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Defining the Brittle Failure Envelopes of Individual Reaction Zones Observed in CO_2-Exposed Wellbore Cement

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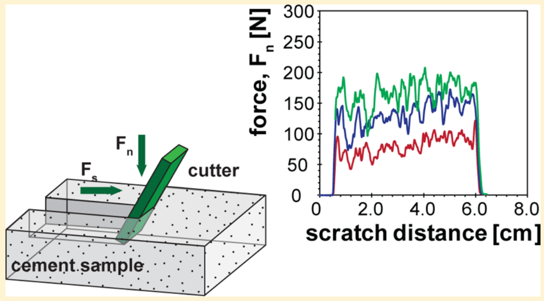
Supporting Information

ABSTRACT: To predict the behavior of the cement sheath after CO_2 injection and the potential for leakage pathways, it is key to understand how the mechanical properties of the cement evolves with CO_2 exposure time. We performed scratch-hardness tests on hardened samples of class G cement before and after CO_2 exposure. The cement was exposed to CO_2-rich fluid for one to six months at 65 °C and 8 MPa P_{total}. Detailed SEM-EDX analyses showed reaction zones similar to those previously reported in the literature: (1) an outer-reacted, porous silica-rich zone; (2) a dense, carbonated zone; and (3) a more porous, Ca-depleted inner zone. The quantitative mechanical data (brittle compressive strength and friction coefficient) obtained for each of the zones suggest that the heterogeneity of reacted cement leads to a wide range of brittle strength values in any of the reaction zones, with only a rough dependence on exposure time. However, the data can be used to guide numerical modeling efforts needed to assess the impact of reaction-induced mechanical failure of wellbore cement by coupling sensitivity analysis and mechanical predictions.



1. INTRODUCTION

To achieve safe and long-term geological CO_2 storage, it is key to prevent leakage of the injected carbon dioxide from the storage complex. Reservoir and caprock integrity are important in determining the stability of the storage complex. However, with careful site selection and adhering to safe injection strategies, reservoir and caprock failure or leakage should not be expected, even on the longer term (meaning >10 000 years).[1−7] Therefore, one of the most likely leakage points within a complex are the wellbores penetrating the caprock.[8−10] It has been argued that most leakage events are caused by improper cement emplacement,[11] potentially coupled to cement shrinkage,[8] leading to the creation of leakage pathways.[10] Induced CO_2−cement−brine interactions along pre-existing pathways could further impact the integrity of a cement seal by self-sealing of fractures and interfaces[12−20] or reaction-induced weakening of the cement.[21−23]

In the case of injection wells, damage to the wellbore cement can occur as a result of mechanical work done by the state of stress, as well as chemo-mechanical changes due to CO_2 exposure. Stress fluctuations within the wellbore, e.g., temperature and pressure changes during well shut-in, can cause contraction and expansion of the casing steel.[24−26] Depending on the mechanical response of the cement, such fluctuations can either lead to brittle failure of the cement in the form of shear failure, radial cracking or disking, or to more plastic deformation, leading to the debonding of the cement−casing or cement−rock interfaces.[27] It has been argued that, for this reason, injection wells should be drilled and completed fit-for-purpose instead of using reworked wells.[9] The stress-induced effects will be less for legacy wells, located away from the injection well. However, they may still be impacted by the chemical attack following CO_2 injection. It is the latter type of wells that our study focuses on.

