The effect of organic retarders on grout thickening and setting during deep borehole disposal of high-level radioactive waste

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ABSTRACT

Deep borehole disposal (DBD) is being increasingly seen as a viable and potentially superior alternative to comparatively shallow mined repository concepts for disposal of some high-level radioactive wastes. We report here details of proof-of-concept investigations into the use of cementitious grouts as sealing/support matrices for use in low temperature DBD scenarios. Using the cementitious grout to fill annular space within the disposal zone will not only support waste packages during placement, but will also provide a low permeability layer around them which will ultimately enhance the safety case for DBD. Grouts based on Class G oil well cement are being developed. The use of retarders to delay the accelerated onset of thickening and setting (caused by the high temperature and pressure in the borehole) is being investigated experimentally. Sodium gluconate and a polycarboxylate additive each provide sufficient retardation over the range 90–140 °C in order to be considered for this application. Phosphonate and sulphonate additives provide desirable retardation at 90 °C. The additives did not affect grout composition at 14 days curing and the phases formed are durable at elevated temperature and pressure.

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1. Introduction

Advantages associated with safety, cost, and ease of implementation, and the ability to drill deeper larger diameter holes (Juhlin and Sandstedt, 1989; Beswick, 2008; Beswick and Forrest, 1982; Exxon Neftegas; Sakhalin-, 2013), means that the use of deep boreholes to dispose of high level radioactive wastes (HLW, including spent nuclear fuel (SF)) is now being increasingly seen as a viable alternative to emplacement in geologically shallow, mined repositories (Chapman and Gibb, 2003; Beswick et al., 2014). The disposal of wastes generated during the production of nuclear energy is of significant importance to the overall nuclear fuel cycle and is currently receiving particular attention around the world. Even though considerable research has been performed in developing waste repositories several hundreds of meters below ground, there is currently no operational facility to provide ultimate waste disposal. Therefore, the development of an alternative more advantageous concept for the disposal of HLW is of particular interest to those involved in the nuclear fuel cycle.

The concept of deep borehole disposal (DBD) of radioactive waste is a multi-barrier approach that places greater emphasis on the performance of geological barriers rather than engineered systems. A large diameter borehole (up to ~0.65 m) is drilled up to 6 km deep into the granitic basement of the continental crust and is subsequently cased (Beswick et al., 2014). Packages of radioactive waste are then emplaced into the bottom 1–2 km of the borehole (the disposal zone) within which they are sealed using materials known as sealing and support matrices (SSMs). These SSMs fill the annular space between the waste packages and the casing, and between the casing and the borehole wall. SSMs provide mechanical support against buckling and damage caused by the load stresses from overlying packages, act as a seal/barrier to the ingress of saline groundwater to the waste container, thus prolonging container life, and provide a barrier to the migration path for any gaseous corrosion products. The borehole itself is then permanently sealed above the disposal zone to the surface.

DBD has significant advantages over disposal in repositories only a few hundred meters deep (such as geological disposal facilities, GDFs) (Gibb, 2010): (i) the safety of the waste is ensured for millions of years due to the isolation provided by the much greater geological barrier, (ii) the boreholes are very deep and waste

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List of acronyms

DBD	Deep Borehole Disposal
HLW	High Level Waste
SF	Spent Fuel
SSM	Sealing and Support Matrix
GDF	Geological Disposal Facility
BWOC	By Weight of Cement
LoI	Loss on Ignition
ASTM	American Society for Testing and Materials
XRD	X-Ray Diffraction
TGA	Thermogravimetric Analysis
DTG	Derivative Thermogravimetric Analysis
DSC	Differential Scanning Calorimeter
LoP	Limit of Pumpability

packages are sealed within a stable geological and hydrogeological barrier, (iii) costs for DBD are estimated to be 20% of those for a GDF per tonne of SF, and (iv) DBD could be implemented approximately 50 years earlier than a GDF for disposal of HLW. The strength of this geological barrier in providing enhanced safety is multi-fold and is based on:

a) The great depth means that the return path to surface for water-borne wastes is an order of magnitude longer.
b) Hydraulic conductivity of the rock at depth is very low.
c) Groundwater density stratification will prevent vertical movement of waste ions and has long-term stability.
d) Isolation from near-surface processes like glaciations is provided.

Building on pioneering work on the disposal of radioactive waste in deep boreholes over the past 25 years ((Gibb et al., 2008), and references therein) the DBD Research Group at The University of Sheffield in the UK is now investigating the use of cementitious grouts as SSMs for emplaced waste packages. These grouts are for use in disposals where temperatures at the surfaces of the packages are below ~190 °C (Beswick et al., 2014). Above this temperature other types of SSMs can be employed (Gibb et al., 2008). The presence of a cement grout around the packages could also help to retard radionuclide migration when the container does eventually fail.

Cementation using specially designed Portland cement grouts is most commonly used within a hydrocarbon or geothermal well to secure the casing after drilling, and to provide a degree of separation between the different fluid chemistries and rock formations through which the borehole passes (Taylor, 1997; Nelson and Guillot, 2006). Because of both the depth and the decay heat from the radioactive waste packages, the temperature reached in the DBD application is similar to the cementing jobs in some hydrocarbon and many geothermal well applications, so the experience of cementing oil and geothermal wells is of benefit to the application to dispose of specific radioactive wasteforms.

