HIGH PERFORMANCE CERAMIC PLUGS FOR BOREHOLE SEALING

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Deep borehole disposal of nuclear waste is under consideration for long term disposition of spent nuclear fuel, sealed sources, and high level waste forms. In the reference design developed by the US Department of Energy, boreholes would be drilled in deep crystalline rock to depths of 3 to 5 km, waste packages emplaced in the lower 2 km of the borehole, and the holes backfilled with a combination of plug and granular materials.

Plugs are critical features of the system design. They serve as structural platforms to bear the backfill column load, and as seals through their low fluid permeability and bond to the borehole or casing wall. Plugs must perform under high hydrostatic and lithostatic pressures, in high mineral content water, and at elevated temperatures due to the geothermal gradient. Conventional methods of well sealing rely on hydrated cements or bentonite materials. Applied extensively in the oil and gas industry where the expected performance horizon is measured in tens of years, these materials are susceptible to degradation in more aggressive thermal and chemical environments. Deep borehole nuclear waste disposal faces the added requirements of assuring performance for thousands of years in potentially larger boreholes.

This paper describes a high performance plug concept which capitalizes on the energy of solid phase reactions to form an in-situ self-sintered ceramic plug. Thermites are a family of self-oxidizing metal/oxide reactions with high specific energy content and the ability to react under water. When the basic formula is modified with additives, the final material can exhibit attractive structural, sealing, and corrosion properties.

In the initial phase of this project, exploratory and scaled tests demonstrated the benefit of carefully tailored formulations that achieved controlled, fine grained, homogeneous, net shape plugs composed predominantly of ceramic material. Laboratory experiments produced plug cores with confined fluid permeability as low as 100 μDarcy, compressive strength as high as 70 MPa (three times the strength of conventional well cement), with the inherent corrosion resistance and service temperature of ceramic matrices. Numerical thermal analyses predicted the in-situ thermal performance of the plugs and surrounding media, showing that they cooled near to ambient temperature (and achieved final design strength) within a day.

Current and future work is focusing on refining the reactant and additive materials to optimize final properties, perform detailed thermal/structural analyses, develop fabrication processes and prototype deployment designs, and test the plug seal and bond quality in mockups of typical well casings. A final demonstration of the project, planned for summer 2016, is a full scale demonstration at depth in a cased well with traditional plug seal and strength diagnostics.

I. INTRODUCTION

Traditional methods of well sealing rely on hydrating cements, developed and applied extensively in the oil and gas industry. Well cements seal both the interior of the well casing and the annular volume between the casing and borehole wall to prevent axial fluid flow in both regions. Portland cement, the most common well cement system, has been engineered for emplacement and setting under a wide range of downhole conditions encountered in traditional petroleum exploration and extraction. In place permeability of plug core material has been demonstrated in the μDarcy range, and overall permeability (including the effects of the seal to the casing surface) in the mDarcy range has been measured[1,2]. It is common to emplace relatively long plug sections in well casing (30 m or longer). Portland cement is, however, a hydrating formulation sensitive to the chemistry and pressure of its emplacement environment, and is susceptible to dehydration and physical degradation at elevated temperatures.

Deep borehole disposal of nuclear waste poses similar challenges due to the anticipated depth of disposal, with the added requirement of performance assurance for very long times, and in potentially much larger diameter boreholes (as large as 0.43 m diameter to accommodate spent fuel assemblies).

In the DOE reference design developed by Sandia National Laboratories[3], holes are drilled in deep crystalline rock to depths of 3 to 5 km and waste packages placed in the lower 2 km of the borehole. Waste packages are emplaced in the borehole using a guide casing, which is then removed to leave the borehole uncased from the top of the waste zone up to a depth of 1 km. Conventional casing and surface conductors are in place in the upper 1 km of the hole. The open borehole is backfilled with a combination of bentonite sealing plugs, cement and asphalt structural plugs, and granular material.

