Lessons Learned from the Development of Cementitious Grouts for Deep Borehole Disposal Applications

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Abstract: The performance of grouts made using oilwell cement is markedly different above 90°C than at lower temperatures, and the rapidity with which grouts thicken can cause failures in well cementing. One grouting application in which such temperatures are encountered is deep borehole disposal (DBD). DBD is a concept for disposing of high-level radioactive wastes where the temperature and pressure will be 90–140°C and 30–50 MPa, respectively. In developing DBD grouts, a number of issues have been identified that will be of interest to well-cementing organizations. (1) The type of retarder used to delay grout thickening above 90°C is of extreme importance, and should be selected based on local temperature, pressure, and geochemical environment. Addition level might vary considerably depending on the retarder used. (2) Temperature and pressure will shorten the time for grouts to thicken, particularly the former. Water content will also affect grout properties such as consistency, viscosity, and flow. (3) The retarder may not influence hardened grout composition, which suggests that only the time at which the cement hydration reactions occur is influenced. **DOI: 10.1061/(ASCE)MT.1943-5533.0002006.**

Introduction

Using deep boreholes to dispose of high-level radioactive waste (HLW, including spent nuclear fuel) is an alternative to emplacement in geologically shallow, mined repositories (Gibb 2015; Gibb et al. 2012; Beswick et al. 2014; Chapman 2014; Brady et al. 2009; Arnold et al. 2013; Al Bloushi et al. 2015). This disposal concept is known as deep borehole disposal (DBD) and is based on the emplacement and sealing of waste packages within the bottom ~2 km (called the disposal zone) of vertical boreholes drilled several kilometers (~5 km) into basement rock (Beswick et al. 2014; Arnold et al. 2010; Bates et al. 2014). This creates significant advantages associated with safety, cost, and ease of implementation over disposal in mined repositories only a few hundred meters deep (Chapman and Gibb 2003; Gibb 2010).

The search for reserves of hydrocarbons and geothermal energy has led to continuous and comprehensive development of all aspects of deep borehole construction (Juhlin and Sandstedt 1989; Beswick 2008; Beswick et al. 2014), including improvements in drilling technology and equipment, and a better understanding of geomechanics in deep stressed rock (Beswick 2008). Advances in drilling techniques have been supported by the use of down-hole drilling motors rather than surface rotation of the drill string (Beswick and Forrest 1982) and have enabled directional drilling of long reach wells extending to more than 12 km [horizontal sections of more than 11 km have been drilled (Exxon Neftegas 2016)]. The ability to drill larger-diameter holes to greater depths has also been developing over the past 10–20 years, and this has put an obligation on organizations involved in radioactive waste disposal to assess and develop concepts such as DBD that are alternatives to shallower mined repositories. As an example, a project to develop DBD in the United States involves drilling a 5-km-deep borehole with a diameter of 431.8 mm (17 in.) in dense granitic rock with a goal of both proving the drilling process and testing deployment of inactive simulant waste packages (Sandia National Laboratories 2014, 2015).

Building on more than 25 years of pioneering research (Gibb et al. 2008, and references therein), the DBD Research Group at the University of Sheffield in the United Kingdom is developing cementitious grouts for use as sealing and supporting matrices (SSMs) (Collier et al. 2015a, b). These materials have two principal functions:

1. To provide a seal/barrier to the ingress of saline groundwater to the waste container, prolonging container life and augmenting the disposal safety case; and
2. To provide mechanical support against buckling and damage caused by the load from overlying containers, thus protecting against container breachment and subsequent radionuclide release before final borehole sealing.

The casing in the DBD disposal zone would be perforated, and upon deployment the SSM would flow around the waste containers and through these perforations, thereby filling the annulus between the container and the casing, and between the casing and the borehole wall. After hardening of the SSM, the casing would be secured to the formation. The preferred SSM is called high density support matrix (HDSM) and would be a lead-based alloy with a eutectic solidus of ~190°C and with very low permeability, which would make it a very good sealing matrix (Gibb et al. 2008). Where there would be insufficient heat to melt the HDSM (Gibb et al. 2012), cementitious grouts are proposed. These DBD grouts are primarily based on Class G oilwell cement [BS EN ISO 10426-1 (BS EN ISO 2009)]. However, because the temperature in the package disposal

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zone is likely to be in the range ~90–140°C, the cement is partially replaced with silica flour to reduce the Ca/Si ratio and ensure the formation of durable and stable crystalline calcium silicate hydrate (CSH) phases such as tobermorite (Bensted 2008; Nelson and Guillot 2006). Minor constituents of the grouts include retarders and possibly fluid loss additives to facilitate the flow/movement of grout through the water in the borehole.