Challenges are associated with down-hole cementing operations created by the elevated temperatures and pressures at the bottom of the boreholes. These high temperature and pressure conditions are due to (i) the local geological environment where ambient temperatures in the continental crust would be in the range of 80–130° C for the depths being considered for DBD (Best, 2003), and (ii) the hydrostatic pressure caused by the head of borehole fluid present. Grout deployment should be within a few

hours of package placement so the radioactive decay heat from that package will not have built up significantly during placement and setting (Gibb et al., 2012). Exposure to these adverse conditions affects the properties of a cementitious grout, giving rise to a reduction in thickening and setting time (Scherer et al., 2010; Jupe et al., 2008) in the fresh state before setting, and after setting and hardening when different crystalline products are formed. Elevated temperature and pressure accelerate the hydration reactions in a cement grout reducing the time to thicken and set (Taylor, 1997; Nelson and Guillot, 2006; Bensted et al., 2008; Shariar and Nehdi, 2012; Zhang et al., 2010). Elevated temperature has a greater influence than elevated pressure over how quickly cement hydration reactions occur (Nelson and Guillot, 2006; Scherer et al., 2010; Jupe et al., 2008). It will also have a greater effect on the composition of the main cement hydrate phases formed (Taylor, 1997; Nelson and Guillot, 2006). 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.

The work presented here reports on Portland cement-based grouting systems that are being developed for DBD cementing operations. A proof-of-concept study has been undertaken, and the influence of a range of additives on grout performance has been assessed. Rheological properties and setting characteristics of fresh grouts have been studied at elevated temperature and pressure, and the early age phase composition has been investigated to confirm the formation of desirable hydrated phases. Four different organic additives were chosen to study the influence on grout thickening/setting properties under conditions representative of those found in deep boreholes. Two of these additives are marketed as retarders and two as superplasticisers or dispersants. The latter have been chosen because superplasticisers restrict chemical reaction between cement particles and mix water, and in doing so may also cause retardation of thickening and setting. Even though the presence of organic compounds will complex any radionuclides and increase their solubility, the release of any waste ions as a result of container corrosion will only occur many years after the borehole has been sealed; this creates a geological barrier where any release of radioactive material will take millions of years to return to the human environment making it radiologically harmless. The results obtained in this study have been used to assess the applicability of using cementitious grouts in this DBD application.

2. Materials and methods

A Class G oil well cement (BS EN ISO, 2009) partially replaced with silica flour was used to make the grout. The cement was supplied by Holcim and was manufactured to BS EN ISO 10426-1/ API Spec 10A, and the silica flour was supplied by Sibelco Ltd (Unimin Silica Flour 350G). Detailed information concerning the oxide composition of the cement and silica flour, the phase composition of the cement, and the particle size characteristics of both powders is given in Tables 1–3 respectively. To enable the grout to flow through water without dispersion, an underwater additive (UCS Pak) supplied by Sika Ltd was used which is reported to contain silica and organic compounds. The products assessed that were marketed as retarders were sodium gluconate and Sika Retarder (a proprietary phosphonate product), whereas those marketed as superplasticisers were Viscocrete 3110 (an aqueous solution of polycarboxylate co-polymers supplied by Sika Ltd) and CD-33L (a sulphonated organic polymer supplied by Baker Hughes). Hereafter, all four additives are referred to as retarders. Each retarder was added to the grout mix water (tap water) by weight of cement (BWOC) prior to the addition of the pre-blended powders. The density of the grout (excluding any retarder) was 1.892 kg/m³.

Grout consistency was determined using a high pressure, high

Table 1
Oxide composition of Class G cement and silica flour.

Oxide	Compositional content (wt%)	
	Class G cement	Silica flour
SiO_2	21.19	98.56
Al_2O_3	3.80	0.27
Fe_2O_3	5.34	0.01
MnO	0.05	0.01
MgO	1.82	0.03
CaO	63.18	0.02
Na_2O	0.07	0.07
K_2O	0.47	0.03
TiO_2	0.95	0.11
P_2O_5	0.07	<0.01
SO_3	2.08	<0.01
LoI*	0.89	0.16
Total	99.91	99.27

Notes. * — Loss on Ignition (ASTMD7348-13).

Table 2
Cement phase composition of Class G cement.

Cement phase*	Phase content (wt%)
C_3S	55.11
β-C_2S	19.18
C_3A	1.03
C_4AF	16.25

Notes. * — calculated from ASTM C150 (ASTM C150/C150M), and using cement chemist nomenclature where $C = CaO$, $S = SiO_2$, $A = Al_2O_3$ and $F = Fe_2O_3$.

Table 3
Physical characteristics of powder particles.

