EOR BY ALKALI FLOODING IN THE VIENNA BASIN: FIRST EXPERIMENTAL RESULTS OF ALKALI/MINERAL REACTIONS IN RESERVOIR ROCKS

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ABSTRACT
The alkali/mineral reactions in Nordhorn sandstone, dolomite and reservoir sandstones from the Vienna Basin have been analysed by static tests using steel autoclaves and plastic bottles to gain first insights into potential dissolution and precipitation within the reservoir during alkali-polymer flooding. The interaction of the rocks with NaOH, KOH, Na_2CO_3 and K_2CO_3 at 60°C and pH values between 11.1 and 13.8 has been tested. Duration of the tests was 26 days for autoclaves and 54 days for plastic bottles. Weak dissolution and precipitation of silica crusts have been observed for the Nordhorn sandstone with NaOH in autoclave tests but not in bottle tests. Dolomite shows strong reactions with NaOH and KOH in all tests resulting in precipitation of Mg-hydroxides and calcite. Weak reactions have been observed for tests with Na_2CO_3 and K_2CO_3. Reservoir sandstones of the Vienna Basin are predominately characterized by high amounts of detrital quartz and dolomite. Strong dissolution of grains and precipitation of calcium-silicates occurred in tests with NaOH and KOH resulting in cementation of pore space. Only weak reactions on detrital dolomite have been observed in tests with Na_2CO_3 and K_2CO_3. Further tests are in preparation to analyze changes in pH and the chemical composition of alkaline solutions during alkali/rock interaction to determine the usability of above listed alkaline solutions for alkali-polymer flooding.

INTRODUCTION
The Neogene of the Vienna Basin hosts several mature oil and gas fields that are produced since the 1940's. The applicability of several EOR methods including alkali-polymer flooding within selected reservoir horizons is currently under investigation. The plan is to inject a pre-flush with low-salinity water, followed by an alkaline solution to generate in-situ soaps for mobilizing the crude oil. Afterwards, the injection of a polymer solution follows to enhance the fluid viscosity and support displacement of chemicals. The selection of the alkali solution that should be used for flooding is strongly depending on interaction of alkaline solutions with minerals in reservoir rocks. Interactions between alkali solutions and formation rocks can cause dissolution of existing minerals, precipitation of new

minerals and therefore result in permeability changes and reduce effectiveness of alkaline solutions [1, 2]. These effects can cause severe problems during injection of alkaline solution thus having a strong potential influence on the economics of alkali-polymer flooding. To obtain better understanding of rock-alkali reactions; a first test series of static tests using steel autoclaves and plastic bottles have been performed. Alkali solutions used for the tests are NaOH, KOH, Na_2CO_3 and K_2CO_3. Rocks used for testing are Nordhorn sandstone, dolomite and reservoir sandstone samples from the formation selected as candidate for alkali-polymer flooding.

EXPERIMENTAL SET-UP

Two experimental set-ups have been used concomitantly due to time-constraints. For the first set-up, steel autoclaves that are normally used for corrosion inhibit testing on coupons have been used. The steel autoclaves have been cleaned to remove any rust. A Nordhorn sandstone sample and a dolomite sample have been used for testing. Both samples were broken into 1-2 cm sized pieces to increase the available surface for reaction and a sample piece was put into an autoclave. The autoclaves have been evacuated and afterwards filled with ~100 ml sodium-hydroxide solution [15 g_{NaOH}/1L synthetic brine (synthetic brine = 22.09 g/L NaCl)]. The NaCl concentration refers to the chloride content in the water from the water treatment plant that would be used together with the alkali solution. The pH of the solution was 13.8. The reason for the high concentration and pH was to create some extreme scenario for mineral dissolution and precipitation. Finally, nitrogen gas was used to apply a pressure of ~10 bar. The autoclaves have been stored in a drying cabinet at 60°C (reservoir temperature) for 26 days.

For the second test set-up, polypropylene bottles have been used. The second test set-up included Nordhorn sandstone, dolomite and reservoir sandstone samples (oil removed). Each rock type has been tested with sodium-hydroxide solution, potassium-hydroxide solution, K_2CO_3 and Na_2CO_3 solution. The concentration of the individual solutions was always [15 g alkali/1L synthetic brine (synthetic brine = 22.09 g/L NaCl)]. The pH of the solutions ranges from 11.30 to 13.54. Each bottle was filled with ~250 ml of solution. A plastic foil was applied on top of the plastic bottles to reduce evaporation. The bottles were then stored in a drying cabinet at 60°C for 54 days. All samples have been cleaned with hot methanol after testing to remove salt crusts.

