

Review

A Review of Potential Cementing Systems for Sealing and Support Matrices in Deep Borehole Disposal of Radioactive Waste

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Abstract: Cementitious grouts are being developed for use as sealing and support matrices (SSMs) in deep borehole disposal (DBD) where temperatures do not exceed 190 °C. They will seal radioactive waste containers into the bottom 2 km of holes drilled up to 5 km deep into the crystalline basement. The temperature and pressure is likely to be similar to those in hydrocarbon and geothermal energy wells, where grout placement and durability are affected. This paper reviews the potential cementing systems suitable for this application and explains why a single solution of a formulation of Class G oil well cement, silica flour, water, fluid loss additive, and retarding admixture has been selected. This type of formulation has been used extensively for over 100 years in well cementing. It should provide the short-term performance and durability required for an SSM, maintaining the seal around the waste packages within the disposal zone long after the boreholes are sealed back to the surface, and thus augmenting the safety case for DBD.

Keywords: deep bore hole disposal; nuclear waste disposal; cementing systems for waste disposal

1. Introduction

Deep borehole disposal (DBD) of high-level radioactive waste (HLW, including spent nuclear fuel) is now seen as a viable alternative to the use of mined repositories located only a few hundreds of meters deep [1–7]. The DBD Research Group at The University of Sheffield in the UK has been pioneering the development of DBD for more than 25 years ([8] and references therein). It is envisaged waste packages will be placed and sealed into the bottom of a 5 km deep borehole drilled into basement granitic rock (called the disposal zone) [4,9–12]. This has significant advantages over a shallow mined repository, which include safety, cost, and ease of implementation [13,14]. The concept is now receiving considerable attention worldwide. [3,15].

A key component of the Sheffield DBD concept is the use of a sealing and supporting matrix (SSM) in the disposal zone which provides two principal functions, both of which will augment the DBD safety case:

- (i) The provision of a seal/barrier preventing the ingress of saline groundwater to the waste container, thus prolonging the container life and delaying the release of any radionuclides into the near field.
- (ii) The provision of mechanical support to protect the container against buckling and damage caused by the load from overlying packages, which could breach the waste container and subsequently release radionuclides before the borehole is finally sealed.

By using a perforated casing in the disposal zone, any SSM deployed around the waste containers would also flow through the perforations and fill the annulus between the casing and the borehole wall. After hardening, the cement would not only fix the casing to the borehole wall but also provide a seal around the waste containers. The preferred SSM is a high-density support matrix (HDSM) of a eutectic lead-based alloy melting at 183 °C at 0.1 MPa pressure, but which melts slightly higher than this at 50 MPa [8]. For waste packages, where insufficient radiological heat is generated to melt the HDSM [16], cementitious grouts are proposed, and possible formulations have been developed by the group at Sheffield [17,18].

This paper reviews potential cementing systems that may be appropriate for use in DBD. The most likely systems have been identified and their properties and most important technical issues in their use assessed and discussed. The details and justification for the selection of a Portland cement system are explained.

2. Requirements of Candidate Cements

For a cementitious SSM, the following points need to be considered:

- The cement slurry must be capable of being placed in the disposal zone where the temperature and pressure during deployment at 5 km deep will be around 120 °C and 50 MPa. Once the slurry has hardened, the radiogenic heating may increase the temperature to around 190 °C.
- It has been anticipated that it will take around 4 hours to lower and place each of the waste canisters using coiled tubing [4], so retardation of the thickening time of any cement slurry will be needed for at least this long.
- Conditions within the disposal zone will be such that the cement slurry must be placed, set, and be durable as a hardened grout in saturated brine groundwater.

While several cementing systems have been developed over the past 30 years as alternatives to Portland cement, their usage in well cementing has been minimal. Table 1 lists possible cements which could be considered as SSMs for deep borehole disposal of nuclear waste.

Table 1. Potential cementing systems.