Powder	Particle diameter (µm)				
	Median	Mode	10th Percentile	50th Percentile	90th Percentile
Class G Cement	16.569	25.332	2.726	16.569	43.554
Silica Flour	16.951	25.332	2.018	16.951	55.958

rates (~5–1000 s^{-1}). A qualitative assessment of particle dispersion for each grout mix in water was investigated by pouring a stream of freshly mixed grout into a beaker of water held at approximately 63 °C, and observing any particle dispersion.

Early age composition was investigated by casting samples of each grout and hydrothermally curing them under water in sealed containers at 120 °C for 3, 7 and 14 days. After each time interval, hydration was arrested using a solvent replacement technique (Collier et al., 2008) and the composition determined by X-ray diffraction (XRD) and thermogravimetric analysis/derivative thermogravimetric analysis (TGA/DTG). The Philips PW1729 X-Ray diffractometer used a Cu Kα radiation source and was operated between 4 and 80° 2θ at 3°/min and the Alphatech SDT Q600 combined TGA/Differential Scanning Calorimeter (DSC) analyzer was operated between 0 and 1000 °C at 10 °C/min with a nitrogen atmosphere.

3. Results

3.1. Grout thickening and setting

The objective of this part of the study was to determine the retarder addition levels required to give t_2 greater than 4 h. Grout consistency is a function of viscosity (BS EN ISO, 2009), but in this investigation it was used simply to determine the retardation effect of the additives. Consistency plots for grouts containing either sodium gluconate or CD-33L are shown in Fig. 1, with the data from all tests summarized graphically in Fig. 2. Upper addition levels for all

temperature, consistometer (Cement Testing Equipment 40–600 HTHP Consistometer) operating at 90, 120 and 140 °C and 50 MPa with a linear 4 h heating/pressurizing regime, after which time the testing temperature and pressure were maintained until the sample consistency exceeded the upper limit of measurement. The times at which changes in consistency occurred were recorded; t_1 was the time at which minimum consistency occurred and t_2 was the time for consistency to reach 70 Bearden units (Bc), the limit of pumpability (LoP) accepted in well cementing applications (Nelson and Guillot, 2006). This value has been taken as the maximum consistency at which a grout will flow around a waste package located at the bottom of a borehole. Drilling engineers are confident that grout could be delivered to the bottom of a borehole approximately 5 km deep in under 4 h, so this was taken as the minimum delay required to reach a consistency of 70 Bc (t_2), although options for faster delivery times are being explored. For each grout where t_2 was greater than 4 h, initial and final set were checked 24 h after mixing using manual Vicat testing equipment (ASTMC191-13). Cement hydration reactions were investigated using an isothermal calorimeter set at 120 °C and flow characteristics were investigated at room temperature (22 °C) and pressure (1 atm) using a modified ASTM flow cone test (ASTMC939-10) recording the time to flow through the testing cone. Once the amounts of retarders that gave acceptable levels of grout consistency had been determined, viscosity was obtained using an Ofite 900 Viscometer operating at temperatures of 22, 45 and 70 °C and at a range of different shear

the proprietary products were based on the manufacturer's recommendations. While carrying out tests at lower temperatures if it became apparent that successful retardation would not be achieved at higher temperatures, testing at the higher temperatures was not undertaken.

As shown in Fig. 1, the progression of consistency for each grout was similar, increasing over the first 10 min of testing (when the temperature was between 20 and 25 °C); this increase is most likely due to the gelling effect of the organic retarders. Following this early thickening, the consistency of all grouts, apart from those without retarders or those made with CD-33L, decreased with increasing time and temperature towards zero Bc (which equates to a torque of 0.00782 Nm, and indicates a very low viscosity, virtually at the limit of measurable consistency for the equipment, hence the flat-lining of the trace for the sample containing 0.75% sodium gluconate). Towards the end of the testing period, the consistency of each grout rapidly increased towards 100 Bc at which point the test was halted.

