

Experimental Study of Genesis of a Geologically Activated and Self-Sealing Cementing Material for Deep Wellbore Plugging and Abandonment

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Abstract

Harsh subsurface conditions pose a widespread challenge for permanently plugging and abandoning (P&A) oil and gas wells. A new, cement-free plugging material is proposed and demonstrated using Nature-inspired geochemical processes to generate stable and resilient, rock-like material that is ideally suited to acidic geofluid, high-pressure, and high-temperature (AG-HP-HT) conditions. These conditions accelerate hydration and carbonation reactions that turn granular ultramafic raw materials into competent rock, dubbed here as "Geologically Activated Cement" (GAC). The results show that within hours to days, and hence relevant to P&A operational timeframes, a magnesium silicate-based, solid, rock-like material can be produced from $\text{Mg}_2\text{SiO}_4\text{-CO}_2$ mixtures. Furthermore, the GAC can self-seal within a few hours when subjected to damage and subsequent flow of acidic fluid under HPHT conditions. This self-sealing behavior provides the potential for a resilient cementing system over geological timescales.

Keywords: Resilient Plug and Abandonment (P&A) System; Acidic Geofluid, High-Pressure, High-Temperature (AG-HP-HT); Ultramafic Mineral Carbonation; Self-sealing; Carbon Sequestration, Storage and Utilization (CSSU)

1. Introduction

When oil and gas wells are at the end of their service lives and no longer economically viable for production, it is required that they be safely plugged before permanent abandonment (Vrålstad et al., 2019). The key goal of this plug and abandonment (P&A) is to permanently isolate all of the formations that are penetrated by the well. It requires setting up multiple plugs along the well. These plugs control the subsurface fluid flow, preventing fluids from migrating along the wellbore over time. The plug also protects the casing from acidic fluids and mechanical impact (Norge, 2013; Oil et al., 2015). However, for deep wells, especially those encountered in deep-water offshore environments, as shown in Figure 1, mainly four harsh subsurface conditions

include high-temperature, high-pressure, the presence of acidic fluid, drilling mud contamination pose a threat to the integrity of traditional materials (Ahmed et al., 2020; Allahvirdizadeh, 2020; Kiran et al., 2017). As a result, pursuing a new and improved cementitious material to remediate wellbore leakage has become urgent and necessary.

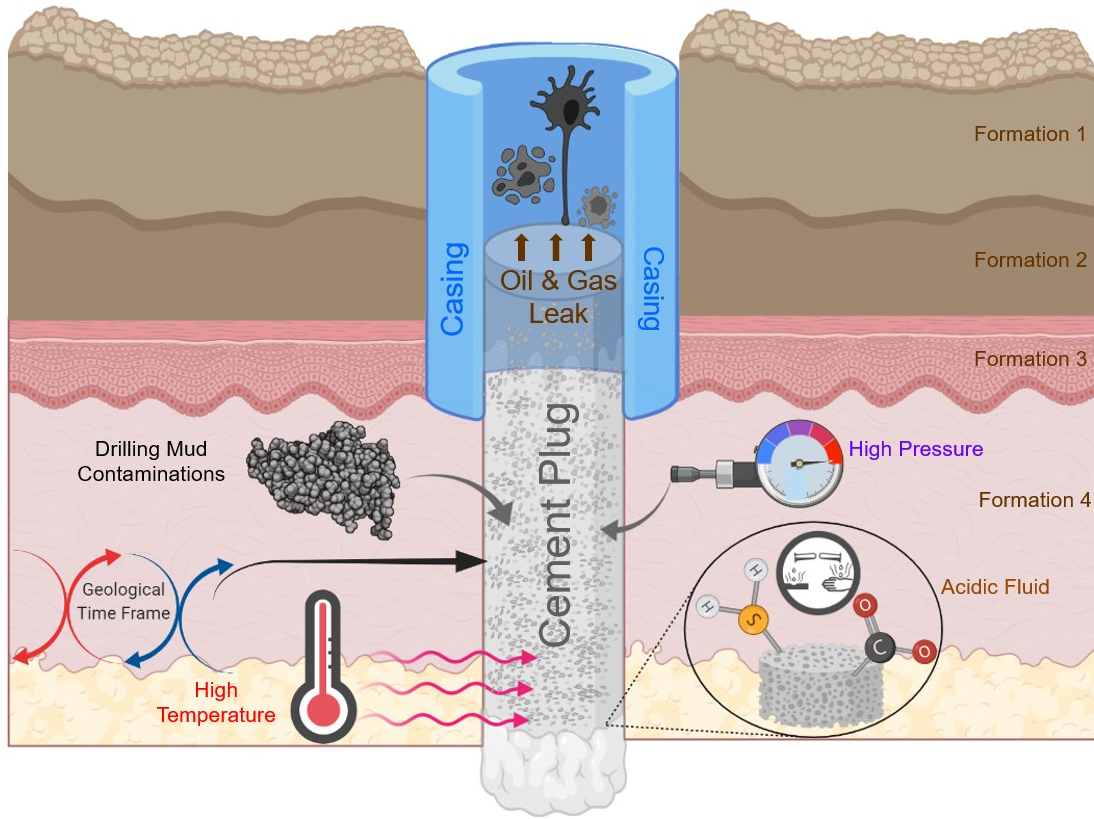


Figure 1. Illustration of four main factors (high temperature, high pressure, acidic fluid, and drilling mud contaminations) that are threatening the integrity of well barrier material in geological time frame.

There is currently a growing interest in developing deep-water P&A technologies. This interest is not only because of an increasing number of deep-water wells waiting to be plugged and abandoned (Aarlott, 2016), but also due to the inadequate performance of the currently-available plugging materials. Although Portland cement (class H and G) is by far the most commonly used plugging material for the offshore abandonment in the worldwide, these materials were initially designed for wells drilled at low pressure and temperature conditions, within competent formations and with the required service life of 20-30 years (Corina et al., 2019; Ingraffea et al., 2014; Vrålstad et al., 2019). Portland cement is also not designed for geochemical compatibility with subsurface

formations (Bachu et al., 2009; Barlet-Gouédard et al., 2009; Dusseault et al., 2000), so the stability over an extended period of time is unknown. When placed in high pressure and high temperature (HPHT) formations, exposed to acidic geofluid (AG), and/or contaminated with the drilling fluid, there is a compounding risk that the current wellbore barrier materials will be insufficient and therefore will allow leakage through the abandoned wellbores (Beltrán-Jiménez et al., 2019; Jiang et al., 2019; Katende et al., 2020; Li et al., 2019; Shadravan et al., 2014). The issue is complex because the leakage pathways could occur at multiple locations along the well and could include damage to the vulnerable interface between the reservoir formation and cement plug (Carroll et al., 2016; Kiran et al., 2017). The microscopic scale of these pathways can make them difficult to locate and mitigate (Norge, 2013).

Current industry practice and regulatory guidelines most likely can reduce leakage of fluids along wellbores, but true prevention remains an unattained goal. By increasing the minimum length of the primary plug and setting multiple well barriers, the expectation is these leakage paths could be reduced and the integrity of the P&A system should be strengthened. However, these two measures fall short of truly preventing leakage of the well, particularly if there is degradation of the plugging material. Furthermore, if plugging fails, remediation is difficult and expensive, and the damage to the environment which is caused by the leaky well can be extensive (Barclay et al., 2001). So it is of utmost importance to seal the well correctly with a material that resists decay of its performance and is able to naturally restore performance even if chemical, thermal, and/or mechanical assault causes it to be compromised at some point during its service life.

