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van Noort, Reinier; Pluymakers, Anne; Li, Kai; Suryanto, Benny; Starrs, Gerry

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Development of tailored wellbore sealants for CCS and other geological storage applications

Reinier van Noort¹*, Anne Pluymakers², Kai Li², Benny Survanto³ and Gerry Starrs³ establish the key properties of wellbore sealants that can help to ensure to long-term seal integrity during CCS, and identify testing methods for these properties.

Abstract

The development of new geological storage applications and other uses of subsurface reservoirs requires tailored wellbore sealants, able to withstand application-specific exposure conditions. For example, wellbore sealants used in reservoirs targeted for CO₂-storage will be exposed to CO₂-rich fluids, that may chemically attack OPC-based sealants, leading to carbonation and potential degradation. During CO₂-injection, local temperature changes around the injection well may also affect the integrity of the sealant-wellbore system, for example causing the formation of annuli between sealant and steel casing due to differences in thermal expansion. The research project CEMENTEGRITY aims to identify the key sealant properties that may help to ensure the long-term integrity of the wellbore-seal system during CO,-injection and storage, as well as the best testing methods for these properties. This is done by testing five different sealant compositions, exposing them to potentially deleterious impacts under different conditions. Here, we report some of the key findings of our project. While CEMENTEGRITY is researching sealants specifically for CO₃-storage, other applications, such as hydrogen storage, or geothermal energy exploitation, will require purpose-built sealants that are similarly tailored to the expected chemical and physical conditions.

Introduction

With geological carbon sequestration (Carbon Capture and Sequestration - CCS) gathering momentum worldwide, one key research challenge is the development of wellbore sealants with improved resistance to exposure to CO₂-based fluids. Wellbore sealants used for decades in hydrocarbon exploration and production wells are based on Ordinary Portland Cement (OPC). However, OPC is known to be vulnerable to carbonation, and during prolonged exposure, such carbonation can lead to degradation (cf. Kutchko et al, 2008; Duguid and Scherer 2010; Zhang and Talman, 2014; Chavez Panduro et al, 2017; Hernández-Rodríguez et al, 2017), potentially leading to loss of seal integrity. Furthermore, OPC is a brittle material that can fracture easily when strained, for example due to changes in the reservoir stress state.

Therefore, in an attempt to ensure long-term wellbore seal integrity, new sealant materials are being developed, many of which are either based on OPC, or on other, similar technologies such as geopolymers or calcium-aluminate cements. However, the successful development of improved sealant materials requires that the key impacts to which sealant materials may be exposed during CO₂-injection and subsequent storage are identified, and that testing methods are developed to thoroughly assess the ability of these materials' ability to withstand such impacts under realistic conditions.

CEMENTEGRITY is a research project funded by a collaboration of national funding agencies through the ACT-mechanism, with partners in Norway, the Netherlands and the UK. The project's main targets are to establish the key properties of wellbore sealants that can help to ensure long-term seal integrity during CCS, and to identify testing methods for these properties. This is done through testing five different sealant compositions (see Table 1), exposing them to key deleterious impacts that would be encountered during CO₂-injection and storage. To eliminate variables caused by differences during sample preparation, all samples tested were prepared centrally by one of our partners,

#	Description	Note
S1	Class G cement with 35% BWOC silica flour	Representative for old wells, and reference for internal comparison
S2	Class G cement with 35% BWOC silica flour, amended for reduced permeability	Field design currently in use, high silica fume concentration
S3	Class G cement with 35% BWOC silica flour and ReStone additive	Blend with modified mechanical properties, and a CO ₂ -sequestering agent
\$4	Calcium-Aluminate Cement-based system	Considered highly acid-resistant; currently used in high-temperature wells
S5	Granite-based geopolymer	1-part system, specifically engineered for CCS

Table 1 The five sealant compositions studied and compared in the CEMENTEGRITY project.

Institute for Energy Technology (IFE) | 2Delft University of Technology | 3Heriot-Watt University

* Corresponding author, E-mail: reinier.noort@ife.no

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and distributed after curing for 28 days under water, at 150 °C and 30 MPa.