As expected, t_2 for the control grout (without retarder) was reached in less than 4 h, confirming the need for retardation. Fig. 2 shows that, to achieve a t_2 greater than 4 h at 90, 120 and 140 °C, sodium gluconate addition levels of at least 0.05, 0.25 and 0.25% BWOC respectively were required. Considerably more Viscocrete 3110 was required to achieve a t_2 greater than 4 h, with at least 0.75, 1.0 and 2.0% BWOC additions needed at the same testing temperatures respectively. With Sika Retarder, only the grout tested at
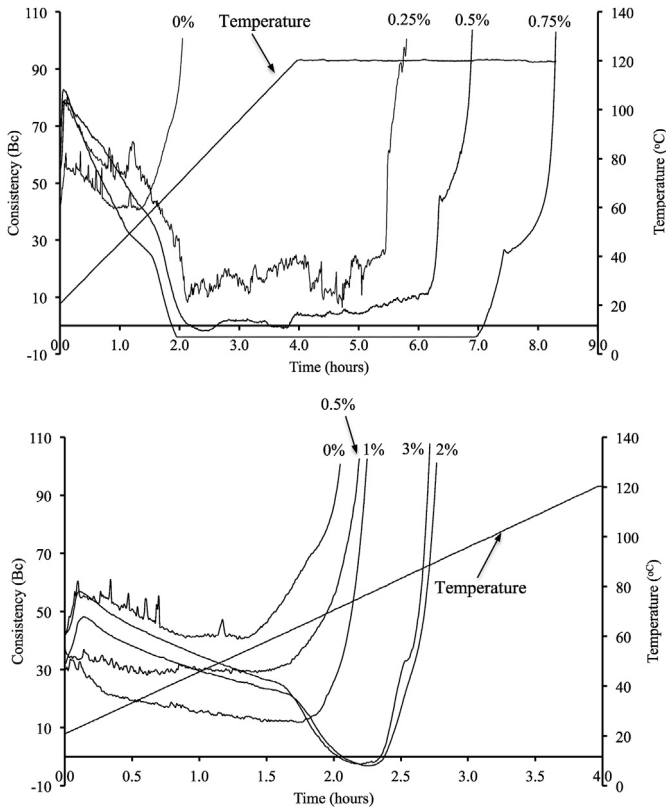
Fig. 1. Comparison of consistency results for grouts containing sodium gluconate (top) (Collier et al., 2015a) and CD-33L (bottom) at 120 °C.
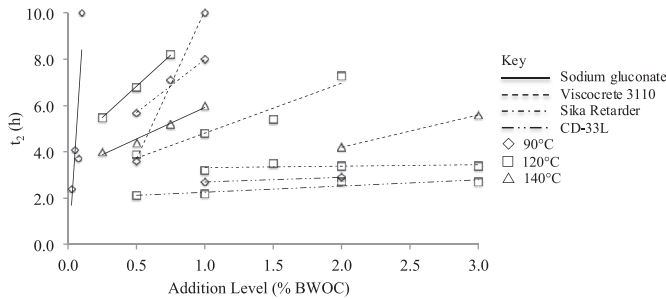

Fig. 2. Changes in t_2 times plotted for all grouts. Notes. t_2 was the time for consistency to reach 70 Bc. Linear trend lines have been added as a visual guide only.

90 °C with an addition of ≥0.5% BWOC gave a t_2 greater than 4 h and it was not possible to produce sufficient retardation at 120 °C with the maximum recommended addition. It was also not possible to produce a grout containing CD-33L where t_2 was greater than 4 h at 90 or 120 °C.

In all grouts where t_2 was greater than 4 h, final set had occurred within 24 h, providing confidence that waste package deployment rates of the order of one a day could be achievable.

3.2. Heat flow during grout thickening and setting

Calorimetry curves for grouts containing sodium gluconate and CD-33L are shown in Fig. 3 with all heat flow events summarized in Table 4. Because the samples were mixed externally to the calorimeter, any heat flow events that occurred before the samples reached thermal equilibrium within the calorimeter were not
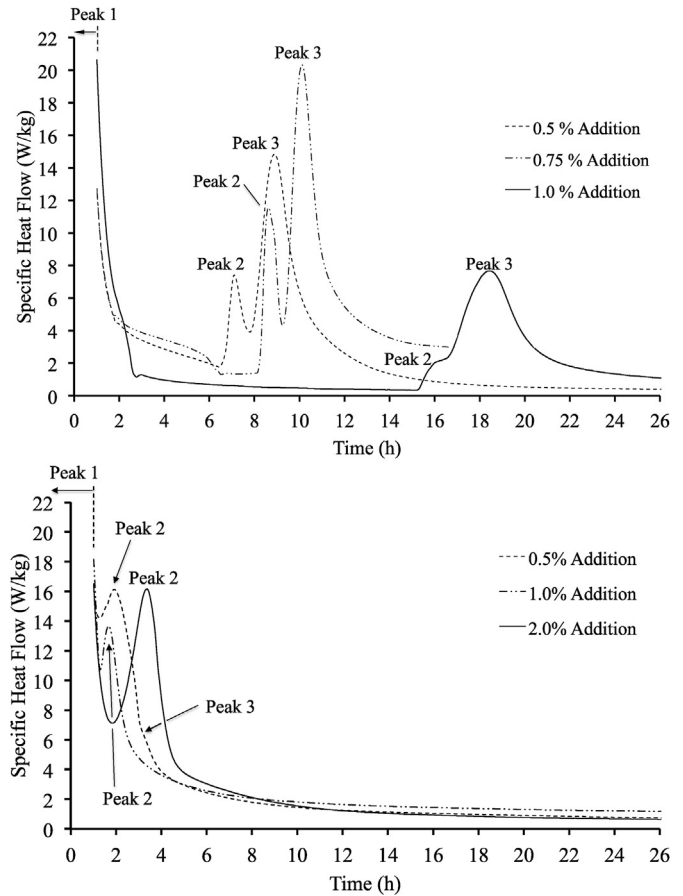

Fig. 3. Calorimetry results for grouts containing sodium gluconate (top) and CD-33L (bottom) at 120 °C.

recorded (time zero was when the grouts were placed in the calorimeter immediately after mixing). The quantity of each retarder used in these tests was based on the consistency results previously obtained.