There is a wide distribution of severity of consequences of failure of a wellbore plugging and sealing system. Many lessons can be learned from perhaps the highest consequence event in the history of the industry, the Deepwater Horizon oil spill at Macondo (Bly, 2011; Group, 2011; Summerhayes, 2011). This experience shows that even when the P&A system has several wellbore barrier elements, if one of them fails to carry out its function properly, the balance of the whole system can be broken by the accumulative effects, which can accelerate the degradation of the system or even lead to the system failure. Therefore, when considering the next generation of barrier materials for P&A, the ideal barrier material not only needs to overcome the challenging conditions but also needs to have resilience. The concept of resilience is often used in the structural engineering discipline to evaluate the performance of structures after they experience an event such as an earthquake (Bruneau et al., 2003). In P&A, the proposed resilience is focused on the

plugging material's self-restoration or self-sealing behavior. When the barrier in the P&A is damaged, it will lose its integrity and the permeability will become larger than prior to the damage. As fluid flows through the material, based on the Darcy's law where permeability can be calculated from flow rate (q), specimen length (l) and pressure drop (Δp), the permeability can stay the same with time t (stable damage), increase with time t (growing damage), or decrease with time t (sealing damage). The latter case comprises resilient behavior and will be taken as evidence of self-sealing within the material (Figure).

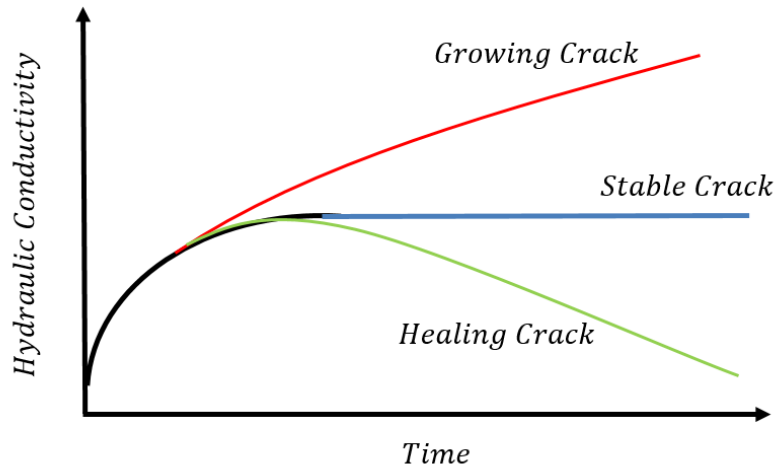


Figure 2. Conceptual illustration of three potential outcomes of permeability evolution of a material that has been damaged, where the reduction with time indicates a resilient response to the damage.

Resilience is difficult to attain with Portland cement-based systems because the properties tend to naturally degrade in acidic environments (Gutberlet et al., 2015). Furthermore, the material has only existed for a short time, geologically speaking, and so there is no relevant data on its performance over geological timescales. On the other hand, many geological materials naturally undergo alterations and many of these result in cemented rocks which have been discovered to be stable under acidic hydrothermal conditions for millenia. Inspired by work on the reaction kinetics associated with the geochemical alteration of ultramafic minerals (Kelemen et al., 2008), the present work focuses on one of these, investigating the feasibility of inducing nature-mimicking carbonation and hydration reactions of ultramafic rocks under wellbore conditions to generate a material that is stable and self-sealing.

Drawing on reaction pathways and kinetics of silicate dissolution and subsequent carbonate precipitation (Lisabeth et al., 2017; Zhu et al., 2016), the principle of the new “Geologically Activated Cement” (GAC) is to place ultramafic minerals, such as olivine, into the wellbore and allow them to hydrate and carbonate in-situ. This approach is a form of so-called "cap rock restoration", novel in that it utilizes geochemical alterations that are ubiquitous, but typically too slow for engineering applications. However, Kelemen and Matter (Kelemen et al., 2008) show that certain temperature-pressure conditions, serendipitously very similar to HPHT reservoirs associated with many deep-water wells, result in drastic speed up of the relevant reactions (Figure) such that processes that would take tens of thousands of years at surface conditions could occur within one day under AG-HP-HT deep-water well conditions. Hence, leveraging this nature-inspired reaction turns challenging AG-HP-HT conditions into an advantage. Furthermore, it hypothesizes that reactions will occur at the surfaces of granular olivine, leaving a cemented material with unreacted olivine at the particle cores. This unreacted material is expected to remain available to carbonate or hydrate in a manner that is restorative, sealing cracks that form as a result of damage to the material during its service life. This work is therefore aimed at proof-of-concept for genesis of GAC and testing the hypothesis that such a material will exhibit self-sealing behaviors under simulated AG-HP-HT, deep-water well-like conditions.

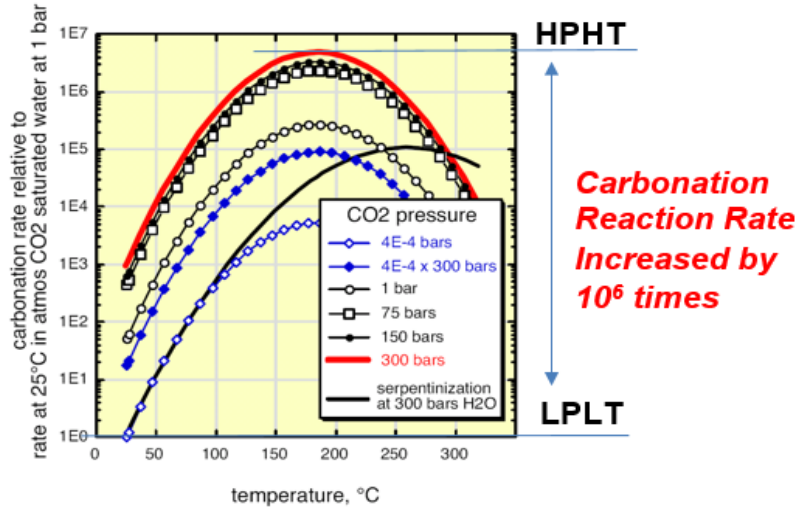


Figure 3. Relative increase in carbonation rate of olivine at elevated pressure and temperature compared to surface conditions (after Kelemen and Matter 2008, with permission).

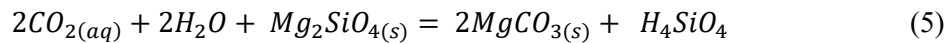
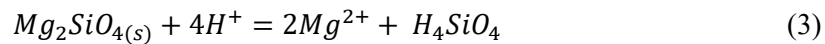
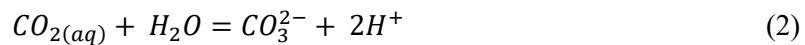
2. Experimental Procedures

2.1 Genesis of GAC Materials

The first objective is the initial exploration of the conditions enabling the necessary reactions to occur at the relevant engineering timescale. The goal is to provide demonstration of pressure, temperature, and fluid chemistry to obtain the desired alteration products.

The apparatus used to generate GAC material at elevated temperatures and pressures is shown in Figure . The syringe pump at the upstream side can provide the pressure up to 68.94 MPa (10,000 psi). The stainless-steel reactor with 203.3 mm length and 15.7 mm internal diameter has a cap at the downstream end and so behaves as a closed system. The external heating is provided by an oven that enables the specimen to be heated up to 250°C. Sodium bicarbonate, which is used as the CO₂ source, will undergo a decomposition reaction and start to produce CO₂ when the temperature is above 50 °C. As the temperature increases, the reaction goes to completion, with the decomposition of all the sodium bicarbonate ($2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + 2\text{H}_2\text{O} + \text{CO}_2(\text{g})$). The chemical composition of olivine fine particles used in the experiment is 90.7% Mg₂SiO₄, 7.6% Fe₂SiO₄ and 0.27% Al₂O₃. Its size distribution is determined by sieving and selecting particle sizes less than 0.075 mm.

