32 MJ/kg for coal, 47 MJ/kg for oil and 54 MJ/kg for natural gas (calculated using standard thermodynamic data [16]). Therefore, hydrogen is considered as the best energy carrier to effectively store the renewable primary energy from sources such as solar or wind, which are used for water electrolysis to produce hydrogen [17–19]. Accordingly, the energy storage capacity of H_2 is very large and H_2 is potentially suitable for use in large scale geological energy storage in porous formations, saline aquifers [20,21], caverns [13,22,23] or depleted oil- and gas reservoirs [21,24], which can all provide large storage capacities [10,25,26]. The specific geologic limitations at particular sites, however, may cause a large disparity of costs for the construction and operation of a storage system [27] between different regions.

Large scale use of subsurface energy storage is accompanied by effects induced by the storage operations [5]. For dimensioning of storage capacities as well as for impact assessment, a process based description of the ongoing processes is required in order to be able to predict these effects. These effects have been investigated only recently for hydrogen storage by Refs. [28–30], who use reservoir simulation tools to assess storage options and individual induced effects.

Injection of H_2 into a porous reservoir, however, will impact the original geological fluid-mineral system [11]. On the one hand, an aqueous solution of dissolved H_2 will change the properties of the fluid system, resulting in a shift to reducing conditions and potentially triggering mineral reactions. For instance, in H_2 gas storage at larger depths under elevated temperatures of up to 60–90 °C, the potential electron donor H_2 will behave more actively to support metal oxidation processes, such as redox reactions of Fe^{2+}/Fe^{3+} and H_2/H_2O. Microbiological activity can promote these reactions, whereas the presence of minerals, such as siderite, dolomite and calcite can inhibit them [11]. In underground reservoirs, stored hydrogen, under the influence of methanogenic microorganisms, undergoes chemical conversion, which results in a decrease in the concentration of hydrogen and carbon dioxide, and an increase in the concentration of methane [31]. Hydrogen can be microbially converted to methane and acetate, which can be converted to acetic acid [32]. Truche et al. [33] point out that at low pH values with hydrogen and oxygen present, pyrite becomes unstable and can be involved in hydrogen sulfide producing reactions. On the other hand, the dissolution of H_2 and aqueous geochemical reactions will also affect the fluid density, which may impact convective flow and transport processes in the fluid system. These process interactions may become very complex considering also potential feedbacks of reactive processes on the transport properties of the porous reservoir, e.g. by mineral precipitation/dissolution and consequential changes in porosity and permeability [34–36]. This requires not only a thorough system understanding but also adequate simulation tools [37]. Coupled simulators being able to enable such studies are provided by e.g. Refs. [38–40].

In order to assess the stability and security as well as the energy storage efficiency of a H_2 storage reservoir over long operation periods, the occurrence and extent of the above effects has to be considered. Therefore, the phase behavior of hydrogen, i.e. H_2 solubility and volume properties of a H_2 gas - aqueous solution system, are basic and essential to understand these effects and the migration and alteration of fluids and minerals induced by a H_2 storage operation. Most of the natural groundwater systems are in a non-equilibrium redox state [41]. Hydrogen uptake kinetics have been studied for a wide variety of hydrogen consuming bacteria [41,42], and can be modelled e.g. with Michaelis-Menten kinetics [43], where the H_2 concentration in the aqueous solution is the most important factor and determines the direction and rate of reaction [31]. Injection of high pressure hydrogen gas into porous underground storage formations will increase the H_2 concentration in the aqueous phase significantly, leading to a promotion of abiotic reactions of hydrogen with minerals of the reservoir host rocks and cap rocks [11]. Due to the low viscosity of hydrogen and its high diffusivity, hydrogen migration within the reservoir is increased in comparison to other dissolved components. However, in a continuous cycle of H_2 storage by alternating injection/extraction, the reservoir matrix may be exposed to hydrogen gas and the pore fluid alternately and repeatedly: In this case, the impact of geochemical reactions will accumulate and intensify. For these reasons, an accurate quantification of the solubility of H_2 under conditions of geological storage, which determines the amount of H_2 available for reactions, is a key issue for an assessment of coupled hydraulic and geochemical processes in the reservoir.

The general cubic equation of state, such as Peng-Robinson type equations, has been widely used for phase equilibrium and volume estimation [44]. As a simplified model and due to the lack of sufficient calibration with experimental data, however, it does not accurately reflect the thermodynamic properties of the system. Due to limitations of the underlying data and methods used, applications of this empirical model are limited with respect to temperature and pressure conditions [45]. A rigorous hydrogen solubility model is required for accurate predictions, especially considering the effects of aqueous solution composition and gas mixtures.

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