Short-term effects of impurities in the CO₂ stream injected into fractured carbonates

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ABSTRACT

After the Paris Agreement in which 195 countries are involved, the Carbon Capture and Storage (CCS) is now an accepted technology in the United Nations Framework Convention on Climate Change (UNFCCC). In Spain, Fundación Ciudad de la Energía (CIUDEN) has successfully completed the full CCS chain, being CO₂ captured in the Technology Development Centre in Cubillos del Sil (León, Spain) whereas that it is geologically stored in a deep saline aquifer, formed by fractured carbonates with poor matrix porosity, located in the Technology Development Plant (TDP) at Hontomín (Burgos, Spain).

The results of the field tests, in which up to 150t of CO₂ and synthetic air (5%v of N₂ and O₂) were co-injected on site, are analyzed in this paper comparing the operational parameters gained during the injection of impure CO₂ (pressures, temperatures and flow ranges) with its corresponding baseline previously determined (i.e. 1500tons of pure CO₂ were injected during the reservoir hydraulic characterization). Besides that, the geochemical reactivity analysis of impure CO₂ injected in this saline aquifer and its correlation with the results from laboratory tests were assessed.

As main conclusions from laboratory scale results, a porosity diminution was measured after the injection of CO₂ with 5%v of SO₂; apart from that, without SO₂, the effluent pH was in the range of 7-8 whereas in case of CO₂ and SO₂, a pH of 1-2 was obtained. Otherwise and focused on field scale tests, a density decrease was detected comparing the base case (pure CO₂) with the CO₂ injection containing 5.1%v of synthetic air. On the other hand, Ca²⁺, SO₄²⁻, Mg²⁺ and K⁺ migration effects in the rock were also detected and analyzed.

1. Objective

The main objective was to carry out field scale injection tests of CO₂ and synthetic air (i.e. O₂ and N₂) into fractured carbonates with poor primary porosity and transmissivity through the fracture network, to identify and assess the impacts of these impurities in the short-term stability of CO₂ storage and their influences on site operation. Laboratory scale test campaign was previously conducted in order to study the chemical interactions between impure CO₂/brine and carbonates reservoir.

2. Introduction

Years of work culminated in the Paris Agreement in which some of the main key points were: 195 countries are involved; reduce the temperature rise to below 2°C it is desired; the Carbon Capture and Storage (CCS) is now an accepted technology in the United Nations Framework Convention on Climate Change (UNFCCC) (Dixon and Gale, 2016; IEAGHG, 2016; Christian, 2015). CCS is recognized one of the key existing technologies to reduce the global emissions of CO₂ into the atmosphere (International Energy Agency (IEA), 2013). Regarding technical aspects, this technology has "a green light" although there are some important uncertainties to be solved (Delgado et al., 2014).
Fundación Ciudad de la Energía (CIUDEN) has successfully completed the full CCS chain, being CO₂ captured in the Technology Development Centre in Cubillos del Sil (León, Spain) whereas it is geologically injected into a deep saline aquifer located in the Hontomín Technology Development Plant (TDP) (Burgos, Spain) (Fernandez et al., 2015).

Regarding CO₂ storage, one of the most important uncertainties of this technology is to understand the physico-chemical processes that take place in the rock-brine-CO₂ system within the seal-reservoir geological complex during and after CO₂ injection and, particularly, the changes induced on operational processes due to impurity effects (Brosse et al., 2005; Michael et al., 2015). CIUDENís activities are focused on this issue including the accomplishment of experiments in laboratory and field scale. It should be noted that selected impurities used in laboratory and their composition are different than in field scale case, with the aim to avoid operations that could cause damages to the geological formations and the facility.

3. Material and methods

3.1. Hontomín TDP

Regarding the geological formations to inject CO₂ in Hontomín TDP, Sopeña Formation (Fm) was selected due to better injectivity conditions during the site hydraulic characterization. This formation presents a poor matrix porosity and permeability through the fracture network, conditioned by hydrodynamic effects induced by the injection of CO₂ and brine and the geochemical reactivity between the mixture previously specified and the reservoir rock. As it is explained in Fig. 1, Sopeña Fm. consists of two different layers: limestones and dolomites; in Table 1, Sopeña Fm. mineralogical composition is showed (Global CCS Institute, 2015).