Oilwell cements, such as Class G or H [BS EN ISO 10426-1 (BS EN ISO 2009)], are most commonly used in hydrocarbon and geothermal wells to secure the borehole casing and provide separation between the different fluid chemistries and rock formations through which the boreholes pass (Bensted 2008; Nelson and Guillot 2006). The composition of a Class G or H cement is similar to that of BS EN 197-1 CEM I (BS EN 2000), the form of portland cement used most commonly in civil/construction applications. However, oilwell cements have low aluminate content to prevent reaction between the aluminate and sulphate ions present in the groundwater, a process which results in the expansive formation of ettringite, which can cause cracking of the hardened paste.

The local geology in DBD will be different from that in hydrocarbon and geothermal wells, but because of the borehole depth and the waste package decay heat, the temperature to which any SSM used in DBD would be exposed is similar to cementing conditions in geothermal well applications. Temperature is known to significantly affect paste performance, particularly above ~90°C. Therefore, because DBD grouts would be used in the temperature range ~90–140°C, the experience and knowledge gained from their development is of interest for organizations involved in oil and geothermal well cementing. This paper identifies and discusses technical issues associated with DBD grouts that could be applicable to well cementing.

Influences of Local Environment on Grout Performance

The near-field conditions in the DBD disposal zone will make post-drilling cementing operations challenging. The principal influences on wet paste performance and hardened paste durability will be from the elevated temperature and pressure, but other, less influential effects are also envisaged. The most likely influences are identified and discussed below.

Temperature

The elevated temperature is principally caused by (1) the local geological environment, where an ambient temperature range of 90–140°C is typical for the depths being considered in DBD, a temperature rise of ~2°C per 100-m-depth increase (Best 2003) and (2) the radioactive decay heat from the waste packages, which generally reaches a maximum at ~1,000 days (Gibb et al. 2012). Grout deployment should be within a few hours of package placement, with the overall grouting/setting process occurring within 24–48 h, so any radioactive decay heat will be insignificant during placement and setting.

In DBD the maximum temperature to which a cementitious SSM will be exposed will affect hardened paste characteristics. DBD grouts are being designed to set between 4 and 24 h after mixing, which will ensure sufficient time for grout deployment and allow a minimum of 24 h from mixing for the grout to set and harden before placement of any subsequent containers. This means that a loading rate of 1 container every 1 or 2 days could be achieved. After deployment of the cementitious SSM, the temperature to which the grout is exposed will rise, particularly once the borehole is resealed above the disposal zone and the local geothermal conditions are re-established. Heat flow modeling has predicted that the temperature in the disposal zone will peak after ~1,000 days, but this is dependent on the contents of the waste containers. In the work being carried out in the DBD Research Group at Sheffield, heat flow modeling is used to select whether HDSM or a cementitious SSM is used for each disposal or set of disposals (Gibb et al. 2012). As an example, Fig. 1 shows a temperature evolution plot for the outer surface of a batch of containers holding 30-year-old UO_2 fuel; in this scenario the local temperature would never exceed the eutectic solidus of the HDSM, so a cementitious SSM would be used. Cement grouts are used in well-cementing operations up to ~400°C [above ~160°C the tobermorite changes to xonotlite, the stability and durability of which is similar to that of tobermorite (Nelson and Guillot 2006)], but our modeling work will ensure that a cementitious SSM will only be used where the temperature never exceeds ~190°C.