Cement Type	Binder	Use in Wells
Portland oil well cement	Calcium silicate hydrate	Used extensively
CSA cement	Ettringite/CSH	No evidence
Alkali Activated systems	Metal aluminosilicate	Claimed suitable but no practical use
Calcium Aluminates cement	Calcium aluminate hydrate	Used as P modified cement. No reports on field durability.
Phosphate cement	Metal phosphate hydrate	Claimed but not used
Pozzolan cement	CSH	Minor use

3. Cement Types

3.1. Portland Cement

Portland oil well cements are commonly used in hydrocarbon and geothermal wells to secure the borehole casing to the formation after drilling, and to provide separation between the different fluid chemistries and rock formations through which boreholes pass. They have been successfully used in deep well applications for more than 100 years [19,20]. While the local geology in the DBD disposal zone is likely to be different to that sought for hydrocarbon and geothermal energy wells, both the borehole depth and the radioactive waste package decay heat mean that the temperatures and pressures an SSM will encounter will be similar to those encountered in these well applications, so the experience gained in cementing hydrocarbon and geothermal energy wells will be valuable in developing grouts for DBD.

The compositions of oil well cements are regulated in the UK and Europe by BS EN ISO 10426-1:2009 [21], and in the USA by American Petroleum Institute (API) Spec 10A [22].

Like construction cements, they contain two calcium silicates, tricalcium silicate (C_3S ; $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$ and $H = H_2O$) and dicalcium silicate (βC_2S , also known as belite), which, upon hydration, form the main binders along with calcium aluminate (C_3A) and calcium aluminoferrite (C_4AF). Both elevated temperature and pressure in deep wells accelerates the cement hydration reactions [23–27], so oil well cements are generally coarsely ground to reduce the surface area and prolong setting. They also contain lower amounts of the fast reacting C_3A than construction cements, which provides a degree of sulphate resistance, preventing the formation of expansive ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26H_2O$) after setting, damaging the hardened binder. API lists eight classes of cement from A to H, designed for different depths and temperatures [22]. As deeper wells are now being drilled and the temperature at which cementing is conducted is increasing, advanced retarders are needed. Class G and H cements have become the most popular products used in hydrocarbon and geothermal energy well cementing. Both are manufactured without additives, such as grinding aids, that can detrimentally affect the performance of retarding agents.

The high temperature and pressure in deep wells influence the properties of a Portland cement grout in several ways:

- 1) Thickening and setting times of the cement slurry are accelerated and retarders are required, which has a significant impact on engineering operations and cost. The performance of retarders can vary widely with temperature and pressure.
- 2) Above $\sim 120^\circ C$, the hardened pure Portland cement binder slowly loses strength as the temperature increases, due to crystallisation of the main calcium silicate hydrate binding phase to a phase known as $\alpha\text{-}C_2SH$ with an increase in porosity, giving rise to a phenomenon known as ‘strength retrogression’ where the strength slowly decreases with time.

To overcome this issue of strength regression with increasing hydrothermal treatment, ground quartz (silica flour) is added and new low Ca/Si ratio crystalline CSH phases (tobermorite and xonotlite) are formed at temperatures above approximately $120^\circ C$ [28,29]. Formation of these phases is slow and is dependent on the temperature and impurities. While alternative sources of silica are sometimes used, including diatomite and perlite (which is $\sim 70\%$ silica), the use of these materials reduces the amount of quartz, and inhibits the formation of tobermorite, which only forms with large amounts of quartz.

Other additives have been developed for well cementing, primarily to control paste thickening and setting, density, viscosity, and loss of mix water (known as fluid loss) [19,20]. The retarders were based on calcium lignosulphonates or hydroxyl compounds, such as sugars or sugar acid salts (e.g., sodium gluconate or sodium heptagluconate, where a paste containing ~ 0.1 wt% sodium gluconate will take about 1 day to set at $30^\circ C$), although phosphonates and other organic products, such as hydroxyacids, can also provide retardation. Inorganic compounds, such as those of zinc, tin, borate, or phosphate, also delay thickening times, but generally a much higher dose is required compared to organic retarders and they do not function well at elevated temperatures [30,31]. Clay products (such as bentonite and metakaolin) have been used to prevent segregation of the cement solids from the mix water because of the high water:solids ratio used to control slurry density, but their effect lessens above $\sim 60^\circ C$. Also, clay materials should be used with caution above $\sim 120^\circ C$ as they react with the silicates to form aluminosilicate phases, such as katoite, in preference to the formation of C-S-H phases. These aluminosilicates have low strength and are detrimental to the overall strength of the hardened cement.