Highlighting that 18 linear meters of chokes are installed at 1000 m depth, in order to produce a pressure drop up to 60 barg. As shown in Fig. 2, these instrumentations cross the packer (grey area).

Regarding HA, with a distance of 50 from HI, the well is equipped with similar instrumentation than injection well (see Fig. 3):

a) P/T sensors to measure at 4 different levels in the open hole (seal and reservoir).

Table 1

<table>
<thead>
<tr>
<th>Hontomín reservoir mineralogy.</th>
<th>Limestone (% w)</th>
<th>Dolomite (% w)</th>
<th>Anhydrite (% w)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sopeña limestone unit</td>
<td>97</td>
<td>3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Sopeña dolomite unit</td>
<td>0</td>
<td>98</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Not to scale

Fig. 1. Hontomín TDP formations.

Fig. 2. X-mas tree and instrumentation of H-I well.
b) 28 electrodes for electrical resistivity tomography (hereinafter, ERT) installed at intervals of 7–8 m.

c) Mobile hydrophones spaced regularly at intervals of 9 m.

Also worth mentioning is the U-tube operating principle due to the important role of this deep sampler during the test campaign conducted on site. The U-tube is a simple positive fluid displacement pump which uses a high pressure gas drive (Freifeld, 2009). Its core is the ball check-valve installed at the top of the hydraulic packer (1428 m depth), and below it, the inlet filter and thin tubing which reaches the bottom hole. This valve contains the only moving part of the system in the borehole. A loop of tubing, with the "sample leg" and "drive leg" as it is shown in Fig. 4, reaches the surface for extracting deep fluid samples. Check-valve is located below a "tee" at the base of the U and permits the fluid to enter into the loop, closing (by application of gas from the surface) when the pressure in the U is increased above the hydrostatic value. The inlet, below the check-valve to prevent the plugging, is manufactured by a sintered stainless steel filter.

For collecting a sample (Freifeld, 2009), once the check valve is open, the U is firstly filled by venting and driving the fluid from the reservoir to the inside of both legs. At this stage the check valve is closed and the sample is recovered by supplying high-pressure N₂ through the drive leg, enhancing the fluid recovery through the sample leg.

3.1.2. CO₂ injection facility

This facility is formed by three cryogenic tanks (50 tons each one), injection pumps, CO₂ heater/gasifier, balance of plant (BOP) and instrumentation and control (I&C) parts.

In order to monitor the synthetic air injection, four different cylinder racks were used in parallel (see TRACING/DOPPING AREA in) Fig. 5. For acquiring representative data to quantify the amount of synthetic air that was injected in the main CO₂ stream during each test, one of the four cylinders rack was located over a scale to provide information which could corroborate the measurements gained from the facility monitoring.

After the injection tests, samples from the borehole were extracted using the U-tube device on a weekly basis, considering a period of three months. Taking into account that the samples were extracted in "reservoir conditions" (pressure and temperature), they were analyzed in two steps:

- Step #1 or gas phase analysis: It was performed using a Fourier Transform Infrared analyzer (FTIR) (see Table 2).
- Step #2 or liquid phase analysis: It was conducted in two different equipments: the ion chromatography and the carbonate analyzer.

In the first case, the determination of anions and cations were
Table 2
Technique and equipment model used during the field tests.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Equipment Model or Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion-exchange chromatograph</td>
<td>METROHM model automatic processor 850 professional IC (METROHM)</td>
</tr>
<tr>
<td>Gas permeameter</td>
<td>VINCI Technologies GasPerm (VINCI Technologies)</td>
</tr>
<tr>
<td>Mercury porosimetry</td>
<td>QUANTACHROME (POREMASTER 60GT) (QUANTACHROME)</td>
</tr>
<tr>
<td>Un-steady state Relative Permeability System</td>
<td>CORETEST SYSTEMS RelPerm (CORETEST SYSTEMS INC)</td>
</tr>
</tbody>
</table>

Fig. 5. Schematic process flow diagram (PFD) of Hontomín TDP.

Fig. 6. Ion concentration for effluents produced during the test (sample B1.4.2).