All samples as well as untreated samples of every lithology have been analyzed using a LEO 1450 EP SEM with an attached EDX system.

Sample Descriptions

<u>Nordhorn Sandstone</u>

The sample can be described as fine-medium-grained, porous sandstone that consists of quartz (96.6%), potassium feldspar (0.9%) and kaolinite (2.5%). The quartz grains exhibit well developed quartz cement overgrowths (plate 1a). The kaolinite is present as cement in pore space and as replacement within potassium feldspar. Under the SEM, the kaolinite exhibits a well-developed booklet structure (plate1b). Pore space consists predominately of primary interparticle pores.

Dolomite

The sample can be described as bluish-greyish dolosparite with trace amounts of calcite present. The sample belongs to the so-called “Hauptdolomit” geological unit; a Triassic dolomite that has sourced the detrital dolomite grains present in the reservoir sandstone samples. SEM images of the untested sample show that it consists of well-developed dolomite rhombohedra with some open intercrystalline pore space (plate 3a).

Reservoir Sandstone

The sample can be described as medium-coarse-grained, moderately to well sorted litharenite (plate 5a, 5b). The mineralogical composition comprises mainly quartz (~46%) and detrital dolomite (~36%), ferroan dolomite cement (~6%), feldspars (~4%), crystalline rock fragments (~2%) detrital limestone (~4%), detrital clay coats on grains (~1%) and calcite cement (~1%). Pore space consists predominately of primary interparticle pores.

RESULTS

Autoclave Tests

Nordhorn Sandstone with NaOH, 1.5% Brine, pH 13.8

The quartz cement surfaces show discontinuous, poorly crystalized encrusting’s (plate 2a) that consist of Si and O based on SEM-EDX analyses. Those crusts are interpreted as amorphous silica crusts that precipitated on the quartz cement surfaces. Similar crusts are also observed on kaolinite cement crystals (plate 2b). Furthermore, the edges of the kaolinite crystals show evidence for dissolution.

Dolomite with NaOH, 1.5% Brine, pH 13.8

Macroscopically, the surface of the tested sample exhibits a whitish staining. The SEM analyses reveal that the dolomite rhombohedra are covered by multiple layers of newly formed mineral that exhibits a webby (“honey-comb”) texture (plate 3b). The size of individual crystals is <1 micron. EDX analyses show the presence of C, O, Mg, Ca and Fe but these results are strongly influenced by the dolomite below. Based on the texture, this newly formed mineral is interpreted as Mg-hydroxide (interpreted as brucite).

The Mg-hydroxide layers are overgrown by round-shaped to elongated crystals that occur either isolated or as aggregates (plate 3b). The crystal surfaces are smooth and round-shaped. Size of crystals is <10 microns. EDX analyses show the presence of calcium and phosphor. The latter could be sourced from the dolomite sample although it has not been detected by EDX analyses before. These crystals are interpreted as calcium-phosphates.

The third newly formed mineral consists of well-developed, prismatic-shaped crystals that overgrow both the webby Mg-hydroxides and the Ca-phosphates. The size of the crystals ranges in the tenths of microns. Based on EDX analyses, those minerals comprise calcium (Ca), carbon (C) and oxygen (O) and are interpreted as calcite.

Bottle Tests

Dolomite Sample with NaOH, 1.5% Brine, pH 13.54

The dolomite rhombohedra are strongly dissolved and almost not recognizable anymore. The complete sample is covered by micrometer-sized micro-pores. The dissolution also created secondary macro-pores (plate 4a). Columnar calcite crystals have been observed but no brucite coatings are present.

Dolomite sample with KOH, 1.5% Brine, pH 13.39

The dolomite rhombohedra show strong dissolution resulting in abundant, ~1 micron-sized dissolution pores (plate 4b). Furthermore, two new mineral phases have formed. The first one comprises 2-4 microns long, prismatic-shaped crystals cover the dolomite surface. Based on EDX-analyses they consist of Mg, Ca and O and probably represent a magnesium-hydroxide. Tiny calcite crystals are present between the prismatic-shaped crystals. The second phase consists of columnar-shaped, ~10 microns long crystals. EDX-analyses show Ca, C and O thus the crystals are interpreted as calcite.

Dolomite sample with Na_2CO_3, 1.5% Brine, pH 11.41

The rhombohedra show only weak dissolution that is mainly evidenced by flaking of several micrometer-sized plates from the crystal surface.

