Overview of current standards and common other testing methods used in wellbore sealant assessment

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Summary:

Wells in reservoirs in which CO_2 is stored will be exposed to a range of conditions that may have a deleterious impact on the integrity of the wellbore sealants, both during CO_2-injection, and in the period after that. The development of sealants that can ensure long-term seal integrity requires 1) identification of the key properties for ensuring such long-term integrity; 2) proper testing methods for these properties based on a thorough understanding of these deleterious mechanisms. As a first step towards identifying these properties, this report provides an overview of current relevant standards, guidelines and regulatory requirements for the assessment of wellbore sealants to be used in CCS operations.

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1. Introduction

The primary objective of the ACT3-funded project Cementegrity is to support the development of wellbore sealants that can ensure long-term sealing integrity during CO_2-injection and -storage. To achieve this, Cementegrity is performing mostly experimental work to assess how five different sealants (three based on Ordinary Portland Cement (OPC), and two not based on OPC) perform when exposed to a range of deleterious conditions that may arise during CO_2-injection and storage. The findings and conclusions from those experimental studies (carried out in WP's 1, 2, 3, 5 and 6) and numerical modelling (WP 4), will be documented as part of WP 7 mainly focused on identifying critical properties that contribute to the enhancement of long-term seal integrity, as well as suggesting best practices for measuring or assessing those properties and how they may be affected by CO_2-injection and -storage.

The successful application of any sealant mixture requires that the material has satisfactory properties throughout its lifetime; i.e., during emplacement, during setting and hardening, during CCS-operation, and beyond. While properties of the sealant mixture before setting, and its behaviour during setting and hardening are of key importance for achieving a successful seal, these properties are not specific to CO_2-storage. Therefore, the Cementegrity project focuses specifically on the properties of the hardened sealants that are required to ensure a proper seal, and how these properties may be affected by exposure to deleterious physical and chemical conditions resulting from CO_2-injection.

To support that work, this report and deliverable for WP 7 of Cementegrity will provide an overview of current relevant standards, guidelines, and regulatory requirements, focusing on international documents, and documents from Norway, the Netherlands and the UK (i.e., the countries in which Cementegrity partners are located). Based on these documents, we will identify the key properties of hardened sealants, with their preferred testing methods as given in these documents. We will also discuss other common testing methods that are of relevance to these properties. Where required, we may also note other analysis methods that are currently not commonly used in wellbore cementing but may have high relevance and applicability. Note that, in the following report, we will list these standard, common, and/or relevant methods, but will not necessarily evaluate them.

1.1. The wellbore-sealant-rock system

Figure 1 schematically illustrates a wellbore-sealant-rock system after plugging and abandonment. During construction of the well, sealants are used in the annulus between wellbore and host (cap-)rock, as well as in the overlapping joints between wellbore casing and tubing. Then, once CO_2-injection is done, a well is plugged with additional emplacement of sealant. At any time, during emplacement of the annular seal and subsequent operations (and beyond), leakages may form 1) along interfaces between sealant and wellbore or sealant and rock; 2) along fractures within the sealant; 3) through the body of the sealant itself, as a result of: a) chemical; b) mechanical; c) thermal effects. Thus, when developing and testing sealants for CCS-applications, we need to ascertain that these sealants can provide and maintain seal integrity, withstanding such effects and potential interplays between these effects after being exposed to CO_2.

1.2. Existing relevant standards, guidelines, and legislative requirements

1.2.1. General

Existing standards and country specific guidelines and/or legislative requirements need to be considered when selecting sealant compositions for a specific application, or when developing new sealant materials. In the following discussion, a distinction needs to be made between standards, guidelines and legislative requirements. Furthermore, as the international standards provide guidance in terms of cement/sealant properties, these can either be referenced or used by the Energy companies to develop bespoke company standards.

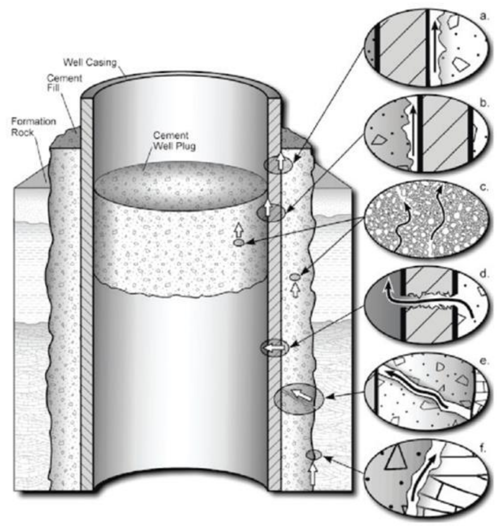

Figure 1. Schematic representation of a plugged well, showing potential leakage pathways (from: Celia et al, 2005).

