

## Review: Role of chemistry, mechanics, and transport on well integrity in CO<sub>2</sub> storage environments



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### ABSTRACT

Among the various risks associated with CO<sub>2</sub> storage in deep geologic formations, wells are important potential pathways for fluid leaks and groundwater contamination. Injection of CO<sub>2</sub> will perturb the storage reservoir and any wells that penetrate the CO<sub>2</sub> or pressure footprints are potential pathways for leakage of CO<sub>2</sub> and/or reservoir brine. Well leakage is of particular concern for regions with a long history of oil and gas exploration because they are top candidates for geologic CO<sub>2</sub> storage sites. This review explores in detail the ability of wells to retain their integrity against leakage with careful examination of the coupled physical and chemical processes involved. Understanding time-dependent leakage is complicated by the changes in fluid flow, solute transport, chemical reactions, and mechanical stresses over decade or longer time frames for site operations and monitoring.

Almost all studies of the potential for well leakage have been laboratory based, as there are limited data on field-scale leakage. Laboratory experiments show that CO<sub>2</sub> and CO<sub>2</sub>-saturated brine still react with cement and casing when leakage occurs by diffusion only. The rate of degradation, however, is transport-limited and alteration of cement and casing properties is low. When a leakage path is already present due to cement shrinkage or fracturing, gaps along interfaces (e.g. casing/cement or cement/rock), or casing failures, chemical and mechanical alteration have the potential to decrease or increase leakage risks. Laboratory experiments and numerical simulations have shown that mineral precipitation or closure of strain-induced fractures can seal a leak pathway over time or conversely open pathways depending on flow-rate, chemistry, and the stress state. Experiments with steel/cement and cement/rock interfaces have indicated that protective mechanisms such as metal passivation, chemical alteration, mechanical deformation, and pore clogging can also help mitigate leakage. The specific rate and nature of alteration depend on the cement, brine, and injected fluid compositions. For example, the presence of co-injected gases (e.g. O<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub>) and pozzolan amendments (fly ash) to cement influences the rate and the nature of cement reactions. A more complete understanding of the coupled physical-chemical mechanisms involved with sealing and opening of leakage pathways is needed.

An important challenge is to take empirically based chemical, mechanical, and transport models reviewed here and assess leakage risk for carbon storage at the field scale. Field observations that accompany laboratory and modeling studies are critical to validating understanding of leakage risk. Long-term risk at the field scale is an area of active research made difficult by the large variability of material types (cement, geologic material, casing), field conditions (pressure, temperature, gradient in potential, residence time), and leaking fluid composition (CO<sub>2</sub>, co-injected gases, brine). Of particular interest are the circumstances when sealing and other protective mechanisms are likely to be effective, when they are likely to fail, and the zone of uncertainty between these two extremes.

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## 1. Introduction

The goal of any CO<sub>2</sub> storage project is to retain 99% of the injected CO<sub>2</sub> in the target reservoir for 100s of years with a maximum CO<sub>2</sub> surface leakage rate of 0.01–0.1% of CO<sub>2</sub> inventory per year (Hepple and Benson, 2005; NETL, 2011). Wells at storage sites can threaten this goal, as they represent a direct connection between the CO<sub>2</sub> storage reservoir and the atmosphere, as well as underground sources of drinking water (Gasda et al., 2004; Metz et al., 2005; Viswanathan et al., 2008; Carroll et al., 2014). These wells penetrate protective geologic formations such as caprock and were originally constructed to produce or inject large volumes of fluids from or into the subsurface. The long-term integrity of wells is of particular concern because of the potential for CO<sub>2</sub> (as a free phase or dissolved in formation brine) to react with and degrade the materials used in well construction. Wells in sequestration projects are generally planned, drilled, and completed following best practices, using best available materials, and following government regulations that were developed to address most of the common problems discussed above. As a result, modern wells have a much higher likelihood for well integrity. However, in many areas that are prime candidates for CO<sub>2</sub> storage there are legacy wells that were drilled when regulations were less restrictive, often using methods or materials that are now outdated (Gasda et al., 2004; Watson and Bachu, 2008; Nicot, 2009).

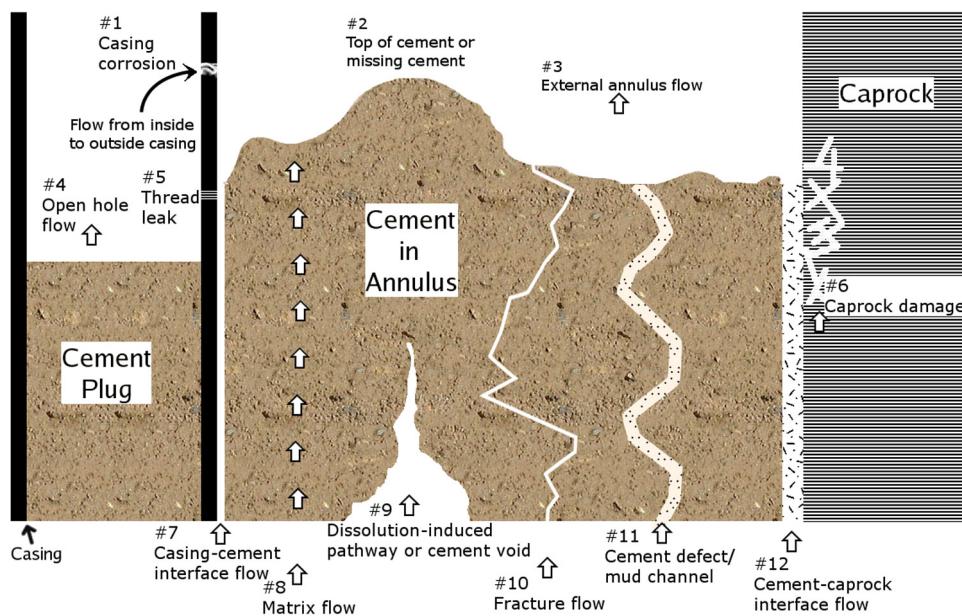
Well integrity can be compromised by defective well completion or as a result of chemical and mechanical stresses that damage the well during the operation or abandonment phases. Possible principle leakage paths are illustrated in Fig. 1 (Viswanathan et al., 2008). Key problems in poor completions include: thread leaks between casing joints, possibly accounting for 90% of all tubular failures (#5; Schwind et al., 2001); inadequate or incomplete cement placement or incomplete cement coverage especially in non-vertical wells (#2, #9); poor cement quality (i.e. high permeability cements; #8); development of mud or gas channels in the cement (#11); failure to adequately remove filter-cake from the borehole and other problems associated with a poor bond between casing/cement

and cement/formation (#7, #12); and formation damage during drilling (#6).

Post-completion problems may be caused by thermal stresses induced by production or injection of fluids; mechanical stresses due to changes in pressure inside tubing or within the injection/production reservoir as well as due to tectonic stresses; and chemical stresses due to fluids and gases within or surrounding the well attacking cement or steel. Potential post-completion leakage pathways include: casing and tubular corrosion which has large financial impacts across all of the oil and gas sector and can allow communication of fluids inside and outside the well (#1; Brondel et al., 1994); fractured cement (#10); dissolution-induced cement defects (#9); formation of microannuli at the casing/cement or cement/formation interfaces (#7, #12); and chemical degradation of the cement resulting in elevated permeability (#8). If fluids migrate past the cement barriers, then flow may occur via open-hole flow within the casing (#4) or by external annulus flow (#3). If fluids escape the multiple barriers in the well system and migrate through the external annulus, they still must have access to permeable formations or the atmosphere in order to impact the environment.