Fig. 7. Ion concentration for the effluent produced during the test (sample B1.3A).

Table 3
Technique and equipment model used during the laboratory tests.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Equipment Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury porosimetry</td>
<td>QUANTACHROME (POREMASTER 60GT) (QUANTACHROME)</td>
</tr>
<tr>
<td>Gas permeameter</td>
<td>VINCI Technologies GasPerm (VINCI Technologies)</td>
</tr>
<tr>
<td>Un-steady state Relative Permeability System</td>
<td>CORETEST SYSTEMS RelPerm (CORETEST SYSTEMS INC)</td>
</tr>
<tr>
<td>Ion-exchange chromatograph</td>
<td>METROHM model automatic processor 850 professional IC (METROHM)</td>
</tr>
</tbody>
</table>

3.2. Laboratory equipments

CIUDEN performed surface campaigns collecting cores from outcrops (analogues) corresponding to the caprock and reservoir, being used in the laboratory tests.

Generally speaking, the laboratory tests were based on the injection of a CO₂ stream with and without impurities in Hontomín analogues according to the following methodology:

- Measurements before the injection:
  - Mass, helium porosity and gas permeability measurement.
  - Analogue saturation with sodium chloride (NaCl) with a concentration of 40 g/l and determining its permeability by CORETEST equipment.
  - The analogue is covered with a thermo-retractable plastic in its lateral area.
  - Set the conditions of the experiment.
  - Inject pure CO₂ or impure CO₂ throughout the cores. The total volume injected was, at least, higher than 5 times the porous volume of the sample.
  - The test duration was five days (8 h/day).
  - Measurements after the injection:
    - Mass, helium porosity and gas permeability measurement.

- Ion chromatography of effluents generated during NaCl saturation and the injection tests.

Worth mentioning the requirements of the samples in order to do these tests were: Porosity ≥5%; permeability >1 mD; diameter: 1,5 cm; length: 1-3 cm. Regarding the procedure basis, Table 3 shows the technique and equipment used for these tests:

4. Results

4.1. Laboratory scale tests

The test matrix is included in Table 4; a comparison between the injection of pure CO₂ and CO₂ containing SO₂ was selected as the case study in laboratory scale. As explained above, it is needed to remind that the selected impurity (SO₂) and the composition of the mixtures used in laboratory were different than the used in the field scale tests, in order to avoid some damage that could be caused to the reservoir and/or the facility.

Based on the steps related in the Chapter 3.2, the following tables (Tables 5–8) show the results gained from each sample considered in the test matrix; the Figs. 6 and 7 are the representation of the data included in Tables 6 and 8.

4.2. Field scale results

4.2.1. Composition of injection stream

Considering the quantity of synthetic air (kg/min) that was injected in each test, the real composition of CO₂ stream was cal-
### Table 4
Laboratory scale test matrix.

<table>
<thead>
<tr>
<th>Type of experiment</th>
<th>Sample type</th>
<th>Sample name</th>
<th>CO₂ impurity</th>
<th>Concentration of CO₂ impurity</th>
<th>P-T conditions</th>
<th>Brine</th>
<th>Brine concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plug Flow (dynamic tests)</td>
<td>Sopórea limestone</td>
<td>B1.4.2</td>
<td>Pure CO₂</td>
<td>0%</td>
<td>150 bar/50° C</td>
<td>NaCl</td>
<td>40,000 ppm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B1.3A</td>
<td>CO₂ + SO₂</td>
<td>5%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: The values presented correspond with the main characteristics of Hontomín TDP.

### Table 5
Physical properties for the sample B1.4.2 before and after CO₂ injection.

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (mm)</td>
<td>42.32</td>
<td>42.12</td>
</tr>
<tr>
<td>D (mm)</td>
<td>37.19</td>
<td>37.19</td>
</tr>
<tr>
<td>m (g)</td>
<td>101.67</td>
<td>100.27</td>
</tr>
<tr>
<td>Φ (%)</td>
<td>18.87</td>
<td>21.02</td>
</tr>
</tbody>
</table>

Notes: L = length, D = diameter, m = mass (dry basis), Φ = porosity.