Durability If Used as an SSM

Oil well cements have been in use for approximately 100 years [32], and whilst problems still exist in some aspects of their performance, their durability in the field, at least over periods of approximately 50 years, has been proven. The high temperature and pressure conditions at the bottom of a DBD borehole will be very similar to those encountered in hydrocarbon and geothermal energy wells, suggesting that cement grouts that perform satisfactorily in those situations should also be appropriate

for DBD applications. While the method of grout deployment in DBD may be very different from that in hydrocarbon and geothermal energy wells, it is likely that techniques used for cementing the latter could be relatively easily adapted for DBD.

Comparing the durability of cements in oil well applications with those required for DBD is difficult because of the different timescales involved. The lifetime of an oil or geothermal well is of the order of 30 years, although longer time periods are now being sought [33], with the cementing job ideally lasting for the length of the well's operational life. An estimation of the ultimate lifetime of DBD is difficult when it is based on the notion of "for as long as possible," in hundreds of thousands or even millions of years [1].

For DBD, the borehole could be expected to remain open and unsealed for up to 2 years while loading continues [34], so this is the lifetime requirement for the support function of the grout. After the disposal zone is fully loaded, the hole will be sealed back to the surface of the earth, and this will allow the density and salinity stratification of the groundwater to reform. Use of a cementitious SSM around the waste packages will delay both container corrosion and the possible release of radioactive waste ions into the near-field environment, thereby augmenting the safety case for DBD. As the ground waters in DBD are likely to be less chemically aggressive than those encountered in conventional well applications, the grouts are likely to be more durable.

Generally, the use of organic materials in cementing radioactive waste for storage and disposal is not approved because they may complex the waste ions, leading to increased radionuclide solubility and an acceleration of the movement of radioactive material to the biosphere. However, organic retarders are likely to be needed as inorganic retarders do not function well at temperature. [31]. This is considered less important in DBD applications for two reasons. Firstly, any radionuclide release will only occur many years after the borehole has been sealed so there is unlikely to be any return to the biosphere, and secondly, the elevated temperature and pressure, coupled with the high pH of the cement grout, will cause decomposition of the organic compounds after grout thickening [35,36].

3.2. Calcium Sulfoaluminate (CSA)/Belite Cement

CSA cements are currently receiving attention due to their low CO₂ footprint and reduced energy requirements [37–39]. They set rapidly and are used in structural applications associated with bridge decks, airport runways, and patching roadways and sidewalks. The principal clinker phases are a calcium sulfoaluminate, ye'elimite, (Ca₄(AlO₂)₆SO₄), also known as Klein's Compound, and belite with other minor phases. CSA cement has been produced in China for a number of years for construction, but the quality can be rather variable. The principal binder in the system is ettringite, which is only stable to around 65 °C, when it loses hydrate water and decomposes, offering limited binder functionality at elevated temperatures [40,41]. CSA cement was considered for cementation of intermediate level radioactive waste (ILW) [42,43], but the consistency of the cement phase composition has been insufficient to allow use in the UK for the storage and disposal of intermediate level radioactive waste (ILW) despite some advantages with its lower pH and reaction with metals.

Companies, including Lafarge–Holcim [38] and Heidelberg Cement [39], are developing CSA/belite products. The Lafarge–Holcim Aether® cement contains 40% to 75% belite, 15% to 35% ye'elimite, 15% to 25% C₂AF (Ca₂Al₂Fe₂O₈), a phase similar to the aluminoferrite phase present in Portland cement), and 0.1% to 10% of minor phases. A small quantity (~5%) of anhydrite (CaSO₄) is also added. The product hydrates in two stages. The first stage is the reaction/hydration of the ye'elimite with anhydrite and water to produce ettringite and a hydrated alumina gel (Al₂O₃·3H₂O). The second stage is the reaction between the βC₂S and 1) AH₃ to form strätlingite (Ca₂Al₂(SiO₂)(OH)₁₀·2.5(H₂O)), 2) C₂AF to form hydrogarnet phases (those based on Ca₃Al₂O₆·6H₂O phases), and 3) strätlingite to form hydrogarnet and C-S-H. The reaction of the ye'elimite with water is rapid whereas that of the βC₂S is slower, giving rise to a dormant period between the two sets of reactions.