Dolomite sample with K2CO3, 1.5% Brine, pH 11.30

The dolomite rhombohedra show no signs of dissolution.

Nordhorn Sandstone with NaOH, 1.5% Brine, pH 13.4

Only traces of silicate crusts have been observed on few quartz cement surfaces.

Nordhorn Sandstone with KOH, 1.5%Bbrine, pH 13.2

The sample shows very weakly developed dissolution pits on quartz cement surfaces. No changes have been observed on kaolinite cement crystals.

Nordhorn Sandstone with Na_2CO_3, 1.5% Brine, pH 11.41

Neither dissolution nor precipitation of new mineral phases has been observed.

Nordhorn Sandstone with K_2CO_3, 1.5% Brine, pH 11.30

Quartz cement surfaces show minor dissolution and very localized precipitation of calcium-silicates has been observed.

Reservoir Sandstone Sample with NaOH, 1.5% brine, pH 13.4

Macroscopically, the sample is more cemented after cleaning than before the testing. Quartz grains show dissolution evidenced by depressions on grain surfaces that are bounded by crusts (plate 6b). Detrital dolomite and dolomite cement rhombohedra are strongly dissolved and partly not recognizable anymore. Furthermore, crystals that resemble brucite in texture and composition have developed. The same crusts found on quartz grains are also present. These crusts additionally form pore-bridging cement between grains (plate 6a). Based on EDX analyses, these crusts consist of Si, Ca, C and O and are interpreted as poorly crystallized to amorphous calcium-silicates.

Reservoir Sandstone Sample with KOH, 1.5% brine, pH 13.2

The detrital dolomite and dolomite cement rhombohedra are strongly dissolved; minerals resembling brucite have formed (plate 7b). Quartz and other siliciclastic grains exhibit dissolution in form of depression on grain surfaces that are bounded by irregular-shaped, poorly crystallized crusts. These crusts consist of Ca, Si, C and O thus being interpreted as calcium-silicates. Overall, the dissolution and precipitation (plate 7a) is less pervasive compared to reservoir rock samples exposed to NaOH.

<u>Reservoir Sandstone Sample with Na2CO3, 1.5% brine, pH 11.41</u>

Detrital dolomite and dolomite cement show 1-2 microns-sized mineral flakes with a platy- to ragged-shaped texture. Based on EDX-analyses, these crystals comprise of Ca, Mg, C and O. The crystal texture and the chemical composition point to a magnesium-hydroxide (?brucite). Quartz grains and other siliciclastic grains show now dissolution or precipitation of new minerals.

<u>Reservoir Sandstone Sample with K2CO3, 1.5% brine, pH 11.30</u>

The rhombohedra of detrital dolomite and dolomite cement are characterized by very thin, rough layer that could represent an overgrowth by irregular-shaped, very fine crystals (probably poorly developed magnesium-hydroxide). The quartz grains and other silicate do not show any dissolution.

DISCUSSION

Autoclave Tests

<u>Nordhorn Sandstone Sample</u>

The Nordhorn sandstone sample showed only weak dissolution and precipitation after 26 days of testing at 60°C. It was expected that more dissolution would have been observed due to the high pH of 13.8, especially as the solubility of silica increases strongly at pH >7.5 [3]. The observed weak dissolution and precipitation of amorphous silica crusts on quartz grains and cement could be explained by two factors; temperature and chemical stability of quartz cement. Strong reaction of quartz with strongly basic NaOH solution was observed at 80°C after 8 days [4] whereas the same works report almost no reaction at 23°C after 265 days of testing. Temperature was considered as a key parameter for quartz solubility. Based on our results, it could be imaginable that a temperature of 60°C was too low for stronger reactions. The other factor could be the chemical stability of quartz cement as this cement had time to precipitate under chemical equilibrium in the subsurface resulting in well-ordered crystals. The diagenetic kaolinite present also only showed weak reactions which was unexpected as kaolinite is considered to be very reactive with NaOH [1], even at room temperature [5]. A reason could be that these experiments have been conducted on powdered or disintegrated samples whereas the kaolinite cement in our study consisted of well crystallized booklets. The observed crusts on quartz and kaolinite cement surfaces were interpreted as amorphous silica crusts. Such crusts precipitate after reaching equilibrium with the solution [4]. The observed low volumes indicated that this equilibrium most likely was achieved near before the end of the tests.