Studies investigating the effect of chemical changes on transport properties show the tendency for cement to self-heal, either by precipitation of carbonates, the formation of a silica-gel layer, or the migration and reprecipitation of alteration products.[12−19] In contrast, a few studies indicate a permeability increase along interfaces, resulting from primary cement dissolution and secondary mineral redissolution.[28−31] Studies coupling reaction to mechanical behavior are less numerous but suggest that the precipitation of carbonates results in (localized) hardening of cement,[32−37] while strength differences across reacted cement zones could lead to decoupling.[21,22] Such chemo-mechanical studies mainly focused on measuring either the strength of bulk-reacted cement via compression tests[21,23,34,38] or the hardness of the individual reaction zones through micro- and nanoindentation tests.[32,33,35,36,39] Understanding of the strength of individual reaction zones is needed to predict changes in the structural integrity of the cement upon CO_2 exposure,[36] although bulk cement tests do not account for strength changes of the individual zones. In addition, hardness only provides a qualitative comparison of zone strength and cannot be directly used in numerical models aimed at predicting the in situ mechanical behavior of the cement sheath after CO_2 injection. Instead, such models

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require mechanical parameters describing the failure behavior of the different zones, such as unconfined compressive strength (UCS) and the friction coefficient (μ), as well as elastic parameters.[40−42]

This study aims to quantify the brittle strength of the individual reaction zones in CO_2-exposed Class G wellbore cement as a function of exposure time. The brittle strength was analyzed in terms of UCS and μ, which delineate the brittle failure envelope of the material. These brittle failure envelopes describe the stress conditions under which the material is intact versus fractured. UCS is related to the intercept of this line in stress space, while μ is related to its slope (see the Supporting Information for more details). As such, our study provides an improved basis for comparing unreacted and reacted cement and the difference in behavior of the differing zones. By employing the mm-scale core-scratching technique,[43−47] we can furthermore use the results of this study to bridge the scaling gap between local material properties, such as those obtained using qualitative microscale hardness tests of individual reaction zones, and bulk sample properties, such as those measured in cm-scale experiments on whole cement samples.[21,32−36,39]

2. MATERIALS AND METHODS

Preparation of the Cement Samples. In total, 12 cylindrical cement samples were prepared using Class G Portland cement (Dyckerhoff AG, Lengerich, well cement). This type of cement was selected because it is widely used for zonal isolation and abandonment of oil and gas wells.[48] The material was prepared according to ISO 10426−1 International Standard (American Petroleum Institute (API) specifications ISO/API 10B[49]), prescribing a water-to-cement ratio of 0.44. After mixing, the cement was poured into cylindrical molds (dimensions: 60 mm diameter, 200 mm in length) and initially cured in a water bath for 24h at ~73 °C. Subsequently, the cylinders were removed from their molds and immersed in fluid-filled, closed-off containers for another six months of curing at ambient conditions. The fluid consisted of a saturated solution created by mixing an excess amount of cured cement with distilled water while boiling for 48 h to prevent carbonation. It should be noted that curing under ambient conditions will result in higher CO_2-penetration depths during batch reaction.[50,51] Because the focus of this study is on the brittle strength properties of individual zones, the width of each zone is not expected to change our findings. Thicker reaction zones are beneficial for our mechanical scratch-hardness testing, which relies on sufficient sampling thickness, i.e., > ~150−200 μm.[46]

By means of computed-tomography (CT) imaging, we selected homogeneous sections of the cylinders for the drilling of smaller samples (25 mm diameter, up to 65 mm in length) used in the subsequent chemical and mechanical experiments (see Figure S2). Prior to CO_2 exposure, the circumferential surface of the samples was cut flat, parallel to the sample axis, on four sides. These flat surfaces were needed to perform the core scratch-hardness tests.

CO_2 Exposure of Cement: Batch-Reaction Experiments. The selected samples were exposed to supercritical CO_2 (sCO_2) and cement-saturated water, i.e., CO_2-saturated solution, for one to six months in a batch reactor. We used distilled water instead of brine as a reaction fluid to study the simplest possible system and to maximize the extent of reaction, resulting in thicker reactions zones needed for mechanical testing.[50] Furthermore, saturation with respect to cement minimizes solid−fluid disequilibrium upon applying the elevated experimental conditions. The reaction setup consisted of a Hastelloy autoclave, located in an oven (see Figure 1). The