Legislative requirements such as the Dutch Mining Law, Decree and Regulations in the Netherlands, to which adherence is mandatory, do not stipulate specific sealant properties considered necessary to ensure (long term) well integrity, instead indicating isolation requirements for subsurface containment and well integrity with the intent for no movement of gas or fluids through a prescribed isolation barrier. Here, the main standards and guidelines, both international and on a national level, provide guidance on cement and sealant properties. These standards include the international ISO 10426-1 and ISO 10426-2 standards (also known as ANSI/API Specification 10A and ANSI/API Recommended Practice 10B-2), the Norwegian NORSOK standard D-010; the UK OEUK *Guidelines on well decommissioning for CO_2 storage* (WDCS) and Guidelines on Qualification of Materials for the Abandonment of Wells (GQMAW); and the Dutch NOGEPA INDUSTRY STANDARD 45 *Decommissioning of* wells. This latter standard refers to relevant sections of the Dutch Mining Regulations. It is important to note that while the applicable well abandonment articles in the Dutch Mining Regulations are also applicable for CO_2 injection wells, at present, sequestration of CO_2 falls outside the scope of NOGEPA 45 standard. However, the standard does provide precedence of accepted isolation methods. In the following chapters, we will discuss these standards and guidelines, focusing on aspects relevant for ensuring well integrity during CCS.

1.2.2. Important properties of sealants, according to standards and guidelines

The guidelines and standards named above all specify what are considered important properties for sealant materials. These specifications will be compared and discussed here, focusing on material-specific properties relevant for CCS. While the API 10A classifies a number of different (OPC-based) wellbore cements, with regards to material properties of cured cements, it only sets requirements relevant for successful emplacement of a seal, including compressive strength after 8 and 24 hours of curing (dependent on cement class and chosen curing regime).

The main requirement given by all these documents is that a material selected as sealant must have low permeability. Here, the D-010 gives a required (maximum) value for the water permeability of ≤5 µD, but also allows for a higher permeability of up to 1000x that of the rock formation the well barrier is placed against. Regarding placement of the barrier, D-010 states that ”The well barrier(s) shall be placed adjacent to a low-permeable or impermeable formation with sufficient formation integrity for the maximum anticipated pressure.”. In addition, D-010 notes that “the zonal isolation material shall as a minimum have a combined permeability and length such that its ability to prevent fluid migration is as good or better than the cap rock it replaces." In contrast to this, the UK WDCS guidelines state the sealant must be "effectively impermeable", and the Dutch NOGEPA 45 guidelines require a "very low permeability". While this "very low permeability" is not quantified, this must be read in reference to the Dutch Mining Regulation (DMR) BWBR0014468, which states (Article 8.5.1.3) that when decommissioning a well, the operator "shall install an effective and durable isolation that prevents flow of subsurface gasses and fluids through the caprock to other rock strata or to the surface." (English translation taken from NOGEPA 45).

Secondly, the sealant material must form a seal where it interfaces with other materials (caprock, steel tubing), to prevent leakage around the seal. While the WDCS and NOGEPA 45 simply state that a material must seal at the interfaces (and be compatible with surrounding materials), D-010 specifies that a sealant must bond to steel tubulars, or have a compensating mechanism if it cannot bond, and that a sealant must have low shrinkage (for annular seals) or long-term positive linear expansion (for internal plugs).

Thirdly, all documents require mechanical properties that are suitable for accommodating expected pressures and stresses (at expected temperatures). What these properties are is not specified further as this may vary widely between applications.

Fourthly, it is required that the sealant can sustain long-term seal integrity under the physical and chemical conditions it is expected to operate at downhole, i.e., that it is able to maintain the properties listed above, and does not significantly deteriorate. This includes minimising the risks of cracking of the sealant, or debonding at the interfaces.

In addition, the sealant must stay in position once emplaced. Furthermore, shrinkage should be low, and should not affect the quality of the seal itself, and of the seal-steel and seal-rock interfaces (i.e., should not cause debonding). Finally, the sealant material itself should not have a negative impact on the steel tubulars and surrounding rock materials it is in contact with.

Table 1. Required properties of sealants, as specified by NORSOK D-010, WDCS, and NOGEPA 45.

