Formed-in-place Ceramic Systems for Sealing and Flow Control in Geothermal Applications

William Lowry¹, Ken Coates¹, Nick Wisner¹, Ken Wohletz¹, Sandra Dunn¹ and Andrew Louden²

¹ Olympic Research, Inc.

² isol8 Ltd.

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ABSTRACT

Conventional oil and gas tools are frequently unsuitable for downhole applications in geothermal wells, largely due to uncased well configurations and their extreme thermal/chemical fluid conditions. Consequently, relatively common O&G tools like bridge plugs and sand control screens are difficult or at times impossible to implement in geothermal wells. In commercial oil and gas, thermite-based tools are being developed for intervention and decommissioning applications, and gaining field experience and credibility. We are developing and testing such systems for geothermal applications, with the objective of forming ceramic sealing and flow control features in-situ. The process uses self-propagating thermite reactions, in which a metal is combined with an oxidizer to release significant amounts of energy in a controlled, nonexplosive manner. These solid phase reactions can be engineered to generate ceramic products with specific physical and flow characteristics. We are developing and testing formulations and wireline deployment tools which yield low to high permeability as needed, and preferentially expand to fill boreholes in both large diameter and slimhole wells. Near term applications are bridge plugs for P&A operations, screens for sand control and borehole stabilization, and lost circulation control during drilling. Laboratory tests have demonstrated the ability to form these products under high temperature and pressure conditions. Field tests are in planning to demonstrate the full-scale performance of these tools. This paper will present the status and results of this demonstration project, in its first year of advanced development for the DOE geothermal technologies program. New developments utilizing thermite tools in the HP/HT oil and gas domain will also be highlighted, particularly those which may have utility in geothermal applications.

1. Introduction

Downhole sealing and flow control systems are being developed using thermite-based reactions to form corrosion resistant, high strength components (Lowry et al., 2017). These systems use the thermal energy of solid phase metal/oxide reactions, supplemented by mixtures of minerals and oxides, to form monolithic ceramic components in place. These highly modified thermite reactions are moderated and controlled, self-oxidized, and run to completion under downhole water pressure. The method is being extended to applications benefitting from intentionally-generated porosity in the ceramic material, including bridge plugs, screen formation, lost circulation control, and borehole stabilization. The technology has application in conventional large diameter boreholes as well as slimhole drilling, and is particularly suited for high temperature, corrosive environments.

Thermites are a class of energetic material that combines a combustible metal with an oxide to release large amounts of thermal energy. A common formulation is the aluminum/ferric oxide system, where aluminum is the combustible metal and ferric oxide (Fe₂O₃) the oxidizer, yielding iron, aluminum oxide, and a large amount of energy upon reaction. The reactants are blended in powder form, compacted into the desired shape, packaged in a sealed aluminum canister, and ignited when placed at the desired location in a well. The reaction progresses at a relatively Aluminothermite is slow pace (fractions of a cm/sec) and is not considered explosive. insensitive as an energetic material due to its high activation energy, but once started will tend to react to completion (even under water, since it is self-oxidizing). The stoichiometric aluminothermite reaction reaches a peak temperature of approximately 2900°C (Fischer and Grubelich, 1999). A variety of additives can be combined with the thermite to alter peak temperature and tailor the final product form. High temperature oxides and mineral additives reduce the peak temperature, moderate the reaction rate, and combine with the thermite reaction products to yield other compounds, such as feldspars. Glass and alkali additives can produce a largely amorphous product with a lower melt temperature than the crystalline form.