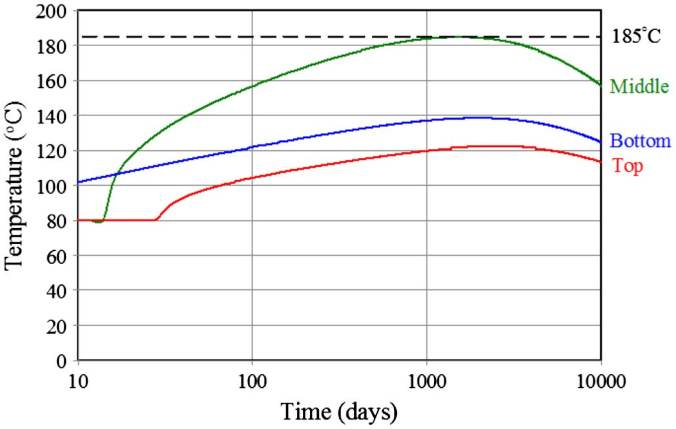

Fig. 1. Evolution of temperature modeled for the outer surface of a batch of five containers emplaced at 7-day intervals for 600 pins of 30-year-old UO_2-65 GWd/t fuel (data from Gibb et al. 2012); top, middle, and bottom data lines refer to the level in the batch stack, and the horizontal line at 185°C is the eutectic solidus of the HDSM at atmospheric temperature and pressure

Elevated temperature accelerates the hydration reactions of cement, reducing paste thickening time (Taylor 1997; Nelson and Guillot 2006; Bensted 2008; Shariar and Nehdi 2012; Zhang et al. 2010; Scherer et al. 2010; Jupe et al. 2008). Temperature also affects the composition and morphology of the CSH binding phases in the hardened paste. The crystalline products being formed are different from those found at atmospheric temperature (Taylor 1997; Bensted 2008; Nelson and Guillot 2006). The phase composition of the hardened cement grout is important in terms of the lifetime of the SSM, and the most durable hydrate phases need to be formed to provide longevity to the DBD concept. Given the correct slurry composition, crystalline tobermorite-11Å $[Ca_5Si_6(OH)_{18}.5(H_2O)]$ will form in the temperature range applicable to DBD. This phase has higher strength, is more stable, and therefore has higher durability than other crystalline phases that may form such as α-C_2SH $[Ca_2(SiO_4)H_2O]$. The formation of tobermorite-11Å rather than α-C_2SH can be assured under these conditions by adding silica flour (quartz) to the cement in order to lower the Ca/Si ratio.

As with DBD, the temperature of any reservoir of steam, hot water, or hydrocarbon source is not only determined by depth, but is also influenced by the local temperature of these intrarock fluids (the fundamental reason for drilling geothermal energy wells). In drilling for steam or hot water, the wells are located in fractured rock formations, which have low density, high permeability, and high thermal conductivity. DBD boreholes would be drilled into granitic basement rock with high density, low permeability, and low thermal conductivity (Bates et al. 2014). In most hydrocarbon-producing areas, the temperature gradient with depth usually varies between 1.1 and 2.9°C per 100 m of depth increase. But in areas where the crust of Earth is thinner (i.e., in geothermal areas), the thermal gradient is much higher, with values as high as 18.2°C per 100 m of depth increase reported (SPE Petrowiki 2016). Therefore, geothermal wells are generally shallower than DBD boreholes, and the temperature is likely to be as high as or higher than in DBD. Indeed, some geothermal energy wells require cement at ~300°C (Nelson and Guillot 2006; Deutsche Erdoel 2016), and some deep wells are being considered where temperatures could even be above the critical point of water (~374°C) (Hefu 2000).

Pressure

After drilling, wells are generally flushed with fresh water to remove drilling muds and other unwanted chemicals, so it can be assumed that any DBD borehole will be filled with water during post-drilling cementing operations. The pressure in a water-filled open hole is governed by the hydrostatic head of water and will be influenced by depth and water density. Geothermal wells can be as shallow as only a few hundred meters deep, but generally they are drilled to depths of ~3 km, although wells deeper than this are becoming more common (Finger and Blankenship 2010; Anger 2016). This is significantly less than the depth of DBD boreholes (~5 km), which means that the hydrostatic pressures at the bottom of geothermal wells will be less than in DBD. However, the presence of high-pressure steam in geothermal wells will increase the overall pressure encountered during cementing.

When assessing the effects of pressure on cementitious SSMs, pressure external to the grout (hydrostatic pressure), as well as pressure caused by the internal expansion of the grout mix water after setting (attributable to the elevated temperature), should be considered. Hydrostatic pressure increases at a rate of ~1 MPa per 100 m of hole depth, so the pressure at the bottom of a 5-km-deep DBD borehole during grout deployment will be of the order of 50 MPa. This pressure will decrease as the hole is filled with waste containers because of the corresponding reduction in hydrostatic head. Most cement hydration occurs within the first 90 days of curing [the quantities of the three primary cement phases reacted by this time have been estimated to be 85, 94, and 100% (Patel et al. 1988)], after which time the amount of free water remaining in the pores will be very little. The increase in temperature in DBD during this 90-day period will be insignificant (the temperature reaches a maximum at ~1,000 days), meaning that the corresponding increase in internal pressure caused by the expansion of the grout mix water will also be insignificant.