<u>Dolomite Sample</u>

The dolomite sample reacted strongly with the NaOH solution which was in good agreement with published data [4]. The presence of brucite and calcite could be explained by the following chemical formula after [6].

$$CaMg(CO_3)_2 + 2MOH \rightarrow Mg(OH) + CaCO_3 + M_2CO_3 \text{ where } M=Na, K, \quad (1)$$

The reasons for precipitation of phosphate minerals are still under investigation. Alkali carbonate crystals were not been found during SEM analyses. Based on the observed crystal structure, brucite would increase micro-porosity and most likely affect wettability if formed within the reservoir.

Bottle Tests

Nordhorn Sandstone Samples

The Nordhorn sandstone samples showed no to very localized weak dissolution and precipitation of new minerals. Interesting to note is that the bottle test sample exposed to NaOH showed less alterations than the autoclave sample. This could be explained by the larger amount of liquids within the bottles which needed longer to achieve equilibrium and maybe also by ambient pressure conditions.

Dolomite Samples

The dolomite samples showed strong reactions both with NaOH and KOH solutions. The dolomite rhombohedra were strongly dissolved and abundant new micro-pores were generated. Calcite had precipitated in both tests whereas Mg-hydroxides had only been observed in the KOH test. Weak dissolution was observed in the Na2CO3 test. The precipitation of radial (“star-like”) iron-rich crystals is still under investigation. Almost no reaction was observed in the K2CO3 test

Reservoir Sandstone Sample

The reservoir sandstone had been strongly altered by NaOH solution. The detrital dolomite and dolomite cement showed the same alteration as observed in the dolomite sample tests. Furthermore, the siliciclastic grains were strongly dissolved. The dissolved material had precipitated as amorphous calcium-silicate crusts. The sample exposed to KOH showed similar dissolution and precipitation features but the alterations were less intensive than compared to NaOH. The sample exposed to the Na2CO3 solution showed minor precipitation of Mg-hydroxides on dolomite rhombohedra whereas the siliciclastic grains remained mainly untouched. A similar but even weaker developed precipitation had been observed in the tests with K2CO3 solution. Again the quartz grains were untouched. The test results for Na2CO3 and K2CO3 solution could be explained by the high reactivity of dolomite towards alkaline solutions [4].

CONCLUSION

A series of static tests using steel autoclaves and plastic bottles to obtain first insights into rock-alkali interactions have been conducted. Based on the test results, the following conclusions can be made:

1) The reaction between rock samples and alkaline solutions can be tested both with steel autoclaves and plastic bottles.

2) Temperature is a key factor for quartz solubility in alkaline solutions. The 60°C in the test set-up resulted in less reaction than the 80°C used in published test results [4].
3) The differences in reaction of quartz grains in Nordhorn sandstone between autoclave and plastic bottle tests are related to higher amount of liquid in the latter and probably also higher pressure conditions in the autoclaves.
4) Dolomite is a highly reactive mineral phase in contact with alkaline solutions, especially NaOH and KOH but also Na_2CO_3 and K_2CO_3. Dedolomitization results in precipitation of micro-porous brucite and calcite and creation of abundant dissolution pores.
5) Reservoir sandstones characterized by abundant detrital quartz and dolomite react with NaOH and KOH resulting in grain dissolution and precipitation of brucite and calcium silicates. This precipitates will have a negative influence on reservoir properties and therefore injectivity. Further testing would be necessary to evaluate the usability of NaOH and KOH for alkali-polymer flooding in the Vienna basin.
6) The weak reactions of reservoir sandstones with Na_2CO_3 and K_2CO_3 solutions compared to NaOH and KOH argue for the use of those solutions for alkali-flooding
7) Additional tests are in preparation to analyze changes of pH and the chemistry of different alkaline solution during contact with reservoir rock samples over time. These tests will also include potential gravel-pack materials (sand, carbolite, glass spheres).

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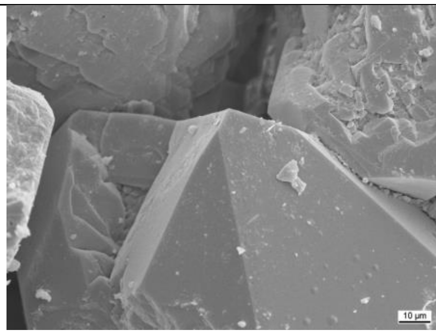