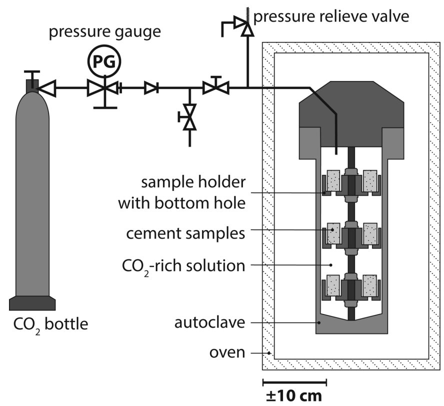

Figure 1. Schematic diagram of the batch-reaction setup.

samples were placed in chemically inert Teflon inserts, employed to prevent chemical interaction between the samples caused by stacking. The samples plus inserts were submerged in cement-saturated solution (same as during curing; initial solid-to-fluid ratio of 0.08, similar to previous studies[33,50]). After the injection of sCO_2 (total pressure, P_{total} = 8 MPa), the CO_2 was mixed with the solution through an internal stirrer for 5 min to reach a fully saturated solution. The autoclave was heated to 65 °C in 3 h while any pressure above the set pressure was bled off.

The autoclave was kept at temperature and pressure for one-month reaction periods at a time for a total period of six months. After each month, sample retrieval was done by reducing the pressure, followed by the temperature, back to atmospheric conditions during a period of about 3 h. Depressurization and cooling was done slowly to minimize the potential for precipitation of carbonates from solution[33] or crack formation,[35] although these processes could not be eliminated completely. Every cycle, two samples were removed for analysis, and the remaining samples were returned to the autoclave for another exposure period at elevated pressure and temperature without replacing the reaction fluid.

Mechanical Properties of Reacted Zones: Scratch Hardness Tests. The unconfined compressive strength and friction coefficient of the zones formed within the CO_2-exposed cement were measured using the core scratching technique[43−47] (see also the Supporting Information for more details). Studies have shown that the scratch-hardness technique is as reliable as conventional testing, such as unconfined strength tests.[46,52] At the same time, the scratch-hardness test is able to resolve strength variations within samples at a much smaller resolution because only 1−2 mm of scratch length is needed to measure rock strength.[46]

Knowing the characteristics of the apparatus, using a given cutter type and back rake angle (15°), a blunt cutter was used to make a groove (or "scratch") with a width w of 10 mm and a depth d of 0.03−0.16 mm at a cutting velocity v of 15 mm/s. For each sample, grooves of several cms in length, with three to six different scratch depths, were made into the reacted zone (Table S1). With each new scratch, the cutter removes a new layer of material, of known thickness, and the normal (F_n) and

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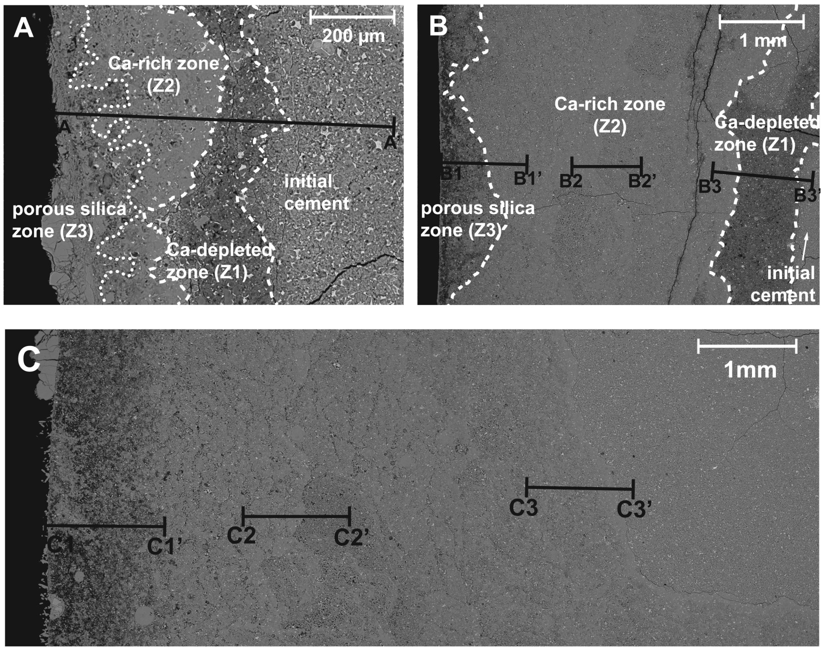