Elevated pressure causes a reduction in grout thickening time (Scherer et al. 2010; Jupe et al. 2008) because, like temperature, it accelerates the cement hydration reactions (Taylor 1997; Nelson and Guillot 2006; Bensted 2008; Shariar and Nehdi 2012; Zhang et al. 2010). However, temperature has a greater influence on cement hydration reactions than pressure (Scherer et al. 2010; Jupe et al. 2008; Nelson and Guillot 2006). While little is known about the combined effect of elevated pressure and temperature on hardened paste composition, the combination could affect the phases formed (Taylor 1997; Nelson and Guillot 2006).

The reduction in availability of hydrocarbons at shallow depths over the past 100 years has resulted in the need to drill deeper wells to access previously untapped resources. Hydrocarbon wells can now be drilled as deep as 10 km, and horizontal drilling to 12 km has also been performed (Beswick et al. 2014). Cementing operations are still employed in these deep wells for the purposes of casing fixation and formation sealing, as well as remedial sealing/engineering operations. The hydrostatic pressure in these deep vertical wells will be higher than in the 5-km-deep borehole for DBD, and up to 70 MPa has been recorded in some high-pressure, high-temperature oil and gas wells (Deutsche Erdoel 2016).

Near-Field Physical Geology

As with selecting sites for geothermal energy and hydrocarbon wells, the choice of locations suitable for DBD will be influenced by geology and near-field chemistry. DBD boreholes will be drilled into dense, low-permeability, granitic basement rock containing few cracks and/or fissures, and downhole conditions will be monitored during drilling using a range of advanced mechanical and electronic monitoring tools already available in geothermal/hydrocarbon well applications.

The physical geology of the surrounding rock will influence the performance of a DBD grout. The rock in the vicinity of the DBD disposal zone will be very dense so little loss of grout mix water to the formation is expected; geothermal and hydrocarbon wells are drilled into fractured rock strata, where loss to formation is likely to be much higher than in DBD. Fluid loss is of concern to well-cementing companies because it severely affects the performance of cementing jobs, and a range of fluid loss additives are used to prevent the process. These additives work by changing the physical and chemical conditions of the wet grout in order to retain the mix water within the slurry (this sometimes results in gelling). Even though fluid loss to formation should not be a major concern in DBD, the flow/movement of the grout through the water in the borehole (and the generation of turbulence around the paste) could cause dispersion of solid particles, the loss of grout mix water, and the ultimate loss of paste cohesion. Therefore, using a fluid loss additive in DBD grouts could help retention of grout mix water and facilitate the flow of the paste around waste packages.

Local Geochemistry

Drilling and engineering operations in DBD or geothermal/hydrocarbon well preparation may cause detrimental chemical reactions to occur. Drilling involves the use of a drilling fluid/mud, and methods to remove it focus on flushing with fresh water. Despite flushing, residual drilling fluids may remain and could interact adversely with any cementitious grout used. Drilling fluids frequently contain surfactants and materials such as bentonite, which can interact with cement grout to weaken the bond between the cement and the casing or formation (Da Silva et al. 2012; Bensted 2008; Nelson and Guillot 2006).

Any pressure differential between the groundwater in the rock and the fresh flushing water present in the borehole will mean that the groundwater will displace the fresh water until pressure equilibrates. This groundwater is likely to be highly saline and may contain carbonates and sulphides that could react with cement pastes in a detrimental manner:

1. Any chloride present may influence the setting characteristics of wet cement paste and may cause corrosion of any ferrous components;
2. Acidic carbonate waters will cause corrosion of hardened cement paste and precipitate calcium carbonates; and
3. Sulphides can attack steel and could oxidize to create sulphuric acid, which will cause corrosion of both steel and cement.