Plate 1a. Quartz Cement, NH Sandstone

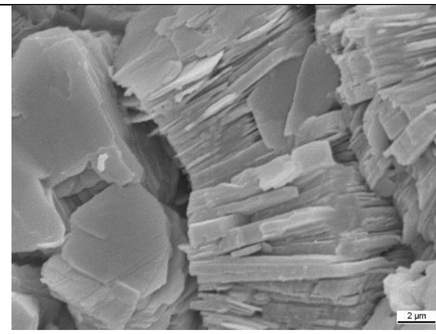

Plate 1b. Kaolinite Cement, NH Sandstone

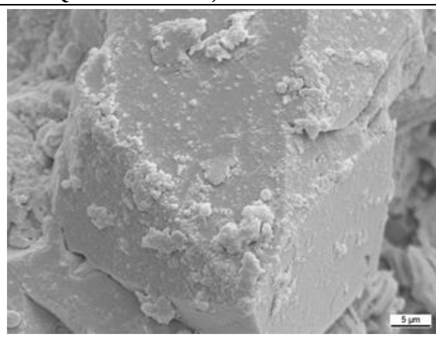

Plate 2a. Quartz Cement, NH Sandstone, after NaOH Autoclave Test

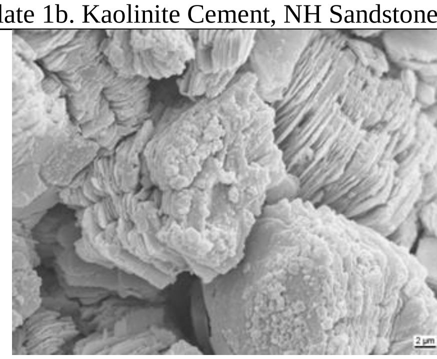

Plate 2b. Kaolinite Cement, NH Sandstone, after NaOH Autoclave test

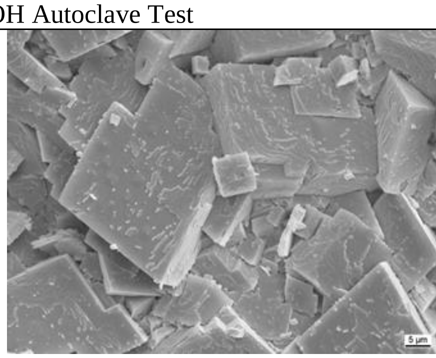

Plate 3a: Dolomite Sample Surface

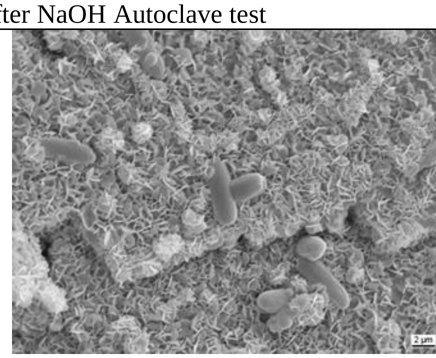

Plate 3b: Dolomite Sample Surface after NaOH auotclave test

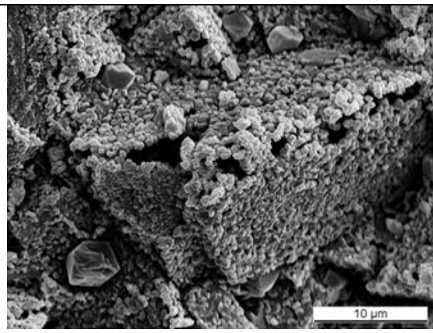

Plate 4a: Dolomite Rhombohedron after NaOH Bottle Test

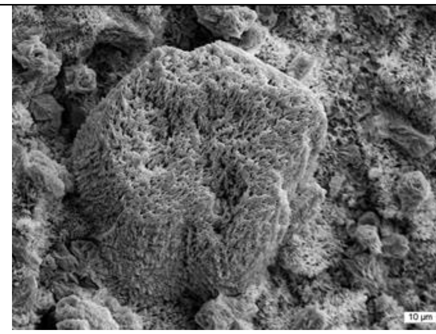