Figure 2. SEM micrographs for CO_2-exposed cement samples after (A) 1 month, (B) 3 months, and (C) 6 months. For the EDX profiles corresponding to the indicated transects, see the Supporting Information. With time, the outer zone becomes more depleted with Ca (Z3) while the Ca-rich zone becomes more pronounced (Z2). After 6 months, the sample appeared to be homogeneously leached of Ca. Note that the cracks are most likely caused by drying of the samples. The transects are related to EDX profiles taken across the samples (see Figure S4 for the profiles).

shear force (F_s) exerted on the cutter are accurately measured ($F \pm 1$ N). From the relationship between the forces, normalized with respect to wd, it was possible to determine the intrinsic specific energy (ε) needed to cut the material (i.e., the intercept with the cutting line), as well as the friction experienced by the blunt cutter, in terms of a friction coefficient (i.e., the slope of the trend). The intrinsic specific energy directly correlates to the unconfined compressive strength of a material[53] (see Figure S10). For homogeneous samples, no significant fluctuations in strength are expected between different cutter depths,[52] resulting in a good linear relationship between F_n and F_s. However, (reacted) cement is very heterogeneous, which may affect this relationship and the determination of ε (see Figure S9). It should be noted that, as described in Section S6, the data-reduction procedure had to be modified to account for the use of a blunt cutting tool.

Prior to testing, the samples were oven-dried at 70 °C for 24 h to remove pore water, after which they were placed in the sample holder of the scratcher. Drying most likely affected the strength[54] but not extensively because it did not lead to visible cracking of the samples. The strength of the unreacted cement was determined before CO_2 exposure to assess the subsequent effect of reaction. After batch reaction, only one reaction zone was scratched at a time to assess its strength. During data processing, force data, obtained on samples of the same exposure time and for the same zone, were combined to limit the effect of sample variability and heterogeneity.

3. RESULTS

Macroscopic Observations and CT Imaging. After exposure, the samples showed clear signs of reaction, with a whitish, coarse-grained layer having formed on the outside of the samples. Furthermore, some specimens showed large calcium carbonate crystals on the outer surface, as identified by optical and chemical analysis. These crystals most likely resulted from secondary precipitation during depressurizing and cooling.[35] Additional post-reaction CT-imaging (medical CT scanner, Siemens Somatom Volume Zoom spiral scanner, resolution 0.5 mm) revealed the development of three distinct reacted zones, each progressing inward with time (see Figure S3). These three zones are consistent with those observed using scanning electron microscopy (SEM), for which details are provided in the below section.

Microscopic and Chemical Analyses. SEM, combined with energy-dispersive X-ray (EDX) spectroscopy (Philips XL-40 FEG SEM, acceleration voltage 30 kV), was performed on the CO_2-exposed samples (see Figure 2 for SEM images and Figure S4 for EDX profiles). After one month of reaction (Figure 2a), already three thin zones can be discerned: (1) a thin (<200 μm) inner zone, also slightly more porous, due to depletion of Ca; (2) a carbonated zone, slightly enriched in Ca and less porous (200−300 μm thick); and (3) an outer-reacted zone (<200 μm), slightly more porous than the original cement and depleted in Ca (see the EDX profiles in Figure S4). With increasing exposure time, the outer zone becomes progressively thicker and more depleted with respect to Ca, especially closer to the edge of the sample, which is in contact with the CO_2-saturated solution (cf. three months; Figure S4b). The inner, Ca-depleted zone becomes more depleted with Ca as calcium diffuses into the carbonated zone to form calcite. After six months of exposure to CO_2-saturated solution (cf. six months; Figure S4c), the sample shows relatively homogeneous profiles of Ca and Si, with a Ca-depleted outer zone but no clear internal carbonated or depleted zones, caused by complete reaction of the sample as also seen in other studies.[36] Most of the cracks seen in the micrographs are related to drying out of the sample material and not the result of drilling-induced damage or the depressurization and cooling cycles, as they show no evidence of reaction.