### Table 6
Ion concentration for effluents produced during the test (sample B1.4.2).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Liquid sample</th>
<th>Cycle</th>
<th>Anion Concentration (ppm)</th>
<th>Cation Concentration (ppm)</th>
<th>pH</th>
<th>Cond (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F⁻</td>
<td>Cl⁻</td>
<td>SO₄²⁻</td>
<td>Li⁺</td>
</tr>
<tr>
<td>B1.4.2</td>
<td>Brine</td>
<td>1</td>
<td>0</td>
<td>23.605</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>2</td>
<td>2.3</td>
<td>23.868</td>
<td>0.0</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>3</td>
<td>22.560</td>
<td>19.9</td>
<td>0.9</td>
<td>14.768</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>4</td>
<td>25.001</td>
<td>0.0</td>
<td>0.3</td>
<td>16.352</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>5</td>
<td>23.223</td>
<td>0.0</td>
<td>2.2</td>
<td>15.221</td>
</tr>
</tbody>
</table>

### Table 7
Physical properties for the sample B1.3A before and after CO₂ + SO₂ injection.

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>L (mm)</td>
<td>46.23</td>
<td>46.23</td>
</tr>
<tr>
<td>D (mm)</td>
<td>37.29</td>
<td>37.29</td>
</tr>
<tr>
<td>m (g)</td>
<td>116.77</td>
<td>115.83</td>
</tr>
<tr>
<td>Φ (%)</td>
<td>8.94</td>
<td>1.95</td>
</tr>
</tbody>
</table>

Notes: L = length, D = diameter, m = mass (dry basis), Φ = porosity.

### Table 8
Ion concentration for the effluent produced during the test (sample B1.3A).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Liquid sample</th>
<th>Cycle</th>
<th>Anion Concentration (ppm)</th>
<th>Cation Concentration (ppm)</th>
<th>pH</th>
<th>Cond (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>F⁻</td>
<td>Cl⁻</td>
<td>SO₄²⁻</td>
<td>Li⁺</td>
</tr>
<tr>
<td>B1.3A</td>
<td>Brine</td>
<td>1</td>
<td>0</td>
<td>25.257</td>
<td>628.4</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>2</td>
<td>0</td>
<td>24.303</td>
<td>1961</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>3</td>
<td>0</td>
<td>23.829</td>
<td>4062</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>CO₂ and brine</td>
<td>4</td>
<td>0</td>
<td>26.018</td>
<td>5700</td>
<td>1.2</td>
</tr>
</tbody>
</table>

![Fig. 8](https://via.placeholder.com/150)

Fig. 8. Real composition of air in the CO₂ stream.
4.2.2. Operation parameters

4.2.2.1. Injection regime and wellhead vs bottom-hole pressure. During the injection of 5.1% of synthetic air, following results were gained as Fig. 9 shows:

4.2.2.2. Storage conditions. Fig. 10 among other parameters, pressure and temperature at the bottom hole are represented to corroborate that CO₂ was stored in supercritical conditions into the reservoir. Taking into account the values of these parameters on the well head (see previous Fig. 9) it is needed to monitor the temperature along the tubing for assessing the injection conditions.

4.2.3. Differential pressure in the bottom hole

Regarding the information given in Fig. 2, two pressure transmitters are installed in the injection bottom hole, being the distance between them of 25 m.

The measured pressure values allowed calculation of fluid density using the hydrostatic pressure equation. Consequently, two different graphs are plotted: first graphic shows the differential pressure and the density calculated during the injection of pure CO₂ (Fig. 11) whereas in a second block of figures, it is represented the comparison of calculated densities between the base case (pure CO₂) and CO₂ containing 5.1% of air, concluding that density value
decreases from 840 kg/m³ to 775 kg/m³ in reservoir conditions (Fig. 12).

4.2.4. Temperature monitoring along injection tubing

Distributed Temperature System (DTS) is a device used to monitor the temperature evolution along the injection tubing (Jenkins et al., 2015). In Fig. 13, the results from the Distributed Temperature Sensing (DTS) are showed for three different stages: formation water, pure CO₂ injection, and CO₂ with synthetic air (5.1%v) injection.