Plugs serve a structural role as platforms to bear the backfill column load (particularly in the larger diameter holes), and a sealing role through their low permeability and bond to the borehole wall material. The environment imposes high hydrostatic pressure (7 MPa at 1000m up to 28 MPa at 3000m), high lithostatic pressure (23 MPa at 1000m up to 79 MPa at 3000m depth, based on an overburden density of 2.7 kg/m^3), high mineral content water, and elevated temperature due to the geothermal gradient (110° C). The geologic media in the emplacement zone will be very low porosity crystalline granite or basalt. Compared to most conventional wells, the deep borehole disposal wells are deeper and potentially larger in diameter than commercial wells, and uncased for much longer intervals.

The objective of this research was to develop high performance plug materials with properties superior to hydrating cements. The initial phase of the project demonstrated that tailored formulations of metals, reactive oxides, and inert diluents could produce uniform, fine grained solid material with a predominantly ceramic matrix product. Best described as a 'self-sintering' process, the thermal plug reaches its final product state through a reaction generating sufficient heat to fuse the material into a formed cylindrical plug.

The plug system is deployed in a cylindrical package, containing the mixed and compacted constituent powders

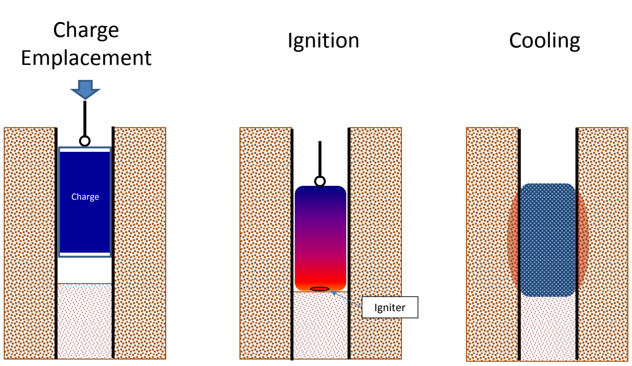

Figure 1. Ceramic plug emplacement process.

(Figure 1). The package is lowered to depth, resting on backfill or a bridge plug. Ignition is initiated at the bottom of the package and progresses upward. Due to either its own mass or a static load placed on top of the package, the hotter, more plastic material in the reaction zone compacts into the borehole volume where it sets and cools. The reaction progresses up the package until all of the material is reacted and solidified in place. Important factors that influence the performance of the thermal plugs are:

- Formation of a low porosity, low permeability plug matrix in place
- Effective bonding (both mechanical and sealing) of the plug to the borehole or casing wall
- Thermal/structural impact to the surrounding borehole rock, or for cased wells, to the casing or casing cement (minimal or no negative impact is preferred)

The following sections describe the basic constituents of the thermal plug material, the predicted thermal response of the plug and surroundings, and the initial properties measured in the first phase of the project.

II. CERAMIC PLUGS

This process is an adaptation of the thermite reaction, modified by heavy dilution with inert oxides. Thermites are a class of energetic materials that combine a combustible metal with an oxide to release thermal energy. Many different combinations of metal/oxidizer are possible. Invented in 1895 by Hans Goldschmidt, thermite has been used in a range of applications capitalizing on its ease of formulation, insensitivity, and large exotherm. Originally conceived as a method of forming metal alloys in a carbon free atmosphere, thermite found widespread use as a field welding process for railroad rails (welding kits are still commercially available and in use), synthesis of refractory materials, simulation of magmas and molten nuclear fuels in experiments, steel structure demolition, and military applications.

The system employed in this development project uses aluminum as the fuel and ferric oxide as the oxidizer:

$$Fe_2O_3 + 2Al \;>\; Al_2O_3 + 2Fe + Heat$$

The reactants are mixed in powder form, compacted into the desired shape, and ignited using an energy source (such as an electric filament) that attains a temperature sufficient to combust aluminum. The reaction progresses at a rate below the speed of sound, hence it is not considered explosive. A thermite reaction is difficult to initiate because of the high temperature required to combust the metal, but once started will burn to completion. It reacts under water and produces no residual gas or vapor. The thermite system described above generates 3956 kJ/kg of available heat at an adiabatic peak temperature of 2862° C (Ref. 4). It is the most common thermite system in use given the low cost and availability of its reactants, and the relatively large specific energy release. The products of the reaction are pure iron and aluminum oxide.