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It should be noted that we did not analyze the reaction fluid, as a detailed study of the chemical evolution of the cement upon CO_2-exposure was not an aim of our study. Therefore, we cannot comment on its equilibrium state during the batch tests. However, the depressurization and cooling of the autoclave must have disturbed the equilibrium state of the solution. Furthermore, the subsequent removal of samples after each exposure period slightly changed the solid-to-fluid ratio. This may have resulted in a larger extent of the reactions throughout the samples. Despite these fluctuations, the reaction zones that have formed within our CO_2-exposed Class G cement are the same as those identified for the reaction zones seen in Class H cement.[51] We will use the nomenclature as defined by Kutchko et al.[51] to describe the zones that have formed from the outside of the cement inward: Z3, the porous silica, gel-like outer zone; Z2, the carbonated zone; Z1, the Ca-depleted, inner zone; and the apparently unaltered inner core, if present.

Mechanical Strength from Scratch Hardness Tests. The UCS-values obtained for unreacted and CO_2-exposed cement are summarized in Figure 3, as a function of exposure time. The unconfined compressive strength of the unexposed samples was on the order of 51.5 ± 10.6 MPa after six months of curing, with a friction coefficient μ of 0.42 ± 0.0085 (see the Supporting Information for a description of the calculation procedure). The outer-reacted degradation zone (Z3) shows a rough decrease in UCS with exposure time, ranging from 4.4 to 32.7 MPa, and μ values of 0.57−0.90 (average 0.79). Note that for the sample exposed for one month, the thickness of the outer layer was in some areas thinner than the maximum scratch depth of 0.15 mm, meaning in those locations the underlying carbonated layer was measured instead. Given the spatial resolution of the measured force data, we were able to separate the data for both layers in these instances. Furthermore, as the outer degradation zone became thicker, the samples were cut lengthwise to reach the inner zones, i.e., after 5−6 months of exposure.

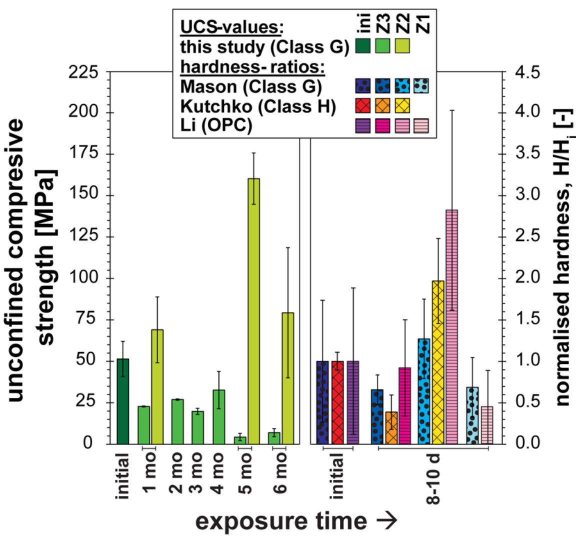

Figure 3. Evolution of UCS (right axis) for cement samples exposed to CO_2-rich solution over time (this study). Hardness ratios (left axis) are shown for other studies performed on Class G cement,[32] Class H cement[36] and ordinary Portland cement (OPC).[33] Note that the error bars for the data obtained in this study are determined by the quality of the data fit (see Supporting Information), while those for the other studies represent the standard deviation for the sample set.