Increasing the amounts of retarder added changed the heat generation characteristics of the grout, especially for the samples containing sodium gluconate. It is difficult to identify any consistent trend in the magnitude of the specific heat flow peaks for each grout in relation to retarder addition level, but as this amount increased, the times at which the heat flow events occurred also increased, particularly when using sodium gluconate.

Three specific heat flow maxima (labeled peaks 1, 2 and 3) were identified for all grouts although peak 3 often merged with peak 2. Peak 1 always occurred at around 1 h, before the sample had reached thermal equilibrium. This peak has been ascribed to the very early hydration reactions between the cement and water or wetting of the cement powder (Taylor, 1997). Sodium gluconate was the most effective retarder for both peaks 2 and 3 with retardation times from 7.0 to 15.6 h for peak 2 and 9.0–18.3 h for peak 3. This compares with 1.6–3.2 h and 3.1–7.0 h for peaks 2 and 3 respectively for the other retarders. Also significantly less sodium gluconate was needed than any of the other retarders.

Several of the calorimeter traces showed marked differences when addition levels were increased. For example, in the trace for the grout containing 1.0% sodium gluconate, peaks 2 and 3 were significantly smaller than at lower addition levels, and the times at which they occurred were much later than at lower levels. Additionally, no peak 3 heat events could be identified for either of the

Table 4
Summary of calorimetry data.

Retarder	Heat flow peaks	Magnitude and time of heat flow events (W/kg) (h)					
		Addition level (% BWOC*)					
		0.5%		0.75%		1.0%	
Sodium Gluconate	Peak 1	>12.5	<1.0	>12.5	<1.0	>20.6	<1.0
	Peak 2	7.0	7.0	11.2	8.6	1.4	15.6
	Peak 3	14.6	9.0	19.9	10.0	7.6	8.3
		Addition Level (% BWOC*)					
		0.5%		1.0%		2.0%	
Sika Retarder	Peak 1	>9.8	<1.0	17.9	1.1	>9.8	<1.0
	Peak 2	13.4	2.9	16.0	3.1	7.2	2.6
	Peak 3	4.4	5.6	3.8	7.0	16.2	4.9
Viscocrete 3110	Peak 1	>20.1	<1.0	>15.5	<1.0	>18.1	<1.0
	Peak 2	13.9	1.6	18.4	2.1	14.8	2.6
	Peak 3	3.9	3.4	5.1	3.9	5.1	4.1
CD-33L	Peak 1	>14.4	<1.0	>18.1	<1.0	>16.5	<1.0
	Peak 2	16.0	1.8	13.5	1.6	15.7	3.2
	Peak 3	6.7	3.1	**	**		

Notes. * — By Weight of Cement. ** — it was not possible to identify this heat event.

1.0 and 2.0% CD-33L samples, and only a hint of a peak 3 heat event could be identified in the sample containing 0.5% CD-33L.

3.3. Grout rheology

Fig. 4 shows the results of the flow cone tests. The flow time of the grout containing Sika Retarder increases with increasing addition level up to ~0.75% after which is decreases. For sodium gluconate, Viscocrete 3110 and CD-33L additions, the results show a decrease in flow time with increasing addition levels with the exception that for sodium gluconate additions beyond 0.6% BWOC there is an increase in flow time.

These results demonstrate the potential for reducing the water content in all grouts except for those containing Sika Retarder. Reducing the quantity of mix water in any grout will produce a less permeable matrix when hardened, which would provide better sealing of waste packages in a borehole against the ingress of saline groundwater.

A summary of the viscosity results for all grouts is shown in Fig. 5, which displays viscosity at each testing temperature when measured using a shear rate of 5.1 s^{-1}. This low shear rate was used to replicate the low shear experienced by the grouts after deployment in the borehole without any additional pressure applied by
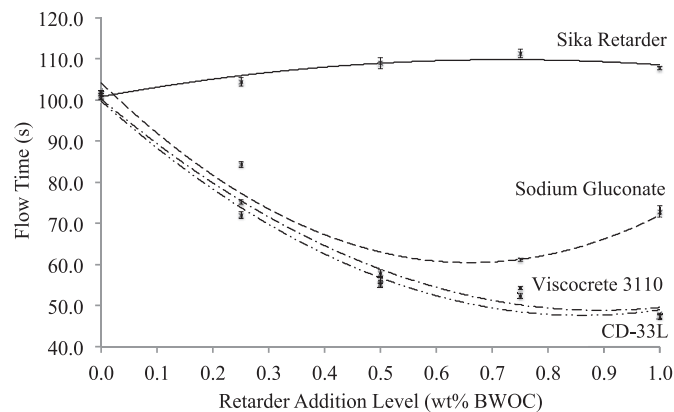
Fig. 5. Grout viscosity results measured using a shear rate of 5.1 s^{-1}. Notes. Addition levels used were 1.0% Sika Retarder, 0.5% sodium gluconate, 1.0% Viscocrete 3110 and 1.0% CD-33L, all BWOC.

pumping.