The proportion of well integrity problems arising during the completion stage, as opposed to the operational or abandonment phases, has not been formally investigated. A common hypothesis from field experience is that most problems originate because of poor completion and inadequate cement coverage creating leakage pathways or leaving the well more susceptible to subsequent mechanical, thermal or chemical stresses.

In this review we evaluate the evolution of leakage risk over time as a consequence of chemical, mechanical, and transport processes. Because CO<sub>2</sub> must be stored for long periods of time to mitigate climate change, relevant time scales range from seconds and days for stresses associated with well completion and operations, to decades and centuries for processes associated with corrosion, dissolution and precipitation. Of particular interest to the carbon storage community is the ability of potential wellbore leakage pathways to seal in the highly reactive system involving



**Fig. 1.** Schematic diagram of an abandoned well showing principle leakage pathways. Note that cement plugs can have many of the same problems as cement in the annulus. These pathways may originate during well completion activities or as a result of stresses occurring during the life of the well. Pathways are not drawn to scale; the plug may have a 10 cm diameter while the cement annulus will be closer to 2 cm.

Modified from Viswanathan et al. (2008).

carbon steel casings, alkaline Portland cement, and CO<sub>2</sub>-rich, acidic brines. This work highlights significant advances on the evolution of well integrity since the review of Zhang and Bachu (2011) and expands upon the geochemistry-focused review of Carey (2013). This review was developed as part of DOE's National Risk Assessment Partnership (Pawar et al., 2014) and includes work conducted by members of the partnership as well as important contributions made throughout the CO<sub>2</sub> sequestration community.

## 2. Key processes controlling leak path evolution

Quantifying the behavior of well leakage over time requires understanding the coupling of leak path geometry, geochemical reactions, geomechanics, and advective and diffusive transport processes at conditions and time scales relevant to geologic carbon storage. Over the past decade researchers used both laboratory experiments (static and flow-through experiments) and numerical modeling to understand the complex relationship between well materials and the reactive fluids in geologic carbon storage systems. Coupled processes are critical to understanding well integrity as it is the physical-chemical interactions with materials and at interfaces that allow fluid flow. Below we identify the major chemical and mechanical alteration processes important to well integrity (Section 2.1) and coupled chemical, mechanical, and transport processes that lend themselves to sealing or opening of leakage pathways (Section 2.2).

### 2.1. Fundamental reaction mechanisms

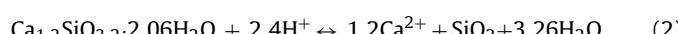
#### 2.1.1. Cement alteration

Most studies on chemical interactions of CO<sub>2</sub> and brine with well materials have focused on ordinary Portland cements. These cements are commonly used in well completions and abandonment and are known to be reactive in geologic CO<sub>2</sub> storage environments (Carey et al., 2007; Duguid and Scherer, 2010; Huerta et al., 2013; Kutchko et al., 2009, 2008, 2007; Mason et al., 2013; Scherer et al., 2011; Walsh et al., 2014a,b). Collectively, these studies confirm that reactions between Ca-containing solid phases, especially portlandite, and CO<sub>2</sub>-saturated brine are so fast that cement alteration is limited by the diffusion of reactants and products, which results in a series of reaction fronts that divide the cement into distinct zones (Carey et al., 2007; Kutchko et al., 2009, 2008, 2007; Mason et al., 2013; Walsh et al., 2014a; Zhang et al., 2015). The zones consist of unaltered cement, a zone depleted in portlandite, a calcium carbonate zone, and a residual amorphous silicate zone, presented in the order from inner unreacted cement to the cement-brine interface in Fig. 2.

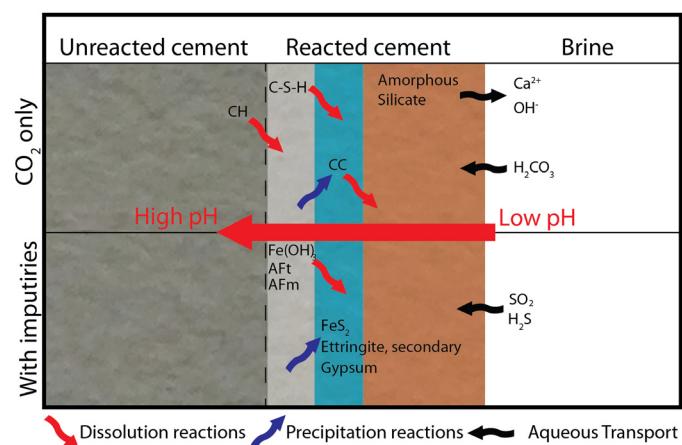
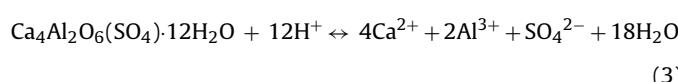
Despite the complex nature of cement, typically only a few mineral phases and associated chemical reactions suffice to model cement alteration (Table 1). Aqueous complexation reactions include CO<sub>2</sub> dissolution into the brine and the formation of a weak acidic solution rich in dissolved carbonate species. The dissolution of CO<sub>2</sub> lowers the pH and dissolves many cement phases, including portlandite (CH),



calcium silicate hydrate (C-S-H, composition varies),



monosulfate (AFm),



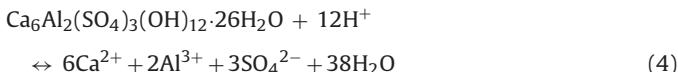
**Fig. 2.** Schematic of interaction between well cement and CO<sub>2</sub> with and without H<sub>2</sub>S/SO<sub>2</sub> impurities, where the phases are described in Table 1 and the reactions are described in the text. The alteration products noted in the CO<sub>2</sub> only gas stream also occur when impurities are present. (Kutchko et al., 2007, 2011; Mason et al., 2013; Zhang et al., 2013).

**Table 1**

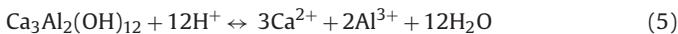
Primary cement phases in ordinary Portland cement and secondary alteration products when cement is reacted with CO<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> saturated brines.

| Phase                                | Formula  | Notes  |
|--------------------------------------|--|--|
| <i>Primary phases</i>                |  |  |
| Portlandite (CH)                     | Ca(OH) <sub>2</sub>  |  |
| Calcium-silicate-hydrate (C-S-H)     | Ca <sub>x</sub> SiO <sub>2+x</sub> ·xH <sub>2</sub> O  | Idealized formula, x = 1.7   |
| Monosulfate (AFm)                    | Ca <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> SO <sub>4</sub> ·6H <sub>2</sub> O<br>Ca <sub>4</sub> Fe <sub>2</sub> (OH) <sub>12</sub> SO <sub>4</sub> ·6H <sub>2</sub> O                                   | Variable composition between the Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> end members   |
| Trisulfate (AFt)                     | Ca <sub>6</sub> Al <sub>2</sub> (OH) <sub>12</sub> (SO <sub>4</sub> ) <sub>3</sub> ·26H <sub>2</sub> O<br>Ca <sub>6</sub> Fe <sub>2</sub> (OH) <sub>12</sub> (SO <sub>4</sub> ) <sub>3</sub> ·26H <sub>2</sub> O | Variable composition between the Al <sub>2</sub> O <sub>3</sub> and Fe <sub>2</sub> O <sub>3</sub> end members.<br>Ettringite is the Al <sub>2</sub> O <sub>3</sub> end member |
| Katoite                              | Ca <sub>3</sub> Al <sub>2</sub> (OH) <sub>12</sub>   |  |
| Gypsum                               | CaSO <sub>4</sub> ·2H <sub>2</sub> O   |  |
| <i>Secondary alteration products</i> |  |  |
| Calcium carbonate (CC)               | CaCO <sub>3</sub>  | Calcite, aragonite, and vaterite   |
| Decalcified C-S-H                    | Ca <sub>r-y</sub> SiO <sub>2+y-x</sub> ·(x-y)H <sub>2</sub> O  |  |
| Friedel's salt                       | Ca <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> Cl <sub>2</sub> ·6H <sub>2</sub> O  |  |
| Ettringite                           | Ca <sub>6</sub> Al <sub>2</sub> (OH) <sub>12</sub> (SO <sub>4</sub> ) <sub>3</sub> ·26H <sub>2</sub> O   | From H <sub>2</sub> S and SO <sub>2</sub> impurities   |
| Gypsum                               | CaSO <sub>4</sub> ·2H <sub>2</sub> O   |  |
| Amorphous silicate                   | SiO <sub>2</sub> or<br>Ca <sub>x</sub> Na <sub>1-x</sub> Al <sub>y</sub> Si <sub>6-y</sub> O <sub>12</sub> ·nH <sub>2</sub> O  | Outer layer has been modeled as amorphous silica and as amorphous silicate with a zeolite-like structure   |
| Amorphous alumina                    | Al(OH) <sub>3</sub>  |  |
| Amorphous iron hydroxide             | Fe(OH) <sub>3</sub>  |  |
| Brucite                              | Mg(OH) <sub>2</sub>  |  |
| Pyrite                               | FeS <sub>2</sub>   |  |
| Amorphous iron sulfide               | FeS  |  |

