

## ON THE EFFECTS OF BRINE EXPOSURE ON MECHANICAL STRENGTH OF A GEOPOLYMER SEALANT FOR CO<sub>2</sub>-GEOSEQUESTRATION

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### ABSTRACT

When considering the storage of CO<sub>2</sub> in saline aquifers, or depleted hydrocarbon reservoirs, the salinity of the pore fluid can affect the durability of wellbore sealants based on Ordinary Portland Cement (OPC), and hence the integrity of the wellbore seals, leading to an increased risk of CO<sub>2</sub> leakage [1, 2]. In addition, seal integrity may be impacted by mechanical failure due to stress-strain alterations caused by salt crystallization [3, 4]. Such integrity issues are highlighted in several laboratory research and field-scale observations [5-8].

Geopolymers (GPs) are promising alternatives to OPC; they can be synthesized through the alkali activation of low Ca-content aluminosilicate precursors using sodium/potassium hydroxides, sodium/potassium silicates or a combination of these. Low chemical shrinkage, high acid resistance, good strength development, and simple production systems with lower greenhouse gas emissions compared to the production of OPCs are among the most promising features of GPs [9, 10]. However, large uncertainties remain regarding the application of GPs as wellbore sealants, particularly in CO<sub>2</sub>-storage operations [11-15]. One key challenge here is the impact of brine exposure on the performance of GP systems. Experimental studies in which GP samples were exposed to brine in an autoclave under static conditions report both positive [16-18], and negative [10, 19, 20] effects on the mechanical properties of the exposed GPs. The different outcomes reported may be due at least partially to the static nature of the reported exposure experiments, which will lead to the establishment of an equilibrium between the aging medium and the pore solution, or even saturation of the brine with certain elements [8].

The present work addresses this challenge, through a set of dynamic-exposure experiments, where a flow of brine is forced through a granite-based GP system under pressure-temperature conditions that are representative of those encountered downhole, to investigate the impact of this brine on GP mechanical strength and permeability. Alterations of the microstructure of the GP system were investigated using Scanning Electronic Microscopy (SEM).

The normalized solid precursor was prepared through mixing small portions of micro-silica and Ground Granulated Blast Furnace Slag (GGBFS) with a local granite rock (see Table 1), following

procedures similar to those described by Khalifeh, et al. [21]. A potassium silicate solution ( $\text{SiO}_2/\text{K}_2\text{O}=2.14$ ) was used as alkali reactant, while  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{KNO}_3$  were employed as retarder agents. The GPs were prepared in a high-speed blender, in accordance with API RP 10B-2 [22]. The constant concentration of the retarders was selected based on previous experiments [23]. The prepared slurries were conditioned at  $60^\circ\text{C}$  and 150 rpm using an atmospheric consistometer (according to API RP 10B-2 [22]), and then cured for one week in autoclaves in water and at  $90^\circ\text{C}$  and 13.8 MPa.

Exposure, followed by mechanical testing our samples was carried out in a triaxial apparatus, at a temperature of  $90^\circ\text{C}$ , and a hydrostatic confining pressure of 13.8 MPa (see Figure 1a). To carry out a test, first axial and radial stresses were monotonically increased to reach a hydrostatic confinement pressure of 13.8 MPa. Next, samples GP-2 and GP-3 were flooded with constant flow rates (0.001-0.002 mL/min) of brines with NaCl concentrations of 0 and 0.5 wt.%, respectively, while sample GP-1 was not exposed to any flow. Sample permeabilities were tracked during flooding (samples GP-2 and GP-3 only), through continuous monitoring of the injection pressures (see Figure 1b). After three weeks, compressive strength of the samples was measured through deviatoric experiments, by monotonically increasing the axial stress (i.e., mimicking consolidated-drained (CD) tri-axial testing conditions) with a constant loading rate of 10 MPa/min.

As shown in Table 2, while flooding with distilled water (GP-2) resulted in lowering of the compressive strength compared to reference sample (GP-1), flooding with brine resulted in improved mechanical strength of the material. In addition, brine injection resulted in lower permeability compared to distilled water flooding. It should be noted here, though, that the permeability of both distilled-water-flooded and brine-flooded samples ( $0.141 \mu\text{D}$  and  $0.065 \mu\text{D}$ , respectively) are well below the limits recommend by American Petroleum Institute (API) for typical wellbore isolation systems ( $0.2\text{--}200 \mu\text{D}$ ) [24]. The higher compressive strength and lower permeability of GP-3 likely arise from the reduced alkali leaching at higher salinities, as previously argued by Giasuddin, et al. [17] and Nasvi, et al. [18]. However, to confirm this hypothesis, further research is required to investigate the impact of brine concentration on the degree of alkali leaching, especially through analysis of the alkali contents of the effluents. SEM micrographs of the GP samples, presented in Figure 2, show a high degree of homogeneity and a very dense microstructure of all GP samples, to which their good mechanical properties could be ascribed. No significant differences were observed in the microstructures of the three samples, suggesting that exposure to a flow of brine did not cause any significant degradation of samples GP-2 and GP-3.

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Table 1. Chemical analysis of the solid phase used in the experiments.