The results show that at 22 °C, the viscosity of the grout containing either Sika Retarder or sodium gluconate is significantly higher than that of the control. The viscosity of the Viscocrete 3110 grout was similar to that of the control, while the viscosity of the CD-33L grout is lower. Increasing the testing temperature to 45 °C reduced the viscosities of all the retarded grouts to less than that of the control, particularly for the mixes containing Viscocrete 3110 or CD-33L. At the highest testing temperature (70 °C) the viscosities of all retarded grouts were very similar and were all significantly lower than the control, approximately 30 cP compared to approximately 70 cP respectively. The effect of temperature on the control grout was different to those containing Sika Retarder, sodium gluconate and Viscocrete 3110, but was similar to that containing CD-33L grout although no meaningful trend could be identified in terms of the effect of temperature on the viscosities of the control and CD-33L grouts. It should be noted that the flow results obtained when testing at room temperature are not always consistent with the viscosity results. A reduction in flow time, which should correlate with a reduction in viscosity, was not always observed when using a retarder, as with the flow and viscosity results measured at room temperature for the samples containing Sika Retarder, sodium gluconate and to a lesser degree Viscocrete 3110

Fig. 4. Grout flow test results. Notes. The curves represent polynomial fits to the data, added as a visual guide only. Previously published data for Viscocrete 3110 and CD-33L (Collier et al., 2015b) are displayed here for comparative purposes.
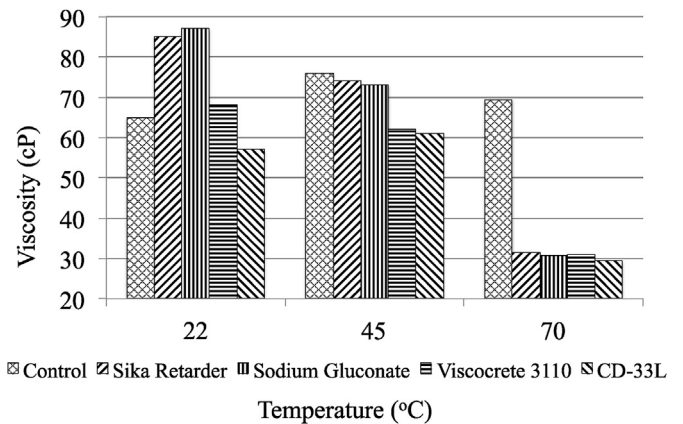
(this anomaly is not observed at elevated temperature). This may be due to the differences in shear stresses applied to the grouts during the testing processes; the level of shear applied in the viscosity testing may be greater than that in the flow testing where the shear applied in the latter test only results from the gravitational flow of the grout itself. This suggests that the grouts exhibit shear thickening (rheopectic) characteristics.

Any grout with t_2 consistency time greater than 4 h was poured through water held at 63 °C and its dispersion observed. Generally all the grouts flowed freely through the water with only a small amount of particle dispersion. Any particles that did disperse soon came to rest on the top surface of the settled grout.

3.4. Phase composition of hardened cement paste

The waste packages will be located in the lower 1–2 km of the boreholes (the disposal zone) and, having sealed the borehole above the disposal zone, any radionuclides released will take a very long time, depending on the route of migration, to return to the biosphere (of the order of a million years or more (Chapman and Gibb, 2003; Brady et al., 2009)). Consequently, the use of SSMs to seal individual waste packages within the disposal zone is not absolutely essential. However, any sealing of the packages which prolongs the life of the containers, and hence the primary containment, as well as restricting the migration path of any gaseous corrosion products, will be advantageous when making the safety case for the overall DBD process. This can be achieved by designing the grouting system to form stable and durable cement hydrate phases at the elevated temperatures.

Example XRD diffractograms and TGA/DTG traces for grout samples containing sodium gluconate are shown in Figs. 6 and 7 respectively.

The main crystalline phase identified in all samples was quartz (SiO_2) from the unreacted silica flour. Two crystalline calcium silicate hydrates were identified by XRD, α-C_2SH ($Ca_2(SiO_4)H_2O$) and Tobermorite-11 Å ($Ca_5Si_6(OH)_{18}.5(H_2O)$), along with an amorphous material, usually referred to as C–S–H (Taylor, 1997), which was responsible for a "hump" centered at approximately 37° 2θ in all XRD traces. While crystalline portlandite ($Ca(OH)_2$) was not detected by XRD, the TGA/DTG results identified a loss centered at approximately 450 °C in all samples suggesting it is amorphous (Midgely, 1979), and this phase will carbonate as evidenced by the detection of calcite by TGA/DTG. A small quantity of unreacted brownmillerite (Ca_2FeAlO_5) was detected in each sample. The same phases were identified in each sample type, which suggests that

