Available online at www.sciencedirect.com

ScienceDirect

Procedia Earth and Planetary Science 17 (2017) 265 – 268

Procedia Earth and Planetary Science

15th Water-Rock Interaction International Symposium, WRI-15

Modeling of hydrogen genesis in ophiolite massif

Pierre Bachaud[a,1], Clémentine Meiller[a], Etienne Brosse[a], Isabelle Durand[a], Valérie Beaumont[a]

[a]*IFP Energies Nouvelles, 1-4 avenue du Bois-Préau, 92852 Rueil-Malmaison Cedex, France*

Abstract

Natural hydrogen is a promising energy source, but its economic viability remains to be assessed. The present study consists in a modeling methodology applied to hydrogen genesis in Oman ophiolite. With the use of several fluid-rock interactions codes, we modeled groundwaters in fractured harzburgites. The hydrogeological system considered is the following: shallow circulations (above 50m-deep) lead to alkaline springs and fuel deeper flows responsible for serpentinization and hydrogen generation. Numerical results were compared with field data (water compositions, mineralogy, *etc.*), and a good agreement was obtained. An interesting point evidenced by our model is the major role played by carbonates in this system. Where present, these minerals act as carbon buffers, and lead to formation of methane rather than hydrogen.

Peer-review under responsibility of the organizing committee of WRI-15

Keywords: H_2; serpentinization; reactive transport modeling; Oman.

1. Introduction and geological settings

Whereas natural hydrogen (H_2) is a promising and theoretically carbon-free energy source, its potential to constitute an economically viable resource remains to be assessed. In that regard, fluid-rock interactions modeling can help to develop a better understanding of the processes that lead to its formation. The present work consists of applying different simulation tools to model water circulation inside Oman ophiolite, a relatively well-known system due to the numerous studies describing the hydrology, hydrogeology and geochemistry of this region[1-4], and the evidences of hydrogen genesis in ultramafic rocks[5].

* Corresponding author. Tel.: +33 147 527 415.
E-mail address: pierre.bachaud@ifpen.fr

Peer-review under responsibility of the organizing committee of WRI-15
doi:10.1016/j.proeps.2016.12.051

The ophiolite nappe of Oman, standing on the Arabian continental margin, is a remnant of the Thetysian oceanic lithosphere emplaced by obduction and exhumation during late Cretaceous. Its mantellic section is composed of ultramafic rocks (harzburgites), in which olivine and pyroxenes are the most abundant minerals[6]. Serpentinization is the geochemical alteration of this protolith. It consists of a progressive retrograde metamorphic hydration, which leads to serpentine, magnetite and brucite formation. Hydrogen is the product of reduction of water (H_2O into H_2) induced by the oxidation of Fe(II) into Fe(III)[7]. Previous studies described in a fairly accurate way groundwater circulations in the Oman ophiolite [1-3,5]. Meteoric waters infiltrate the fissured zone located near the surface (about 50 m thick), and react with the protolith. The combination of relatively low hydraulic conductivity and significant storage leads to non-negligible residence times in this shallow horizon. This process produces moderately alkaline waters presenting a very high Mg/Ca ratio[3], and partially altered harzburgites. In a lesser extent, these shallow waters supply deeper circulations in the fractures, producing small hyperalkaline springs characterized by higher temperatures (sometimes above 35 °C), a very low magnesium content, and a high calcium concentration that leads to spectacular calcite precipitations by reaction with atmospheric CO_2[4]. These waters also present a highly reducing nature, which most remarkable consequence is the discharging of H_2 gas at the outlets[5].

2. Modeling tools and methods

The modeling strategy that has been followed makes use of several tools and methods to predict fluid-rock interactions.

The Global Energy Minimization method (or GEM) is used to calculate the stable assemblage of a given composition system, by minimizing the Gibbs free energy of the different phases under the constraint of mass conservation[8]. The associated code used in the present study is Arxim-GEM, a tool based on a similar algorithm as the one presented by[9]. Thermodynamic properties of pure end-members come from[10] and[11] databases. The fluid behavior is described by an equation of state (eCPA[12]), specifically parameterized for H_2-H_2O systems. The use of the GEM method is justified in the Oman ophiolite case by the important role played by ferroan and magnesian solid solutions in the serpentinization process. Solid solutions stable compositions at given temperature and pressure conditions, and associated thermodynamic parameters, are calculated considering ideal mixing of the end-members.

The Law of Mass Action approach (or LMA) solves the 0D speciation problem under the constraints of mass conservation and chemical equilibrium between aqueous species. Contrary to the previous method, distance from equilibrium is introduced in solution-minerals reactions, allowing the addition of kinetic constraints to the mathematical system. Arxim-LMA[8], a batch calculator in which only fixed-composition phases can be considered, is used in this study.

Arxim-LMA can be coupled with the reservoir simulator Coores to perform reactive transport. A sequential splitting strategy is used to solve successively the multiphase flow and the reactive transport[13]. This calculation code cannot simulate reactive transport in fractured system, and the ophiolite hydrogeological network has to be approximated by a matrix-type porous medium. Due to the fact that gaseous hydrogen transport properties were poorly constrained at the time of the study, important numerical difficulties were observed when solving reactive transport in presence of a gaseous phase. For that reason, the choice was made to artificially modify gases solubility to reduce the problem to a monophasic aqueous system.

3. Simulations parameters and results

Shallow circulations (above 50 m-deep) were simulated using Arxim-LMA, considering the flushing of a porous media by a solution. The rainwater composition given by[3] is used for the injected fluid, and the flushing flow rate corresponds to the effective infiltrations estimated by[2] (about 18 mm/year). 10 000 years are simulated. Harzburgites mineralogy comes from the work of[6], and solid solutions compositions are calculated by Arxim-GEM simulations (Table 1). The initial porosity is set to 10%. Kinetics parameters are taken from the USGS compilation[14], and the floating spheres texture model is used for each solid phase[8].