Required sealant property	NORSOK D-010	WDCS	NOGEPA 45
Permeability	≤5 µD	effectively impermeable	very low – the sealant is to prevent movement of subsurface gasses and fluids through the caprock to other rock strata or to the surface
Form a seal at interfaces	by bonding or compensating mechanism	provide a seal	provide a seal
Mechanical properties	FEA to be performed to ensure 40% safety factor	suitable	Suitable
Long-term integrity	Key integrity indicators should not indicate deteriorating long-term trend	no significant deterioration, able to withstand downhole fluids at foreseeable PT	sustained functional properties under foreseeable conditions
Remain in position intended at depth	-	noted	noted

Volume stability	Low shrinkage or long-term expansion	consider "risks of cracks and de-bonding over time"	"risks of shrinkage and debonding should be considered"
Compatibility with surrounding materials (steel and/or rock)	"shall not detrimentally affect" steel tubulars in contact	compatible with adjacent geology	-

1.2.3. "Key integrity indicators"

With regards to long-term durability, and the impact of CO_2 on sealant integrity, the NORSOK D-010 lists "key integrity indicators". These are properties that, when testing a sealant for a specific application, should be measured on both exposed and reference samples, to assess how much they change due to exposure. Properties that could similarly be considered "integrity indicators" can also be found in the UK *Guidelines on Qualification of Materials for the Abandonment of Wells* (GQMAW).

The Key Integrity Indicators given by D-010 include compressive and tensile strength, permeability, and Young's modulus. Of these, the D-010 only gives a required (maximum) value for the water permeability of 5 µD (or 1000x the permeability of the rock formation, whichever is greater), which is a little more limiting than the 10 µD (nitrogen) permeability mentioned by the GQMAW. Of specific relevance for CO_2-storage, the requirement for chemical stability included in NORSOK D-010 means that exposure (to CO_2 and other chemicals that may be encountered) should not "substantially affect" the required integrity; i.e., the "key integrity indicators" should not change substantially (negatively) due to exposure.

The GQMAW similarly states, with respect to durability, that a barrier material "should not degrade such that its sealing capability or position is compromised", and further suggests that this is assessed for an arbitrary duration of 1 million days (or circa 3000 years). The NOGEPA 45 likewise notes that a sealant material must have "durable, long lasting isolation characteristics", and "sustained functional properties under foreseeable downhole conditions, including corrosive fluids". However, the DMR which references the EU CCS Directive guidelines (2009/31/EC) refer to permanent containment of the stored CO2, quote "*The selection of the appropriate storage site is crucial to ensure that the stored CO2 will be completely and permanently contained.*", unquote.

For qualification testing of cements, ceramics and similar sealant materials (which includes geopolymers), the GQMAW requires assessment of permeability, UCS, tensile strength, shear bond strength, swelling and shrinkage, thermal expansion coefficient, and tendency to creep. Furthermore, the GQMAW requires assessment of the impact of aging on permeability, UCS, tensile strength, shear bond strength, swelling and shrinkage, and mass, indicating these are important indicators for sealant integrity. While the NOGEPA 45 asserts that cement-based materials have been the norm in well isolation globally, it allows for other materials to be used on exemption, and refers to the GQMAW (Issue 2, 2015) with regards to qualification of such alternative materials.

The NORSOK D-010 and GQMAW thus identify important parameters and properties that can be used to assess the impact of CO_2 (and other deleterious effects expected during CCS) on wellbore sealant materials, when developing or testing such materials. The GQMAW further refers to several standard methodologies that can be followed when measuring these properties.

In addition to that, the API 10A and API 10B-2 standards provide instructions of how to measure certain key sealant properties, such as UCS, as well as descriptions of methods for other important properties, including permeability. While these standards do not discuss cement durability, API 10B-2 does note that compressive strength measurements before and after exposure of a cured cement to representative downhole conditions "may be used to test cements or cement blends for resistance to thermally induced strength retrogression."

Table 2. Key integrity indicators: properties to be tested before and after exposure, to ensure integrity can be maintained.

Integrity indicator property	NORSOK D-010	GQMAW
Permeability	X	X
UCS	X	X
Young's modulus	X	recommended
Tensile strength	X	X
Mass (change)	-	X
Shear bond strength	-	X
Swelling and shrinkage	-	X

Legislative requirements (where present) such as Dutch Mining Law, -Decree and -Regulations often do not stipulate specific cement/sealant properties and focus more on the conditions and emplacement requirements for the cement/sealant (e.g., length of cement column or plug, placed against an effectively sealing caprock) with a view to ensuring (long-term) well integrity (pre and post abandonment).
Given the country specific differences in aforementioned guidelines and legislation, for the purposes of the CEMENTEGRITY project the most stringent requirements and conservative assumptions shall be used to compare the results of the experimental work.