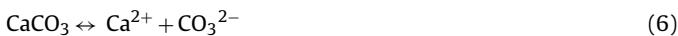
trisulfate (Aft),



and katoite



Monosulfates and trisulfates have variable compositions between their aluminum and iron endmembers. The dissolution rates for portlandite are typically faster than C-S-H by as much as four orders of magnitude (Baur et al., 2004; Galí et al., 2001; Marty et al., 2009). Faster portlandite dissolution rates are responsible for the development of the portlandite depleted zone (Carey and Lichtner, 2007; Mason et al., 2013). The calcium carbonate zone forms as dissolved calcium from the cement minerals diffuses away from the unaltered cement and carbonic acid diffuses toward the portlandite depleted zone, leading to the precipitation of calcite or a mixture of calcite, aragonite and vaterite (CC).

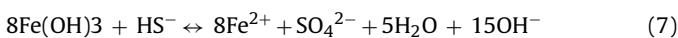


The residual amorphous silicate zone, located at the cement interface where the fluids are the most acidic, is a by-product of restructuring of calcium-free C-S-H phases with dissolved sodium and aluminum to form an amorphous aluminosilicate (identified as having a zeolite structure similar to mordenite in the work of Mason et al., 2013). Cement alteration can be modeled by explicitly accounting for chemical reactions among the phases in Table 1 (Carey and Lichtner, 2007; Marty et al., 2009; Wolery et al., 1990; Zhang et al., 2013) or as a series of moving chemical fronts controlled by portlandite and calcium carbonate solubility (Kutchko et al., 2007; Walsh et al., 2014a). Cement alteration is initially fast and slows down at later times. The extent of alteration and the relative width of the layers depend on the duration, the specific reaction conditions, and the initial cement composition. The initial cement properties, in particular the ratio of the initial portlandite content to porosity, determine the evolution of cement properties. Portlandite-rich cement results in localized “sharp” reactive diffusive fronts characterized by calcite precipitation, leading to significant porosity reduction, which eventually clogs the pore space and prevents further acid penetration (Brunet et al., 2013).

### 2.1.2. O<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> impurities in the CO<sub>2</sub> stream

The chemical alteration model for cement requires some modification to account for the effect of O<sub>2</sub>, H<sub>2</sub>S, and SO<sub>2</sub> impurities in the injected CO<sub>2</sub> captured from power plant exhaust and other industrial sources. The presence of O<sub>2</sub> in the injected CO<sub>2</sub> stream is not expected to result in different reaction pathways. We note that cement phases are already present in their oxidized forms of Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup>.

In contrast to O<sub>2</sub>, H<sub>2</sub>S and SO<sub>2</sub> impurities modify the redox potential and drive a second set of alteration reactions. Kutchko et al. (2011) observed that cement exposed to a mixture of CO<sub>2</sub> and H<sub>2</sub>S underwent a sequence of oxidation-reduction and sulfidation reactions in addition to the alteration zones observed when cement is in contact with brines saturated with only CO<sub>2</sub> (Fig. 2). When the brine is saturated with both H<sub>2</sub>S and CO<sub>2</sub>, the resulting carbonation zone contains secondary ettringite and unidentified particles rich in iron and sulfur, as well as pyrite in the outer rim of the carbonation zone. The formation of ettringite is attributed to a two-step reaction (Kutchko et al., 2011; Zhang et al., 2013). In the first step, H<sub>2</sub>S is oxidized by the dissolution of Fe<sup>3+</sup> bearing minerals in the cement to form SO<sub>4</sub><sup>2-</sup>. The equation below uses iron hydroxide as a proxy for any Fe<sup>3+</sup> bearing minerals in the cement:



In the second step, SO<sub>4</sub><sup>2-</sup> reacts with Al(OH)<sub>4</sub><sup>-</sup> from the dissolution of Al-bearing minerals to produce ettringite (Eq. (4)). The formation of pyrite is attributed to a direct reaction between H<sub>2</sub>S and Fe<sup>2+</sup> from the reduction of Fe-bearing minerals in cement.



Kutchko et al. (2011) concluded that the Fe<sup>3+</sup>-containing phases are the key for cement-H<sub>2</sub>S reactions.

The dominance of the sulfidation reactions may also depend on the amount of H<sub>2</sub>S. Studies with abundant H<sub>2</sub>S (e.g. 66 mol% in Jacquemet et al., 2008) observed iron reduction in the cement minerals to form sulfides (Jacquemet et al., 2012, 2008; Kutchko et al., 2011). In contrast, studies with much lower concentrations of H<sub>2</sub>S yielded cement alteration rates and products similar to those observed in the experiments with 100% CO<sub>2</sub>.

The alteration products generated by reacting well cement and a mixture of CO<sub>2</sub> and SO<sub>2</sub> are similar to those between cement and CO<sub>2</sub> and H<sub>2</sub>S. Dissolved CO<sub>2</sub> reacts with portlandite and C-S-H to produce CaCO<sub>3</sub> precipitates such as calcite, aragonite, and vaterite, while SO<sub>2</sub> is oxidized by either O<sub>2</sub> or Fe<sup>3+</sup> containing phases to form SO<sub>4</sub><sup>2-</sup>. Dissolved SO<sub>4</sub><sup>2-</sup> then reacts with Ca<sup>2+</sup> and various Al and Fe-bearing minerals to form ettringite and gypsum.

### 2.1.3. Pozzolan additives

Additives are commonly combined with the ordinary Portland cement to reduce slurry density, improve acidity resistance, and reduce costs in oil and gas operations (Lyons, 1996; Neville, 2004; Sideris et al., 2006; Türkel et al., 2007). Pozzolan is a generic term for reactive additives, such as fly ash, volcanic glass/ash, silica flour, and ground blast furnace slag. Fly-ash is one of the most common additives in oil and gas well cement formulations and can comprise up to 75% of the cement volume (API, 2011, 1997; Kutchko et al., 2009; Lyons, 1996; Massazza, 1993; Nelson and Guillot, 2006; Neville, 2004; Sideris et al., 2006; Türkel et al., 2007). The chemical reactions for a fly ash-amended cement are identical to those outlined in Fig. 2 (with the exception of reduced portlandite content in the cement), because mixing fly ash, which contains amorphous aluminosilicate, crystalline and amorphous SiO<sub>2</sub>, small amounts of lime (CaO), and hematite (Fe2O3) (Papadakis, 1999; Shehata et al., 1999) with neat cement converts the portlandite and gypsum in the neat cement into C-S-H, mono- and tri-sulfate phases during the hydration process (Papadakis, 1999).