The Heidelberg Cement CSA/belite product known as Ternacem (or Belite Calciumsulfoaluminate Ternesite, BCT) appears to be similar to the Lafarge–Holcim Aether, but also contains ternesite ($\text{Ca}_5(\text{SiO}_4)_2\text{SO}_4$) as well as $\beta\text{C}_2\text{S}$ and CSA.

Durability If Used as SSM

The large amounts of $\beta\text{C}_2\text{S}$ in CSA cement suggests it may have properties similar to that of the former API Class J cement (a combination of $\beta\text{C}_2\text{S}$, silica flour (ground quartz), and a small amount of calcium carbonate), although the prior formation of ettringite may be a problem. Class J cement was designed for use in high temperature deep well applications due to the slow hydration of the $\beta\text{C}_2\text{S}$ and its slow reaction with quartz, so retarding admixtures were rarely required when this cement was used at circulating temperatures less than ~ 150 °C. [20,44]. However, unless specially manufactured for nuclear waste disposal, this system appears no longer to be available because the well cementing industry believes that similar properties can be obtained with other classes of cement combined with silica flour and retarders [20].

While both Lafarge–Holcim and Heidelberg Cement are reported to be developing CSA/belite cements, they are not yet commercially available. In addition, the ettringite formed in this product decomposes at the temperatures encountered in DBD so it will not function as a binder and the properties at elevated temperatures are unknown.

3.3. Pozzolan Cements

Pozzolan materials are siliceous and/or aluminous phases which do not hydrate on their own, but when ground to a fine powder will react at room temperature with water and calcium hydroxide, the so-called ‘pozzolan reaction,’ to form cementitious phases similar to the C-S-H produced in Portland cement hydration. The resulting binder is less permeable than that from just Portland cement and usually provides superior durability. Pozzolan materials include industrial by-products, such as pulverised fuel ash (PFA, also known as fly ash), blast furnace slag (BFS), and silica fume, as well as naturally occurring materials, such as metakaolin, volcanic ash, and glass, and a range of other waste ashes, such as rice husk ash.

In well operations, the use of specific pozzolans in combination with Portland cement can provide a lighter weight slurry, which reportedly performs better in deep borehole applications [20]. However, the evidence to support this advantage is limited, and the use of pozzolans has generally been avoided in hydrothermal cementing because tobermorite is not formed unless there is a large amount of additional quartz present and there is a detrimental effect on permeability [45].

An amorphous hydrothermally altered silica, Microsilica 600 (MS600), produced by Golden Bay Cement in New Zealand, is now being used with Portland cement to produce an amorphous binder rather than tobermorite, which performs much better in the carbon dioxide rich waters of the geothermal wells in New Zealand [46]. While the reason for the enhanced durability is not entirely clear, one possible explanation is that MS600 reacts more quickly with the $\text{Ca}(\text{OH})_2$ from cement hydration than does the dissolved CO_2 in the groundwater to rapidly form an amorphous product, which only carbonates slowly to provide an expansive product which forms an impermeable carbonation sheath. Carbonation of tobermorite results in a reduction in solid volume so no protective sheath is formed.

Durability If Used as an SSM

Some pozzolan cements (similar to lime–quartz systems) only begin to react above 90 °C. While this type of system may be suitable for use in DBD, there is little proof that this type of system will perform any better than conventional oil well cements in downhole conditions, particularly where uncertainties exist about the formation of durable high strength phases, such as tobermorite.

3.4. Alkali Activated or Geopolymeric Systems

Geopolymer cements are inorganic systems based on the activation and hardening of an amorphous aluminosilicate material using very strong (>5 M) alkaline chemical activators, such as waterglass (sodium silicate, $\text{Na}_2(\text{SiO}_2)_n\text{H}_2\text{O}$, e.g., sodium metasilicate, Na_2SiO_3) and sodium or potassium hydroxide [47–49]. The aluminosilicate materials include calcined clays, such as metakaolin, BFS, PFA, or natural pozzolans. The binder is an amorphous aluminosilicate where aluminium substitution in the silicate network requires a charge balancing cation, usually Na^+ but it can be calcium ions (such as that from BFS or PFA).