Although the available UCS data for the inner-reacted, carbonated zone (Z2) is more limited than for the outer layer, it shows a rough increase in strength with exposure time, from one to five month with UCS values increasing from 69.1 to 160.3 MPa. After six months of exposure, the strength of this layer appears to have decreased significantly to values slightly lower than those measured after five months of exposure (UCS = 79.3 MPa; see Table S2). The friction coefficient is in the range of 0.38 to 0.63 (average 0.57). Overall, it can be seen that the rough trend suggests localized strengthening of the cement by up to a factor of 1.5−3 through the formation of carbonate-rich, dense zones, although there is significant variation in the measurement. It should be noted that the Ca-depleted, inner zone (see Figure 2a and b) was either too thin to measure its strength or could not be reached.

4. DISCUSSION AND IMPLICATIONS

Previous studies have shown that the unconfined compressive strength of the initial (fluid-saturated), unreacted cement varies strongly, with UCS = 45.1 ± 16.8 MPa[21,23,34,55−59] and μ = 0.54 ± 0.21.[23,34,55−57] The large range of reported strength values is mainly caused by the water-to-cement ratio but also by the range in available cement classes, and additives (e.g., fly ash), as well as curing time and conditions (temperature and pressure).[11] Upon CO_2 exposure, the variability in degree of carbonation, and hence bulk strength, resulting from factors like curing conditions and additives is even further complicated by the chemical environment (temperature, pressure, and fluid), as wet sCO_2 generally results in only a single reaction front, as opposed to the different zones seen in samples reacted with CO_2-saturated brine.[21,51,60] Triaxial compression experiments can be employed to determine the bulk strength of reacted cement. However, this only results in a single strength value representing the sum of the individual reacted zones.[21,23,34,38] Few studies have focused on determining the mechanical behavior of CO_2-exposed reaction zones in wellbore cement,[32,33,35,36,39] in part due to the difficulty of measuring the mechanical strength of the separate reaction zones, as well as due to sample heterogeneity on the μm to mm scale. We will compare our brittle strength data to results obtained on reaction zones in additive-free cement,[32,33,36] similar to the cement used in this study, and make inferences for wellbore stability.

Strength of Individual Reaction Zones in Additive-Free CO_2-Exposed Cement. Studies investigating strength changes for the different reaction zones are limited and show large variations[32,33,36] (cf. Figure 3). After about 8 to 10 days of exposure to brine and sCO_2, nanoindentation tests on reacted Class G cement showed varying results for Z2, from local weakening to significant strengthening, as across the zone hardness changed by 27 ± 48%.[32] In contrast, nanoindentation tests on Ordinary Portland Cement (OPC)[33] and Vickers Hardness microindentation tests on pozzolan-free Class H cement[36] showed more significant strengthening for the same zone, by 181 ± 120%[33] and 150 ± 52%,[36] respectively. This is in line with the bulk strength measurements made on fully carbonated cement (in effect representing Z2), which showed an increase in UCS by 160%.[34] However, the outer, porous silica layer (Z3) showed contrasting mechanical behavior, with weakening by 34 ± 17% for Class G cement[32] to strengthening by 24 ± 21% for Class H cement,[36] while OPC showed strength changes ranging from 66% weakening to 51% strengthening.[33] The inner, Ca-depleted layer (Z1) showed a

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clear weakening for all three cement types (Class G: 31 ± 36%;[32] OPC: 56 ± 55%;[33] Class H: 24 ± 21%[36]).