Pozzolan-amended cement allows faster penetration of CO<sub>2</sub> than neat cement under typical CO<sub>2</sub> sequestration conditions with very high dissolved CO<sub>2</sub> concentrations. Carbonation depth was measured to be 20 times higher than neat cement after 9 days exposure to CO<sub>2</sub>-saturated brine for cement with 35 vol% pozzolan and 65 vol% class H cement (Kutchko et al., 2009, 2008). Further, the neat cement showed progressively slower rates of penetration in time, possibly due to the precipitation of calcium carbonate. The cause of fast CO<sub>2</sub> penetration in pozzolan-amended cement is not clear. A possible explanation is that combined higher porosity and lower portlandite content for calcite precipitation leads to faster diffusion and a more permeable carbonate zone and therefore a higher penetration/alteration depth (Fig. 6 in Brunet et al., 2013). Despite the extent of alteration, the altered pozzolan cements maintained a good hydraulic barrier with permeability values well below the American Petroleum Institute recommended maximum value of 200 μD (Kutchko et al., 2009).

Impurities in the CO<sub>2</sub> stream further alter pozzolan-amended cements. In one study, H<sub>2</sub>S penetrated the cement more rapidly than CO<sub>2</sub>, but the resulting reaction products impeded further penetration of CO<sub>2</sub> (Kutchko et al., 2011). Two other studies found that the H<sub>2</sub>S impurity altered the cement chemistry considerably

farther into the cement than CO<sub>2</sub> alone, and resulted in significant alteration of the surface region of the cement (Zhang et al., 2015), including porosity (Zhang et al., 2013).

#### 2.1.4. Steel corrosion

Steel casing (i.e. pipe) is the third component of the steel–cement–caprock system that determines well integrity. The steel casing must have adequate strength to contain the fluids within the well and to resist external stresses. Although casing rupture does occur, the most common problems are associated with leaking pipe connections and corrosion of steel. The steel used in most wells is low-cost, low-carbon steel that is not corrosion resistant. The near surface environment is particularly problematic, as the greater availability of oxygen can cause surface and conductor casing to rapidly deteriorate without adequate cement protection (Fig. 1, #1) (Talabani et al., 2000). For steel casing, factors that can exacerbate corrosion problems include sand (introduced during hydraulic fracturing or during production of poorly lithified reservoirs, resulting in metal erosion), the presence of oxygen, hydrogen evolution (which can cause embrittlement), chloride and sulfate-rich formation waters, acids used to stimulate the formation, in situ H<sub>2</sub>S and CO<sub>2</sub>, and the higher temperature and pressure that occur at drilling depths (Rahman and Chilingarian, 1995; Talabani et al., 2000).

Choi et al. (2013) recently reviewed casing corrosion issues specifically relevant to CO<sub>2</sub> sequestration. CO<sub>2</sub> transforms the oxygen-free subsurface to a highly corrosive environment primarily because of carbonic acid (Han et al., 2011a; Nešić, 2007). The key half-cell reaction is:



which is balanced by the dissolution of iron:



Corrosion can be rapid and destructive because it allows fluids to communicate between the inside and outside of the well. Uniform corrosion rates of bare metal can reach tens of mm/year for unpassivated low-carbon steel in the presence of high-pressure CO<sub>2</sub> (Han et al., 2011a). Fortunately, cement carbonation appears to passivate and protect the steel surface, despite its more acidic pH. Han et al. (2011b) reported reductions in corrosion rates by a factor of 20 due to formation of iron carbonate scale on the steel casing. These reduced corrosion rates still have a potential impact on well integrity, because CO<sub>2</sub> storage wells need to operate for decades and to protect against leaks for centuries. We currently lack a good basis for predicting the impact of corrosion rates on well integrity in the presence of passivating iron carbonate scales.

In addition to these general reactions that are expected to cause relatively uniform corrosion over large areas, there will also be localized CO<sub>2</sub>-induced corrosion rates (Kermani and Morshed, 2003). These effects can be more rapid and penetrating than uniform corrosion. Factors that exacerbate localized corrosion include stress-induced defects, incomplete passivation layers, mechanical damage to passivated surfaces, and some dissolved chemical species such as acetic acid or H<sub>2</sub>S (Kermani and Morshed, 2003).

Corrosion of low-carbon steel can be prevented through the use of corrosion inhibitors or cathodic protection among other measures. However, one of the most important methods for protecting against corrosion of external casing is an adequate coverage with cement, particularly on the surface casing in the subsurface across formations with problematic fluids (Choi et al., 2013; Rahman and Chilingarian, 1995; Talabani et al., 2000).

#### 2.2. Geomechanical factors

The stresses acting on a well are an important factor influencing the risk of a leakage event. Wellbore stresses will change over time, as a result of shifts in pressure due to pumping or leakage, fluctuations in subsurface temperature (also potentially a byproduct of injection or leakage), or due to natural variations in subsurface conditions (tectonic stresses and seismicity). These changes can directly affect the permeability of any of the previously discussed well leakage pathways through several mechanisms. Variations in the normal stress on a fracture have a non-linear effect on fracture transmissivity related to the surface roughness (Bandis et al., 1983; Barton et al., 1985), while shear motion will induce preferential flow pathways that depend on the direction and extent of the relative displacement between the two fracture surfaces (Detwiler and Morris, 2014). Likewise, multicomponent and multiphase flow along fractures are also strongly influenced by changes in stress on the well, due to the coupling between the effective stress and the aperture distribution (Walsh and Carroll, 2013), and this effect varies with the relative permeabilities of the component fluids. In the event of CO<sub>2</sub> leakage, these complexities interact with chemical reactions that occur between cement, steel, rock and carbonated brine. The chemical alteration within the reaction zones changes the mechanical properties of the fracture interface, potentially resulting in collapse of the fracture aperture (Walsh et al., 2014a,b). Due to the interplay between these different processes, the coupled effects of mechanics, chemistry and flow should be incorporated into an assessment of wellbore leakage.

There are a multitude of processes throughout a well's construction and use that contribute to its stress state. As a well is drilled, subsurface stress is concentrated in the surrounding formation – the forces previously born by the excavated rock are redistributed to the intact material around the hole. While analytical expressions can be found to describe the resulting stress distribution (e.g. Bradley, 1979; Peška and Zoback, 1995), in reality, the stress state around the well is more complex: a product of a dynamic layered environment consisting of the well casing, the surrounding well cement, drilling fluid filter cake (if present) and a zone of damaged rock from the drilling process, within the larger (largely undamaged) far-field formation (e.g. Gray et al., 2009; Nygaard et al., 2014).

After the hole is drilled and the well casing inserted, well cement is introduced in the annulus between the casing and the formation. Pouring and setting of cement occurs in a far-from-pristine environment. In particular, the drilling fluid used to create the borehole, along with any subsurface liquids and gases, can produce fluid channels that decrease the bonding strength between the cement and the casing and the formation and may be the source of preferential flow pathways (Agbasimalo and Radonjic, 2012; Agbasimalo, 2012; Randhol, 2008). Mixing between these liquids and the well cement negatively impacts the cement's mechanical properties (El-Sayed, 1995).