A key aspect of the initial development effort was understanding the benefits of diluting the thermite system with non-reacting oxides. In the course of the testing work, the thermite system (the stoichiometric mixture of aluminum and iron oxide) was diluted as much as 1:1 with silica and alumina. The result was significant suppression of the peak temperature, slower and more controllable reaction rates, and a product with a very fine matrix structure (Figure 2).

Figure 2. Thermal plug sample removed from granite block test (7.6 cm diameter plug, high dilution of thermite with aluminum oxide)

III. THERMAL RESPONSE

During the formation of the ceramic plug, a discrete amount of thermal energy is released and diffuses into the surrounding media. In order to predict the transient effects and the peak temperatures experienced by the adjacent media, scoping calculations were performed using a chemical equilibrium code to define the thermal source. A transient finite element model predicted the resulting temperature response.

III.A. Thermal Source Term

The thermal source term is defined by the plug's peak temperature upon completion of reaction, its enthalpy, and its thermal conductivity. The peak reaction temperature of various mixtures was estimated using NASA's Chemical Equilibrium with Applications code (CEA) and manual thermodynamic calculations. CEA calculates chemical equilibrium product concentrations from any set of reactants and determines thermodynamic and transport properties for the product mixture, using a minimization of energy approach[5]. It is based on an ideal mixture model, an equation of state for perfect gases, and condensed species that have no volume in the reaction products. CEA calculated peak temperatures for the thermite mixtures when the molar composition was at or near stoichiometric ratios. For the more dilute formulas the peak temperature was estimated by manual thermodynamic calculations. Using the peak temperature and product concentrations calculated by CEA for the base thermite, the amount of energy released as the thermite cooled was compared to the energy needed to heat the mass of diluent. The peak temperature of the diluted mixture was the temperature reached when these two energies balanced. To exploit the beneficial effects of diluents, it is necessary to understand the impact of additional inert material on the reaction peak temperature. While the stoichiometric aluminothermite achieves a peak temperature of nearly 3000° C, dilution with inert oxide can reduce the peak to less than 1700° C. In Figure 3 the peak temperature as a function of aluminum oxide dilution is estimated (where dilution is the fraction of final product mass). As dilution increases from the stoichometric mix, peak temperature drops and a plateau is reached near 2100° C (the melting point of alumina), then the temperature continues to decrease. Above about 50% dilution the peak temperature drops to just below 1700° C. In the small scale tests conducted, the reaction

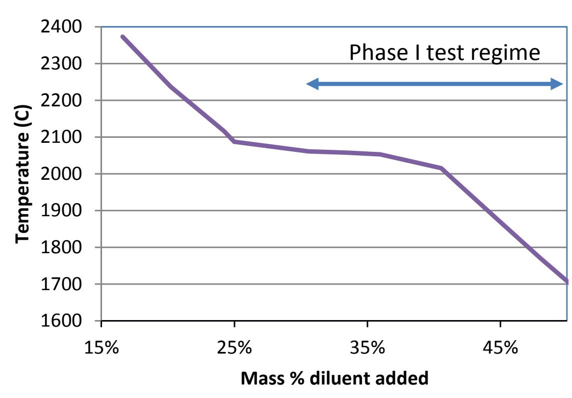

Figure 3. Adiabatic reaction temperature reduced with dilution of thermite system with additional aluminum oxide.

would not reliably self-propogate at dilutions greater than 51%. This temperature suppression allows a degree of control over the thermal impact to the borehole wall.

III.B. Transient Thermal Response

The LISA 8.0 generalized finite element analysis program[6] was used to perform transient thermal analysis. The initial baseline calculations simulated the transient response of a thermal plug placed in the borehole with an initial temperature equal to the peak temperature of the diluted thermite reaction. A medium dilution aluminothermite/silica mixture was used, with a peak temperature of 1646° C. Thermal properties for the plug and granite are listed in Table 1. The temperature dependent specific heat is shown in Figure 4, for the specific composition of the plug, and accounts for phase changes of the constituents using thermodynamic property tables from the CEA library. The temperature dependent composite thermal conductivity of the plug is also shown in Figure 4, which considers matrix porosity and inclusions of high conductivity metal (iron, in this case).

Table 1 Thermal properties of the plug and granite.