The geochemical conditions relevant to DBD are currently unknown, although internationally accepted requirements for geological disposal of radioactive waste exist (IAEA 2003; Ojovan and Lee 2014). However, there will be significantly less carbonates and sulphides in DBD boreholes than in hydrocarbon and geothermal energy wells, so the primary influence of local chemistry in DBD will be from chlorides. Issues associated with casing corrosion will be the same for DBD as for geothermal and hydrocarbon wells, with low pH conditions (such as those caused by the presence of chloride or sulphide phases) eventually causing pitting and corrosion of the steel casing (Nelson and Guillot 2006). In DBD there is also the corrosion of the waste containers to consider, but these are likely to be made from high-grade stainless steel [Nirex Report N/124 (Nirex 2005)], and therefore they will corrode significantly less than any mild steel casing. Corrosion is a concern in hydrocarbon and geothermal energy wells, and methods to prevent it using copper inclusion/coating techniques or to develop better-performing materials such as corrosion-resistant alloys (CRAs) are being addressed (Gatekeeper 2014; Roscoe Moss Company 2016).

Chemical reactions may occur between the cement paste and the host rock in either DBD or geothermal/hydrocarbon wells. One of these reactions is an alkali-silica reaction (ASR), which can cause severe deterioration of the hardened paste (Silva and Milestone 2016). In this reaction, the alkaline cement pore solution (containing sodium and potassium released from the cement as it hydrates) reacts with any siliceous component of the host rock and forms an alkali silicate gel. The formation of this gel is expansive and can cause cracking of the rock and the hardened cement paste. The conditions that facilitate ASR in DBD will be the same as those for geothermal energy and hydrocarbon wells.

Grout Deployment

DBD grout deployment will be different from the placement of cement paste in geothermal and hydrocarbon wells, and the methods used may influence loss of grout mix water, dispersion of solid particles, and loss of hardened grout integrity. In the cementation of the casing in geothermal and hydrocarbon wells, the grout is deployed down the center of the casing and returns to the surface up the annulus between the casing and borehole wall. This process is meant to ensure that a good cement seal/sheath is produced on the outside of the casing and that a good bond is made between the casing and the borehole wall (in practice, this is often not achieved). In DBD, cementing the casing in the disposal zone (where the casing is perforated) would be different from well cementing and would form part of the SSM deployment process. Methods for DBD grout deployment include the following:

1. Deploying the grout on top of a preplaced waste container so that it flows down in to the annulus between the container and the casing, through the casing perforations, and into the annulus between the casing and the borehole wall; and
2. Placing the grout into the disposal zone before a waste container, which is then released into the fluid grout and upon sinking displaces the grout upward, forcing it to flow through the perforations in the casing and around the container to fill both annuli.

The density of the grout ($<2{,}000\ \mathrm{kg/m^3}$) will be higher than that of the water in the disposal zone, so the water will be displaced in both the methods described above. DBD grout deployment requires careful development because the paste must flow through water and around/through intricate constrictions, which may cause significant solid particle dispersion. While any dispersed solid particles are likely to settle and harden, the porosity and permeability of the resultant hardened paste may be higher than that of the original undispersed grout.

Until relatively recently, remedial cementing work undertaken in geothermal or hydrocarbon wells was generally performed using wire line equipment [and utilization of equipment such as a dumper bailer apparatus (Nelson and Guillot 2006)]. However, over the last few years, an increasing amount of remedial cementing has been performed using coiled tubing, which has advantages such as operational flexibility, shorter deployment times, and the ability to use the equipment for other remedial applications such as descaling using water-powered drilling heads on the end of the coiled tubing rig. Coiled tubing could be a viable option for DBD grout deployment.

Radiological Environment

In DBD, the waste packages will contain either vitrified HLW or spent fuel. Emission of alpha (α) and beta (β) particles from the surface of the containers will be prevented because of the absorption by both the matrices within the containers (the glass matrix in the case of vitrified HLW and any metallic filler in the containers of spent fuel) and by the container itself (stainless steel). This means that only the impact of the gamma (γ) radiation on the cement grout requires consideration.