As the cement cures, it undergoes a two stage process of hardening (conversion of the liquid cement into a solid body) and shrinkage (a reduction in volume upon curing of the solid cement) (Gray et al., 2009; Randhol, 2008; Ravi et al., 2002). Hardening has little effect on the stress of the cement (as the cement is generally considered to remain under hydrostatic stress throughout), though it will affect cement rheology. Shrinkage, however, results in a change in the cement's stress state, which can potentially lead to plastic deformation of not only the cement, but also the casing and formation, or debonding at either the casing or formation interfaces (Ravi et al., 2002). In addition, the casing may not be located in the center of the borehole, and thus shrinkage can result in an uneven distribution of stress in the cemented annulus (Gray et al., 2009). In time, the surrounding rock can creep toward the borehole,

gradually applying far-field stresses to the cement. These diverse processes create a range of possible stress conditions for cement that include hydrostatic, completely detached from the rock formation, and in stress-continuity with the rock formation.

Over its lifetime, a well is subjected to variations in pressure induced by processes internal to the well (resulting from stimulation processes, mechanical testing, and injection and production), by changes in the formation (again due to injection or production from either the well itself or an adjacent source), and by natural fluctuations (e.g. tidal variations). The well is also subject to thermal stresses that accompany fluid flow during injection and production. For example, Thiercelin et al. (2007) calculate stresses induced in cement for a number of these processes. Thermal stresses are particularly important when supercritical CO<sub>2</sub> is injected into the subsurface (Nygaard et al., 2014), and most notably if injection follows a cyclic pattern causing fluctuations in the thermal field and associated stresses (De Andrade et al., 2014). Cyclic stresses may encourage growth of fractures within the well cement or result in debonding between the cement and formation (De Andrade et al., 2014; Heathman and Beck, 2006; Shen and Pye, 1989). Fluctuations in stress also play a role in determining the active flow pathways due to the coupling between applied stress and fracture permeability.

### 2.3. Impact of coupled chemical, mechanical, and transport processes on well integrity

Field observations show that CO<sub>2</sub> has migrated over substantial distances along sections of the wellbore above a CO<sub>2</sub>-containing reservoir. Crow et al. (2010) observed carbonation of cement more than 60 m above a natural CO<sub>2</sub> reservoir adjacent to shale. Similarly, Carey et al. (2007) found evidence of CO<sub>2</sub> migration 3 m above a CO<sub>2</sub>-enhanced oil recovery reservoir along the interface between cement and caprock. They also saw unusual silica-carbonate bands within the shale-fragment zone indicating mobilization and deposition of silica (Fig. 6 in Carey et al., 2007). In both of these studies, the amount of migrating CO<sub>2</sub> was not possible to quantify. The cement barriers remained intact and the observed carbonate precipitates in void spaces suggests the leakage path was sealed during the operation of the site. The field observations in the two studies cited suggest a barrier failure, but as emphasized by King and King (2013), the failure of a single barrier does not necessitate leakage to the atmosphere. Neither study observed evidence of CO<sub>2</sub> migration to the surface or sustained casing pressure indicative of a breach of the well annuli. Combined with observations from experiments and numerical simulations described below, these findings suggest that under some circumstances coupled processes can help limit leakage.

In this section we draw on a variety of laboratory experiments as well as numerical simulations that characterize how coupled flow, geochemical reactions and mechanical alteration change permeability of fractures within the cement and at the cement–caprock and cement–steel interfaces. Collectively the studies described below find a reduction of fracture permeability due to swelling of the amorphous silica layer, precipitation of carbonate minerals and/or concurrent chemical alteration and deformation of the cement asperities that allow fluid flow. Instances of sustained or increasing permeability were attributed to large initial fracture apertures or high fluid flow rates that promote dissolution-dominated environments.

#### 2.3.1. Coupled chemistry and diffusion

Good quality cement that is well bonded to casing and formation rock provides a barrier that permits transport of CO<sub>2</sub> only by diffusion or by very slow flow that is effectively diffusion-like in character. In addition, capillary entry pressures in good quality cement will prevent the supercritical CO<sub>2</sub> phase from entering

the cement further limiting any flow processes to CO<sub>2</sub>-saturated brine (Carey and Lichtner, 2011). The rate of progress of chemical alteration of cement under diffusive CO<sub>2</sub>-saturated brine transport (leakage pathway #8 in Fig. 1) is insufficient to pose a threat to well integrity. This conclusion is based on the slow rates of diffusive transport, the tens of meters of transport distance in wellbore cement, and the fact that the thickness of diffusion-controlled alteration zones shown in Fig. 2 is limited by the growth of a dense carbonate zone in neat cements serves as a barrier to further cement degradation (Kutchko et al., 2007, 2008; Matteo and Scherer, 2012). Kutchko et al. (2008) estimated a penetration depth of only about 1 mm after contacting the CO<sub>2</sub>-saturated brine for 20–30 years. Simulations conducted under the same diffusion controlled conditions suggest that higher amounts of portlandite and lower initial porosity further limit cement degradation (alteration zones varied between 0.5 and 6 mm after 200 days of exposure to CO<sub>2</sub>-saturated brine, Brunet et al., 2013). While pozzolan-bearing cements carbonate at faster rates than neat cements (Kutchko et al., 2009; Crow et al., 2010), these cements maintain relatively low permeability and thus the mass flow rate is effectively limited to low values.

#### 2.3.2. Coupled chemistry and flow

Flow of CO<sub>2</sub> and CO<sub>2</sub>-saturated brine can occur where a leakage pathway exists due to a poor completion or due to mechanical damage (leakage pathways #7, #10, #11, and #12 in Fig. 1). Under fluid flow conditions, fresh reactants (H<sup>+</sup>, H<sub>2</sub>CO<sub>3</sub>, etc.) are continuously supplied while reaction products including calcium and carbonate species are removed. In this environment, the residence time or the time scale over which the CO<sub>2</sub> is in contact with cement, determines the relative rates of cement dissolution compared with precipitation or other processes that reduce pore space and permeability to seal the fracture pathway. Thus, the combination of fluid residence time and aperture width can cause wellbore cement pathways to seal or open as a consequence of chemical reaction. The relative magnitude of the two competing processes ultimately controls the cement properties and long-term leakage potential.

A summary of experimental studies of the permeability evolution of fractured wellbore components using flow-through systems is shown in Table 2. Most of the experiments involved flow through pre-fractured cement samples. Some studies used HCl solutions as a surrogate for the acidic CO<sub>2</sub>–brine system and conditions ranged from ambient conditions to pressure and temperatures above the supercritical point of CO<sub>2</sub>. The majority of studies observed a drop in permeability with time. Two studies (Luquot et al., 2013; Huerta et al., 2015) showed an increase in permeability under conditions associated with larger apertures and higher flow rates, while decreases in permeability were associated with smaller apertures and lower flow rates. These results are consistent with the concept that permeability evolution is governed by a competition between advection of acidic solution and precipitation of supersaturated solutions (see below). The studies attributed permeability reduction to a variety of effects including relative permeability (due to exsolution of CO<sub>2</sub> along the length of the core), precipitation of carbonate, and swelling of the amorphous silica residue that remains after cement reaction with the acidic solution.

A similar set of studies examined the permeability evolution of the cement–rock interface (Table 2). Permeability decreases were found in two studies and attributed to several mechanisms including relative permeability effects, fines migration, reprecipitation of cement phases, silica gel swelling, and mechanical closure of the aperture under confining stress. A permeability increase was found in an experimental setup that included large fracture apertures (Cao et al., 2013), which is consistent with the Luquot et al. (2013) observations on aperture/flow control of permeability evolution. A fourth study (Walsh et al., 2014a,b) found both an increase and decrease in permeability depending on the initial fracture geometry.

**Table 2**

Summary of experimental studies that evaluate permeability evolution of wellbore systems for CO<sub>2</sub> and brine leakage.