A perturbation is produced close to 1000 m depth, as is shown in Fig. 13; the reason was that 18 linear meters of chokes were installed inside the injection tubing at this depth to generate a pressure drop for avoiding to reach values higher than the Leak-off test pressure (LoT) of reservoir formation (Birkholzer et al., 2015; Bachu, 2015) with the consequent negative effects such as induced seismicity in surface and leakages affecting potable groundwater resources (Jones et al., 2015; Birkholzer et al., 2015). A temperature decrease is generated as well, due to the Joule-Thomson effect, as consequence of the fast CO₂ expansion at the choke outlet (Fig. 13).

According to the data gained during the CO₂ injection in the well head (Fig. 9), the bottom hole (Fig. 10) and the DTS, it can be assured that the injection was performed in liquid-phase along the tubing. Consequently, the coupling between well head pressure (WHP) and bottom hole pressure (BHP) due to monophasic flow conditions during injection was confirmed.

4.2.5. DOTs₁ gas phase analysis

Figs. 14 and 15 represent the results obtained for the gas phase from the tests performed by pressure vessels used to store fluids at above atmospheric pressure (DOTs) (see step #1 previously explained in the Chapter 3.1.2).

After the injection of impure CO₂, different extractions were carried out in order to analyze the reservoir behaviour after the injection of CO₂ with the impurity of 5.1%v of air (see step #1 explained in the Chapter 3.1.2); analogously to the base case previously presented, following figures (Figs. 16 and 17) represent the results obtained for the gas phase.

4.2.6. DOTs liquid phase analysis

Fig. 18 represents the composition of CO₂ in the liquid phase for different samples, i.e., the quantity of CO₂ dissolved at atmospheric pressure (see step #2 previously explained in the Chapter 3.1.2)

₁ DOT is a pressure vessel used to store fluids at above atmospheric pressure.
Carbon dioxide sequestered will be trapped by physical and chemical processes. Focusing on chemical trapping, a distinction between aqueous phase trapping (solubility and ionic trapping) and mineral trapping can be done (Talman, 2015). Considering the duration of the test, it is clear that the second case is not the scope of this work so only the expected reaction with the aqueous phase should be taken into account, i.e. solubility of water in the injected high-density CO₂ - stream and hydrolysis reactions or ionization of water (Talman, 2015):

\[
\text{CO}_2 (aq) + H_2O \rightarrow H^+ + HCO_3^- \\
\text{CO}_2 (aq) + H_2O \rightarrow 2H^+ + CO_3^{2-}
\]
Several trace impurities also undergo hydrolysis reactions; these are H₂S, SO₂ and NH₃; considering the scope of this work, SO₂ is included in this section with a higher degree of detail. SO₂ forms the strongest acid, it will protonate HCO₃⁻ to form CO₂ (aq).

Regarding the laboratory results previously described, if we compare the values of porosity between the injection of pure CO₂ and CO₂ with 5.1%v of SO₂, in the second case, the result was much lower (≈80%). In our opinion this effect could have two possible causes: first hypothesis is the samples were extracted from the pressure chamber suffering both fast cooling and expansion at the end of each test, and consequently, the Cl⁻ and Na⁺ precipitated into the rock matrix with the final diminution of porosity; other possibility is based on the fact that due to the high concentration of SO₂ (5.1%v is not common in flue gases to be captured (Global CCS Institute, 2014)), the porosity was decreased due to the precipitation reactions such as the carbonate and sulphate formations. This last hypothesis should be studied deeply in future longer laboratory tests.

Focused on the field scale tests, DTS monitors the temperature evolution along the injection tubing. At this point, it was obtained that higher the concentration of air in the CO₂ stream, higher is the Joule-Thomson effect (i.e. diminution of the temperature with the variation of pressure). As a future work, these measurements have to be compared with the theoretical values provided by TREND software (Span, 2015).

Finally, it is needed to highlight that during the following 11 days after the injection of impure CO₂, the gas phase samples gained were the same nature as the base case (i.e. injection of pure CO₂). At this point, Reader is reminded that 150t of impure CO₂ were injected, and in our opinion that quantity was not enough to achieve clear results for determining how the reservoir behaviour is in terms of structural trapping at Hontomín site.