To ensure adequate performance in the field, testing of the hardened grout under irradiation is recommended. However, by reviewing the available literature, an initial assessment of likely performance can be made. Cementitious pastes are reported to have high radiation durability (Mobasher et al. 2015; Abdel Rahman et al. 2015); indeed, grouts based on BS EN 197-1 CEM I portland cement [BS EN 197-1 (BS EN 2000)], equivalent to ASTM C150/C150M Type I cement [ASTM C150/C150M (ASTM 2016)], are used in the United Kingdom with pozzolanic material (blast furnace slag and fly ash) to directly encapsulate/immobilize intermediate-level radioactive waste (ILW) and produce a stable and durable wasteform with a high pH (to reduce radionuclide solubility) capable of immobilizing a range of radioactive ions (Glasser 1992, 1993, 1997, 2001; Sharp et al. 2003; Hutson 1996; Gougar et al. 1996). In developing these United Kingdom ILW encapsulation grouts, irradiation testing was performed at a dose rate of 1×10^4 Gy/h up to a total dose of 10 MGy over a period of 2 years (used to simulate the effect of irradiation between 50 and 100 years at 50°C) (Palmer and Fairhall 1992; Wilding 1992; Richardson et al. 1989). Apart from a small amount of pore water radiolysis, a slight increase in potassium and sulphate concentration in the pore solution, and the formation of an ettringite phase in some samples at higher dose rates, the work concluded that irradiation had little attributable effect on composition and microstructure. The compositions and characteristics of the Class G grouts being developed for use in the Sheffield DBD concept are very similar to the U.K. ILW encapsulations' grouts described above, so their performance under irradiation is likely to be comparable. The radiation dose rate expected in DBD is an order of magnitude less than in the testing performed on the ILW grouts described above [a typical surface dose rate expected from vitrified U.K. HLW containers will be of the order of 1.6×10^3 Gy/h (BNFL 1990)]. In addition to this, the low aluminate content of Class G cement means that the formation of any additional ettringite phases from irradiation (as in the U.K. ILW encapsulation grouts) is unlikely. This gives confidence in the fact that DBD grouts are likely to be radiologically durable in the short term. However, the CSH phases formed in the U.K. ILW encapsulation grouts are largely amorphous (or at best nanocrystalline), whereas those formed in DBD grouts will be largely crystalline (mostly tobermorite). Little or no work has been performed on the effect of radiation on the crystalline phases formed in DBD grouts. The effect of the total dose should also be considered because the total dose from HLW wasteforms may be of the order of 10 GGy (Ojovan and Lee 2014), which is significantly more than the total exposed dose used in developing the U.K. ILW encapsulation grouts referred to above. Hence, it is recommended that the radiation durability of DBD grouts should undergo a structured testing regime.

Transferable Lessons Learned from the Development of DBD Grouts

Recent research focused on developing DBD grouts has been conducted, with further fundamental work continuing (Collier et al. 2015a, b, 2016, 2017). The work to date has provided information on the performance of DBD grouts which is likely to be of use in geothermal and hydrocarbon well cementing. The principal lessons learned from this work are described below.

Retardation of Grout Thickening

The ability to control grout thickening at elevated temperature and pressure is paramount in operations associated with casing cementation or remedial cementing. If the grout starts to thicken (or ultimately sets) before final placement is completed, major corrective action will be required, which will incur major expense and may significantly delay well production.

In developing grouts for DBD applications our research has demonstrated that

1. Organic materials perform better as retarders of grout thickening than inorganic materials; and
2. The biggest influence over thickening retardation is attributable to the effect of elevated temperature.

Of the organic materials studied in our work, only two types of materials retarded thickening sufficiently over the whole temperature range expected in DBD (90–140°C). Gluconate and carboxylate ether products give the best performance and can retard the time at which grout consistency exceeds 70 Bearden units (Bc) for more than 4 h at temperatures up to 140°C [70 Bc is known as the limit of pumpability for well cement (Nelson and Guillot 2006) and has been taken as the maximum consistency at which DBD grouts can be used (Collier et al. 2016)]. The phosphonate and sulphonate products investigated only give suitable performance up to 90°C. Inorganic compounds of borate, phosphate, zinc, and tin can provide retardation, but only borate retards sufficiently up to 90°C and possibly 120°C (Collier et al. 2017). In all the work performed in establishing these performance data, only the testing temperature was varied, and an ultimate testing pressure of 50 MPa was always used. However, the effect of varying pressure should also be considered.