Material	Thermal Conductivity (W/m-K)	Specific Heat (J/kg-K)	Density (kg/m^3)
Granite	3.0 (constant)	790 (with step change up to 1400 J/kg-K from 700 to 950° C to account for phase change	2750
Thermite / diluent plug	Variable (see Figure 4)	Variable (see Figure 4)	2560

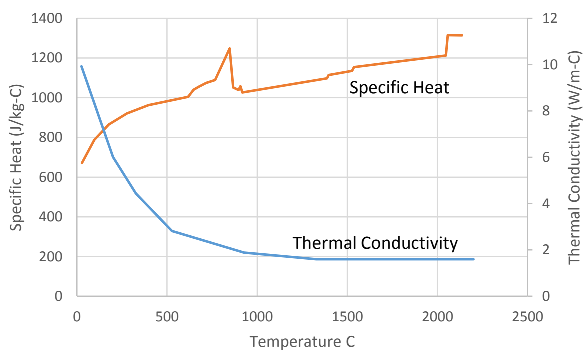

Figure 4 Temperature dependent thermal conductivity and specific heat of the plug material.

The solution mesh represents a quarter circle single element layer in the center of a plug (Figure 5). Two borehole sizes are considered (both uncased). The large hole simulation represents the 0.43m diameter borehole considered for disposal of a spent fuel assembly (Ref. 1), with the outer mesh boundary at 3 m radial distance. The smaller hole is 0.25m diameter, representative of typical commercial wells and potential nuclear material capsule disposal scenarios (outer mesh boundary at 1.77 m).

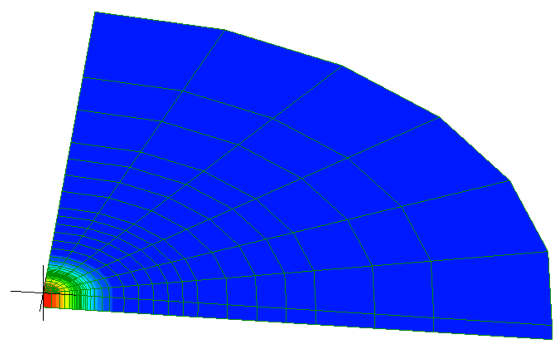

Figure 5. Mesh for the baseline LISA model. For the large hole case the outer radial boundary is at 3 m, for the smaller hole the boundary is at 1.77 m.

Simulations ran to ten hours (sufficient to capture peak temperature gradients), with 1 second time steps and produced a set of radial temperature distribution snapshots (Figure 6). The decay of the source temperature is relatively fast, particularly for the smaller hole diameter which cools nearly to ambient within 10 hours. In both cases the plug/rock interface cools to 700-800° C in the first hour. The estimated depth of penetration of the heat-effected zone temperatures greater than 600° C) is 2 to 4 cm.

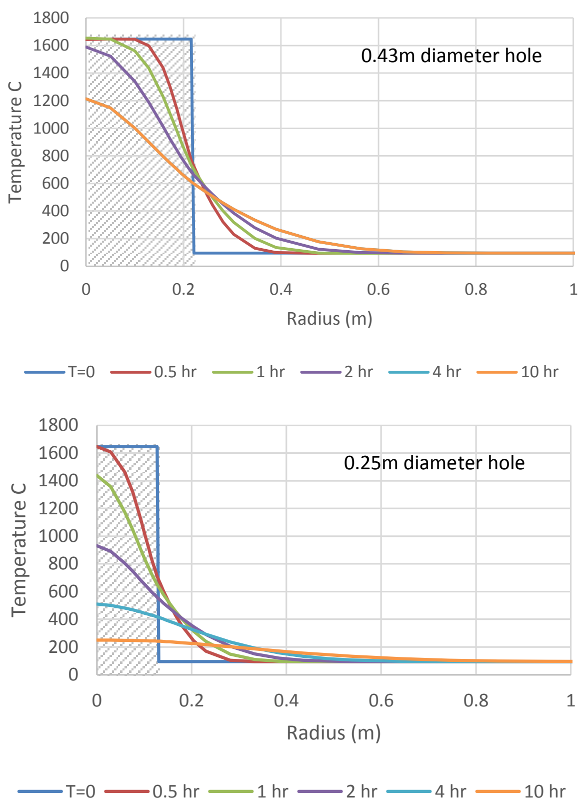

Figure 6 Radial temperature profiles at one hour intervals for the large borehole case (top) and the small borehole case (bottom).