We have identified three critical abilities for any sealant material to be used in CCS; the ability to resist exposure to CO₂-bearing fluids; the ability to withstand thermal shocks or cycling; and the ability to form a seal as part of the well-caprock system. Based on a review of regulations and industry recommendations (Van Noort, 2024), a sealant's permeability and mechanical properties (compressive and tensile strength, Young's modulus, and Poisson's ratio) are the key towards ensuring a material's initial and long-term quality with regards to these abilities. Furthermore, when testing candidate materials, in addition to measuring the impacts of exposure on these key properties, changes in microstructure (porosity) and composition (both chemical and mineralogical) should also be studied.

While our current project is focused on developing and testing sealants to be used in wells in CCS-reservoirs, other geological storage technologies and uses of the subsurface, such as hydrogen-storage or geothermal energy exploitation, will similarly require wellbore sealants tailored to their specific chemical and physical environments. Thus, the concepts and approach for sealant assessment developed in CEMENTEGRITY can readily be applied to the testing of sealants in other geological storage systems, and to the development of tailored sealants for improved wellbore integrity in such applications.

Impact of exposure to CO,-bearing fluids

Wellbore sealants used in wells exposed to CO, during CCS must be able to withstand exposure to CO₃-bearing fluids in order to maintain long-term seal integrity. We are testing the ability of our five sealant compositions to withstand such exposure using two different types of exposure experiment.

Imposed flow experiments are carried out using both wet supercritical CO, and CO2-saturated water. In these experiments, a flow of CO, is forced through cylinders of sealant (with a diameter of 1.5") at 80 °C, using an exaggerated pressure gradient to accelerate exposure. The impact of CO₂-exposure is assessed on a sample-scale by measuring permeability before and after exposure. In addition, we are using a micro-indentation technique to assess local changes in mechanical properties along the sample axis (Van Noort et al, 2023; Lende et al, 2024). In parallel, we are also batch-exposing sealant cylinders (12 mm diameter) simultaneously to either wet supercritical CO₂, or CO₂-saturated water. Using such batch exposure tests we will also expose samples to CO, with key impurities that may impact sealant integrity, such as H₂S and SO_x. After exposure, samples are studied using a range of analytical techniques, including Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS), and CT-scanning.

The results obtained so far show an important distinction between the depths of CO₂-penetration, carbonation, and CO2-induced degradation; and the impact of exposure conditions thereon. For example, samples of Sealant 1 exposed to CO₂-saturated water for 16 weeks in batch-exposure tests show considerable degradation in an outer rim of about 150 µm wide, caused by dissolution of Ca(OH), and the subsequent leaching of Ca²⁺ from C-S-H-gel. Further inwards, these same samples show pore-filling and densification due to carbonation, penetrating up to ~1 mm into the sample. On the other hand, samples of S1 exposed to wet sc. CO, for 16 weeks are densified

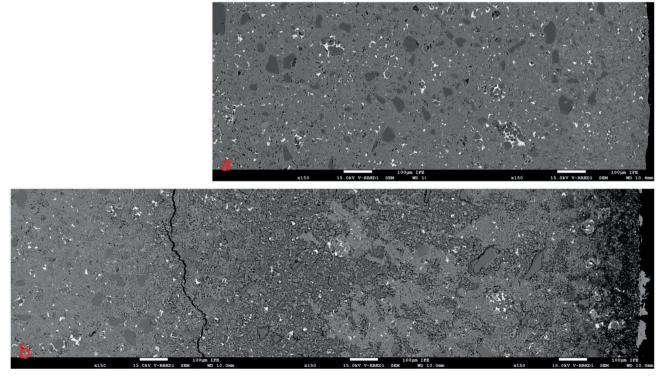


Figure 1 SEM Backscatter electron micrographs showing the impact of exposure to CO2 on sealant S1. a) S1 exposed to wet sc. CO2 for 16 weeks. b) S1 exposed to CO2 saturated water for 16 weeks

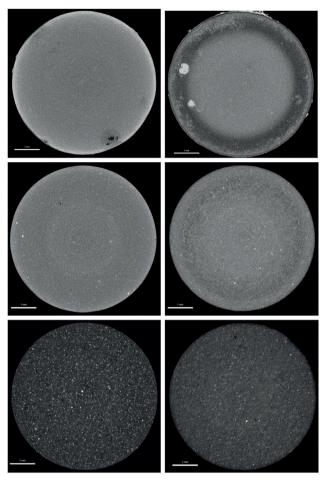


Figure 2 CT-scanned cross-sections of samples S1 (top), S2 (middle) and S4 (bottom) exposed to wet sc. ${\rm CO_2}$ (left) and ${\rm CO_2}$ -saturated water (right).