The core-scratch results obtained in this study are the first to quantitatively report the unconfined compressive strength and delineate the brittle failure envelopes of reaction zones formed in CO_2-exposed cement. Because hardness is not an intrinsic material parameter, it cannot be directly related to unconfined compressive strength. Therefore, we assumed that hardness scales linearly with strength to be able to compare our results to the indentation hardness measurements stated above. For this comparison, we plotted normalized hardness as a function of exposure time in Figure 3 (right axis). Overall, the results obtained by Mason et al.[32] for Class G cement fit reasonably well with our own observations (Figure 3), which show a weakening of Z3 (36−91%), and a strengthening of Z2 (34−211%) with exposure time. Our rough trends fall within the range obtained in the other studies,[32,33,36] i.e., decreasing strength for Z3 with time and increasing strength for Z2. This (rough) time dependence of zone strength may reflect the extent of the reaction, wherein more reaction with time leads to a time-evolution of porosity, affecting zone strength (lower porosity increases strength, and vice versa). Furthermore, our samples suggest a pronounced strengthening of Z2 after five months of exposure (211%) and a decrease in this strength again after six months of reaction (34%). This could be due to the fluctuating chemical conditions resulting from the depressurization and cooling cycles, inherent differences in sample strength at the onset of the batch-reaction phase, or even continued leaching of a fully reacted sample, although we have no means to test these hypotheses.

It should also be noted that the contact areas for the three different methods differ by several orders of magnitude. Nanoindentation tests employ indenters with an area of several nm^2 to μm^2, while the contact area during a Vickers Hardness test is on the order of several 100−1000s of μm^2, with penetration depths going from a few nms to μms. Given the highly porous, heterogeneous nature of cement, this could lead to a large variation in measured hardness, as demonstrated by the data of Mason et al.,[32] Li et al.[33] and Kutchko et al..[36] In contrast, the scratch-hardness tests conducted in this study perform measurements on areas of >1 cm^2, with total scratch depths of several tenths of a mm. However, the irregular shape of the reaction zones, controlled by the inherited heterogeneous micropore structure of cement materials[50,61] (cf. Figure 2a,b), is inferred to affect the force measurement, resulting in force fluctuations of ∼100−200 N, especially for measurements taken on the longer exposed samples (5−6 months). These samples show clear "paleo-fronts" with locally higher and lower porosity developed in Z2, which are remnants of older Ca-rich and Si-rich reaction zones that progressed through the material[22,62] (see Figure 2b,c). This may additionally attribute to the larger variability in force measurements obtained for Z2 compared to Z3 (see Figure S9). Overall, the qualitative trends obtained from indentation tests are in accordance with the quantitative values obtained using the core scratch technique. This suggests that the measured micro- and cm-scale properties are similar, though it should be noted that the large range influences the direct predictive capability of the measurements.

Implications for Wellbore Stability and Future Research. When it comes to wellbore stability, (reaction-induced) mechanical cement failure may not necessarily result in loss of integrity. Rather, knowledge of the location and extent of mechanical failure is needed to assess the potential loss of zonal isolation.[11,63] The latter entails a complex interplay between the chemical interactions of the cement with CO_2-rich fluid, the effect this may have on its mechanical behavior, the state of stress acting on the cement in response to injection of a high-pressure fluid, and (most importantly) how all these factors affect the transport properties of the cement. Under in situ conditions, lab[63,64] and field[65,66] studies suggest that CO_2 penetration, and hence induced reaction, will be limited unless the CO_2 has a way to penetrate the cement along significant portions of the wellbore through either cracks or microannuli. If this is the case, chemical zonation by CO_2 exposure within the cement itself may affect its mechanical behavior and strength, as is also demonstrated in the present study.