2. Technical considerations

In our effort to develop ceramic sealing plugs, thermite reaction experiments under atmospheric air conditions frequently resulted in high gas filled porosity. This is because the powdered reactive material, compacted into solid cylindrical forms at very high pressure (typically 10,000 psi compaction stress), typically retained 35-45% air-filled porosity. When reacting, the product peak temperature reaches 2000-2500°C (depending on the formulation). The air in the pores undergoes adiabatic expansion, resulting in a volume change proportional to the ratio of final to initial absolute temperature, or a factor of 7 to 9. If the reaction products solidify quickly, which is the case of the aluminum oxide or aluminosilicate product forms of the basic aluminothermite reaction with silica additives, the pores will freeze quickly as the product cools to 1800-2100°C. On the other hand, if the reactants are designed to solidify at much lower temperature, such as 1200-1400°C, the product will remain molten long enough for the pores to float out, as is observed in the process of manufacturing glass. This degree of control is illustrated in Figure 1, showing core samples ranging from extremely low porosity (and permeability) to very large, expanded pores, with correspondingly high permeability.



Figure 1: Typical range of porosities and permeabilities attained under atmospheric reaction conditions, in air. The core on the left remained molten long enough for the bubbles to float out, while the sample on the right solidified very quickly after the reaction completed and the pores expanded.

The mechanical properties of the ceramic foam products are important because they influence the ability to drill through the formed product and leave remaining annular material in the hole as a screen or borehole stabilization feature. High compressive strengths are possible in very low porosity products (as high as 30,000 psi measured for ~1% porosity product in the sealing plug application). However, the higher porosities observed in these samples (up to 45%) yielded compressive strengths in the range of 8,000-10,000 psi, which places these materials in the realm of drillable geologic media. Mohs hardness of 5.5 to 7.5 were measured.

When reacting these materials at depths and pressures typical of geothermal applications, however, the hydrostatic overpressure resists formation of gas-filled porosity to a degree proportional to the ratio of final to initial pressure. Since the reactants are packaged in hermetic cylinders, their initial pore pressure is essentially atmospheric. Pore gas will expand when heated to the peak reaction temperature by a factor of 7 to 9 (ideal gas law ratio of absolute temperatures). However, when reacted and then exposed to the downhole fluid pressure the pores are dramatically compressed, by a factor of approximately 200 if the downhole pressure is 3000 psi, for example. Consequently, the net compression of pore gas requires additional non-condensable gas to generate pore expansion.

In the following discussion we address an approach to generating pore volume, and the reaction product conditions necessary to maintain those pores in the matrix.

2.1 Generating porosity under downhole conditions

In order for the thermite mixture to expand, existing pore gas must be supplemented by noncondensable gas during the reaction. One way to accomplish this is by adding a small amount of calcium carbonate ($CaCO_3$) to the mixture. During the thermite reaction, the calcium carbonate decomposes into calcium oxide (CaO(s)) and carbon dioxide (CO₂(g)), at a decomposition temperature of approximately 825° C:

$$CaCO_3 + 178 \text{ kJ/kg-mole} \rightarrow CaO(s) + CO_2(g)$$

It is possible to use the ideal gas law to estimate the amount of pore gas expansion resulting from a given quantity of carbonate material in the reaction. However, the temperatures experienced in the thermite reaction are beyond the typical equation of state data for CO_2 , so review of data and compressibility models was needed to ensure the desired expansion is possible. To understand if CO_2 can provide the necessary expansion, two questions must be addressed: 1) how much CO_2 will be available for expansion while the thermite is reacting, and 2) will the volumetric change in the material be adequate to create the necessary porosity in the final ceramic material.

The critical temperature and pressure for CO_2 is 31.1C (304.3°K) and 7.38 MPa. At atmospheric pressure, CO_2 will be in the gas phase during the thermite reaction. At the anticipated maximum downhole pressures (5000 psi, or 0.035 GPa), the CO_2 will be supercritical, where distinct liquid and gas phases do not exist. Supercritical material has a high density like a liquid, but will expand to fill available space like a gas. A phase diagram for CO_2 under extreme pressures and temperatures is shown in Figure 2 (Boates, Teweldenberhan, & Bonev, 2012). This phase diagram indicates that CO_2 is not undergoing any phase change at the pressures / temperature of interest, and is not in the CO regime.



Figure 2: A standard phase diagram for CO2 (left hand image) is an enlargement of the highlighted area of the high pressure / temperature phase diagram (Boates, 2012).