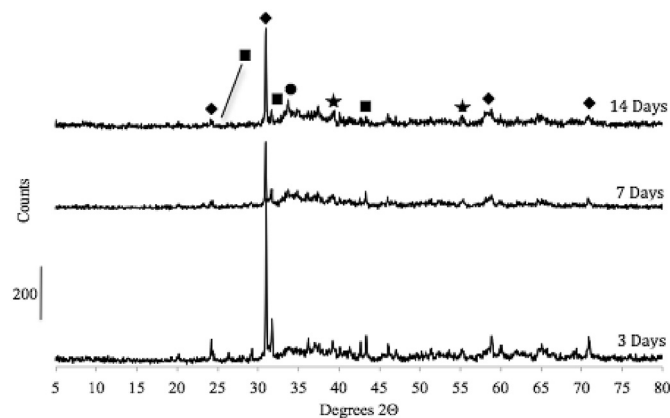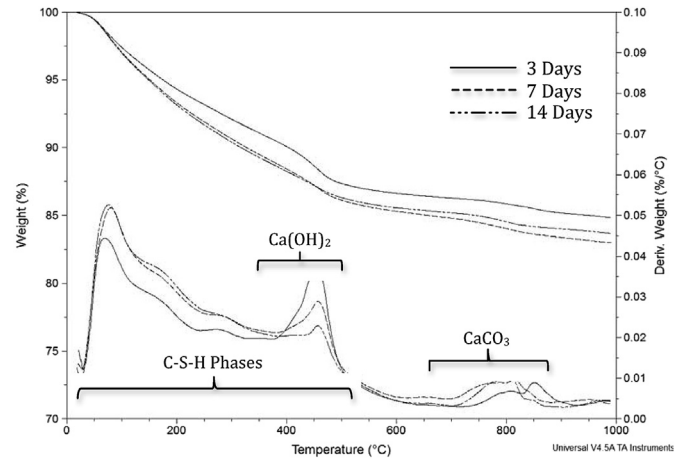**Fig. 7.** TGA/DTG traces for samples containing sodium gluconate.

none of the retarders influenced composition when added at the addition levels used here. Although not displayed here, there was no discernable difference in the compositions of the hardened cement pastes due to the presence of any quantity of each of the retarders. For each grout, the intensity of the quartz XRD reflections reduced slightly between 3 and 7 days suggesting the quartz had reacted slowly with time. α-C_2SH was identified in all samples cured for 3 and 7 days with the intensities of its main reflections reducing with time making detection after 14 days difficult. Tobermorite-11 Å was not detected in any sample after 3 days curing, but small XRD reflections were identified in all samples cured for 7 and 14 days (one of the strongest reflections for this phase at 9.2° 2θ was difficult to identify, but the other main reflections were identified). The quantities of the crystalline calcium silicate hydrate phases increased with time whilst the amount of portlandite decreased. These progressive phase changes follow those suggested in the literature with (1) quartz reacting slowly with calcium hydroxide to form calcium silicate hydrate phases, (2) the early formation of α-C_2SH, the quantity of which gradually reduces with time, and (3) the formation of tobermorite-11 Å following the decline of α-C_2SH (Nelson and Guillot, 2006; Bensted et al., 2008). Although not presented here, TGA/DTG data showed that the quantities of the calcium silicate hydrate phases in samples containing any of the retarders were less than those formed in the control samples.

The phases formed in the hardened grouts after 14 days hydrothermal curing show no effect due to the presence of any retarder, and are typical of those found in oil and geothermal well cementing applications, which suggests a high level of durability for the grouting system.

4. Discussion

4.1. Influence on paste properties

Temperature has a significant influence on the progression of consistency with time, with increasing temperature accelerating the onset of grout thickening in line with published results (Shariar and Nehdi, 2012; Zhang et al., 2010). Elevated pressure also accelerates grouts thickening, but not as significantly as elevated temperature (Scherer et al., 2010). How the grout will be placed in the borehole will require investigation, and should include assessment of whether cooling or agitation during deployment may be required.

The consistency and setting data obtained from this work

Fig. 6. XRD diffractograms for samples containing sodium gluconate. Notes. ◆ – quartz (SiO_2); ■ – α-C_2SH ($Ca_2(SiO_4)H_2O$); ● – tobermorite-11 Å ($Ca_5Si_6(OH)_{18}.5(H_2O)$); ★ – brownmillerite ($Ca_2FeAlO_5$).

demonstrates that cementitious grout formulations not too dissimilar to those used in oil well and geothermal well applications could be suitable for DBD. All of the retarders studied were able to delay the onset of thickening and setting, with sodium gluconate having the greatest influence. However, only sodium gluconate and Viscocrete 3110 appear to provide the level of retardation required for the DBD process up to 140 °C when addition levels similar to those recommended by the manufacturers were used. While Sika Retarder and CD-33L did not delay the onset of thickening enough for the DBD application, their use as plasticizers should not be discounted if they were used in combination with another retarder.

The torque required to stir the wet cementitious paste (which is measured during the consistency testing process) is directly related to consistency by a mathematical relationship described in BS EN ISO 10426 (BS EN ISO, 2009). We intend to exploit this relationship and extract other paste properties such as viscosity and yield stress in further work.

Although both the consistency and calorimetry data indicate that all four additives retard grout thickening time, it is difficult to correlate the two results because the experimental operating conditions are different; similar difficulties have been reported by other workers (Jupe et al., 2008). Consistency testing best replicates the DBD application of the fresh grout because the heating rate from room to test temperature, and the resultant increase in testing pressure, can be used to represent the change in temperature and pressure on the grout as it travels down the borehole before encapsulating the waste package.