The term ‘geopolymer’ was originally coined by Davidovits [50–52], but various names, such as inorganic polymers, hydroceramics, and alkali activated slags, have been used. Geopolymers are currently receiving attention as alternatives to Portland cement for use in transportation, infrastructure, construction, and offshore applications with a few structures built [49,53].

The potential for using geopolymers for well cementing has been recently explored by Nasvi and co-workers [54–58] in laboratory-based studies. Other researchers are now exploring the use of this system, particularly where CO_2 sequestration is being considered, as the system is not readily carbonated [59].

Issues with obtaining a suitable thickening time for these systems have been found although they may have been overcome in a recent reported work [60]. The systems are very similar to those developed at the South West Institute [61] as part of an extensive programme of cement development for geothermal wells coordinated by Brookhaven National Laboratory conducted in the late 1970s. Those cements relied on the activation of a metal oxide or hydroxide with sodium silicate, which dissolved at an elevated temperature to give a metal silicate. Unfortunately, the product formed was porous when the reaction occurred in water whereas in the dry steam conditions of many of the geothermal fields in the USA, a reasonable product could be obtained.

Alkali-activated slag cements have been reported for applications of sealing in salt and sulphur mines and for hydrotechnical operations [62–64], in oil well sealing [65], for CO_2 storage and sequestration applications [56], and in the conversion of drilling mud to cementitious slurries [66–69]. Recent patents demonstrate an ongoing interest in the use of these materials in downhole applications [69,70]. However, variable cracking has been reported in alkali-activated BFS slurries [71].

Sodium silicate-activated BFS and BFS/fly ash cements were developed for potential use in geothermal wells [72,73] with high compressive strengths (>80 MPa), low permeability to water, and good resistance to acid attack. The binding phases formed at elevated temperatures and pressure were dominated by partially crystalline C-S-H phases, including tobermorite. Apart from concerns over being able to control the setting, the practical use of this type of system would need to be addressed, as each aluminosilicate source behaves and reacts differently. Despite these reports, there is little information on whether these types of systems are regularly in use in downhole applications, where the temperature and pressure are similar to that in DBD, and whether there are any products readily available on the market that have seen significant relevant use with good durability.

Durability If Used as an SSM

Most alkali activated systems, such as geopolymers, require very high concentrations (>5 M) of soluble alkali hydroxide or silicate or both to react with an aluminosilicate material. This may cause problems as the deployment/flow of a geopolymeric grout through water at the bottom of a borehole is likely to dilute the alkaline activation component of the grout. Geopolymeric grouts cast in steel moulds and cured before exposure to well conditions prepared by one of the authors showed a promising performance. However, when the same formulation was deployed in a porous mould in an attempt to set the formulation in a water filled autoclave at an elevated temperature, the soluble component diffused from the mix, resulting in a failure to harden or set [74]. This dilution of the alkali activator has been noted before [75], and the same is likely to occur with similar systems that contain other water-soluble activators, such as phosphate bonded cements.

There is a further issue which must be considered. Many of the alkali activated systems rely on alkali concentrations as high as 14 M [76]. This concentration is likely to attack the host rock in a similar way as that shown by da Silva and Milestone [77].

3.5. Calcium Aluminate Cement (CAC) Systems

CAC cementing systems, also known as aluminous cement, high alumina cement, and Ciment fondu, are based on hydraulic calcium aluminate phases. As the production cost is higher than Portland cements, they are only used in limited and specialised applications, such as:

- Where rapid strength gain is required across a broad temperature range, even at low temperatures.
- To prevent biological corrosion due to the presence of aggressive microbes (e.g., sulphides) in applications, such as wastewater processing or sewer structures.
- Where structural strength is required at elevated temperatures, such as in refractory applications.
- As a constituent of blended cements designed for specific properties, such as rapid setting and strength gain applications, e.g., for airport runway repairs.

