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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.

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/m^3.

Grout consistency was determined using a high pressure, high