Plate 4a: Dolomite Rhombohedron after KOH Bottle Test

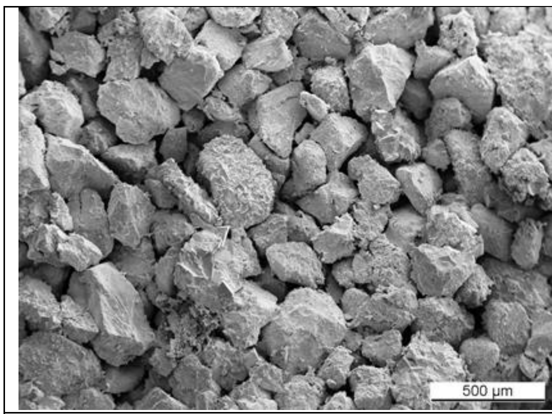

Plate 5a. Reservoir Sandstone Sample

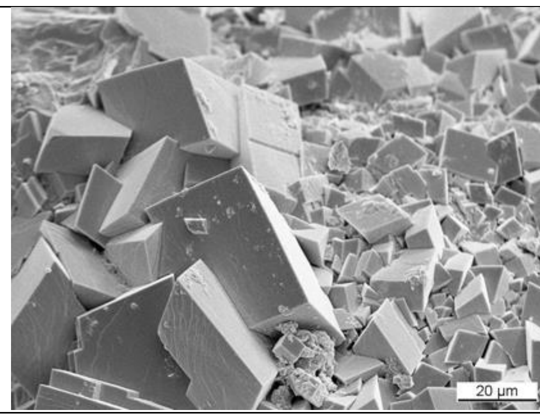

Plate 5b. Reservoir Sandstone Sample, Dolomite Cement Surface

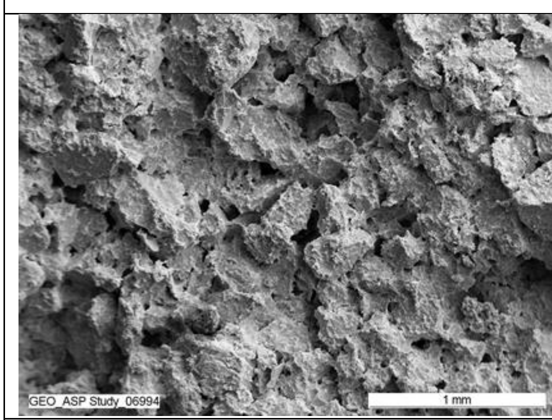

Plate 6a. Reservoir Sandstone Sample after NaOH Bottle Test

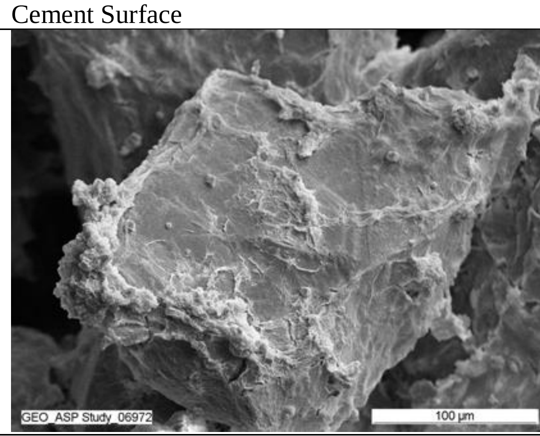

Plate 6b. Reservoir Sandstone Sample, Quartz Grain after NaOH bottle test

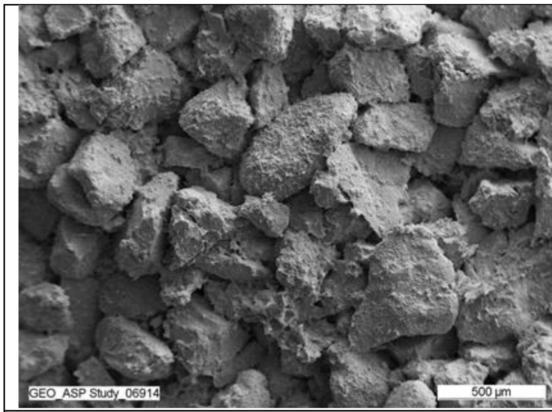

Plate 7a. Reservoir Sandstone Sample after KOH Bottle Test

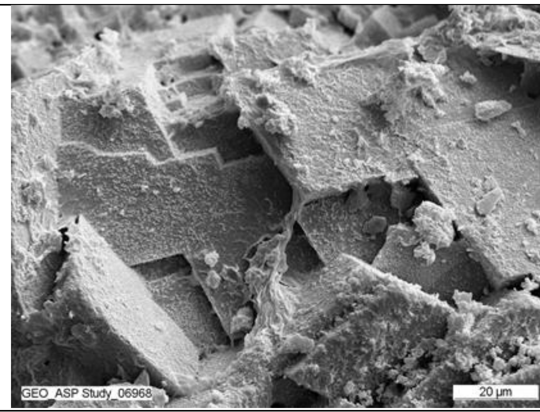

Plate 7b. Reservoir Sandstone Sample, Dolomite Cement Surface after KOH Bottle Test