6. Conclusions

In this work, experiments on laboratory and field scale have been performed to study physical and chemical interactions in the short term between CO₂ and impurities, brine and reservoir rock, in order to assess their influence in a safe and efficient injection and the implications involved for the CO₂ geological storage.

Focused on the laboratory scale, dynamic tests (samples are located in a liquid permeameter where the CO₂ flows through the sample) of analogous from Hontomín reservoir have been done; 150 barg and 45°C were planned as P and T conditions (Hontomín reservoir conditions) and SO₂ was selected as impurity considering a concentration of 5.1%v in the CO₂ stream. As main conclusions, a sample negligible mass diminution (around 1%) was measured after the injection, independently of the degree of impurity; regarding the porosity, it was much lower (≈80%) after the injection of CO₂ with 5%v of SO₂. Besides that, other important differences detected are the effluent pH and the ion migration phenomena. In regards the pH value, for the pure CO₂ injection tests the effluent pH was in the range of 7–8 but if impure CO₂ was injected, the pH obtained was in the range of 1–2 (Pearce et al., 2015). Regarding the second effect with the mixture of CO₂ and SO₂, chemical modifications were detected, being mainly based on the modification of Mg²⁺ and SO₄²⁻ due to migration phenomena produced by the acidification previously explained.

The short-term co-injection of CO₂ and synthetic air (i.e. O₂ and N₂) field scale tests were conducted in order to identify the impact of these impurities in the reservoir behaviour of Hontomín Technology Development Plant. For a synthetic air concentration of 5.1%v and based on the pressure and temperature at the bottom injection well (158 barg, 31°C), it was possible to assure that the CO₂ is stored in supercritical conditions at Hontomín reservoir. On the other hand, DTS data reveal that the injection is performed in monophasic flow (liquid). Consequently, the coupling between WHP and BHP due to single phase fluid conditions during injection was also confirmed.

It was possible to calculate the fluid density using the two pressure transmitters installed at the bottom of the injection well and considering the distance between these two devices. Comparing the base case (pure CO₂) with the case of CO₂ containing 5.1%v of air, the density decreases from 840 kg/m³ to 775 kg/m³ at the storage conditions (i.e. 8% of diminution in the density). Consequently, the storage capacity of the reservoir suffers an impact due to the replacement of CO₂ but also due to the mixture of CO₂ and impurities do not compress to as great a degree as CO₂.

Otherwise, regarding the operation conditions showed in Fig. 9, the well head pressure needed to inject the mixture of CO₂ and 5.1%v of air, increased from 80 bar, corresponding to the case of pure CO₂ to 90 bar. That effect reveals that the higher value of WHP is due to the need to inject a mixture of CO₂ in liquid phase with the impurities (N₂ and O₂) in gas phase. By the foregoing, we can conclude that the injection of N₂ and O₂ in concentrations of 5.1%v of air (79% N₂ and 21% O₂) is less efficient than the injection of pure CO₂.

Several fluid samples from the borehole were extracted using the U-tube. Taking into account that each sample was extracted at the same conditions as the borehole (high pressure and temperature), the gas and the liquid phases were analyzed separately. Regarding the first analysis (gas phase), following main compounds were detected: NO, SO₂, CH₄ and CO₂. The composition of these compounds is showed in Table 9:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO</td>
<td>40 ppm</td>
</tr>
<tr>
<td>SO₂</td>
<td>10 ppm</td>
</tr>
<tr>
<td>CH₄</td>
<td>160 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>1000 ppm</td>
</tr>
</tbody>
</table>

For the case of liquid phase, apparently there were more ions in the brine after the injection of CO₂ (base case), brine (operational reasons) and impure CO₂. In particular, Ca²⁺, SO₄²⁻, Mg²⁺ and K⁺ concentration were increased. This may be due to ion migration effects in the rock according to test duration and the nature of the impurities (O₂ and N₂), no were detected (Talman, 2015). Finally and continuing with the liquid phase analysis, worth mentioning is the fact that the dissolved CO₂ trend is positive although the test durations were not enough (there is more CO₂ dissolved conform over time) whereas the pH behaviour is the contrary (negative trend).

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References