due to carbonation in an outer rim up to $\sim 450~\mu m$ into the sample, with little to no degradation (see Figure 1). Figure 2 presents CT-scanned cross-sections through samples of S1, S2 and S4 exposed for 16 weeks. Comparing S1 and S2, we see that while the lower permeability of S2 leads to a reduced depth of degradation, carbonation proceeded to similar or even somewhat greater depth in S2. Within this carbonated zone, both S1 and S2 show a secondary zone with lower density, possibly

caused by the dissolution of Ca(OH),; this impact is more severe in S1 than S2. In contrast, samples of S4 show little to no significant change after exposure to CO2-saturated water or wet sc. CO2, though the latter did result in minor densification at the sample surface.

In the samples exposed to an imposed flow of wet sc. CO, or CO₂-saturated water, we see that the effects of carbonation penetrated both more deeply and more irregularly for the former, leading to a pH-decrease in the pore fluid (due to dissolution of Ca(OH)₂) and an increase in material hardness and strength (due to precipitation of Ca-carbonates in the pore network). However, minor degradation was only observed in some samples exposed to CO2-saturated water, and limited to the area directly around the injection point. Here again, sample S4 showed little to no change resulting from exposure to either CO₂-saturated water, or wet supercritical CO₂.

These results show that degradation of OPC-based materials mostly takes place when they are exposed to a sufficiently large volume of hydrous fluid, while direct exposure to sc. CO, does not cause significant degradation. Our results are also showing that pressure-driven (imposed flow) vs diffusive (batch) penetration of CO₂-bearing fluids into a sealant may result in different depth of CO₂-penetration and degrees of degradation and carbonation. We are now using our results to elucidate different strategies by which sealants able to resist CO₂-exposure could be developed: 1) sealants that are not affected by CO₂-based fluids; 2) sealants that form stable carbonation reaction products that improve its properties; 3) sealants with very low permeability to limit CO₂-penetration. Finally, our results show the importance of exposing sealants to realistic in-situ conditions, and in a manner that accurately simulates how CO2 or other reactive fluids might penetrate and attack the sealant, to capture how the interplay between CO₂-sealant-interactions may accelerate or limit further ingress.

Impact of temperature changes

Injection of cold CO, into a relatively hot reservoir can lead to significant changes in temperature, which may be locally exacerbated by the Joules-Thompson effect when CO, is injected into a depleted reservoir. When injection is not continuous, periodic

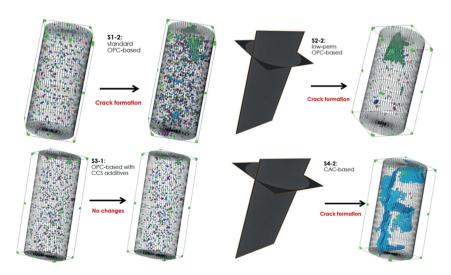


Figure 3 CT-scans of cylinders of S1-S4 before and after unconfined exposure to thermal shocks.



injection can thus lead to temperature cycles, as the injection well and reservoir area around it cool down during injection, and then warm up when injection is paused. Such temperature changes may impact the integrity of a sealant directly, as differences in thermal expansion within the sealant may induce stresses and cracking. Furthermore, temperature changes may also affect the integrity of the sealant-wellbore system by causing the formation of annular cracks between sealant and (steel) casing, or between sealant and surrounding caprock.

Therefore, when developing new sealant materials, it is important to assess how these materials behave when they are exposed to thermal changes. To address this, we have exposed samples of our five sealants to thermal shocks and cyclic thermal changes under a range of confinement conditions. Before and after exposure, we used CT-scanning to assess microstructural changes. In addition, we conducted unconfined compressive strength tests to quantify the damage induced.

Unconfined thermal shocks were applied by dropping hot sealant cylinders, heated to 120 °C, into a water bath at 20 °C. CT-scans, taken after eight such exposures (see Figure 3, and Li and Pluymakers, 2024), showed the development of large cracks in samples of S1, S2 and S4, while samples of S3 and S5 showed no cracking. In contrast, thermal cycling under confined conditions, by rapidly flowing 5 °C water through a central bore through samples of S1-S4 kept at 120 °C in a triaxial apparatus, did not lead to crack-formation, even at confinement pressures as low as 1.5 MPa.

