

## ***Interactive comment on “Qualitative and quantitative changes in detrital reservoir rocks caused by CO<sub>2</sub>-brine-rock interactions during first injection phases (Utrillas sandstones, Northern Spain)” by E. Berrezueta et al.***

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Dear Editor,

The authors would like to thank the anonymous reviewer for her/his contributions to this manuscript. We must acknowledge that the incorporation of the recommended suggestions improved the quality of the manuscript.

All referee's comments are answered bellow and included in the revised version of the manuscript highlighted in green. Furthermore, other changes are highlighted in

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red (ref#1). The detailed corrections were uploaded as a pdf supplement file (revised manuscript 2).

GENERAL COMMENTS This study deals with the effect that the injection of “wet” CO<sub>2</sub> under supercritical CO<sub>2</sub> conditions may exert on the Utrillas sandstone stability in the context of geological CO<sub>2</sub> 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 CO<sub>2</sub> 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.

Answer: We kindly appreciate the comments of the referee that allowed improving the manuscript. Changes have been made following the referee's comments (explained bellow) concerning the sections: Abstract (p 1); section 3.1. Experimental setup and procedure (p7 line 9-13); section 5 Discussion (p14-15); section 6 Conclusions (p 16) and Fig. 8 following the modifications included in the discussion section.

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

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CO<sub>2</sub> under supercritical conditions may affect the rock stability.

Answer: We used the right terminology indicated by the referee along the manuscript to clarify. It is the CO<sub>2</sub>-rich brine that interacts with the rock in our experiments. Thanks to the reviewer's comments that allowed to improve the interpretation that the changes seen in porosity correspond to the outermost rock areas that are in direct contact with the acidified brine. This has been included in the abstract, discussion and conclusions sections.

Second comment. According to the described experimental protocol (pg. 2250 and 2251), the authors were able to study the DO CO<sub>2</sub> 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 CO<sub>2</sub> and the six sandstone cubes. I recommend a clear explanation of the experimental conditions in the reactor (pg. 2250 and 2251): Were the samples (six cubes) immersed in brine (600 cm<sup>3</sup>) to ensure that they were fully saturated (brine occupied all pore space) before the start of the experiment under supercritical CO<sub>2</sub> conditions? For how long? This is just briefly explained in Introduction (pg. 2247 line 10).

Answer: Clarified the experimental set up and procedure as follows: (p7 lines 9-13): "The experiments began with the saturation of rock samples (6 cubes of 27 cm<sup>3</sup> of sandstone sample) with natural brine by 3 cycles during 72 h. 0.3 dm<sup>3</sup> of this brine was extracted and analysed before CO<sub>2</sub>-rich brine exposition occurs. Then, the rock samples (6 cubes of 27 cm<sup>3</sup> of sandstone sample) were introduced into the chamber and fully immersed in the rest of brine (0.3 dm<sup>3</sup>) and at the end of the experiments analyzed and noted "after CO<sub>2</sub>-rich brine"."

Comment: 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.

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Answer: Yes, there were no significant changes in quartz content.

Comment: 2) Regarding the experiment under SC conditions, I understand that the six cubes of approx. 180 cm<sup>3</sup> were placed into the reactor immersed in 300 cm<sup>3</sup> of remaining brine. What is the volume of the reactor? Were the six cubes fully immersed?

Answer: We clarified in the previous comment about the experimental setup and procedure. The maximum capacity of the reactor is approx. 3000 cm<sup>3</sup> (detailed p 7, line 3).

Comment: Was there a cap space occupied by non-dissolved SC CO<sub>2</sub> (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 CO<sub>2</sub> was dissolving. Is this what occurred?

Answer: Yes. The presence of non-dissolved SC CO<sub>2</sub> in the brine was not in contact with the rock. This occupied the top of the test chamber. Sample+brine+CO<sub>2</sub> were up to supercritical conditions for 24 hours. Sample+brine+CO<sub>2</sub> were 6 hours in conditions below 38°C and 7.8 MPa: 3 hours from ambient conditions to supercritical conditions and 3 hours to go from supercritical conditions to ambient conditions.

Comment: 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).

Answer: Yes, the brine pH was measured before brine was in contact with CO<sub>2</sub> and after the experimental test. Brine chemical studies carried out in the present work are listed in section 3.2 Methodology of study.

Comment: 3) During these 24 h, the progressively acidified brine was reacting with the minerals of the rock samples (pg. 2253: 95 % quartz, 1-5 % 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

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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?

Answer: We think that the acidified brine interact with the brine that is filling the pores. The low compressibility coefficient of a fluid in the case of an increase of pressure and temperature (as in our experiment) do not favour displacements of the fluid.

Comment: 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  $\text{pH} > 3$ ), Si, Al (it also could precipitate if  $\text{pH} > 5$ ), 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  $\text{SO}_4$  decrease? Was that  $\text{CaSO}_4$  and/or  $\text{MgSO}_4$  could precipitate some how? 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.

Answer: The elements analysed for the whole rock and brine, after/before interaction with  $\text{CO}_2$ -rich brine, were conditioned to techniques available in our research centre. We have included information about it in p8 line 30. This About dissolution process that could take place under our experimental conditions, we have included information about it in p 14 line 1-4. "According to the bibliography dissolution of clay and feldspar of the matrix could take place due  $\text{CO}_2$ -rich brine. In this case,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Si}^+$  could be releases but they do not show relevant variation in the brine analysis after  $\text{CO}_2$ ". The  $\text{SO}_4$  variations could be explained for example as gypsum precipitation. In p 13 line 28 we explained the possibility that these changes could be "due to local mineral precipitation of Mg, Ca and Na minerals, evidenced by an increase of these oxides in the chemistry of the rock after the experiment". We have included the term "(e.g. gypsum..)" p13 line 29. We did not produced the PHREEQC models referred, therefore we have commented the limitations of the chemical studies in the conclusions in the sense that a way to improve the understanding of the chemical processes occurring in our experiments would be important to expand the number of analyses, the num-

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ber of elements to analyze and to improve the accuracy by more precise techniques. In addition, the incorporation of PHREEQC models would facilitate the interpretation of results. This comment was included in the manuscript in p16 lines 22-24 "Some improvements would allow understand the chemical processes occurring in the experiments: e.g. number of analyses, elements to analyse, accuracy of techniques and the use of PHREEQC models."