Element	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CaO	$\text{Fe}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	MgO	$\text{TiO}_2$	MnO	L.O.I
Normalized precursor	63.1	12.97	9.94	1.49	3.81	2.34	4.54	0.8	0.19	0.82

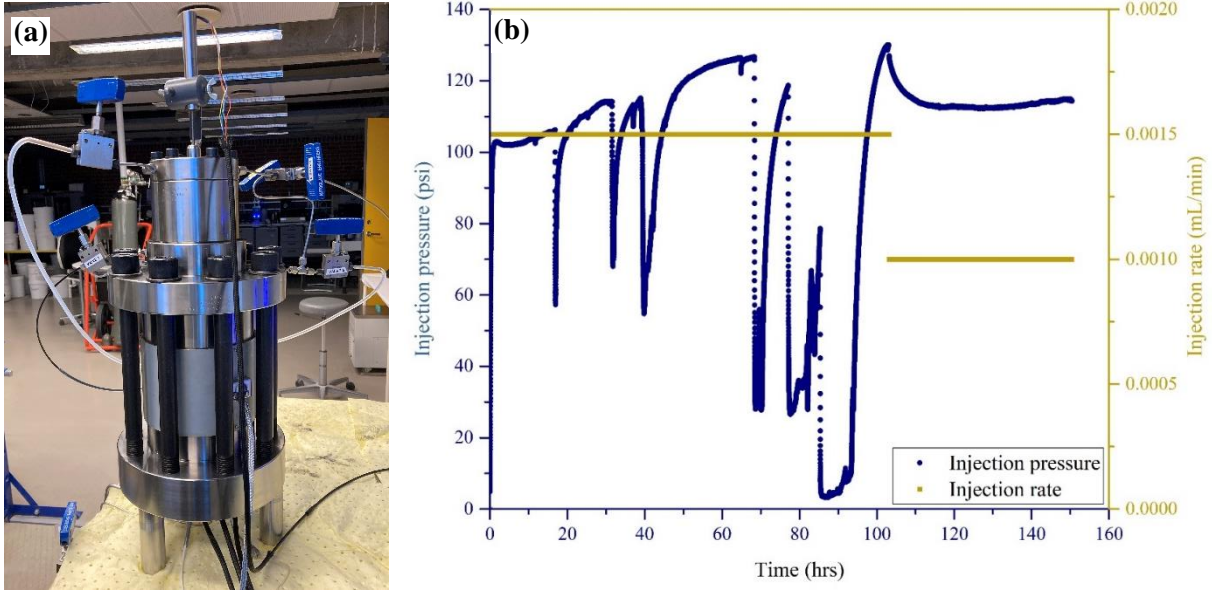
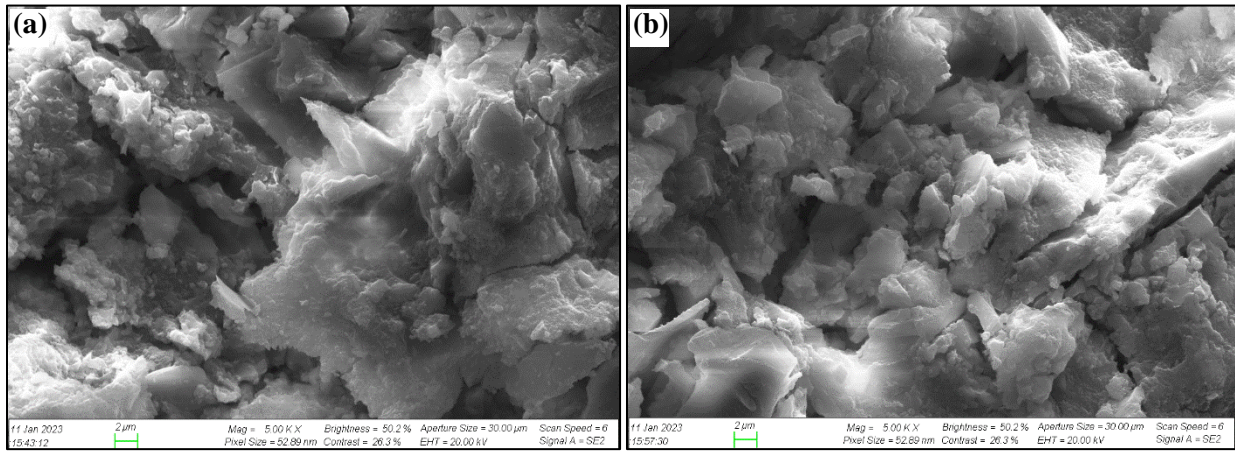


Figure 1. An illustration of (a) the in-house tri-axial instrument and (b) the injection pressures and rates measured throughout the water flooding of the GPs in tri-axial experiments.

Table 2. A list of tri-axial experiments performed in the present study.

Sample No.	Injected fluid	NaCl concentration (wt.%)	Test duration	Compressive strength (MPa)	Permeability (mD)
GP-1	-	-	3 weeks	45.63	-
GP-2	Distilled water	0	3 weeks	41.17	0.000141
GP-3	Brine	5	3 weeks	56.20	0.000065



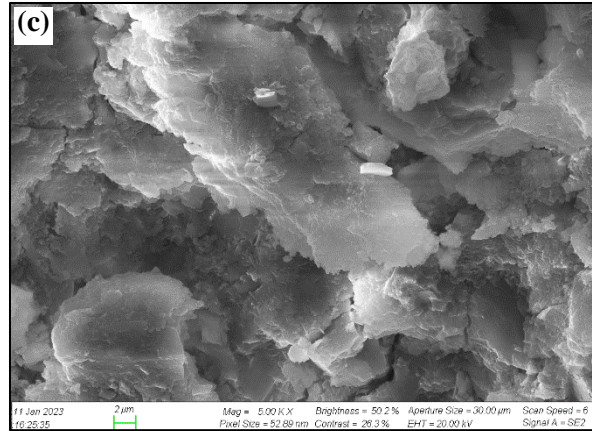


Figure 2. SEM analysis of (a) GP-1, (b) GP-2, and (c) GP-3 after tri-axial experiments.

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