2. Standard and common testing methods for wellbore sealants

In the following overview of standard and common testing methods used in the development and assessment of wellbore sealants, we will first consider preparation and testing of the sealant slurry, as well as sample curing and aging. Next, we will discuss methodologies applied to hardened sealant samples, and exposure of sealants to CO_2 and other deleterious conditions that may occur during CO_2-injection and -storage. As Cementegrity is mostly concerned with how a sealant performs once emplaced, we will focus mainly on these methodologies for hardened sealants, assuming that adequate placement has been obtained and position maintained.

2.1. Sample preparation and curing

The API 10B-2 standard gives detailed instructions for the preparation of (cement-based) sealant samples in the laboratory, as well as descriptions of the mixing equipment to be used. These instructions were developed to be representative of mixing conditions encountered in the field, while also ensuring that thoroughly mixed sealants are used consistently across projects, laboratories, and operators. When developing sealants for CCS applications that use similar mixing procedures as current cement-based sealants, it is recommendable to follow the preparation instructions given in these standards, while for sealants that are prepared differently, it may be necessary to develop alternative mixing procedures that achieve a comparable outcome.
For tests performed on cured samples (such as compressive strength testing and permeability measurements), API 10B-2 suggests curing is done at a project-dependent curing temperature and pressure, without specifying the pressure medium used in case of curing at elevated pressure. Such conditions could, for example, reproduce those expected in the targeted application of the sealant, but reference PT-schedules are also provided. For testing of materials used in annular seals in wells drilled during CCS-operations, curing should in general be done (in water or brine) at expected in-situ PT-

conditions. However, for materials used in plugs that are used to seal wells once CO_2-injection is completed, exposure to CO_2 already during curing might be more representative.

2.2. Tests performed on sealant slurries

Once mixed, a sealant slurry must fulfil a number of criteria that determine whether it can successfully be transported downhole and, once there, form a high-quality seal. These criteria are dependent on the targeted application, and expected conditions in the wellbore (e.g., depth, pressure, temperature, etc.). For most if not all of these, test procedures are provided in API 10B-2, and standard equipment based on these procedures is available. Such properties include slurry density, rheological properties and gel strength (typically measured together in a rotational viscometer), static fluid loss, slurry stability, thickening time, and volume changes upon hardening. As Cementegrity is mainly focused on the material properties and behaviour of hardened sealants, these tests will not be addressed here.

2.2.1. Testing of mechanical properties

Along with its permeability, a material's mechanical behaviour under stress, and at in-situ pressure and temperature conditions, is key in determining whether this material can be used as a downhole wellbore sealant. Of the mechanical properties, the uniaxial Unconfined Compressive Strength (UCS) is easiest to measure, for example following procedures such as those outlined in API 10B-2. However, this UCS may be less representative of a sealant's behaviour downhole. Therefore, UCS is commonly supplemented by further uniaxial, and triaxial experiments. In these further tests, cylindrical samples are either unconfined (uniaxial) or confined radially (triaxial) using a fluid pressure medium, and then compressed along the axial direction, commonly up to their failure point, or even beyond. Experimental procedures for such tests are, for example, described in ISRM (1983), API TR 10TR7 (2017), and ASTM D7012-23 (2023). From loading curves obtained in such experiments, in addition to the yield or failure strength (at the set confinement pressure), the Young's modulus can be calculated, which gives insight in a sealant's elastic behaviour before it fractures. Poisson's ratio, indicative of the volume change of a material when stressed, can be calculated from the obtained data if radial (or volumetric) strain is tracked. When a series of samples is tested at different confining pressures, the material's friction angle and cohesive strength are also obtained, which allows for failure envelopes to be plotted.

One additional mechanical property that is usually measured when assessing wellbore sealant materials, is their tensile strength. For sealants (and other rock-like materials), this is most commonly done using a version of the Brazilian disc test, in which a disc of sealant material is split through radial compression, and the stress needed for the disc to split is correlated to the material's tensile strength. Note that for materials that can undergo high elastic strain before splitting, this method may yield unreliable results as it assumes the disc to be perfectly cylindrical. For a description of this method, see ASTM C496 (2017).

When considering these mechanical testing methods, we should note that such methods typically proscribe fixed strain rates at which they are to be carried out, as the rate at which such tests are carried out can impact the values obtained in multiple ways. While tests are to be carried out under fully drained conditions, allowing any pore fluid to escape when the loading rates is sufficiently slow, for low-permeability materials with water-filled pores, compression at the prescribed (relatively rapid) rates can lead to pressure build-up in these pores, which can in turn lead to a lower observed compressive strength.