The predominant reactive phase in CAC is monocalcium aluminate (CA, CaAl_2O_4). When mixed with water, this undergoes a series of complex hydration reactions which lead to the formation of a mixture of hydrate types known as the hexagonal hydrates, CAH_{10} ($\text{CaAl}_2\text{O}_4 \cdot 10\text{H}_2\text{O}$), C_2AH_8 ($\text{Ca}_2\text{Al}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$), cubic hydrates C_3AH_6 ($\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$), and alumina gel ($\text{Al}(\text{OH})_3$). The curing temperature influences the type and quantity of these phases formed. Hexagonal CAH_{10} and C_2AH_8 undergo what is termed a 'conversion reaction', decomposing to a mixture of cubic C_3AH_6 , $\text{Al}(\text{OH})_3$ gel, and water, causing an increase in porosity accompanied by a decrease in strength.

Retardation has been an issue with CACs at elevated temperatures, and work at Brookhaven National Laboratory has dealt with this by adding a second component, such as phosphate (discussed below) or fly ash plus sodium silicate [78].

CAC cementing systems have high resistance to chemical and acid attack [79], so they have been used for lining waste-disposal wells [80]. However, despite this acid resistance, these systems are poor at resisting alkali attack, and could not be used in the disposal of alkaline wastes unless it was neutralized prior to disposal. CAC systems are stable and durable in very high temperature applications, and so can be used as thermal cements and in fireflood and thermal recovery wells. This high temperature performance is primarily due to the absence of hydrated phases, such as that formed in Portland cement pastes. It is also reported that these systems can be employed in hot dry rock geothermal energy recovery and for more general utilization in geothermal wells. A noteworthy point is that these cements can be utilized as a base for specially prepared calcium phosphate cements [80]. Despite the claims detailed above, there is little evidence that CAC cements are regularly used in downhole applications where the temperature and pressure are similar to DBD.

3.6. Phosphate Cements

Phosphate cements, also known as chemically bonded phosphate ceramics (CBPCs), were used principally for dental applications, but recently, they have been considered for use in other applications, including structural ceramics, waste processing, oil well operations, and bioceramics. They differ from the more usual calcium-based cements as the reaction to form a hardened paste is an acid–base reaction between metal cations and soluble phosphate anions to form insoluble crystalline metal phosphate hydrates in the presence of water, rather than by direct hydration reactions. To date, work has focussed on compounds of calcium, zinc, and magnesium as the source of cations. The reaction is achieved by mixing an oxide or hydroxide with either phosphoric acid or an acid phosphate, such as ammonium or potassium diphosphate solution, and occurs rapidly at room temperature, giving a product with ceramic-like properties. By controlling the reaction rate between the acidic and basic components, bonds can develop between precipitating particles and grow into crystalline structures to form a ceramic-like material. Because the precursor components rapidly neutralize each other during mixing,

the resulting paste has rapid setting properties and a near-neutral pH and has been developed as a patching material [81]

Wagh [82], has championed a magnesium phosphate cement called Ceramicrete, formed by mixing magnesium oxide powder and soluble phosphate powder with water in a process similar to that for making concrete. The wet mix can be pumped, gunned, or sprayed with commercially available equipment. The resulting product is reported to be non-porous and with a high compressive strength. A number of advantages over Portland cement systems have been reported, including reduced density, reduced permeability, higher strength, and increased resistance to acidic and carbon dioxide corrosion (a major issue in geothermal energy well cementing). He has reported Ceramicrete as being applicable for oil well/geothermal well applications ([82] and the references therein), but there is little practical experience with these systems in the field.

A phosphate modified aluminous cement produced by reacting CAC cement with a source of phosphate has been referred to as a calcium aluminium phosphate (CAP) cement [83,84]. It is reported to resist carbon dioxide induced corrosion, protect pipes and casing, develop high strength, and is acid resistant. While a number of papers report its use within the temperature range of 60 to 370 °C, there are no durability test reports of field performance. This system, containing PFA partly as a filler material but which forms apatite phases under hydrothermal conditions, was developed commercially by Halliburton Energy Services as ThermaLock™ Cement [85], to resist carbon dioxide induced corrosion and protect the cement and casing.