Comment: 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.

Answer: It was a natural brine obtained in a borehole from a saline aquifer. We clarified in the text. (p 6 line 25-26).

Comment: 5) Did depressurization of the experiments lasted 3 h (pg. 2251)? Why did it take so long?

Answer: The time to reach experimental values (ca.3h) has followed the recommendations of the manufacturer of the test chamber, as well as the time for the process of depressurization and temperature drop. We have clarified in the text. (p 7 line 19).

Comment: During this step, the brine pH likely increased as  $\text{CO}_2$  degassed, allowing carbonation and formation of  $\text{CaCO}_3$  and  $\text{MgCO}_3$ . Was this contemplated? Is this the reason to observe a decrease in Ca and Mg (Table 2)?

Answer: This is a possibility that we had not contemplated as we did not find any  $\text{CaCO}_3$  and/or  $\text{MgCO}_3$  precipitates, but we agree that this possibility exists and we have included it in the text. p 14 lines 12-14. "The higher amount of carbonic acid originates from the  $\text{CO}_2$  dissolution in the brine, and could allow carbonation and formation of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  due to the depressurization process followed".

Comment: How were the samples prepared to ICP-EOS analyses?

Answer: Brine samples before and after having contact with SC  $\text{CO}_2$  are collected in sealed recipients and sent to an accredited lab (IGME) for analysis by ICP-OES. Term

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included in p 8 line 29.

Comment: Did you filter the samples? Please explain.

Answer: The brine was extracted from the chamber after experimentation. This was decanted and separated into liquid and solid. The result of the analysis of the brine before and after experimentation appears in Table 2. We changed to clarify in the table 2 the terms "Rock before CO<sub>2</sub> and brine" and "Rock after CO<sub>2</sub> and brine" by "Brine before CO<sub>2</sub>" y "Brine after CO<sub>2</sub>". The solids recovered were described by binocular microscope and shown in Figure 7.

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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub>-rich brine or CO<sub>2</sub> percolating through? b) "SC CO<sub>2</sub> 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 CO<sub>2</sub> diffuses into the pore structure. Again, do you mean the CO<sub>2</sub>-rich brine diffuses through?

Answer: In fact, considering the experimental set up the acidic brine is interacting with the rock samples. But the evidenced changes evaluated are mainly physical features (porosity increase..) that indeed reflect a chemical interaction. On the other hand the result of chemical analyses of brine and rock, before and after contact with SC CO<sub>2</sub>

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indicate no significant changes, considering the accuracy of the techniques. This does not rule out a possible chemical effect of the acidified brine in the rock matrix including some carbonation and/or MgSO<sub>4</sub> and/or CaSO<sub>4</sub> precipitation. Besides, we can not exclude matrix solution (feldspar / clay) of sandstone as indicated by previous studies as noted above p14 lines 1-4. In this sense the conceptual model is now better described p 15, lines 3-29 and modifications included in Fig. 8 and figure captions Now written in the discussion: p 14 lines 18-21 "the changes in the porosity configuration measured (Table 1), are limited to external areas of the sandstone blocks exposed to CO<sub>2</sub>-rich brine and probably due to local chemical changes; and may represent the early physical display of the chemical influence of the CO<sub>2</sub>-rich brine on the rock".

#### SPECIFIC COMMENTS

Comment: pf 2250, line 16. How "standard commercial CO<sub>2</sub> at 45 bars" relates to the cylinders? What does it mean?

Answer: The two cylinders correspond to CO<sub>2</sub>-supplying cylinders of standard industrial CO<sub>2</sub>. We changed "commercial" by "industrial" in the text (p 6, line 27).

Comment: pf 2250, line 18. What do you mean with "possible leaks"?

Answer: In case there is any failure in the chamber dealing with gas loss, the pump will maintain the experimentation conditions.

Comment: pg2252, line 26. Was ICP-EOS used?

Answer: Yes. We included the term ICP-OES instead ICP in the text p 8, line 27.

Comment: pg 2254, line22. 172 100?

Answer: p 10 line 16: Changed: "The maximum and minimum area of pore were 172100  $\mu\text{m}^2$  and t 9.2  $\mu\text{m}^2$ , respectively." by: "The maximum and minimum area of pore was 172100  $\mu\text{m}^2$  and 9.2  $\mu\text{m}^2$ , respectively".

Comment: pg 2256, line 24, "the chemical composition of the brine. . ."

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Answer: p 12 line 4: Changed: "The composition of the brine was analysed before and after the 24 h testing and the results are shown in Table 2". By: "The chemical composition of the brine was analysed before and after the 24 h testing and the results are shown in Table 2".

Comment: Table 2: please remove "pH unit"

Answer: OK.

Changed in Table1 terms: "Before SC CO2-brine" and "After SC CO2-brine" by "Before CO2-rich brine" and "After CO2-rich brine".

Please also note the supplement to this comment:

<http://www.solid-earth-discuss.net/7/C1368/2015/sed-7-C1368-2015-supplement.pdf>

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