In addition to destructive testing (i.e., fracturing samples), certain mechanical properties can also be assessed by non-destructive methods, such as by the sonic method described in API 10B-2 for monitoring compressive strength during curing, which is commonly used to track strength development against time.

Recent research has shown that the mechanical properties of (cement-based) wellbore sealants, such as compressive strength and Young's modulus, can also be correlated with some accuracy to indentation depth using indentation testing techniques and equipment similar to the Rockwell hardness test (for example, see Yan et al, 2023 and references therein). Similar results may also be obtained using a (micro) scratch test method (Liu et al, 2020). The use of such methods is particularly interesting as micro-indentation methods allow for multiple localized measurements within a single sample cylinder, rather than measuring the mechanical properties of the full cylinder, while scratch methods can be used to measure changes along selected lines across a sample. Thus, these methods offer the possibility of more accurately assessing changes in mechanical properties caused by CO_2-exposure, as well as the distribution of such changes. Note that the measurement of hardness is also recommended, though not required by the GQMAW when qualifying new sealant materials.

2.2.2. Sealant permeability and porosity measurements

The other key parameter determining whether a material can be used as a wellbore sealant is its permeability. Sealant materials need to have a low permeability to inhibit fluid flow through the seal itself. Accordingly, maximum allowable permeabilities are given in some documents, such as NORSOK D-010 (5 µD water permeability, or 1000x the permeability of the surrounding rock) and GQMAW (10 µD nitrogen permeability). While several different methods exist by which permeability can be measured, most involve observing a flow of fluid through the sample.

API 10B-2 describes a simple permeability test, to be carried out using water or gas, where a constant flow of the chosen fluid is forced through a cylindrical cement sample from one side, while the other side is open to the atmosphere. The pressure needed to force this flow through the sample is measured at the upstream side and used to calculate sample permeability.

Similar constant flow tests are also commonly performed in more complex apparatuses, which allow for elevated temperatures, and in which both the up- and downstream side of the sample can be at elevated pressure, while the sample itself is confined at a set pressure (cf., Rod et al, 2019; Beltrán-Jiménez et al, 2022; Hatambeigi et al, 2023). Such apparatuses thus enable permeability measurements under pressure and temperature conditions similar to those expected in-situ, allowing for a more accurate permeability measurement.

Alternative to measuring the pressure difference over a sample when a constant flow is applied through this sample, permeability can also be measured using a transient pressure pulse method. Here, instead of a constant flow, a pressure pulse is applied to the sample, and its decay through the sample monitored to calculate sample permeability. The key advantage of this method, especially for samples with low permeability, is the shorter measurement duration, as there is no need to wait for a steady flow through the sample to establish (cf., Bello and Radonjic, 2014; Ridha et al, 2012; Skadsem, 2021).

While the above methods depend on measuring pressure differences over a sample when a fluid flows through it, for water-filled samples of porous materials (i.e., cement-based and most other sealants commonly used), permeability can also be correlated to electrical impedance (i.e., frequency-dependent resistivity). While such electric measurements can be very rapid, and may enable in-situ monitoring of cement permeability/integrity, they are not as commonly used in research, probably because the interpretation of permeabilities from results can be relatively complex, and requires material-specific constants (cf. Ridha et al, 2012).

When assessing a sealant specifically for use in a CO_2-storage reservoir, it can be important to measure its permeability to CO_2 in particular, by exposing a sealant core to a flow of CO_2 using a method otherwise similar to that described above. This will be further discussed below, in chapter 2.3, as this can be combined with testing the ability of a sealant to withstand exposure to CO_2.

In addition to permeability, porosity, the volume fraction of void space within a solid material, can also be of importance. One standard technique for the measurement of porosity is porosimetry, where a non-wetting liquid (e.g., mercury) is pushed into a sample at high pressure, yielding measurements of pore volume and pore diameter. Alternatively, pycnometer-based measurement techniques measure the drop in pressure when a known volume of gas (commonly He, because of its low molecular diameter) at elevated pressure flows into a chamber containing the sample, or into the sample itself directly. Both these methods only assess the interconnected pore volume, into which the fluid used can flow. In addition, porosity can also be assessed from Scanning Electron Microscope images taken using back-scatter electrons on resin-impregnated polished sections (Wong et al, 2006; Edwin et al, 2019), or from X-ray Computed Tomography (CT-scanning).

