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Solid Earth
Discussions

Interactive comment on “Qualitative and quantitative changes in detrital reservoir rocks caused by CO_2-brine-rock interactions during first injection phases (Utrillas sandstones, Northern Spain)” *by* E. Berrezueta et al.

Anonymous Referee #2

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General comments

This study deals with the effect that the injection of “wet” CO2 under supercritical CO2 conditions may exert on the Utrillas sandstone stability in the context of geological CO2 sequestration.

In the paper the authors present an exhaustive characterization of the samples before and after the experiment that was carried out by using optical and electron microscopy techniques (OpM and SEM) and image analysis. The high capability of these techniques to explore the rock changes in order to acquire quantitatively and qualitatively

information on changes in mineralogy, texture and porous network distribution is extensively shown along the paper, and it is pointed out in the conclusions.

Regarding the effect that “wet” SC CO2 exerts on the rock stability I have some comments mainly addressing the experimental methodology. Some clarification should be given to improve the quality of the description and to confirm that the proposed conceptual model does account for the changes observed in the samples after the experiment.

First comment. During CO2 injection, under CO2 supercritical conditions, supercritical CO2 will remain as (1) supercritical CO2 (SC CO2) that is not dissolved with the brine and (2) as supercritical CO2 that dissolves in the brine and becomes dissolved CO2 (DIS CO2) under supercritical conditions. Do the authors study the effect that DIS CO2 exerts on the sandstone under supercritical conditions? In the abstract (“…exposed to supercritical (SC) CO2 and brine”), in the experimental setup and in discussion this is not clear. What does “wet” CO2 mean in the abstract? The authors should clarify along the paper (abstract, materials and methods and in the discussion) on how the CO2 under supercritical conditions may affect the rock stability.

Second comment. According to the described experimental protocol (pg. 2250 and 2251), the authors were able to study the DO CO2 effect on sandstone stability (reactivity). However, I have some doubts on the procedure of the experiments and how the followed steps could affect the interaction between DO CO2 and the six sandstone cubes. I recommend a clear explanation of the experimental conditions in the reactor (pg. 2250 and 2251):

1) Were the samples (six cubes) immersed in brine (600 cm3) to ensure that they were fully saturated (brine occupied all pore space) before the start of the experiment under supercritical CO2 conditions? For how long? This is just briefly explained in Introduction (pg. 2247 line 10). During this step, considering the low reactivity of quartz -the main mineral in the sandstone (95 wt. %)- the chemical composition of the brine (which is not acidic brine) could likely undergo small variation. Was this the case?

Note that unsaturated samples would not be representative of the reservoir sandstone under field conditions.

2) Regarding the experiment under SC conditions, I understand that the six cubes of approx. 180 cm3 were place into the reactor immersed in 300 cm3 of remaining brine. What is the volume of the reactor? Were the six cubes fully immersed? Was there a cap space occupied by non-dissolved SC CO2 (which is less dense than the liquid brine)? If the six cubes were fully immersed, they were in contact with the brine that for approximately 27 h (3 h+24 h) was being acidified as SC CO2 was dissolving. Is this what occurred? Was the pH measured? In pg. 2259 (line 4) it is stated that pH decreased from 7.2 to 5.2 (also shown in Table 2).

3) During these 24 h, the progressively acidified brine was reacting with the minerals of the rock samples (pg. 2253: 95 % quartz, 1-5 5 % of hematite and limonite and 5 % of feldspar, clays (muscovite, chlorite, illite, and kaolinite)). Considering the acidic pH and experimental temperature (38 C), dissolution of some of these minerals could occur as the acidified brine interacted with the mineral surfaces present at the cube surfaces and within the cubes through pores (rock porosity ranged from approx. 5 to 20%; pgs. 2253 and 2254). Could the brine filling the pore space -if rock cubes were previously fully saturated- be displaced by the acidified brine during the experiment?

4) If dissolution could take place, all minerals, except quartz, likely dissolved (Fe oxide and hydroxide, feldspar and clays) from which Fe (although it precipitated at pH > 3), Si, Al (it also could precipitate if pH > 5), Mg, Na, Ca and K could likely be released. In Table 2 concentrations of these elements were not given. Please give more details. How could SO4 decrease? Was that CaSO4 and/or MgSO4 could precipitate somehow? Was the brine in equilibrium or supersaturated with respect to these or other phases (pg. 2258; line 25? This could be easily checked with PHREEQC. Regarding the brine used in the experiments, where is it coming from? Was it extracted from the aquifer? Table 2 head states “natural” brine. Please explain.

5) Did depressurization of the experiments lasted 3 h (pg. 2251)? Why did it take so long? During this step, the brine pH likely increased as DO CO2 degassed, allowing carbonation and formation of CaCO3 and MgCO3. Was this contemplated? Is this the reason to observe a decrease in Ca and Mg (Table 2)? How were the samples prepared to ICP-EOS analyses? Did you filter the samples? Please explain.

Third comment. Considering the experimental setup –as I understand it- I do not see any other way, other than the acidic brine interacting with the cube samples, that SC CO2 could contact the solid samples. This implies that only chemical processes could affect the rock stability (reactivity). In this case, the conceptual model based on the effect that injected CO2 exerted on the quartz matrix and quartz skeletal grains leading to detachment and partial re-adjustment of the quartz volume proposed in the paper cannot account for the underwent processes. If my interpretation is not correct, in the revised ms, please improve the explanation of the experimental procedure so no one else is confused (pg. 2260):

a) “initial CO2 input would mix with brine and percolate through the rock pore system generating a mechanical dragging force probably opening/widening some of the inter quartz-particle cracks”. Is CO2-rich brine or CO2 percolating through?

b) “SC CO2 continues to diffuse into the pore structure causing accommodation inside (small fractures) and between quartz grains, producing instability in the rock cohesion”. I do not understand how SC CO2 diffuses into the pore structure. Again, do you mean the CO2-rich brine diffuses through?

Specific comments

pf 2250, line 16. How “standard commercial CO2 at 45 bars” relates to the cylinders? What does it mean? pf 2250, line 18.What do you mean with “possible leaks”? pg 2252, line 26. Was ICP-EOS used? pg 2254, line22. 172 100? pg 2256, line 24, “the chemical composition of the brine…” Table 2: please remove “pH unit”

Interactive comment on Solid Earth Discuss., 7, 2243, 2015.