Durability If Used as an SSM

Attempts to employ the ThermaLock cement system in geothermal wells in New Zealand encountered significant problems with flash setting [74]. Detailed investigatory work has shown that these systems are strongly dependent on the composition and properties of the CAC and PFA used and appear to have a short shelf life. Major problems were encountered in developing consistent formulations which demonstrate repeatable performances when it was considered for waste immobilisation [86].

3.7. Other Cementing Systems

Several other cementing systems have been reported for use in well applications. However, even less is known about them than the systems detailed above, and they have not been manufactured in reasonable quantity to make them readily available on the market.

Schlumberger offers a system they call CemCRETE™ [19,87]. This product appears to control the particle size distribution to provide better particle packing so the solids content of the paste is increased so that it is higher than in conventional Class G or H pastes, resulting in a slurry with higher density, reduced porosity and permeability, and increased compressive strength [88]. It is also claimed that lower concentrations of most admixtures can normally be used. Schlumberger have also produced a range of products, including Lite-CRETE™ (for low density requirements in the range 1.20–1.56 g/cm³), SqueezeCRETE™ (for the penetration of small/narrow gaps in remedial hole cementing), DensCRETE™ (for high-density requirements above 2.52 g/cm³), and DeepCRETE™ (where the acceleration of setting and development of compressive strength is required).

Halliburton–Baker Hughes also offer a similar system designed for possible use in CO₂ sequestration, with the trade names, Evercrete™, Set for Life™, and PermaSet™, with some formulations that can be used up to over 300 °C.

Since the 1970s, investigations have been performed into whether Portland cement can be introduced into drilling fluid (mud) and converted into well cement. If successful, this conversion could reduce mud disposal costs, significantly improve annular cementing efficiency, and reduce costs associated with staffing/manpower, equipment, time, and materials [89]. Little detail exists on how this conversion could give desirable cementing properties, but some researchers have suggested the use of BFS [19,66–68]. Additions of ground granulated BFS (GGBS) to a mud along with a suitable

alkaline activator, such as sodium hydroxide or calcium hydroxide, could form C-S-H-type phases similar to those from the hydration of Portland cement but with lower Ca/Si ratios [90]. The lower Ca/Si ratio could ensure the formation of higher strength crystalline C-S-H phases. Little information is available on their properties.

4. Selection of an SSM Cementing System for DBD

In reviewing the potential cementing systems that might be applicable to DBD, several other points arise which help in determining a suitable cementing system for SSMs.

4.1. Proven Durability

Portland cement-based systems are by far the most commonly used in hydrocarbon and geothermal well cementing with over 100 years of knowledge, experience, evidence and supporting literature, and proven reliability of their use [32]. No other system can provide this level of credibility, and indeed many have not been tested in field trials. API Classes G and H well cements are now the preferred options for well cementing with quartz flour additions and have been used successfully in deep wells where temperatures and pressures are well in excess of those being considered for DBD, particularly when used with additional quartz flour [91]. A cementitious SSM can be expected to provide sealing and support functions whilst the borehole remains open during the waste package deployment phase (estimated at 2 years), much shorter than the required lifetime of hydrocarbon or geothermal wells of ~30 to 50 years. As the near-field ground water chemistry in DBD is likely to be less aggressive than in geothermal wells, these hardened oil well cement grouts should be durable over the short-term DBD waste package deployment phase before the final hole well sealing takes place. Moreover, the use of a system with a proven durability of over 50 to 100 years will enhance the longer-term durability of the DBD application.

The hydrate phases formed in Portland cement systems have been shown to chemically retain a range of waste cations and anions [92,93]. Portland composite cements are currently used in the UK for ILW encapsulation/immobilisation with proven durability [94–99]. Therefore, if a waste package does rupture in DBD (before or even after the final borehole sealing), the hardened paste will retard any release of radionuclides to the biosphere. Significantly less is known about the retention of radioactive waste ions for other cement systems.

4.2. Placement

Discussions with well cementing engineers and practitioners, and suppliers of cement products and auxiliary additives and admixtures, show suitable formulations using a Class G cement and silica flour can be prepared which would meet the demanding conditions of placement in the disposal zone of DBD.