2.2.3. Bond strength and hydraulic sealability

An important property determining how well a sealant can maintain seal integrity in a geological system undergoing change is the strength of the bonds that it forms with the steel wellbore, and with the surrounding rock. In particular, the annular contact between sealant and wellbore is a key nucleation site for the formation of leakage pathways, which can for example be induced by mechanical (fluid pressure, vibrations) and thermal effects. Therefore, a range of different tests has been developed and applied for assessing bond strength (see for example Carter and Evans, 1994). Typically, these tests measure the force required to create slip along a bonded contact surface created by casting and curing a sealant in contact with a piece of steel or other material (shear bond strength testing), though tests measuring the bond strength using tensional loading have also been used (e.g., Ladva et al, 2005). Alternatively, hydraulic sealability tests measure the fluid or gas pressure needed to break through a cemented interface (Van Eijden et al, 2017). Contact geometries for bond strength tests can be a flat surface (Ladva et al, 2005), a sealant cast around a central piece of steel (Carter and Evans, 1964), or a sealant cast within a steel tube (as in Patent No US11054353B2).

2.3. Assessment of CCS-specific impacts on seal integrity

For most regular applications, a sealant material's mechanical properties and permeability, and the evolution of these parameters with time under in-situ conditions, are sufficient for estimating whether a successful seal can be maintained. However, during CCS, sealants may be exposed to additional mechanical, chemical and thermal effects that can be deleterious to sealant integrity by either impacting a sealant's mechanical properties and/or permeability, or otherwise interfering with its ability to maintain seal integrity. Therefore, when assessing sealants for CCS, either in general, or for a specific project, these additional effects need to be accounted for in experimental tests where samples are exposed to these effects and their impact is measured. Currently, such loads and stress/strain are typically simulated using Finite Elements Analysis software.

2.3.1. Exposure to CO_2

The most important effect to which sealants will be exposed in any CO_2-storage project is the CO_2 itself. By dissolving into the pore water, CO_2 has a major impact on pore water chemistry, which may then induce fluid-mineral interactions such as leaching and dissolution in the sealant material. New solid phases may also form and precipitate. These reactions will in turn impact a sealant's mechanical properties, and permeability. Furthermore, depending on its water content, CO_2 may also remove water from the pore network, by displacement or evaporation, and thus change the exposure scenario.

Exposure of sealants to CO_2 is most commonly done in batch experiments, where a larger number of cured sealant samples (typically cylinders) is placed together in an autoclave or similar pressure vessel, which is then filled with water or brine, pressurized with CO_2, and heated. In this manner, larger number of samples can be exposed simultaneously, using a relatively simple setup that is easy to monitor and run. Samples can be placed under water (to be exposed to CO_2-dissolved water) or above water (to be exposed to water-saturated CO_2), and different water and CO_2 compositions can be used to mirror desired conditions (cf. Kutchko et al, 2006; Duguid et al, 2011; Liteanu and Spiers, 2011; Zhang and Talman, 2014; Chavez Panduro et al, 2017). Similar experiments can also be carried out using a flow-reactor, in which the fluids

surrounding the sample(s) are refreshed continuously, but flow is not forced through the sample (Duguid and Scherer, 2010).
However, during such batch exposure tests, the depth of CO_2-ingress is mostly controlled by initial pressure-driven penetration into the sample, followed by very slow diffusion-controlled transport. As a result, only the outer skins of sealant samples are commonly exposed, making it more difficult to assess the impact of exposure on the material's compressive strength, permeability, and other properties by methods based on testing of the full sample.
Alternatively, samples can be exposed in flow-through (core-flow) setups, where a flow of (water-saturated) CO_2 or CO_2-saturated water is forced through a cylindrical sample (cf. Walsh et al, 2014; Lende et al, 2021). This flow can be forced at constant flux, or at constant differential pressure; and exposure can be carried out at elevated temperature and confinement pressure. Such tests are considerably more complex, and thus expensive, to monitor and run, and only allow for small numbers of samples to be exposed simultaneously (typically limited by the number of apparatuses available). However, depending on sample permeability, the selected pressure gradient or flow rate, and duration, they do allow for full exposure of a sealant sample, and can give a more reliable estimate of CO_2-penetration rates, that are easier to extrapolate to field dimensions and timescales. Furthermore, monitoring of flowrates and up- and downstream pressures allows for sample permeabilities to be estimated and monitored during ongoing tests. Despite the complexities of such tests, it can be recommendable to run parallel exposures to both a flow of (wet) CO_2 (at in-situ pressure and temperature, so likely supercritical) and CO_2-saturated water, as then the impacts can be compared, and worst-case scenarios can be identified.
Furthermore, flow-through experiments can also be carried out on fractured (or otherwise damaged) samples, to assess how reactive flow through a leakage pathway may alter that pathway's permeability (see for example e.g., Abdoulghafour et al, 2013;2016; Van Noort, 2023).
After exposure, the sample mechanical properties and permeability can be measured using the same procedures as described above, and are ideally compared to identical samples aged under similar pressure and temperature conditions, but without CO_2. These permeability measurements before and after exposure are best performed under conditions where there is a single flowing fluid phase (for example by using water) to ensure permeabilities are measured accurately and reproducibly, and are not impacted by multiphase flow effects. Additional analyses may be carried out to investigate the impact of CO_2-exposure on sealant microstructure, (mineral) composition, and integrity, such as microstructural analysis (see below), as well as standard analyses such as XRD, XRF, TG/DTA, etc.
Finally, as most CO_2-storage projects will be injecting CO_2 with a certain (varying) combination of impurities into a reservoir that will contain water, methane, and/or other fluids, the impact of these impurities on cement seals needs to be taken into consideration, and additional exposure testing to impurity-bearing CO_2 may be warranted in line with CO2 specifications defined for transport, flow assurance & specific selected storage complex reservoir.