In this system, the dissolution and precipitation reaction can be represented by the following steps (Gerdemann et al., 2007; O'Connor et al., 2005a):



Here the system consists of dissolution and hydration of CO₂ in water (equation 1 & 2), the dissolution of silicate minerals using magnesium silicate as an example (equation 3), and the precipitation of carbonate (equation 4). If we add the first four equations, then it yields a net aqueous carbonation reaction, which is represented by equation 5.

The experimental procedures are as follows: firstly, the fine olivine particles and sodium bicarbonate are thoroughly mixed. Secondly, each ingredient is prepared under the ambient atmosphere and temperature based on the proportion information provided in Table 1. Note that based on the stoichiometric calculations implied by equation 1 to 5, the ideal ratio of bicarbonate of fine olivine particles should be 2.4:1. In present experiment work, this ratio is increased to 4.8:1 in order to increase the carbonation level of the fine olivine particles. Then, the reactor is loaded by the solution with a volume of 39.2 mL, which is its full capacity. When the reactor is sealed, the oven is turned on to 180°C and the upstream pressure is adjusted to 13.79 MPa (2000 psi). After 24 hours of HPHT curing, the post-reaction products are taken out from the system after releasing the pressure and turning off the oven.

Table 1. Summary of proportion of each ingredients for carbonation reaction

	BB/OFP	DW/OFP	Water to Solid Ratio
Based on Stoichiometry	2.4	0.25	0.07
In Present Work	4.8	0.5	0.08

*OFP = olivine Fine Particles; Bicarbonate = BB; Distilled Water = DW;

The product is observed and analyzed under Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). To improve the image quality, the samples were carbon-coated prior to SEM/EDS analysis. Images, maps, and spectra were obtained at 20 KeV, and

various magnifications, from a larger field of view to a higher magnification that reveal characteristics of the interfaces and surface properties of the new generated cementitious material.

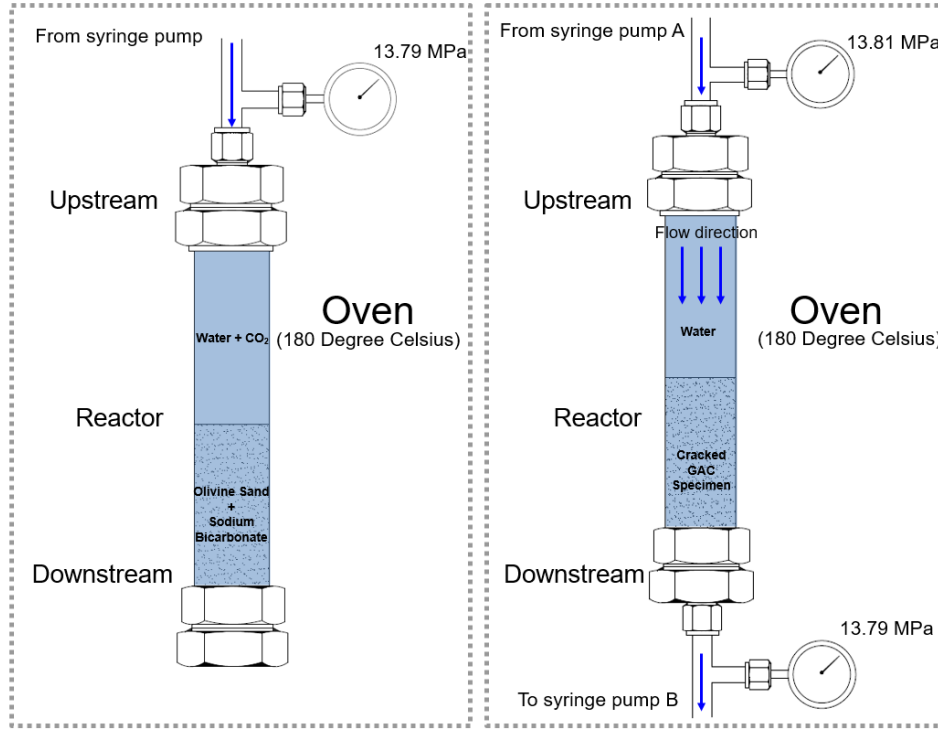


Figure 4. Left: laboratory setup for carbonated olivine generation; Right: experimental setup for the self-sealing test.

2.2 Self-Sealing of GAC Materials

The second objective is to test the self-sealing hypothesis for the GAC by measuring the evolution of permeability of damaged GAC subjected to flow of fluid under wellbore-like conditions. The experiments entail firstly inducing damage to the GAC, that is, inducing cracks. Thermal shocking was found to be the most convenient because it does not require removal of the GAC from the steel tube in which it is generated. It was also found that, by carefully repeating the same procedure, the crack widths generated by the thermal shock could be reasonably consistent from one test to another, ranging 0.1 to 1 mm. Several methods were explored, but the most effective was found to be pouring boiling water on the room temperature specimen (which includes the stainless steel tube).

After inducing cracking, the self-sealing experiments are performed with a wellbore-analog setup, which is illustrated in Figure (right). The reactor loaded with cracked GAC is placed inside

an oven. Pressure is applied at both ends of the reactor by two syringe pumps. The instrumentation on these pumps enables monitoring and recording the change of pressure and flow rate in the system.

Before a self-sealing test is started, the upstream pressure and downstream pressure are both increased to 13.79 MPa and the oven is set to 180 °C. This is followed by a brief (60-90 minutes) waiting period for the temperature of the specimen to equilibrate to the oven temperature. After that, the pressure at the upstream is increased from 13.79 MPa to 13.81 MPa. This pressure difference will drive the fluid flow to penetrate the cracked specimen and flow to the downstream end of the specimen. Immediately after the upstream pressure is increased, the flow rate is monitored and measured using the downstream syringe pump displacement. The testing time for the self-sealing of GAC usually takes 10 to 20 hours. The pressure at upstream and downstream ends remain unchanged during testing, controlled independently by two syringe pumps. As the control group, the class-H cement is cured in the same HPHT reactor and is tested under the same experimental conditions as the GAC. Besides control experiments with Class H cement, two types of self-sealing tests are performed where the fluid is taken alternatively as carbonic acid (pH~3) and distilled water with anhydrous citric acid (pH~4).

3. Results

3.1 Genesis of Geologically Activated Cementing Materials

As shown in Figure 5, the initially loose olivine fine particles (Figure 5a) with the maximum particle size less of 75 microns, has been turned into solid material. Recall this end product is obtained after subjecting the mixture of olivine sand, water, and the CO₂ source (in this case degenerating sodium bicarbonate) to 13.79 Mpa (2000 psi) of pressure and 180°C of temperature for 24 hours. This cementitious and hardened solid becomes firmly lodged in the reaction chamber (Figure 5b), which is expected because the overall is accompanied by volumetric increase (Kelemen et al., 2008; Zhu et al., 2016).