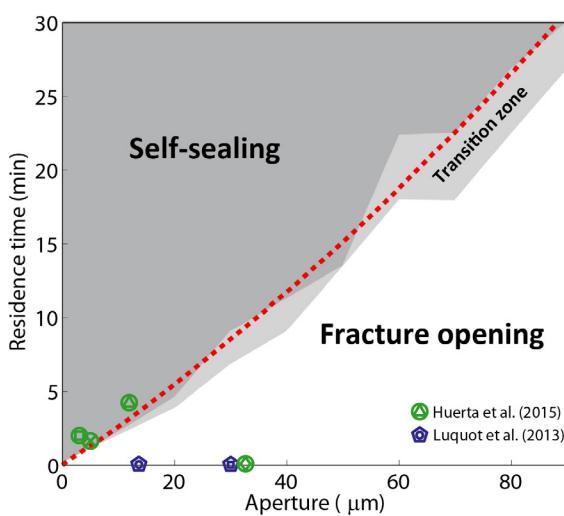
| Fractured cement experiments                |                      |          |                            |  |
|---|----------------------|----------|----------------------------|--|
|   |                      |          |                            | Relative permeability effects  |
| Bachu and Bennion (2009)                    | scCO <sub>2</sub>    | Hi PT    | Permeability drop          |  |
| Wigand et al. (2009)                        | scCO <sub>2</sub>    | Hi PT    | n/a                        | Carbonate precipitation  |
| Yalcinkaya et al. (2011)                    | CO <sub>2</sub>      | Unclear  | n/a                        | Widening of apertures  |
| Liteanu and Spiers (2011)                   | scCO <sub>2</sub>    | Hi PT    | Permeability drop          | Carbonate precipitation  |
| Huerta et al. (2013)                        | HCl                  | Ambient* | Permeability drop          | Carbonate precipitation  |
| Luquot et al. (2013)                        | scCO <sub>2</sub>    | Hi PT    | Permeability drop and rise | Carbonate and silica gel precipitation   |
| Abdoulaif et al. (2013)                     | scCO <sub>2</sub>    | Hi PT    | Permeability drop          | Silica gel precipitation   |
| Wenning et al. (2013)                       | HCl                  | Ambient  | n/a                        | Modified fracture geometry   |
| Huerta et al. (2015)                        | CO <sub>2</sub>      | Hi P     | Permeability drop          | Silica gel and carbonate precipitation   |
| Cao et al. (2016)                           | CO <sub>2</sub>      | Mod. P   | Permeability drop          | Carbonate precipitation  |
| Cement–rock interface experiments           |                      |          |                            |  |
| Newell and Carey (2013)                     | scCO <sub>2</sub>    | Hi PT    | Permeability drop          | Relative permeability, fines migration and cement precipitation                  |
| Cao et al. (2013)                           | CO <sub>2</sub>      | Mod PT   | Permeability rise          | Aperture widening  |
| Mason et al. (2013) and Walsh et al. (2013) | CO <sub>2</sub> (aq) | Hi PT    | Permeability drop          | Chemical alteration and mechanical deformation; and possible silica gel swelling |
| Walsh et al. (2014a,b)                      | CO <sub>2</sub> (aq) | Hi PT    | Permeability drop and rise | Chemical alteration and mechanical deformation                                   |

In order to investigate the relationship of permeability, aperture and flow rate observed in experiments, Brunet et al. (2016) developed a reactive transport model calibrated against the experiments of Huerta et al. (2015). The model calculates change in fracture permeability as a consequence of diffusion and dispersion when CO<sub>2</sub>-saturated water reacts with cement. The authors conducted 250 simulations with aperture width ranging from 6 to 90 μm, initial flow rates from 0.0015 to 0.130 ml/min, and fracture length from 109.6 to 328.7 mm. Each fracture was exposed to CO<sub>2</sub>-enriched water for more than 100 days. The results suggest that the long-term permeability of the fracture depends on both the initial fluid residence time (i.e., the fluid flow rate) and aperture width (Fig. 3). There is a clear division between fracture sealing and opening conditions. The fracture has a tendency to fill with calcite for residence times above the threshold and remain open when

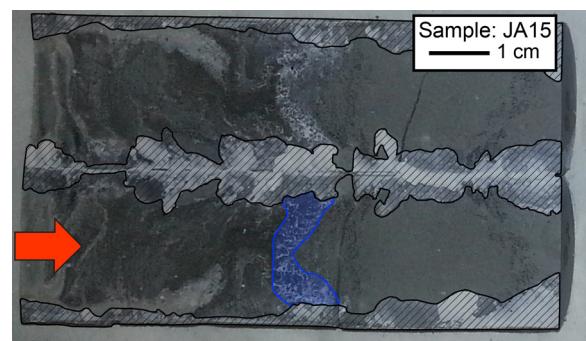
the residence times are below the threshold. A narrow transition zone is observed around the threshold, where both fracture sealing or opening behavior occurs and the permeability changes are sensitive to specific conditions.

The simulated relationship for the critical aperture is consistent with experimental observations of Huerta et al. (2015; Fig. 4). For some simulated cases with initial residence times below the critical threshold, carbonate minerals precipitate at some point, however at an insufficient amount to clog the fracture or are dissolved by continued acidity, leading to no change or increased fracture permeability. Similarly, Luquot et al. (2013) observed and concluded that longer fractures and smaller apertures (longer residence time) tend to seal while fractures tend to open in flow regimes with shorter path lengths and/or larger apertures.

Although the critical threshold parameter is based on data from fractured cement, it is also consistent with observations for CO<sub>2</sub> interactions at cement/rock interfaces. For example, Newell and Carey (2013) observed self-sealing behavior in a composite cement/siltstone core using a brine flow rate of 0.25 ml/min



**Fig. 3.** Illustration of the critical threshold between fluid residence time and initial fracture aperture on the ability of CO<sub>2</sub>-H<sub>2</sub>O-Ca reactions to seal or open fracture pathways within cement–cement interfaces based on numerical simulations. The green and blue symbols represent the initial aperture and residence time of experiments from Huerta et al. (2015) and Luquot et al. (2013), respectively (Brunet et al., 2016). (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)



**Fig. 4.** Open core showing the cement fracture surface after reaction with CO<sub>2</sub>-rich brine (modified from Huerta et al., 2015). Red arrow indicates flow direction. Hatched sections denote no-flow regions where caulk was used to seal the outer boundary of the core prior to reaction. Downstream calcium carbonate precipitated and is inferred to be the mechanism for sealing the conductive pathway. Carbonate zones are shown on both fracture surfaces, but only highlighted in blue on one side of the fracture. (For interpretation of the references to color in figure legend, the reader is referred to the web version of the article.)

and a CO<sub>2</sub> flow rate of 0.08 ml/min. Although the alteration zone extended 5 mm into the cement, the effective brine permeability decreased from ~200 to 90 mD due to the transition to two-phase flow and then further declined to 35 mD. The permeability drop is not attributed to carbonation of cement but rather to the migration and precipitation of alteration products derived from cement within the defect. Cao et al. (2016) observed a permeability increase of 3 times in a composite cement/sandstone core using a CO<sub>2</sub>-saturated brine flow rate of 0.5 ml/min. The permeability increase was attributed to the cement dissolution/degradation at the cement–sandstone interface. At a much higher flow rate of 2 ml/min, Cao et al. (2013) observed a permeability increase of 8 times within 8 days during a flow experiment with a composite cement/sandstone core with a large defect void at the cement–sandstone interface that served as the major conductive flow path. Both the high flow rates and large void (similar to large aperture size) contribute to the observed permeability increase.