Prior work discussing equations of state for carbon dioxide in higher temperature / pressure ranges was reviewed. Most considered pressures from 50 - 300 MPa and temperatures up to 1100° K. Available on-line databases of thermodynamic data were also reviewed. Again, data were typically available for high pressures, but data above 1200° K were not available.

A method to predict gas expansion at higher temperatures is needed. For the purposes of this analysis, the specific volume is used to estimate how much the generated gas will expand. The ideal gas law is the simplest equation of state for substances in the gas phase. It provides a good approximation of the behavior of many gases, but does not include intermolecular attraction forces or the volume occupied by the molecule. Thus, the equation generally produces reasonable results at higher temperature and lower pressure, as the potential energy due to intermolecular forces becomes less significant compared with the particle's kinetic energy, and the size of the molecules becomes less significant compared to the empty space between them. At high pressures, the volume of a real gas is often considerably larger than that of an ideal gas (due to repulsive forces of more densely packed molecules). The deviation from the ideal gas behavior is described by the compressibility factor, Z. This factor can be thought of as the ratio of the actual volume of a real gas to the volume predicted by the ideal gas at the same temperature and pressure as the actual volume. Figure 3 shows the calculated specific volume of CO_2 as a function of temperature for several pressures (atmospheric, 3000 and 6000 psi), along with data obtained from the National Institute of Standards and Technology (NIST). As expected, the ideal gas law calculations closely match the data under atmospheric pressure (absolute errors varied between 0.01 -0.68%). At high pressures and temperatures below about 400°C, the ideal gas law significantly over-predicts the specific volume (errors as high as 155%, for 3000 psi and 0°C). As temperature increases, the ideal gas law under predicts the gas volume. Figure 4 provides compressibility factors for high pressures and temperatures. At the reduced temperature anticipated during the thermite reaction (9.1), Z > 1 for all reduced pressures. Thus, use of the ideal gas law for these analyses will conservatively predict the volumetric expansion of entrained gases in the mixture.



Figure 3: Calculated vs. measured specific volume as a function of temperature for CO₂ at various pressures. Inset shows calculation error to real value.



Figure 4: Nelson-Obert generalized compressibility chart for high reduced pressures and temperatures. Dotted lines represent pseudoreduced specific volume, $v'_R = v/(R T_c/P_c)$.

The ideal gas law can then be used to estimate the mass fraction of calcium carbonate material necessary to achieve the desired expansion of the reaction product pore space. For example, to double the pore volume in a 5000 psi overpressure environment, approximately 6% CaCO₃ would be added to the thermite formulation. This is a relatively simple method and reasonable quantity of additive.

The above calculations indicate that enough CO_2 can be generated, even under maximum anticipated downhole pressures, to both maintain the same porosity of initial thermite mixture and to expand the reacted material to fill the void between the emplacement package and the borehole wall. The next question that must be addressed is if the generated gas will remain gaseous, disassociate, or react with other downhole elements.

Gibb's free energy can be used to determine how equilibrium will occur in a chemical reaction. The equation for disassociation of CO_2 is:

$$2CO(g) + O_2(g) \leftrightarrow 2CO_2(g); \Delta G = -565110 + 173.72T (J)$$

At lower temperatures, ΔG is very negative; the chemical reaction is highly driven to occur and CO₂ will be predominant. As temperature increases, ΔG becomes less negative. ΔG is 0 at 3250°K, and the system would be in equilibrium. Because ΔG is linear as a function of temperature, and the concentration of CO/CO₂ is 0 at 0K and 1 at 3250°K, the ratio of the two compounds can be estimated. For the reaction temperature of 2500°C (2773°K), the ratio of CO/CO₂ would be 0.85, indicating the CO₂ will breakdown. If CO₂ decomposes, both CO and O₂ will be produced, but we assume that the oxygen is readily recombined with other materials at these temperatures. La Chatelier's principle states that as pressure increases a chemical reaction will shift to the side of fewer moles of gas, which favors creation of CO₂. Boats (2012) indicates

that CO_2 will not dissociate until very high temperatures at elevated pressures (Figure 2). For purposes of creating porosity in the reacting thermite, having the gas be CO or CO_2 is inconsequential, but it is important in determining if the gas will be available for expansion or will be consumed in reactions. Note that this analysis did not consider gas interactions with solid materials, since those are expected to be slow (diffusion limited) and the thermite reaction/solidification process occurs relatively quickly.