From the decomposition reaction $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + 2\text{H}_2\text{O} + \text{CO}_2(\text{g})$, we can see that the Na₂CO₃(s) will remain in the post-reaction system as a residue. This residue is in addition

to the reaction products. To exclude the possibility that $\text{Na}_2\text{CO}_3(\text{s})$ is contributing the binding ability in GAC, another control group test was performed. It entails repeating the same test procedures described above but replacing the fine olivine particles with the same size of silica sand particles. At room temperature, the solubility of the magnesium carbonate is $1.06\text{e-}2$ g/100 ml whereas the Na_2CO_3 is 7.1 g/100 ml. The huge difference between the solubilities provides a method by which to distinguish magnesium carbonate and sodium carbonate through a test of solubility performed on the products from the olivine sand mixture system and the silica sand mixture system.

The olivine GAC material is created as described above. The contrasting system using silica sand is produced using the same method. The result is a slurry like material after taking out of the reactor.

Both products are submerged in water and stirred for ten minutes. The pre-stir mass and post-stir mass are recorded in Table 2. The mass of magnesium carbonate cementing material from the olivine system does not change at all after stirring. However, the product from the silica sand mixture system is completely dissolved in the water. We see, then, that Na_2CO_3 binder dissolves rapidly, and the binder for the olivine-based GAC does not measurably dissolve, and thus the results from the solubility test exclude the possibility that Na_2CO_3 is the binder in GAC.

Table 2. Results of the solubility test

	Mass of solid (pre-stir)	Mass of solid (post-stir)
Products from olivine system	1.9 g	1.9 g
Products from silica sand system	1.5 g	0.0 g

While solubility provides evidence that Na_2CO_3 is not the binder, it is worthwhile to explore in more detail to ascertain the composition of the GAC binder. Taking part of the GAC material and analyzing it under XRD shows that the product is a mixture of magnesium carbonate (MgCO_3) and remaining fine olivine particles (Figure 6). It demonstrates that within the timeframe of hours to days, i.e. relevant to P&A operations, the system of fine olivine particles (Mg_2SiO_4)

and CO₂ at temperatures and pressures relevant to the challenging conditions of the deep-water well, has the ability to produce sandstone-like material which is cemented by magnesium carbonate. At the same time, the dissolution-precipitation reaction in this sandstone-like material has not completed yet within this timeframe, which leaves unreacted Mg₂SiO₄ particles widely distribute in the GAC and thus providing the material needed to repair further damage by generating new carbonate binder through reapplication of the carbonation reaction.

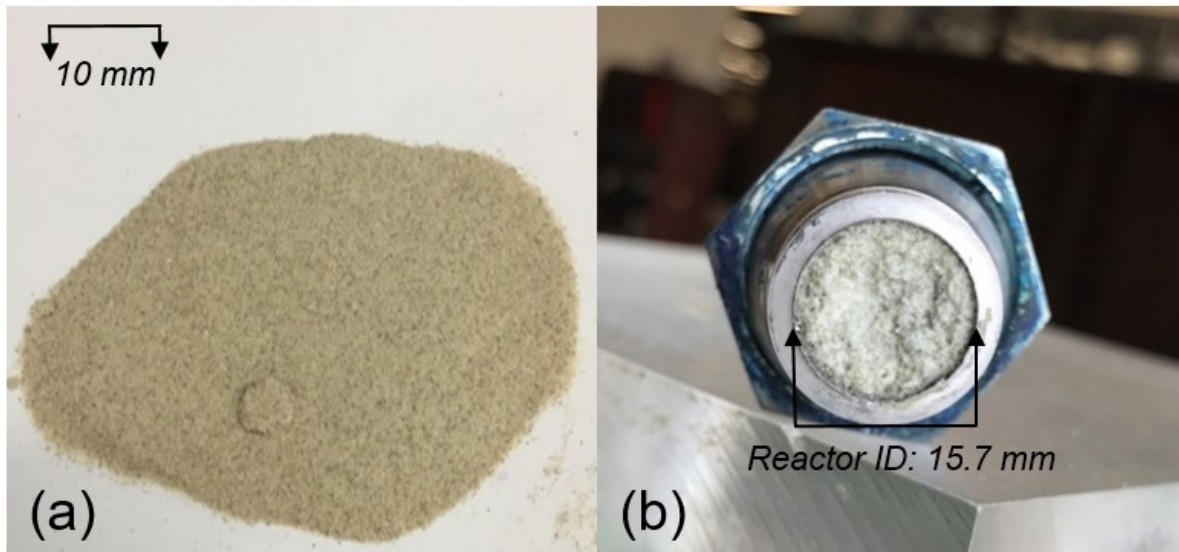


Figure 5. (a) Pre-reaction: loose olivine sand; (b) post-reaction: hardened carbonated masses in the reactor.

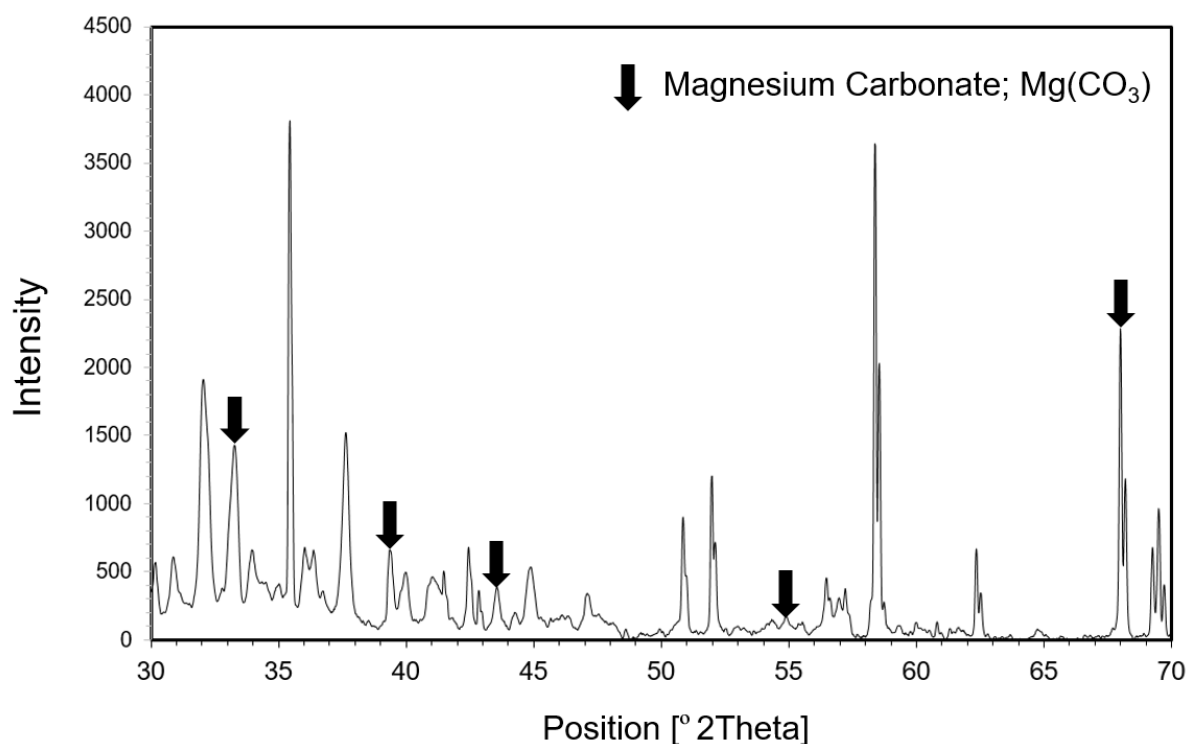


Figure 6. The results of XRD of the reaction product (the black color arrow labels on the are the reference locations of different phases of Magnesium Carbonate in the Power Diffraction File (PDF)).