Suitable slurries using recognised retardation and fluid loss additives can be prepared with a thickening time of greater than 4 hours that could be placed in water at a 5 km depth and these have been demonstrated by work carried out by the Sheffield DBD Research Group.

4.3. Regulation

As with any concept of radioactive waste disposal, rigorous assessment and regulation by governmental bodies is essential, and safety must be assured by the production of a safety case. An example of this process is the significant work that has already been carried out in developing the safety case for the Geological Disposal Facility (GDF) preferred by the UK government for the disposal of ILW and HLW wasteforms [100]. When developing a safety case for DBD, any organisation is likely to find it easier and more acceptable to utilise materials already in use in radioactive waste processing operations. Therefore, the use of grouts similar to the Portland cement-based systems already used in the UK to produce ILW wasteforms should make it more straightforward and acceptable when developing a safety case for DBD.

4.4. Availability

Class G oil well cements are readily available in any country, along with the admixtures (retarders, superplasticisers, etc.) and other components regularly used in oil well cements.

4.5. Financial Consideration

The cost of Portland cement is significantly less than any other cementing system. A typical price of Portland cement is around US\$125/tonne [101], but it is difficult to obtain similar up-to-date information for alternative cement products in large amounts. CAC cement is always substantially more expensive than Portland cement (US\$200–500/tonne) [19]. Davidovits reported in 2005 [51] that the costs of the principal components of two geopolymer cements were more than 3 and 4 times that of Portland cement (~US\$400 and ~US\$330 per tonne of GA and M9 cement, respectively, excluding the cost of sand and aggregate, based on an exchange rate of 1:1 US\$:€).

4.6. Engineering and Placement

Significant differences are likely to exist between cementing a hydrocarbon or geothermal well and deploying or placing a DBD grout [102]. In the former, the grout is pumped down through a tube in the centre of the well, returning to the surface up the annulus outside the casing. The Sheffield DBD Research Group have proposed deploying a known volume of grout to the disposal zone just before or after placement of the waste package(s). Engineers involved in drilling and well cementing have intimated that engineering a solution to this issue should be achievable.

4.7. Radiation Stability

The radiation durability of an oil well cement system is likely to be high in this DBD application in the short-term [102]; a typical surface radiation dose rate expected from containers of vitrified UK HLW is an order of magnitude less than that used during the radiation durability testing of the UK ILW encapsulation grouts where no significant detriment to composition or microstructure was observed over a 2-year period.

4.8. Potential System for SSMS

When the points in Sections 2 and 4 are considered and following discussions with well operators, a generic formulation based on API Class G cement has been selected. The Sheffield DBD Research Group has recently demonstrated that Portland cement-based systems show great potential to perform as required under the conditions likely to be experienced in DBD [17,18,102]. However, their performance as sealing matrices still needs to be assessed. The experimental work performed to date has been carried out at the laboratory-scale (approximately 0.5 L) so further work is needed at a larger-scale.

5. Summary

Cementitious grouts based on Class G oil well cement have been shown to be suitable for providing low temperature sealing and support matrices (SSMs) for deep borehole disposal (DBD) applications. These SSMs will seal the containers of high level radioactive waste within a disposal zone located in the bottom ~2 km of holes drilled into the basement rock of the continental crust. The elevated temperatures and pressures in the disposal zone will be similar to those encountered in hydrocarbon and geothermal energy applications, although the chemistry of the groundwater local to the disposal zone is expected to be more benign.

Partial replacement of the cement with silica flour is required to lower the Ca/Si ratio to ensure the formation of the most durable cement hydrate phases; a fluid loss additive is required to enable the grout to flow/move through water in the boreholes without the solid particle dispersing; and retarding

admixtures are required because the elevated temperature and pressure will cause an acceleration of the thickening time.

This system has been selected based on the fact that over the past 100 years, it has demonstrated it can provide the short-term performance and durability required for DBD across the range of temperatures and pressures likely to be experienced. In the longer-term, the seal around the waste packages should be maintained after the boreholes are sealed to the surface, which will augment the safety case for DBD.

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