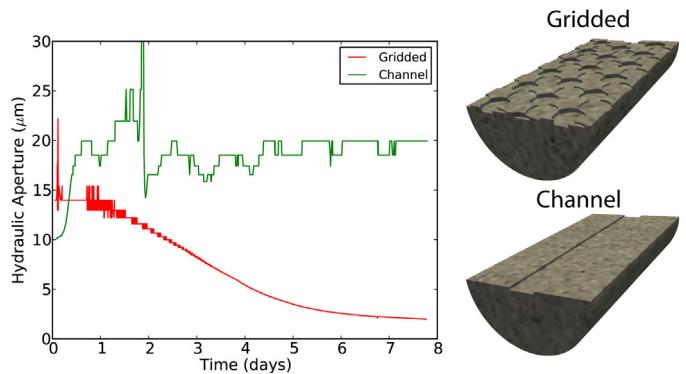
Fig. 3 implies that for fractured cement with hydraulic aperture size of 90 µm or less, sealing can be observed when critical residence time is 30 min or longer. This short residence time indicates that in geological CO<sub>2</sub> storage systems, where cemented intervals are 10s of meters in length, the residence time is likely to be long (assuming there is not a large fracture). Thus, fracture sealing may be more common than fracture opening. This might also explain the lack of observations of CO<sub>2</sub> at the surface in field sites showing cement carbonation at depth (Carey et al., 2007; Crow et al., 2010).

The critical aperture threshold is a useful metric to better define wellbore risk over time, however it does not consider the role of other factors identified in experiments such as portlandite or fly ash content or mechanical deformation of the altered cement. In addition to carbonate mineral precipitation in fracture pathways, it is possible that swelling of the amorphous silicate layer may also contribute to the reduction in fracture permeability (Walsh et al., 2013; Abdoulghafour et al., 2013; Huerta et al., 2015). This mechanism was called on to explain decreases in fracture permeability, because the increased volume associated with the calcium carbonate alteration zone was not sufficient to counteract the overall increase in porosity caused by cement dissolution.

### 2.3.3. Coupled chemistry, mechanics and flow

Chemical and mechanical alterations are tightly coupled and represent an active area of research. Chemical alteration has the potential to change the local stress and aperture fields within the cement as was observed when calcium carbonate precipitated in fractures of cement/basalt samples exposed to CO<sub>2</sub>-saturated groundwater and wet supercritical-CO<sub>2</sub> (Jung and Um, 2013; Jung et al., 2013). Carbonate precipitation caused some fractures to open as a result of crystallization-induced pressure, as well as isolating other cement fractures (also see Wigand et al., 2009). Combined fracture opening and isolation consequently reduced the permeability by an order of magnitude (Jung et al., 2014; Um et al., 2014).

The mechanical factors affecting flow along cement interfaces are further complicated by the structural changes induced by reactions with CO<sub>2</sub>-saturated brine. Reactions between carbonic acid and cement are often accompanied by an increase in porosity (Kutchko et al., 2007; Rimmelé et al., 2008). While this increased porosity would normally be indicative of enhanced permeability, decreased permeability can be induced by changes in the mechanical properties of the altered zones, by weakening asperities that maintain contact between cement and rock in the fracture (Walsh et al., 2014a,b). Nano-indentation measurements of the reaction layers reveal that both the amorphous and depleted regions have lower elastic moduli and hardness than the unreacted cement (Kutchko et al., 2009; Mason et al., 2013; Walsh et al., 2014a). Zhang et al. (2013) found that acid gas impurities had a similar impact on the mechanical properties of the cement alteration zone. These



**Fig. 5.** Hydraulic aperture as a function of time in samples of mated cement/caprock half cores with distinct flow-path geometries.

Modified from Walsh et al. (2014b).

findings are also consistent with the effects caused of calcium leaching from cements exposed to uncarbonated brines (Constantinides and Ulm, 2004; Ulm et al., 2003). These results illustrate several ways that well integrity and risk of CO<sub>2</sub> leakage are controlled by coupled geomechanical and geochemical alterations of well materials.

The extent to which reaction-induced changes in structural properties affect transmissivity depends upon the interface geometry (Walsh et al., 2014b). To illustrate this, Fig. 5 compares results from core-flow reaction experiments performed under confining stress representative of subsurface conditions. During the experiment, carbonated brine was introduced into a core consisting of half-cement and half-caprock samples. The contacting surfaces were imprinted with two distinct geometries: a single flow channel and a grid of circular apertures. The hydraulic aperture increased over time in the channel sample, whereas a consistent decrease in aperture was observed for the gridded sample. The difference in behavior is explained by the manner in which the reaction fronts affect the contact between the sample half-cores. In the gridded sample the reaction fronts removed significant amounts of portlandite and CSH from the asperities maintaining the fracture, resulting in weakened mechanical properties that allowed the asperities to deform. This deformation results in an overall decrease in the hydraulic aperture despite an increase in the cement porosity. Conversely, in the channel sample, although the reaction fronts decreased the contact area between the two half cores, sufficient unreacted cement remained at the contact to support the stress on the fracture. In this case, the permeability is increased slightly due to the increased porosity.

Walsh et al. (2014b) developed a coupled chemical-mechanical-transport model that ties the extent of deformation of the cement asperities to chemical alteration of the cements. Although empirical in nature, the model could be used to refine the relationship between residence time, chemical alteration, mechanical deformation and the ability of flow pathways in the cement to seal or open. Briefly, the model captures the response of the fracture with a set of simple models representing the inelastic deformation of the unreacted cement and each alteration layer. The relative contributions of each layer to the effective stress change as the relative contact areas of the reaction zones evolve, which in turn influences the mechanical and hydraulic apertures of the fracture. The contact areas and depth of the alteration zones are modeled using an idealized representation of the cement chemistry in which portlandite, calcite, and zeolite equilibrium conditions are enforced as a series of discrete reaction fronts. The equilibrium conditions are coupled by diffusive transport between the fronts, which also determines the rate of front propagation.

### 2.3.4. Coupled casing corrosion and flow

There has been relatively little work on the geochemical and hydrologic behavior of the casing/cement interface (leakage pathway #2 in Fig. 1). In the absence of a defect at this interface, the cement protects steel from corrosion due to high-pH pore fluids that create a protective iron-oxide coating. Well integrity risks at the cement/casing interface are considered separately from the evolution of the permeability along fractures within the cement and along cement/caprock interface, because the consequences of chemical reactivity of the steel casing allow for the development of flow paths that are distinct from the cement/caprock aperture controlled processes discussed above.

In wells with casing made of corrosion-resistant alloy, the chief concern for this interface would be the possible dissolution of cement. However, at present there are no studies that have directly examined this system. Carey et al. (2010) examined the more common situation (particularly in non-CO<sub>2</sub>-specific wells) in which there was a microannulus between low-carbon steel and cement. They found that steel was far more reactive than cement during flow of a mixture of CO<sub>2</sub>-brine at sequestration conditions (Fig. 6). The steel showed evidence of extensive corrosion reactions that were limited to some extent by deposition of an iron carbonate. Cement, on the other hand, showed evidence only of diffusion of CO<sub>2</sub> and carbonation of cement. The cement did not erode or noticeably dissolve. Although this study indicates that the more vulnerable component of the interface system is steel, permeability gradually decreased with time, which was attributed to the accumulation of iron carbonate deposits within the interface. The long-term fate of steel in this situation is unknown. It is possible that the iron carbonate scale may provide lasting protection; it is also possible that corrosion may eventually penetrate through the steel wall, allowing communication between the interface and the well interior.