To better observe the GAC microstructure and identify the elemental composition of the materials, GAC is then put under SEM and EDS, as shown in Figure (~600 microns across). The GAC is shown to be comprised of olivine particles bonded together by a material that almost certainly is magnesium carbonate (MgCO_3). The analysis leading to this conclusion begins with selection of several points in Figure 7 for elemental analysis (EDS). The EDS results for the selected points and their element spectrums (percentage by weight) are shown in Figure 8. From these data, clearly different chemical compositions can be found among the five selected points. For example, the point 1 does not contain any C (Carbon) but is rich in O (Oxygen), Mg (Magnesium) and Si (Silicon). Thus, it is inferred to be magnesium silicate (Mg_2SiO_4). However, points 4 and 5 contain C (Carbon), O (Oxygen) and Mg (Magnesium), but without any Si (Silicon). So they are inferred to be the carbonation reaction product of magnesium carbonate (MgCO_3). For points 2 and 3, they are containing the C (Carbon) and Mg (Magnesium)/Fe (Iron) at the same

time, which is taken to imply they consist of product of mixture of carbonated and unreacted olivine.

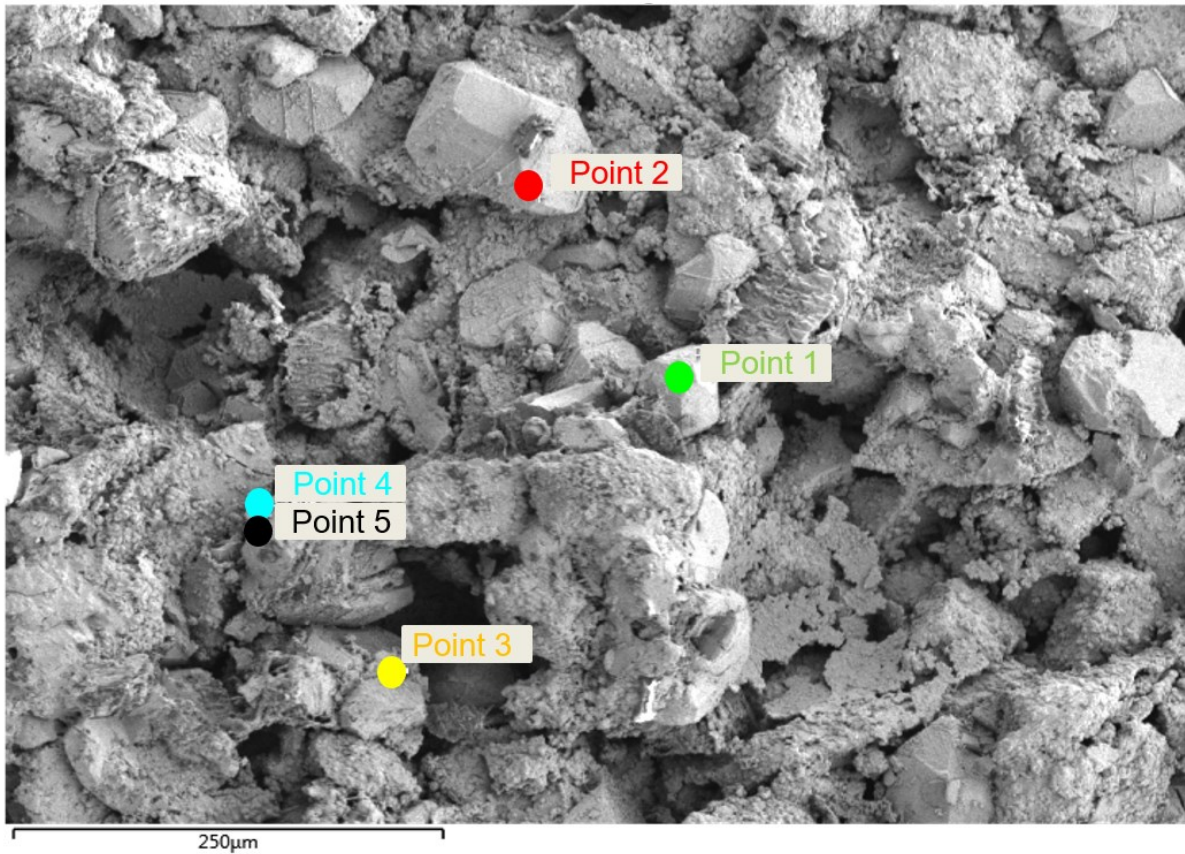


Figure 7. Post-reaction products under SEM and point 1-5 are selected for EDS analysis

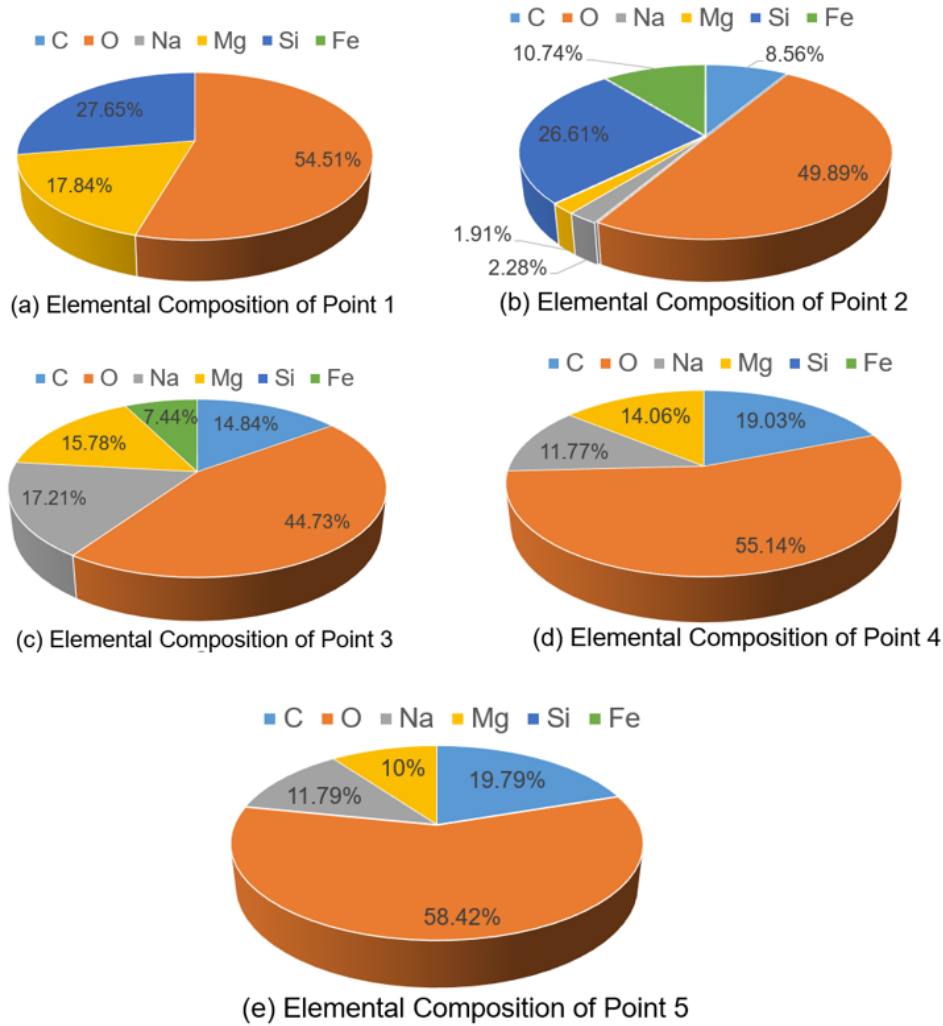


Figure 8. Element spectrum of selected points in Figure 7

3.2 Self-Sealing Behavior

With the proof-of-concept for genesis of GAC established, the attention turns to behavior of the material when it is damaged and as it subsequently interacts with flowing fluids. The overall idea is to compare GAC with class-H cement to determine if it is prone to increasing permeability or decreasing permeability with time. The scenario in which the permeability increases with time is taken to imply that, once it is initially damaged, fluid interaction with the material further degrades it as a plugging material. The scenario in which the permeability decreases with time is taken to imply resilience of the material in that it is able to heal the damage and self-restore as a competent plugging material.