This discussion addressed the predictability of pore gas generation via addition of carbonate materials to the thermite formulations, since very little data exists at the temperature conditions of the thermite reactions. The following conclusions are drawn from the study:

- Pore gas expansion will likely be even greater than that predicted by the ideal gas law, due to the compressibility effects at very high temperatures.
- The gas generated due to decomposition of carbonate material in the thermite reaction will likely remain as a combination of CO or CO₂, both having a similar effect upon pore expansion.
- The quantities of carbonate material required (3-6% by mass fraction of the total thermite formula) are reasonable and easily compounded in the blending process.

2.2 Maintaining the porosity in the final solidified product

Because the compositions and rheological properties of the thermite-created ceramic foam are similar to volcanic lava, which also develops porosity during its solidification (the pores are called vesicles), this study uses a published background on understanding of how vesicles develop and how they control many of its physical properties. The following sections of this report describe the basic physics of vesicle bubble growth and development of a foam, characterization and physical properties of vesicular lavas, and some calculations that predict the porosity of thermite-created ceramic foams at various temperatures and pressures. A major uncertainty in understanding the development of porosity is the origin of the gas in the pores. Certainly, there is enough air trapped in the granular mixture to expand upon heating to create porosity, but the magnitude of that result depends on how much of the air reacts with the thermite materials during high temperature oxidation-reductions reactions and ends up in solid phases. By addition of carbonates, vapor phases such as carbon dioxide and carbon monoxide are generated. In this fashion there is better control on the amount of gas-filled porosity that will result. Given the experimental reproducibility of porosity in thermite formulations and suitability of the vesicular lava analog, then there will be a strong correlation of the engineering properties of these foams to their composition-determined porosity. The analog system is well studied and demonstrates that the gas phase segregates from the melt to form gas bubbles that tend to grow, buoyantly rise, and coalesce near free and fixed surfaces. The amount of bubble growth is limited by melt viscosity and surface tension, but where the volume fraction of bubbles increases to the point where they start touching and coalescing (generally above a volume fraction of 0.74), a foam exists that develops connecting flow paths for permeability. Viscosity and the surface tension of the melt determine the extent of bubble growth and coalescence in the foam and at what temperature range the resulting textures become frozen in size and shape as temperature falls below those with viscosities of solidification.



Figure 5: Illustrations of foam formation. From left to right, a photomicrograph of bubble coalescence during foam formation, a sketch of foam formation at the upper free surface of a porous liquid, a numerical simulation of how increasing surface tension with melt solidification cause bubbles to coalesce and decrease in number, and a sketch of porosity increase from a critical foam at 78% void fraction where bubbles become interlocked to a fully developed foam at 97% where bubbles are coalesced and bounded by polyhedral surfaces. (From Proussevitch *et al.*, 1993; Cashman, *et al.*, 1994; Aref and Vainchtein., 2000; Mangan and Cashman, 1996).

There are limitations in applying the lava analogy. First, the energetics of bubble nucleation in the analog are determined by volatile specie supersaturation in the melt, but the solubility of volatile species (dominantly CO and CO_2 for the formulations discussed) is not known. From compositional considerations the solubility is likely insignificant, even at high temperatures and pressures where solubility generally tends to increase. Nucleation energies are also influenced by heterogeneities in the melt (boiling stone analogy) such that nucleation is favored at sites along the boundary of crystals grown or sintered in the melt, the latter of which may preserve some original pore space. This phenomenon is well known for lavas rich in crystals for which vapor bubbles readily form between the interstices of crystals, known as diktytaxitic texture in lavas. Another unknown for application of the vesicular lava analog are the energetics of bubble coalescence and foam formation, which are strongly dependent upon the surface tension of the melt on bubbles. The viscosity of the melt also plays a role for the thinning of bubble walls and their gradual deformation from spherical to polygonal as melt is squeezed out from the bubble walls. Given these unknowns the following predictions from the analog must be carefully applied through empirical methods for the formulations considered.