It is difficult to ascertain the exact mechanism by which thickening is delayed, but by using a variety of techniques to study wet paste properties such as consistency, viscosity, and calorimetry (which measures both the heat evolved during the hydration reactions and the times at which these reactions occur), the effect of retarder addition on paste thickening can start to be understood. It is apparent that the usual cement hydration reactions continue after retardation, and it has been observed that a higher testing temperature results in a higher rate of increase of final thickening. It is also important to replicate the downhole environment as accurately as possible, and consistency testing is the most appropriate technique available to do this. Additionally, once thickening has occurred and the consistency has risen to 100 Bc, all grouts investigated in our work set within 24 h.

Composition will affect grout retardation and thickening, with water content very influential. In our work we have seen that grouts with lower water content are thicker and more viscous, and the time taken to reach 70 Bc is less. Water content is important in DBD because the grouts will be used to seal around the waste containers; a grout with a low water content will produce a hardened paste with less pore space and lower permeability and will produce a better seal. However, there must be sufficient water present to enable mixing, as well as pumping/flow during the deployment process. Similarly, in well cementing, one of the purposes of the grout is to seal across formations, where less mix water will give better sealing performance. Therefore, in both DBD and well cementing, there must be a balance in selecting the grout water content to ensure correct grout mixing and deployment over the desired time period.

Wet Paste Properties during Grout Deployment

Having investigated the deployment of DBD grouts, we have seen that the dispersion of solid particles from the wet paste is influenced by how much of the grout surface is exposed to the borehole fluids. By limiting this exposure, retention of the solids in the paste is better, and paste cohesion is maintained. This is one reason why the primary cementing operation in hydrocarbon and geothermal wells is achievable without significant dispersion of solids from the wet paste. Other cementing/concreting jobs [such as those using tremie pipe equipment (EFFC/DFI 2016), where the end of the pipe through which the paste is pumped is kept beneath the upper surface of the paste] are based on this principal.

In developing our grouts we have identified that there are influences on wet paste properties and grout cohesion that can be controlled by mix design. Using materials such as fluid loss additives, the surface charges on the cement particles can be changed and the chemical interactions between the cement and water can be influenced. This not only influences grout water retention, but also restricts the mixing of external water/fluids into the cement paste. The quantity of mix water present will affect cement paste cohesion; grout with lower water content and less permeability will be more coherent and expose less surface to the local water present.

The effect of any minor additives on wet paste properties should be considered, particularly when also considering the effect of elevated temperature and pressure. Some additives/retarders we have studied cause an increase in grout consistency and viscosity at atmospheric temperature and pressure, which may cause problems during mixing, whereas additives designed to reduce viscosity will allow the quantity of mix water to be reduced (the primary function of plasticizers/superplasticizers). However, when used at elevated temperature, the general effect of the retarders/additives studied in our work is a reduction in plastic viscosity with increasing temperature, particularly with retarded grouts (Collier et al. 2016).

Durability

Grouts used for DBD or well-cementing applications will have different durability requirements. In DBD, the borehole is expected to remain open and unsealed for a period estimated to be up to 2 years (Gibb 2010), so this is the lifetime requirement for the support function of the grout. Over this period, loading of the disposal zone will occur, followed by borehole sealing. Final sealing of the borehole will cause the reformation of groundwater density and salinity stratification characteristics, and the host geology will return to predrilling conditions. Therefore, it is the final borehole seal that is primarily responsible for the overall durability of DBD, and this is of the order of hundreds of thousands or even millions of years (Gibb 2015). However, a cementitious SSM will provide additional sealing around the waste containers, delaying the release of any radioactive waste ions into the near field, thereby augmenting the DBD safety case. The lifetime of a geothermal or hydrocarbon well is of the order of 30 years [although longer time periods are more desirable [Sullivan et al. 2010)], and the cementing job should ideally last for the length of the well's operational life.

Therefore, it is difficult to compare the durability requirements for a DBD grout with those for well cements. The initial requirement in DBD to support waste packages for up to ∼2 years is considerably shorter than the usual working life of a well, so in this aspect the performance of DBD grouts as supporting matrices should be assured. The ability of a DBD grout to provide additional sealing to prolong the lifetime of components in the disposal zone is advantageous in enhancing the safety case, but it is difficult to quantify this influence. However, the chemical and physical conditions to which a geothermal well cement is exposed will be significantly more aggressive than for a DBD grout, so the latter is likely to be significantly more durable.