An important research question is whether carbonated cement can protect steel from corrosion. If there is flow of CO<sub>2</sub>-saturated brine, either migrating along the cement/caprock interface (#12) through fractures in the cement (#8) or other mechanisms shown in Fig. 1, it could carbonate the cement that is in contact with the steel. In a field sample, Carey et al. (2007) found evidence of CO<sub>2</sub>

leakage along the casing/cement interface in the form a carbonate rind attached to the cement surface adjacent to casing. The casing was not damaged, because the well was under cathodic protection. The origin of the CO<sub>2</sub> creating this deposit is unknown, but may have been derived by leakage through joints in the casing. A limited number of experiments show that casing corrosion rates are less than they would in the absence of carbonated cement (Han et al., 2012). On this topic, as for many questions related to wellbore integrity and risk, there is still much to learn through combinations of theoretical, experimental, computational and field research.

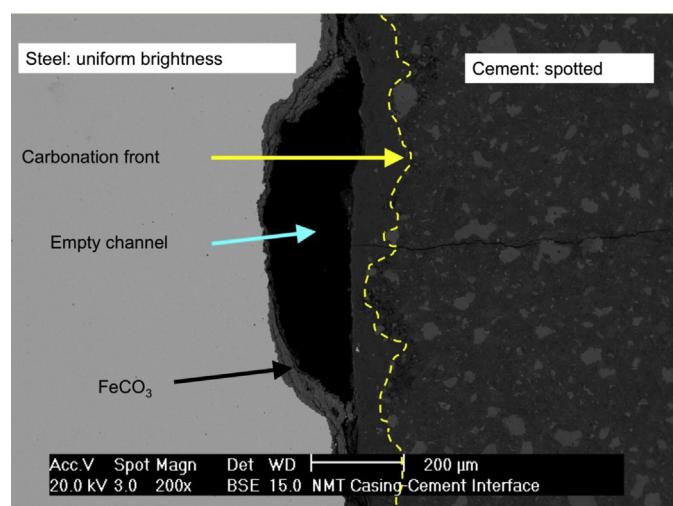
## 3. Conclusions

This review summarizes recent research outcomes that have significantly advanced understanding of the basic science, causes, and impacts associated with well leakage. Wellbores and their immediate environments are chemically and mechanically complex, and represent an important leakage risk for CO<sub>2</sub> storage systems.

Important progress has been made in understanding the chemical alteration of cement, especially the ordinary Portland cements that are most commonly used for wellbore completions and abandonment. Although cement is a complex material, typically a relatively small number of reactions suffice to model these systems, and most thermodynamic parameters of the reactions are well defined. Kinetics has been measured for some reactions of interest, but empirical determination of rate expressions are needed for most. Both experimental and theoretical considerations have confirmed that cement alteration is limited by the diffusion of reactants and products, and that these processes result in discrete reaction fronts and defined alteration zones. Pozzolan (fly ash) amendments can accelerate these diffusion rates, but in experimental systems the effective permeability remained low and within the range of current standards. Additional reactions must be considered to account for H<sub>2</sub>S and SO<sub>2</sub> impurities in the injected CO<sub>2</sub>, but these are also chemically tractable. Changes in oxidation, redox-potential and sulfidation reactions associated with these impurities can affect dissolution and precipitation rates and cement mineralogy, but these effects are concentration dependent, and at low concentrations permeability and performance are expected to be similar to those observed with pure CO<sub>2</sub>.

Carbon steel, as used in most oil and gas wells, is highly susceptible to corrosion by CO<sub>2</sub>-bearing fluids. In the presence of high pressure CO<sub>2</sub> and the resulting carbonic acid, low-carbon steel can erode at rates of millimeters per year. However, if there is good contact between steel and cement, the high pH of cement passivates and protects steel. Passivation may also be crucial where CO<sub>2</sub> manages to migrate along the cement–steel interface, because iron carbonate precipitation provides additional protection against corrosion, reducing rates of corrosion by more than an order of magnitude in some circumstances. Thus the presence of cement is a minimum requirement for demonstrating that steel in existing wells will not be damaged by injected CO<sub>2</sub>. Less well understood is whether carbonated cement can provide protection to steel casing. In this situation, the high pH environment of unreacted cement is lost but the potential to provide a barrier to flow of corrosion reactants and an environment for carbonate precipitation persists. However, even this level of protection may not be adequate to maintain wellbore integrity for the decades and even centuries that may be required of CO<sub>2</sub> storage systems.

We are still in the early stages of understanding how chemical alteration affects the physical properties of wellbore cement. Evidence suggests that well permeability can decrease when



**Fig. 6.** Back-scattered electron micrograph of the interface between steel (solid white material left) and Portland cement (spotted material right). The experiment involved flow of a mixture of supercritical CO<sub>2</sub>-brine through notches cut into the steel. The steel corroded forming iron carbonate deposits while the cement carbonated without a significant loss of material.

Modified from Carey et al. (2010).

reacting with CO<sub>2</sub> rich brines, thereby lowering the risk of leakage in abandoned wells. Geochemical and geomechanical interactions between well cements and supercritical CO<sub>2</sub> or CO<sub>2</sub>-saturated brine can in some circumstances promote sealing and closure of leak paths. Studies have investigated different interface materials (e.g. cement-to-cement or cement-to-rock) and geometries, the role of oxygen and acids, and the impacts of driving force and residence time. CO<sub>2</sub>-promoted sealing is a function of portlandite abundance and cement porosity, as well as flow rates and residence time along the leakage path. Similar phenomena were observed at the cement–rock interface under CO<sub>2</sub> storage conditions. These protective processes were observed under both diffusion dominated and convection dominated flow regimes, and with a range of expected pressures and fluid chemistries. A more complete understanding of the mechanisms and limitations of this self-sealing phenomenon is important in several respects. In areas where good wellbore records exist and the well materials and construction are well characterized, it may reduce the need to recomplete all the wells in the area of review. And in cases where there may be unknown or uncharacterized wells, CO<sub>2</sub>-promoted sealing may provide an additional measure of protection from wellbore leakage risks.

At present we have a relatively poor understanding of the role of stress in the wellbore environment. In addition to geomechanical stress associated with well construction and surrounding geological formations, there will be additional thermal stress from the injection of cold CO<sub>2</sub> whose effects on wellbore integrity remain largely unknown. Similarly, it will be important to define the pressures that will result in damaging interface bonds in the well. The cumulative stresses at well interfaces are likely to have important effects on some of the mechanisms previously discussed. Any separation of cement from steel will cause discontinuities in cement-induced passivation, and can introduce larger diameter pores and flow paths that can reduce or reverse the self-sealing effects.

Computational tools to simulate and predict these effects are under development within a framework to quantify and integrate wellbore leakage risks. Reactive transport models have been developed that tie the extent of reaction to mechanical alteration, and that account for the precipitation of fracture filling minerals (e.g. Huerta et al., 2014; Walsh et al., 2014b). To scale these models to full wellbore systems several challenges must be addressed, paramount among them the computational effort required. Although chemical reactions, CO<sub>2</sub> and brine diffusion, dissolution and precipitation occur at scales of microns and smaller, the wellbores and potential leakage pathways are on the order of 1000 m. Process complexity must also be addressed, including chemical kinetic and equilibrium reactions, diffusion and advective transport, thermal and mechanical stress and mechanical deformation. To fully capture these processes, including interactions with reservoirs, caprock, and overlying aquifers, is computationally prohibitive with high fidelity full physics and chemistry models. The National Risk Assessment Partnership for CO<sub>2</sub> storage (Pawar et al., 2014) has developed reduced order models for wellbore systems and each of these interacting components, coupled within an integrated assessment framework (Jordan et al., 2015; Harp et al., 2016). However, to date these models do not consider changes in wellbore permeability due to chemical, mechanical and transport processes.

To advance understanding of and models for risk of wellbore leakage at CO<sub>2</sub> geological storage sites, it is important that carefully designed field research be conducted at demonstration-scale projects. Direct observations from field site characterization and monitoring campaigns will be needed to develop further, test and validate the complex, integrated models needed to assess risk of wellbore leakage.

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