Both fluids used in the study of self-sealing have a low pH. The first is citric acid and the second is carbonic acid, with the latter a common cause for low-pH fluids in the subsurface including deep-water wells. As previously described, for each self-sealing experiment, the flow rate was recorded as it evolved in time in response to a fixed pressure difference at the two ends of a pre-damaged sample. Based on the flow rate and pressure difference, the permeability is computed according to Darcy's law as equation 6 (Verruijt, 2016), where k is the intrinsic permeability (m^2), q is flow rate (m^3/s), μ is the viscosity ($\text{Pa} \cdot \text{s}$), L is the sample length (m), A is cross-sectional area of flow (m^2) and Δp is pressure drop (Pa)

$$k = q \times \mu \times L / (A \times \Delta p) \quad (6)$$

The evolution of the flow rate is therefore used to ascertain evolution of the permeability of damaged class-H cement and GAC specimens. The results are shown for these two materials in Figure 9(a) and 9(b), respectively. The results firstly show that the class-H specimen exhibits permeability that is increasing with time. As shown in Table 4, the flow rate of water through the damaged class-H specimen is increased by 70%, from 0.024 ml/min to 0.041 ml/min after six hours of core flooding with citric acid under HTHP conditions. This increasing permeability with time corresponds to the “unstable” behavior (Figure 2) and suggests that baseline class-H cement is not resilient when subjected of damage and subsequent flow of acidic fluid.

In contrast to the unstable behavior of class-H cement, Figure 9(b) shows that the permeability of GAC is decreasing with time with flooded with citric acid under HTHP testing conditions. As detailed in Table 3, the GAC specimen undergoes a reduction of flow rate (and hence permeability) of about 75% (Figure 9(b)). The GAC therefore demonstrates resilience when subjected to damage and the experimental results provide evidence for the capacity of GAC to self-heal when subjected to injection of citric acid under HTHP conditions.

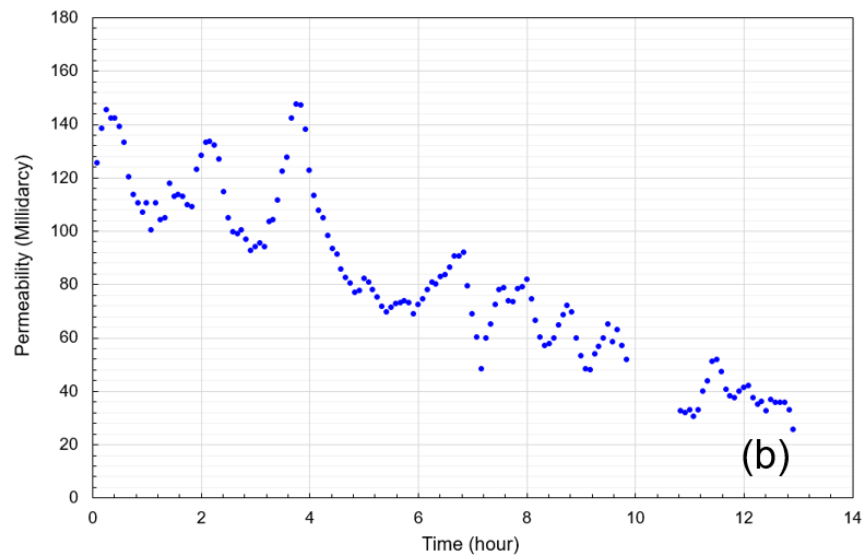
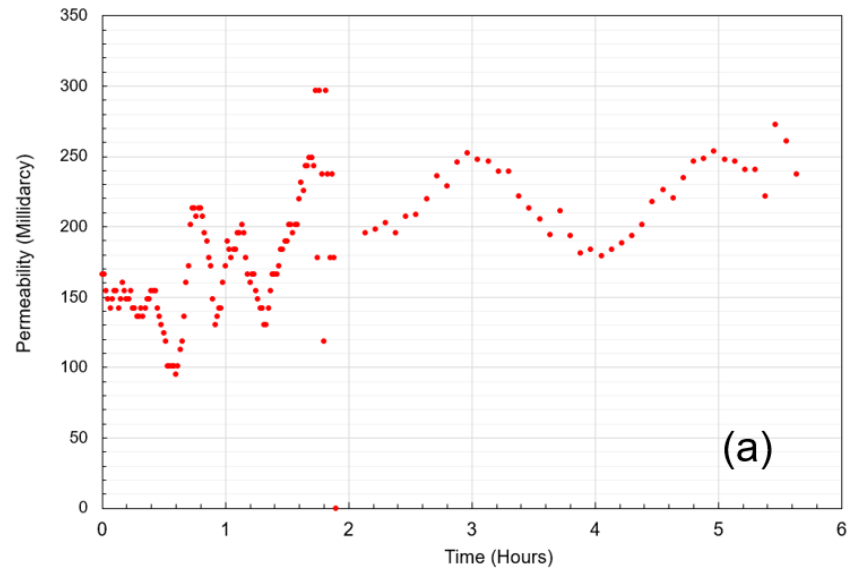
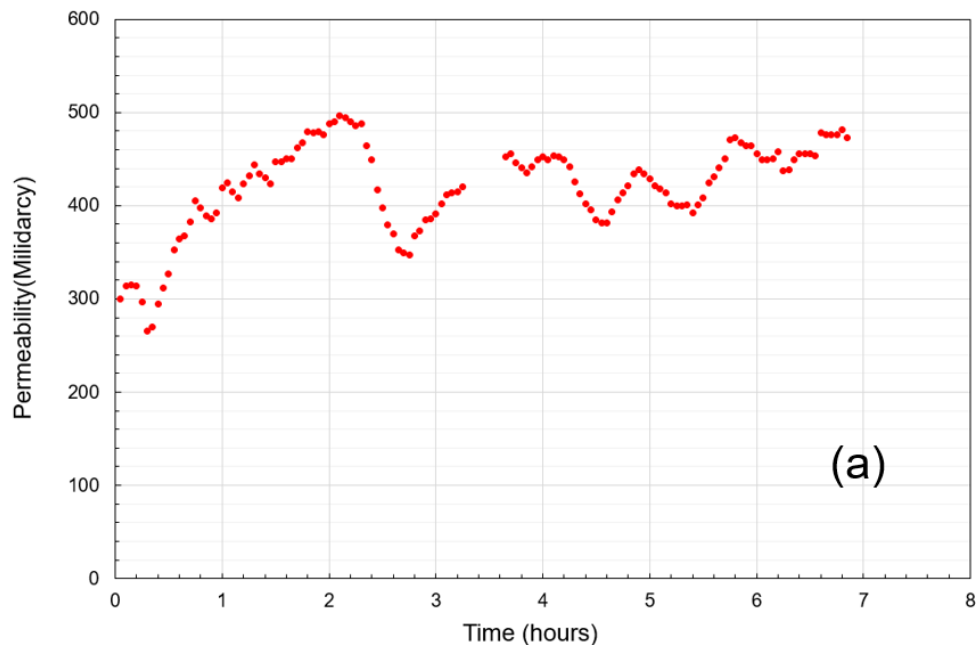


Figure 9. (a) permeability change of class H cement during HPHT self-sealing tests (citric acid group); (b) permeability change of GAC during HPHT self-sealing tests (citric acid group).