The flow data for the grouts obtained at room temperature are useful in comparing the influence of retarder type, but ideally these data need to be obtained and compared at temperatures and pressures representative of those down the borehole. Additionally, the overall sealing of waste containers should be confirmed at temperatures and pressures representative of those in an actual disposal. The applicability of setting the LoP (70 Bc) as the limit in DBD for the ability of the grout to flow around waste containers can also only be assessed by carrying out waste encapsulation tests in conditions representative of those down a borehole.

The method of grout mixing, which is likely to take place at the wellhead, also requires investigation. Although the major oil well cement testing standard (BS EN ISO, 2009) stipulates that any grout testing should be performed using vertical mixers similar to that used here, the most common mixing systems used in the field for oil and geothermal well cementing applications are based on a jet mixing process where pressurized water is combined with cement powder to form a slurry (Nelson and Guillot, 2006). Assessment of the potential for using this type of jet mixing process, or any other type of process, in DBD and its subsequent effect on grout rheology, will be required. This is likely to be complex because of the differences in grout rheology during mixing (at atmospheric temperature and pressure) and during deployment in the borehole, and will need to be conducted at high temperature and pressure.

To provide a good seal for the waste packages against groundwater ingress, low permeability of the hardened grout will be required which means that a low grout water content and use of a superplasticiser may be necessary. However, this will also be governed by the ability to mix the grout under atmospheric conditions at the wellhead.

Further work is required to evaluate how the grout should be mixed and deployed, how readily it will encapsulate and seal waste packages down the borehole, and what its long-term durability will be in the DBD process. Because of issues associated with the difficulty of testing at high temperature and pressure, it is likely that small-scale trials of grout deployment and waste package encapsulation will be needed to fully investigate applicability.

4.2. Applicability to DBD

The results generated in this study demonstrate that the cementitious grout being developed can be used to encapsulate containers of HLW when located in the disposal zone. The grout will remain sufficiently fluid to flow around emplaced waste packages, will set within the desired time, and the cement hydrate phases formed will have high durability similar to those formed in hydrocarbon and geothermal well cementing applications.

Various DBD concepts are being developed internationally (Beswick et al., 2014; Brady et al., 2009), and some of these utilize materials based on well drilling fluids (mixtures of water and bentonite) to fill the annuli in the waste package disposal zone, but this use of such fluids provides very little package support and provides no barrier to corrosion or gas migration (Brady et al., 2009). By contrast, using a cementitious grout to fill these annuli has several advantages: 1) the waste packages will be physically supported during the disposal zone loading process which will prevent/reduce container buckling and reduce the subsequent risk of container breaching, 2) the hardened grout will provide a low permeability layer around individual waste packages restricting/limiting ingress by groundwater and delaying corrosion of the container, 3) the hardened grout will restrict the movement of any gases produced as a consequence of container corrosion when it does occur, and 4) cement hydrates have the potential to immobilize many waste ions (Gougar et al., 1996) by surface adsorption or lattice incorporation that may eventually be released from the waste packages.

The strength of the geological barrier in the DBD concept is multi-fold and is based on the provision of a longer waste ion return path due to the great depth of the borehole, the low hydraulic conductivity of the rock at depth, the groundwater density stratification and its long-term stability, and the isolation of the waste packages from near-surface processes like glaciations. The work presented here demonstrates that the cement grouts being developed can be used as SSMs to fill annuli in the disposal zone, which will add to near-field safety, augment the overall far-field geological barrier, and thereby enhance the overall safety provided by DBD.

5. Conclusions

The following specific conclusions can be drawn from this work:

- Sodium gluconate and Viscocrete 3110 offer the potential to provide the amount of retardation required for use in DBD and also increase fluidity. The quantity of sodium gluconate required to be added to the grout to ensure it retains the desired fluidity for 4 h at 90, 120 and 140 °C are 0.05, 0.25 and 0.25% BWOC respectively. Similarly, 0.75, 1.0 and 2.0% additions BWOC of Viscocrete 3110 are required to ensure sufficient fluidity for 4 h at 90, 120 and 140 °C respectively. At the addition levels recommended by the manufacturer, Sika Retarder only provides the desirable retardation properties at 90 °C and has little influence on fluidity. CD-33L increases grout fluidity and retards consistency, but the amount of retardation is insufficient for DBD applications at the addition levels recommended by the manufacturer.
- The phase composition of the hardened cement paste after 14 days hydrothermal curing is not affected when compared to the retarder-free control grout. All phases present in the hardened cement pastes are in line with those reported in the literature and have demonstrated durability at temperatures and pressures similar to those in the DBD application.
- In all grouts where retardation was greater than 4 h, final set is achieved within 24 h.

This work demonstrates that cementitious grouts similar to those used in oil well and geothermal well applications, where the onset of grout thickening and setting can be delayed for the required time period, would be suitable for application as SSMs in DBD up to temperatures of 140 °C. Using the grouts to fill annular space within the disposal zone will not only support waste packages during placement, but will also provide a low permeability layer around the packages which will ultimately enhance the safety case for disposing of high-level radioactive waste using this DBD concept.

Acknowledgments

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