Engineering properties of interest for application of thermite ceramic foams are all strongly correlated to porosity, with decreasing values of thermal conduction, uniaxial compressive strength, elastic modulus, longitudinal wave speed, and quality index with increasing porosity. Poisson's ratio increases with increasing porosity. These property variations measured in the vesicular lava suggest a similar behavior for design of ceramic foams. For example, by analogy, ceramic foams of 0.75 porosity are expected to have a permeability of about 1 Darcy (~10-12 m^2).

The model developed above shows that the gas-filled porosity is strongly a function of temperature and hydrostatic pressure. An aspect of the lava analog that has not been quantified is the decreasing volume of the gas phase with falling temperature. As temperature falls below solidification temperatures (glass transition temperatures for non-crystalline materials), expected in the range of 600 to 1000°C for lavas, the bubbles are frozen in size and position, and no longer contract. Vesicular lavas do show deflation features in cases where the bubbles reach their full size (by gas mass) at temperatures well above solidification. However, such deflation is offset by continuous gas diffusion from the melt into bubbles during cooling, such that bubbles may not collapse much with cooling. Hence, for a practical application to thermite formulations, the calculated gas volume fraction at solidification temperatures (800 to 1400°C) may be the most useful for estimating final porosity.

Hydrostatic pressure does limit the growth of gas porosity, and calculations show for the formulations studied here that the critical porosity for foam development may require added volatile constituents for application at hydrostatic pressures above 1.0 MPa (~100 m deep in water filled boreholes). For deep applications, formulations with increased gas-generating constituents will be required. In order to calculate critical porosity (~0.75) at 10.0 MPa (~1000 m depth in water), volatile constituents must be increased and bubble volumes at elevated temperature (solidification temperature assumed to be greater than 600°C) are required. For example, altering the formulation by added calcium carbonate to sufficient levels increases dilution to 70%, producing 0.78 porosity. These calculations appear to support an approach to creating porous thermite materials at higher pressures.

In applying a vesicular lava analogy to thermite-created ceramic foam formulations, the following considerations apply:

- Lavas have similar rheology properties (density, viscosity, surface tension, and thermal conductivity) to those of thermite-based formulations and provide a useable analog;
- Air that fills the intergranular porosity in compacted formulations either contributes to oxidize solids or is largely driven out of the reaction zone before being trapped in the melt.
- Thermite product melts have insignificant solubility of volatile phases.
- Thermite formulations are sufficiently oxidized to form an insoluble gas phase from additives such as carbonate or carbon.
- Solidification at 800°C or above is complete enough to freeze pore shapes and sizes so that no further pore space collapse occurs with further cooling.

Given these assumptions, conclusions from this work focus on the permeability characteristics of the product forms:

- Permeability develops from intersecting (coalesced) gas bubbles, forming a percolating pathway like a granular material.
- For pores to connect, the bubble walls must fail, generally thought to come about by stretching and thinning where a bubble grows next to a boundary, such as another bubble or a fixed or free boundary.
- Such permeable foams are more likely to form in lower viscosity and lower surface tension thermite products.

- More bubble porosity produces more permeability, although experimental evidence also suggests that the composition of the reaction product can produce different permeability at similar porosity.
- More bubbles are promoted by increasing the volatile phases (i.e., more trapped gas more permeability).
- Using additives to lower the melt viscosity and surface tension may also encourage bubbles to grow and connect.
- Adding more graphite to form more carbon monoxide or more calcium carbonate to release more carbon dioxide is desirable.
- For application in environments of increased hydrostatic pressures more carbon phases need to be added to form critical porosity for permeable foam development.
- Increased additives increase dilution of thermite formulations with concomitant decreased combustion temperature and reaction rates.