IV. TEST RESULTS

A range of tests evaluated product characteristics in samples from 7.6 cm diameter up to 25.4 cm. Most of the tests were conducted in steel pipe, although several were performed in holes bored in granite blocks. Key results are highlighted below.

IV.A. Compressive strength

Five samples from the granite block test series were subjected to standard unconfined compressive strength tests. Each was approximately 7.6 cm diameter, in length ranging from 10 to 12.7 cm. The cylinders were tested to failure in a compressive test machine. The ultimate compressive strengths are listed in Table 2. The highest strength result was the high dilution alumina sample at 75.89 MPa, and the lowest the silica diluted sample at 46.21 MPa. In all cases these compressive strengths are significantly higher than those expected for standard well cements (ranging from 10 to 20 MPa).

Table 2. Ultimate unconfined compressive strengths of samples from the small granite block tests.

Plug Reactants	Compressive Strength (MPa)
High dilution SiO_2 (1 sample)	46.21
Medium dilution Al_2O_3 (3 samples)	67.97 (σ = 0.99)
High dilution Al_2O_3 (1 sample)	75.89

IV.B. Permeability

The core material permeability was evaluated to understand the effects of formulation and compaction during the reaction process. Reaction temperature, solidification temperature and viscosity of the various components, and cooling rate will influence the final plug properties. Of particular interest is the final plug permeability, dictated by the porosity and pore connectivity of the material. Routine core analysis was conducted on plug samples and a sample of the granite used in the block tests. Samples were prepared by reacting 7.6 cm diameter charges in steel pipe molds under a range of compaction loads (on the top of the sample during the reaction). Plug compositions were chosen to evaluate the effect of total dilution, compression loads, and diluents. The plugs were then cored and tested under confining pressures up to nearly 69 MPa. Figure 7 illustrates the two most pronounced effects. The top three samples show the impact of dilution: increasing the dilution decreases the permeability by more than an order of magnitude. Diluting with a low melt temperature oxide (silica) yielded a much lower permeability, near 20 μDarcy, at maximum confining pressure.

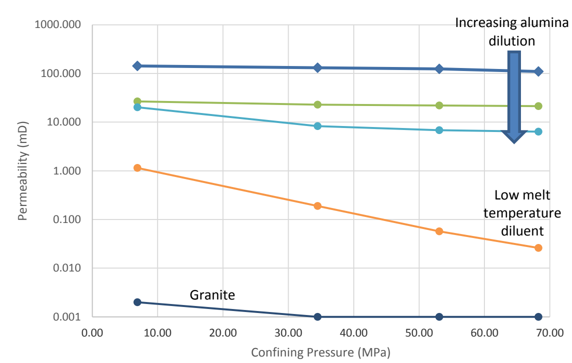

Figure 7 Increasing dilution, and diluting the thermite system with a low melt temperature oxide (silica) yielded low permeabilities in confined measurements.

IV.B. Scaled granite block tests

A number of tests were performed in core holes formed in granite blocks. These were useful scoping experiments which yielded a large amount of thermal response data to be used in subsequent modeling. One pair of experiments demonstrated the similar performance of the plug material in both dry and saturated conditions. In Figure 8 a 7.6 cm diameter plug is shown in a dry block (top) and a block submerged in water during the test (bottom). Both of these tests produced nearly identical reaction rates (0.45 cm/sec vertical propagation rate measured by thermocouples spaced up the plug/rock interface). In each case a thin (2-3 mm thick) layer of perlitic friable material remained bonded to the plug material after the block was separated, and a similar layer was on the surface of the opposing granite piece. This heat-effected layer likely formed from to the expansion of water in the granite pores and minerals, since the tests were not pressurize and interface temperatures exceeded the boiling temperature. Tests under pressurized conditions will evaluate this effect in the following work.