To better understand these differences in how well the sealants tested were able to withstand thermal changes, we measured their specific heat capacities, thermal conductivities, and thermal expansion coefficients, and used these measurements to calculate their thermal diffusivities, and the thermally induced maximum stresses and loading rates in our samples. A material cracks when this stress exceeds the tensile strength of the material plus any applied confining pressure, though thermally induced subcritical cracking may also weaken materials experiencing many temperature cycles. Indeed, these measurements show that, compared to S1, S2 and S4, S3 has a considerably higher thermal diffusivity, and the lowest Young's modulus. As a result, S3 experienced the lowest thermally induced loading rates and maximum stresses, thus explaining why S3 remained intact while all other samples developed cracks. Similar measurements on S5 are pending.

Two important findings from this work, so far, are a) the key importance of a sealant's thermal properties, in correlation with its tensile and compressive strengths, for determining its ability to withstand thermal changes, and b) when assessing the potential impact of thermal changes on wellbore seal integrity, it is important to assess this under in-situ conditions, taking into account confinement of the sealant, as this confinement will play a large role in limiting thermal damage.

However, the impact of temperature changes should be considered for the full wellbore system, as differences in thermal expansion coefficient between steel casing and annular cement seal may cause stress concentrations at the interface between these materials, potentially leading to the formation of micro-annuli, and leakage. Further work is now ongoing on composite samples consisting of a steel tube within a sealant sheath, to assess the impact of thermal change on the integrity of this interface.

Monitoring interface integrity in the sealantwellbore system

A good seal requires a tight contact to be formed between the sealant and the adjacent materials (casing steel and/or caprock). Such a tight contact can be formed as a result of the curing sealant binding to these materials, but could alternatively be created through the use of sealants that expand upon curing. While the creation and maintenance of a tight seal is controlled by the full wellbore system, the bond strength between sealant and steel can be a key parameter in that system. We are measuring this bond strength for our five sealant compositions using a direct shear method, where a cylinder of sealant is pushed out of the steel tube it was cured in (Patent No US11054353B2).

Additionally, the security of a geological storage scheme would be greatly enhanced by the facility to monitor the ongoing integrity of the sealant-wellbore system (both the sealant-steel interface, and the sealant material itself), in-situ. In some circumstances this might be achievable by use of electrical properties measurements. Such properties can be analysed by means of impedance spectroscopy, whereby a material system's







Figure 4 Post-curing sealant/steel interface appearance for Sealants S1 to S3.

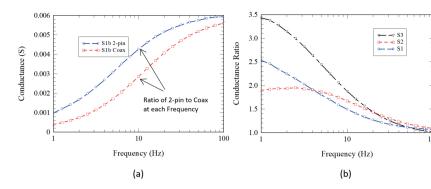


Figure 5 (a) Conductance of 2-pin and coax electrode configurations for Seglant S1 and (b) Conductance ratio of 2-pin to coax electrode configurations for Sealants S1 to S3

response to a frequency-variable alternating voltage stimulus, mediated through a suitable electrode interface, can provide insight into aspects of the system's underlying microstructure. In the case of hydraulic sealants, as considered by CEMENT-EGRITY, the response will be influenced by the water containing pore-network configuration (including its bulk porosity, pore size distribution, tortuosity, permeability, etc.) and, at low frequencies (<1000 Hz), the conditions at the sealant-electrode interface. We have been performing impedance spectroscopy measurements on sealant samples that are identical in form to those configured from steel tubes for push-out Bond Tests (replicating a well-head in miniature), but with additional imbedded electrodes. Two different electrode set-ups, coaxial and parallel pair, have been employed. In the coaxial type a single stainless-steel electrode is placed through the centre of the sample, while the steel tube acts as the other electrode. This configuration includes the sealant/steel interface as part of the measurement. In the parallel pair type, twin stainless-steel electrodes are placed through the centre of the sample, and measurements are obtained between them, facilitating assessment of the sealant bulk electrical properties.