Similar behavior is observed for injection of carbonic acid under HPHT conditions. Specifically, the class-H cement again shows increasing permeability with time by about 50% after 7 hours of testing (Figure 10(a)). Again, this unstable behavior suggests that the class-H cement does not self-restore the damage when subjected to carbonic acid at HPHT conditions. Of course this only considers the first few hours, and other modes of self-restoration could be relevant on longer time scales. But, it could also be argued that if the material becomes damaged, restoration on the timeframe of hours is a desirable characteristic of a material, and on this time frame, class-H cement evolves in the direction of increasing rather than decreasing permeability.

Once again, and in contrast to the class-H cement, the GAC shows decreasing permeability when subjected to carbonic acid flowing through under HPHT conditions. As shown in Figure 10(b), the permeability of cracked GAC decreases from around 130 mD to 68 mD after 12 hours, giving an roughly 50% reduction relative to the initial permeability and demonstrating self-repair of damage within hours.



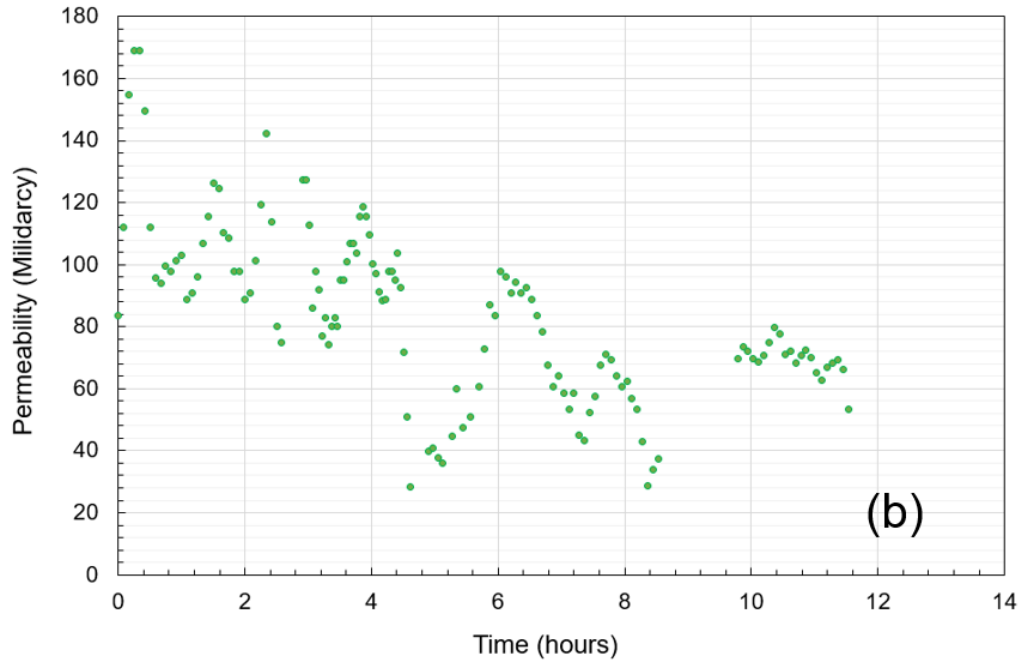


Figure 10. (a) Permeability change of class H cement during HTHP self-sealing tests (carbonic acid group);(b) permeability change of GAC cement during HTHP self-sealing tests (carbonic acid group).

Table 3. Self-sealing data of class H cement and GAC under HTHP testing conditions

Acid source	Specimen name	Testing time (hours)	Initial flow rate (ml/min)	Final flow rate (ml/min)	Initial Permeability (mD)	Final Permeability (mD)	Permeability change percentage	Tendency
Citric acid	Class-H	6	0.024	0.041	150	260	+73%	Unstable
	GAC	13	0.107	0.026	144	36	-75%	Sealing
Carbonic acid	Class-H	7	0.085	0.1275	300	450	+50%	Unstable
	GAC	12	0.022	0.011	130	68	-47%	Sealing

4. Discussion

4.1 Binding mechanism of GAC

The binding mechanism of GAC is inferred from XRD and EDS compositions and SEM microstructure. It is conceptually illustrated in Figure 11. Before the carbonation reaction, the CO_2 is firstly dissolved in the water to form the carbonic acid (pH 3~4), which is represented by equation (2). The carbonic acid is surrounding the magnesium silicate (MS) in the form of a film around the particle. Although the dissolution-precipitation reaction is already happening at this moment, it is at an extremely slow rate (in the timeframe of geological time). However, once the pressure-temperature contains an ideal range (180°C and 13.79 MPa in our proof of concept), the rate of dissolution-precipitation reaction will be dramatically increased. Then, the periphery of the olivine particle is carbonating first and the reaction product of the carbonation will surround the MS particle until it completely covers it. The magnesium carbonate (MC) is not only functioning as the binder among the each particles to form the hardened solid product, but also is the main strength source of the GAC. Furthermore, the generated MC is also filling the pore space between the MS, which causes the reduction of the pore volume and leads to denser structure. As shown in previous studies (Chizmeshya et al., 2007; Lisabeth et al., 2017; O'connor et al., 2005b), there will be volume expansion occurring during the olivine carbonation reaction. However, due to the limitations of the current experimental setup, how much the volume is expanded and what was the expansion induced stress remains a topic for future investigation.

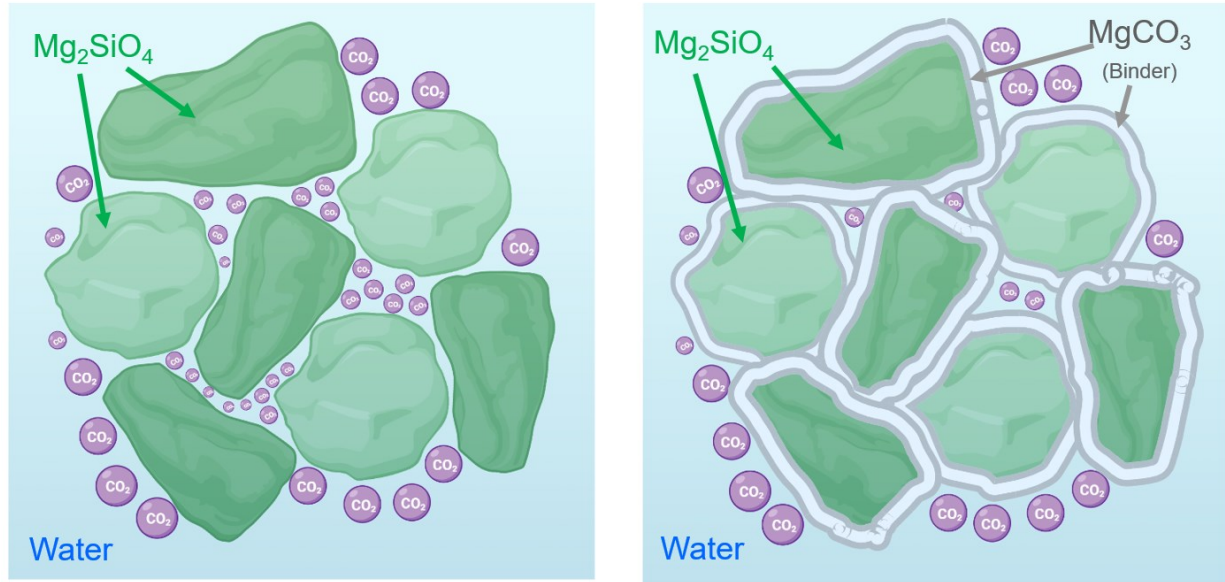


Figure 11. Inferred binding mechanism of Geologically Activated Cement material.