2.3.2. Microstructural analyses to assess the impact of CO_2

Microstructural analyses can provide key information regarding the depth of CO_2-ingress, and the impact of CO_2 on the sealant material. While specific methods for microstructural analysis are not proscribed in standards or regulations, certain techniques are commonly used.
One such method is X-ray Computed Tomography (often referred to as CT-scanning), in which X-rays are used to build a (usually) 3-dimensional image based on density contrasts. While submicron resolutions are possible, as resolutions are dependent on sample size and scanning time, in practice resolutions of several to tens of microns are used. As much of the CT-scan is automated, the method does not require intensive sample preparation, and no knowledge about the composition of the sample scanned is needed (or gained), it is often used to objectively assess CO_2-ingress based on the density (porosity) changes caused by chemical interactions induced by CO_2, as well as to identify cracking and other damage in

cements (e.g., Gawel et al, 2017; Skorpa et al, 2017; Chavez Panduro et al, 2019; Vrålstad and Skorpa, 2020; Yang et al, 2021; Beltrán-Jiménez et al, 2022).

To gain a more complete, and finer image of microstructure and (mineral) composition, and the impact of CO_2-exposure thereon, Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDS or EDX) can be used. Here, the most interesting results are typically obtained using a Backscatter Electron detector (BSE), on a polished (and resin-impregnated) cross-section through the sample (e.g., Kjellsen et al, 2003; Wong et al, 2006; Edwin et al, 2019, etc.). In this way, a clear view of the microstructure of the sample will be obtained, and, when combined with EDS, the depth to which CO_2-exposure has impacted the sealant can be assessed. Furthermore, sealant porosity and individual (mineral) components in the sealant can be identified. Likewise, reaction products and other effects, such as a changes in porosity due to dissolution and leaching of elements, caused by exposure of the sealant to CO_2 can be seen. However, proper performance of such analysis requires high quality sample (surface) preparation, in particular for the quantification of porosity, and this requires a skilled operator (cf. Kjellsen et al, 2003)). Furthermore, as using this method individual components in the sealant may be identified, such analyses may not be desirable from the point of view of confidentiality.

2.3.3. Thermal shocks and thermal cycling

In certain CO_2-storage scenarios (such as injection into a depleted gas reservoir, as planned in, for example, the Porthos CCS project centred on the harbour of Rotterdam), for vapour/gas or dense/liquid CO2 transport and injection operational phases sealants will likely be exposed to rapid changes in temperature; i.e., thermal shocks, and/or thermal cycling as a result of the Joules-Thomson effect. In the context of CO_2-injection, expected thermal shocks are rapid decreases in temperature, while heating afterwards will likely be slower. Such thermal shocks and thermal cycling may impact the integrity of the material used as an annular seal, and may also impact the bonds this seal forms with the central (steel) wellbore and surrounding rock. Therefore, when relevant thermal shocks or cycling are to be expected, these potential impacts need to be assessed beforehand.

The impacts of thermal loading are not yet as commonly assessed as some of the other damage mechanisms discussed here, but a range of methods is described in scientific literature. The easiest method for inducing a thermal shock, is to heat a sealant sample in an oven, and then quickly quench it in a temperature-controlled fluid (e.g., a water bath – cf. Absi and Glandus, 2004 and references therein). Damage induced by one or more shocks induced in this manner can then be assessed with microstructural analyses, or may even be observed optically. The impact on mechanical properties can be measured through any of the methods described above.

However, while relatively simple to perform, the outcome of this test may be less representative, and the test is relatively sensitive to operator variability (time between removal from oven and quenching; orientation in which the sample is dropped, etc.).