In our initial experimental samples mild steel was used as the outer casing. Following the sample curing regime (autoclaved in water at high temperature and pressure) the casing was found to have corroded, with the degree of corrosion on the inner surface (i.e. the sealant-steel interface) dependent on the specific sealant composition (see Figure 4). Interestingly, the condition of the interface was found to directly influence the impedance measurement characteristics, with the degree of corrosion related to the conductance of the samples between 5 Hz and 20 Hz. In particular, it was found that the ratio of internal 2-pin conductance to that of the coaxial conductance at ~15 Hz, once the measurements were scaled to account for electrode dimension differences, was correlated to the visible extent of corrosion. This is illustrated by Figure 5.

While these are preliminary findings, the results demonstrate the potential for monitoring sealant conditions, and the sealant-steel interface, using electrical impedance measurements. Such measurements may be useful in conjunction with mechanical bond testing for the assessment of sealant performance.

Conclusions so far, and ongoing work

The suitability of a material as a wellbore sealant for wells used in CO2-storage reservoirs depends on the material's

ability to form a seal as part of the well-caprock system; its ability to resist exposure to CO₂-bearing fluids; and its ability to withstand thermal shocks or cycling. Key properties assuring that a material can create and maintain a seal, and to assess material integrity after exposure to deleterious effects include permeability, mechanical properties, microstructure (porosity), and composition (both chemical and mineralogical). Thus, when developing and assessing new sealants for CCS, these properties should be measured, and then changes to these properties induced by exposure to CO2-bearing fluids and to thermal changes should be determined. These exposures should be carried out under realistic conditions, to ensure that representative results are obtained, though, alternatively, exposures could be performed under conditions that exaggerate their impact, to better assess enhanced effects through comparison to reference compositions.

Through testing five different sealants, covering a range of compositions, CEMENTEGRITY works to identify the key material properties controlling a sealant's ability to form and maintain a seal with long-term integrity, as well as the best testing methods for these properties. Exposure tests show large differences in impact depending on sealant composition, and whether samples are exposed to CO₂-saturated water (as is often done in experiments) or wet sc. CO, (which may be more representative of conditions encountered in-situ). While the latter resulted in deeper penetration of carbonation into the sealant material, especially in imposed-flow tests, such exposure also led to considerably less degradation of exposed sealants compared to exposure to CO2-saturated water. These results also demonstrate the importance of separately assessing the depths of CO₂-penetration, carbonation, and degradation, to fully understand how a sealant may perform when exposed to CO₂. Work is now ongoing to expose sealant samples to CO₂ containing impurities such as H₂S, that may commonly be co-injected in industrial CCS-operations. As such impurities may cause acidification, as well as otherwise enhancing reactivity within the CO₃-wellbore system, we need to develop an understanding of how such impurities may affect a sealant's ability to withstand exposure.

Experiments exposing sealant samples to thermal shocks and thermal cycles show how temperature changes may directly induce damage in these materials. However, these tests also show that thermal damage may, for example, be prevented by developing materials with high thermal diffusivity. Furthermore, our results show that even a low confinement pressure can be sufficient to suppress thermal effects and prevent crack-formation, further demonstrating the importance of testing materials under representative conditions. However, as steel and sealant materials typically have different thermal properties (especially expansion coefficients), thermally induced effects may be localised at the interfaces between these materials and cause the formation of micro-annuli there. Therefore, we are now performing similar experiments on composite samples consisting of a steel tube within a sealant sheath, monitoring changes in interface integrity induced by thermal cycling, under different confinement conditions.

Finally, the security of any geological storage facility can be greatly enhanced if we can monitor the integrity of its seals, and seal-steel interfaces in-situ. Here, our research shows that monitoring of electrical properties of the wellbore system could be a promising monitoring method, that might help us to identify changes in seal integrity at an early stage.

While the experimental studies in CEMENTEGRITY are being carried out in the context of CO₂-storage, similar assessments will need to be carried out on other geological storage applications or use of the subsurface in order to develop sealants that can create and maintain a permanent seal, resisting exposure to the chemical environment created by injection and storage, and withstanding thermal and other physical changes that may damage the seals, or the seal-steel and seal-rock interfaces. Thus, CEMENTEGRITY may provide a roadmap for the testing of sealants being developed for not only CO₂-injection and storage, but also for, for example, hydrogen storage, and geothermal energy exploitation.

Acknowledgement

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