4.2 Self-sealing mechanism of GAC

The self-sealing mechanism is inferred to rely on the unreacted olivine particles that are shown by SEM-EDS to be widely dispersed in the GAC (recall Figure 7). In fact, XRD further shows that the proportion of olivine that is reacted in the original GAC formation is relatively small, leaving a large amount available for future reaction. So, in the presence of acidic fluid and under HPHT conditions, the rate of hydration-carbonation reaction of remaining olivine particles will be rapid enough to enable effective sealing of the breakage flow paths using the products from the mineral carbonation reaction (mainly magnesium carbonate). Specifically, because of the presence of a carbon source (i.e. carbonic acid), there is a supply of CO_3^{2-} ions. Additionally, because of the HPHT conditions, the Mg^{2+} ions will be continuously released via dissolution of unreacted olivine. Thus, the self-sealing of GAC could be achieved many times owing to a large source of Mg^{2+} and CO_3^{2-} . When present, movement of these ions is presumably by a combination of advection as well as diffusion that is driven by the concentration difference. Hence, when damage occurs and the precipitation reaction begins repair, the ions locally deplete as they form solid reaction products. But, subsequent movement of Mg^{2+} and CO_3^{2-} will be impacted by the concentration difference, leading reactants to repair locations where cracking has exposed to the

fresh olivine. By this process, the fracture will be sealed by the new binder MgCO_3 which is generated from the carbonation reaction.

4.3 Carbonation level and reaction rate

Using carbonation to activate binders is not new. Indeed, natural formation of carbonate binders is one of the most common geochemical processes that occurs in nature. Representing various reactants, products, and processes, rock that owe their binding to carbonate formation include limestone, beachrock, dolomite, and magnesite. All of them are considered as the main rock-forming carbonate minerals in nature and proven to possess chemical and physical properties that allow the rock to remain competent for millions of years (Ashraf, 2016; De Silva et al., 2006; De Silva et al., 2009). While drawing inspiration from these systems is a starting point for developing cap rock restoration systems that are intended to seal for millions of years, the ubiquitous problem is that these natural geological processes occur over geological time scales that greatly exceed the time scales needed for engineering applications. Thus, for practical engineering purposes, how to enhance the carbonation level and reaction rate to create natural carbonate like binders in a short time is a recurring research theme (Gerdemann et al., 2007; Power et al., 2013). In the context of using GAC as the barrier material, the ongoing issues will be to reduce permeability and bound the range of fluid flow rate for which self-sealing is still effective. Some considerations for both of these ongoing objectives are briefly described in this section.

Under our current experimental conditions, the permeability of GAC is falling into the range of 10-500 mD after 24 hours of reaction, which is equivalent to the permeability of many sandstone formations. Although it is relatively high when compared with other plugging materials, it is anticipated that the permeability GAC can be further reduced by increasing the carbonation level, that is, the ratio of the amount of carbonated olivine in the post-reaction products over the total amount of fresh olivine in the pre-reaction product. For example, previous research has shown that the longer reaction time can enhance the carbonation level (Case et al., 2011; Giammar et al., 2005; O'Connor et al., 2005a; O'Connor et al., 2005b; Oelkers, 2001). Since the time frame of P&A is geological time, this extremely long service life may be beneficial for the ongoing increase of carbonation level and could further reduce the permeability. Furthermore, the carbonation level can even more substantially increased if the current MC-surrounding-MS

binding pattern can be improved. As shown in Figure 11, since the reaction will first start from the periphery of the olivine particle, the reaction will stop once the newly generated MC completely covers the unreacted MS, which leaves a low carbonation level around the center area in the MS-surrounding-MS structure. This binding pattern has also been observed in some previous studies (Ashraf, 2016; Guan et al., 2018). So, it is likely that the ratio of surface area to volume, which is directly related to the particle size distribution, is important and can be optimized to obtain both short term permeability and proportion of unreacted olivine that will remain for self-sealing after initial carbonation takes place.

While the matrix permeability of the GAC is related to the carbonation level, the self-sealing ability of GAC is proposed to be largely determined by the carbonation reaction rate. Because self-sealing is almost certainly rate-dependent, it is likely that fluid transport could, at some point, become so rapid that reactants, most notably Mg^{2+} ions, will be swept away by advection before they are able to participate in a precipitation reaction that will seal a fracture. So, the efficacy of self-sealing must rely on the comparison between the reaction rate and the fluid flow rate. When the reaction rate is significantly larger than the leak flow rate, the fluid can be gradually trapped by the newly generated binder until the flow path is completely sealed. Thus, the maximum effective flow rate of self-sealing is associated with temperature, pressure, fracture width, and presumably a variety of other parameters. The work presented in this paper conceptually demonstrated the self-sealing ability under the combinations of certain representative challenging factors, but future studies are needed in order to investigate how the interplay between the reaction rate and transport rate determines the ability of the material to self-seal.

5. Conclusions

Experiments provide proof-of-concept for genesis and self-sealing of Geologically Activated Cementing materials (GAC). These experiments are performed at conditions that are both ideal for olivine carbonation and similar to HPHT conditions in many deep wells including deep-water reservoirs. The products of GAC genesis experiments were analyzed and identified under XRD, SEM/EDS, and solubility tests. Permeability testing of damaged specimens of both GAC and class H cement provide measurement of the evolution of transport properties when subjected to flow of acidic fluid under HPHT conditions.

The results of these experiments demonstrate that combining a CO₂ source and olivine (Mg₂SiO₄) mimics the natural process of olivine weathering via dissolution and subsequent carbonate precipitation. However, because of the HPHT conditions, the reactions occur on a time scale of hours to days, thereby making the process relevant to engineering applications. In this way, an approach is developed that transforms sand into a sandstone-like material within a day. By using a binder that does not rely on Portland cement, the reactions proceed with minimally processed materials and lead to product(s) that are more chemically similar to natural materials such as limestone and carbonate-bound sandstone.

Besides the improvement in potential for long-term chemical stability that is expected from a material that emulates natural carbonates that can be stable for millions of years, GAC is shown in these experiments to have a self-sealing capacity in the presence of acidic fluid under HPHT conditions. These conditions are ideal for self-sealing of GAC, but are adverse conditions for class-H cement. The data show that damaged class-H cement experiences continued increase in permeability during the hours following damage and commencing of flow of acidic fluid. In contrast, GAC experiences significant reduction in permeability over a period of hours. This result indicates that the GAC can effectively seal the breakage flow paths by the products from mineral carbonation reaction. Our experimental results therefore clearly show the potential of GAC to perform under the low pH and HPHT conditions which usually threaten most of the current plugging materials. We therefore propose GAC as a demonstration of a new direction in wellbore plugging materials, emulating natural rocks for which long term stability is well-established and turning the low pH and HPHT conditions from a threat to an advantage by seeking in nature to find desirable reactions for which the kinetics are optimized under wellbore conditions. This concept is proposed to provide resilience to failure and therefore the potential to be an important advanced material for the next generation of resilient wellbore cementing and plugging systems.

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