Using the core-scratching technique, our study for the first time managed to obtain brittle failure envelopes for the individual zones developing in CO_2-exposed cement, confirming qualitative hardness trends observed in previous studies.[32,33,36] These envelopes may be used in numerical studies predicting stress changes in the wellbore and potential cement failure in response to CO_2 injection,[41,42] taking into account chemo-mechanical alteration of the cement. An increase in strength for Z2 suggests expansion of the brittle failure envelope and potentially also the poro-plastic end-cap toward higher stresses. In contrast, Z3 and Z1 are suggested to have smaller failure envelopes due to chemo-mechanical weakening. Existing stress path calculations have shown that lowering of the effective stress acting on the well, e.g., due to high internal pressure in the well or pore pressure decrease in the surrounding rock, can result in stress paths moving toward the brittle failure envelope and potential shear failure of the cement sheath.[41,42] In contrast, increasing effective stresses, e.g., due to heave of the reservoir in response to CO_2 injection, will move the state of stress in the well toward the poro-plastic end-cap.[41] Whether failure or yield is obtained depends strongly on the initial state of stress in the cement sheath, as it determines how far the cement is from the failure envelope.[41,42,63,67] Even though the initial state of stress in wellbore cement is difficult to determine,[67] brittle shear failure seems to be most likely under high τ_m and low σ_m stress conditions (see Figure S1). Since brittle failure is often associated with dilation, this may lead to the formation of permeable pathways depending on the self-healing capability of the cement.

Because this study is only concerned with the brittle failure envelopes of the reacted cement zones, to get the full picture of the mechanical behavior of cement (and the potential creation of leakage pathways under in situ conditions), we would also need to understand the poro-plastic behavior leading to permanent, plastic deformation. In addition, understanding of the elastic behavior, i.e., Young's modulus,[32,33,35] is needed to predict the likelihood of decoupling between different layers. With the creation of weak, porous zones, such as Z1, it also means that cement strength is perhaps not controlled by the strongest (i.e., least porous) zone but rather by the mechanically weakest zone (i.e., the most porous zone). Potential for decoupling between Z2 and the unreacted cement core, due to the mechanically weak porous, Ca-depleted zone (Z1)[21,22,33] has been observed. At the same time, shrinkage of the Si-rich, outer gel layer (Z3) has been noted.[68] Provided that these processes also take place under in situ stress conditions, both decoupling and shrinkage may lead to the formation of microannuli in the wellbore system. However, not all studies show this decoupling,[34] and given the wide range of observed mechanical behavior and strength changes resulting from

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exposure, it is not possible to draw a firm conclusion on the effect that CO_2-induced reactions have on cement resistance to failure.

To resolve this strength uncertainty, we could perform more chemo-mechanical experiments on reacted cement to obtain a statistically relevant data set. This would require the measurement of hundreds of samples, which is not an easy feat. At the same time, this would still not solve the problem of a broad data range due to sample variability, just that of obtaining a stronger average. Instead, statistical tools, such as sensitivity analysis combined with numerical modeling, could prove useful in assessing the in situ mechanical behavior of wellbore cement and study worst-case failure scenarios leading to continuous flowpaths. The current quantitative (this study) and qualitative[32,33,35,36,39] experimental data could serve to guide these modeling efforts. Future experimental work could focus on other key issues, such as quantifying the plastic behavior of reacted cement, the tensile strength of cement, and understanding the material interface decoupling (cement-casing and cement-rock), or even cement−cement decoupling, as well as the potential for fracture−annulus healing.[18,20,69] This is needed to better assess the likelihood of the formation of long-range leakage pathways and their permeability. In addition, it should not be forgotten that cement placement in the wellbore plays the most significant role in determining the overall long-term integrity the CO_2 storage.[9] During the cement job, large annuli can occur, thus limiting the safe storage of fluids for long periods of time. In this context, the integrity of CO_2 storage should be defined in terms of both initial cement placement and subsequent chemical and mechanical effects of CO_2 on the cement and wellbore integrity.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge at The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03097.

> Details of the theoretical background behind key geomechanical principles, the scratching technique, and the data processing method; tables showing experimental data and UCS and μ values; and figures showing schematic diagrams, x-ray attenuation profiles and CT images, raw data, and best linear-fit regressions. (PDF)

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Notes

The authors declare no competing financial interest.

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