Grout Composition

Our work has demonstrated that DBD grout thickening time must be retarded, and formulations capable of providing sufficient retardation have been developed and are being optimized (Collier et al. 2016). There is little difference between the grout formulations used in DBD and those ordinarily used in well cementing, and the primary components of each are BS EN/API Class G or H well cement [BS EN ISO 10426-1 (BS EN ISO 2009)] and silica flour. Because of this, the primary hydration products are also very similar. At elevated temperature and pressure, the calcium phases in the cement in both grout systems react with the fine quartz in the silica flour initially to form α-C_2SH [$Ca_2(SiO_4)H_2O$], which then leads to the formation of tobermorite [$Ca_5Si_6(OH)_{18} \cdot 5(H_2O)$] (Nelson and Guillot 2006; Bensted 2008). We have found that the presence of any minor additives, such as retarders, does not influence the phases formed, and the formation of tobermorite ensures the development of the most durable cement hydrate. However, because the quantity of additive required is extremely low (possibly <1% by weight of cement), any influence on the resultant phase composition may be undetectable, as the detection limits of equipment such as X-ray diffraction (XRD) may be as high as 5% by weight.

The use of organic additives in the encapsulation/immobilization of U.K. ILW is discouraged because they might cause complexation of any radionuclides present and increase their solubility. The conditions to which the grout will be exposed in DBD are different from those in either ILW cemented wasteforms or in a geological disposal facility (where the wasteforms are stored in a vault a few hundred meters underground) because

1. The high temperature and pressure down the borehole, and the highly alkaline environment of the cement grout (pH ∼ 12), will quickly cause degradation of any organic compounds present, thereby reducing the influence on radionuclide solubility; and
2. Any release of waste ions as a result of container corrosion will only occur many years after the borehole has been sealed, and because of the geological barrier any radioactive material released will take millions of years to return to the human environment, which would make it radiologically harmless.

Therefore, the use of organic materials in DBD should not be discounted, particularly when they have been shown to provide better performance than inorganic materials.

Many minor additives are used in well cementing and include accelerators, retarders, weight-reducing compounds, fluid loss additives, and dispersants (the latter are also known as superplasticizers) (Nelson and Guillot 2006), and because of this a number of complex chemical and physical interactions can occur between grout components. However, the number of additives used in DBD grouts has been minimized to avoid complications in performance, so there should be less influence on phase composition.

Consideration should be given to the effects of minor chemical additions on paste performance. Use of a fluid loss additive will augment the performance of DBD grouts by retaining mix water during the flow of the paste. Our work has demonstrated that without any type of fluid loss additive, dispersion of solid particles from the paste is likely, will detrimentally affect paste cohesion, and may ultimately cause complete dispersion of the grout. Some well-cementing additives marketed for a specific purpose may also influence paste performance in other ways. For example, a carboxylate ether product assessed in the development of DBD grouts is marketed as a dispersant, but it also delays cement hydration reactions and significantly retards thickening time at high temperature and pressure.

Summary of Principal Lessons Applicable to Well Cementing

In developing cementitious grouts for use in DBD applications, a number of fundamental technical issues have been identified that will be of interest to organizations involved in geothermal energy or hydrocarbon well cementing, as follows:

- The type of retarder used to delay grout thickening is of extreme importance and should be selected based on downhole conditions of temperature, pressure, and local geochemical environment. Temperature is critical because, while some types of retarder perform satisfactorily up to 90°C, they do not work as desired at higher temperatures, suggesting that the mechanism of retardation changes. The choice of retarder should not just be restricted to products marketed specifically for that purpose because a number of materials promoted for other applications may be appropriate. Retarder addition level may vary considerably depending on what other additives are used.
- The temperature at which the grout is deployed has the most influence on wet paste properties such as consistency/thickening, viscosity, and flow, so testing must be conducted appropriately. The ability to mix the grout must also be balanced with producing the desired physical properties of the hardened paste.
- Elevated pressure has less influence over wet and hardened grout properties than temperature.
- The presence of a retarding additive does not influence the phases formed in the hardened grout in the short term. This suggests that the retarders only affect the time at which the cement hydration reactions occur and should not affect durability.
- The geological and geochemical conditions relevant to DBD will be less aggressive than in hydrocarbon or geothermal energy wells and will therefore have less influence on grout durability.
- Even though grout deployment will be different in DBD than in well cementing, the ability to retain the cohesive nature of the wet paste is important in both applications. Therefore, the use of additives to retain grout mix water is advised.

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