Several more complex methods have been reported in the literature, that may result in a more reproducible, and more representative test. One such method uses a copper rod of which the temperature is controlled with a heating-cooling platform, to induce thermal stress to a composite sample consisting of steel wellbore, cement anulus, and surrounding rock (cf. Albawi et al, 2014; De Andrade et al, 2015; Torsæter et al, 2017). Acoustic emissions during testing, as well as post-exposure microstructural observations may be used to detect damage and debonding caused by thermal variations induced through the copper rod.

As part of the Cementegrity project, alternative methods are being developed by Li and Pluymakers, who expose sealants to thermal shock by flowing a cold fluid (for example cooled water) through a hot sealant sample. This sample is either heated in an oven (unconfined) or held in a triaxial apparatus adapted specifically for this purpose (cf. Li and Pluymakers, 2023). Due to the low permeability of typical sealant materials, these methods may require a central bore, but this is not necessary when composite samples

consisting of a sealant surrounding a representative steel wellbore can be used. The use of a triaxial apparatus, in which a sample can be confined under in-situ pressures, allows for more representative testing as such pressures may help limit the damage caused by thermal variations.
Furthermore, the effect of thermal shocks or cycles on sealant integrity is correlated with the thermal stress felt by the sample and its mechanical properties. This thermal stress, for a given imposed temperature change, is controlled by the material's specific heat capacity, thermal conductivity (which together give heat diffusivity); and thermal expansion coefficient. These properties can readily be measured for any material using standard methods and equipment (such as those described in ASTM E228-22, 2023).

2.3.4. Cyclic mechanical loading

In addition to the direct impact of thermal shocks and cycling on sealant integrity, cyclical changes in injection pressure and temperature will also cause cyclical variations in the effective mechanical stress on the sealant. Such cyclical stress changes themselves may also impact sealant integrity through inducing mechanical fatigue. This is typically assessed using cyclic loading tests, where the effective stress on a sealant sample is varied cyclically between set maximum and minimum percentages of fracture strength (which is either calculated, or measured beforehand on samples of the same material), while measuring the induced strain. Typically, this is done for hundreds of cycles. Conditions should be chosen to be representative of, or exceed, expected conditions. Confinement (i.e., triaxial testing) is generally recommended during such tests.

3. Summary

Based on the above review of regulations and recommendations, regarding the integrity of sealants based on cements, ceramics and similar materials, we can identify the following properties as being considered key properties for ensuring long-term sealant integrity, also in the context of CCS:

- Permeability
- UCS
- Tensile strength
- Young's modulus
- Poisson's ratio

Furthermore, to fully understand long-term sealant integrity in any specific operation, including CO_2-injection and -storage, samples need to be aged and/or exposed to relevant deleterious conditions, and differences in the key integrity indicators between an exposed sample, a sample aged under reference conditions, and a sample before exposure or aging need to be noted. Such exposure and aging likely needs to be performed, at least in part, under accelerating conditions to better visualize effects within laboratory timescales, and allow for extrapolation to required timescales under more realistic conditions (such as the 3000 years given by the GQWAR). In addition to the key properties for ensuring sealant integrity, additional properties should be observed before and after exposure, as these can be important indicators of alteration in sealant materials. These properties include:

- Mass (or density)
- Microstructure
- Chemical and mineralogical composition
- Porosity

For most of the key properties and indicators listed above, standard test methods exist, or else well-established methods are available. In many cases, these methods can be used directly. However, they may need to be adapted to accommodate materials that may have properties that are quite different from those (OPC-based) materials for which these methods were developed, to ensure fair and realistic values are obtained and compared. Likewise, other methods may need to be adapted to accommodate the specific requirements of CO_2-exposure; e.g., the direct measurement of permeability (change) when samples are exposed to a flow of CO_2.

Furthermore, multiple standard or common methods may exist for measuring the same property; for example, compressive strength may be assessed through UCS, triaxial testing, or micro-indentation testing. Here, the best methods will need to be selected based on accuracy/representativeness, reproducibility, cost, and convenience. Where standard or common methods do not exist, new methods may need to be developed (based on existing methods). Further standardization, or at least concordance, may be useful here to ensure reliability and comparability of results from different projects.

One challenge in assessing and developing new materials is that, even with (largely) standardized tests, differences between laboratories or studies may arise due to minor variabilities in execution, sample preparation and curing, etc. To limit the impact of such differences, we recommend that studies include an internal reference, such as the simple OPC-based sealant S1 in Cementegrity, to which measurements and observations on other samples may be compared. Further agreement or even standardization of such a reference composition would then also facilitate comparisons across studies and laboratories.

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