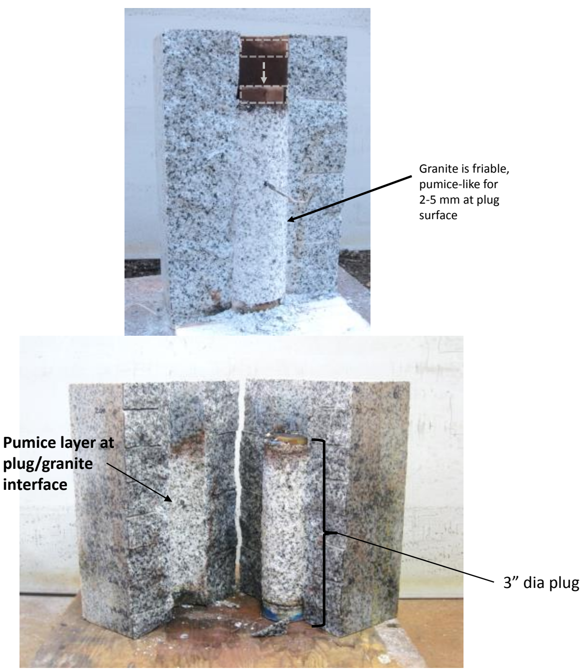

Figure 8 Small granite block experiments showing the results of a dry test (top) and a saturated test (bottom) in 7.6 cm diameter holes cored in granite blocks.

V. CURRENT AND FUTURE WORK

This effort was the first phase of a project evaluating the viability of the ceramic plug concept for deep disposal applications. The research was exploratory in nature, including scoping level calculations and experiments. The project is now in its second phase, with the objective of developing materials, designs, and emplacement approaches for application in deep cased and uncased boreholes in saturated conditions. The main activities are to optimize the plug materials for a range of performance requirements, and develop engineering designs of the emplacement package and manufacturing processes. Specific focus areas include:

- Understanding the thermal/structural interactions at plug-rock and plug-casing-cement-rock interfaces throughout emplacement and cooling cycle
- Understand the thermal/hydraulic effects at the plug/rock interface under high pressure saturated conditions
- Measure seal quality and bond strength in cased wells
- Understand the expected long term corrosion performance of the plug material
- Develop a prototype system, compatible with existing well service practices and hardware

The final activity of this phase, planned for summer 2016, is a demonstration test in a conventional cased well, using standard well field performance evaluation methods.

VI. CONCLUSIONS

In the initial phase of this project, exploratory and scaled tests demonstrated the benefit of engineered formulations that achieved fine grained, homogeneous plug samples composed predominantly of ceramic material. Numerical simulations estimated the thermal effects of emplaced heat sources to understand the depth of the thermally effected zone in the rock and its cooling rates. Exploratory tests evaluated thermite formulations, constituent particle sizes, reaction rates, peak reaction temperatures, and the composition of the final products. Samples were prepared for quantitative confined permeability and unconfined compressive strength measurements. Scaled granite block experiments evaluated reaction controls and consistency, and the impact of the thermite reactions on the granite material under atmospheric (non-pressurized) conditions.

Thermal simulations showed that the temperature pulse from the full scale plugs can thermally perturb several centimeters into the rock (600 to 800° C). The thermal field is short-lived, decaying to near ambient in several days. Scaled experiments demonstrated that diluted thermite reactions could form net shape plugs in place with performance characteristics exceeding well cements. By varying dilution ratios, it was shown that relatively ‘cool’ plugs could be formed with reduced or no detrimental thermal impact to the borehole wall. Confined permeability below 100 μDarcy was measured, and unconfined compressive strengths as high as 76 MPa were measured (over three times the strength of a typical well cement). Repeatable reaction rates and plug formation under water were observed.

The initial effort demonstrated the viability and potential of ceramic plugs formed in place for challenging geotechnical sealing requirements. The technology has application in deep nuclear waste disposal, oil and gas, geothermal, and CO_2 injection programs where highly corrosive and high temperature environments exceed the operating capability of hydrating cements.

The subsequent effort will optimize the reaction chemistry for specific performance requirements, perform more comprehensive numerical simulations to evaluate the coupled processes, develop the prototype plug design, and demonstrate a prototype plug in an actual cased well environment.

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