3. Applications

The initial application considered in the project was that of a ceramic screen to replace metallic slotted casing or screens. The screen formation process is depicted in Figure 6. The reactive package (tool) is lowered into the borehole and landed upon a platform, such as a ceramic plug. The thermite reaction is initiated at its base, and the package is consumed as it sinks into the molten reaction products. If the thermite is formulated to develop a foam, then it expands to fill the hole and retains or increases its volume. The reaction proceeds until all of the tool is consumed, then it cools to ambient conditions (simulations suggest that this can occur in less than 24 hours). At this point it can be drilled out to leave a screen-type geometry in place. Scoping experiments showed that screen-type flow properties could be developed in atmospheric laboratory experiments and some degree of porosity control was achievable. In practice, these emplacements would range from 5' to 20' in length, the upper limit defined by tool clearance and lubricator geometry at the wellhead. Multiple emplacements could be formed in series to form longer screen sections. Since the reaction products are typically aluminosilicate materials, very good corrosion properties are expected.

In the course of experimenting with porosity generation for screen application, we discovered the ability to form hollow, expanding plug forms that filled the borehole. These plugs can be formed while freely suspended by a wireline in the borehole, which means they can act as structural platforms in environments where conventional bridge plugs are not suitable, such as uncased wells (note that the ceramic plugs by themselves do not typically form absolute seals in the wells, unless combined with other sealing media). These ceramic plugs then enable operators to cement only as much of an uncased well as is needed to form a seal and satisfy the decommissioning requirements, since otherwise in open geothermal wells the entire hole may need to be cemented. The ceramic plug also complements the ceramic screen emplacement process, since the ceramic screen needs to be emplaced on a platform to complete the formation.



Figure 6: Ceramic screen formation process.



Figure 7: Ceramic plug formation process (shown in cased well, but also applicable to open boreholes).

A third potential application is that of lost circulation control and borehole stabilization. This application would be a substitute for the cementing option in lost circulation control, which typically is implemented when all other options are exhausted and the drill string has been retrieved. The reactive package is placed at the base of the borehole, reacted to fill the hole, and the molten products fill the fractures and solidify relatively quickly. The solidified product material is then drilled through when cooled. Lost circulation is one of the most expensive problems facing drilling operations, particularly in geothermal applications, so the market for this can be significant.



Figure 8: Lost circulation and borehole stabilization process.

4. Progress to date, and field test plans

4.1 Engineering the tool and control system

The emplacement tool consists of a reactive thermite package suspended below a control, initiation, and monitoring module, deployed on either wireline or slickline (see Figure 9). The upper module contains the control and sensing electronics, housed in a thermal management package to maintain the electronic components at their desired operational temperature in geothermal well conditions. Below that module is suspended the thermite package, a hermetic aluminum cylinder containing the compacted thermite material and initiation module at its base. Initiation of the reaction occurs by a signal from the control unit, applying current to resistive filaments embedded in a thermite mixture designed to reliably initiate and propagate the reaction. The reaction propagates up the thermite cylinder, consuming the aluminum tube, expanding to fill the hole and retaining the expanded product cylinder in place as the reaction completes. When the reaction reaches the top of the thermite package, the connection to the upper tool components is melted and severed, allowing retrieval of the tool.

Reliably packaging the thermite compacts requires careful use of high temperature sealants (to provide hermetic seals at the ends of the packages) and coating of the package to prevent excessive corrosion of the package before firing. We have tested a number of sealants and adhesives for the tubing endcaps under pressure and temperature, and shown successful sealing at temperatures of 200°C and 3000 psi for sustained time periods. Several viable surface coating approaches have been tested, ranging from shrink fit fluoropolymer tubing to industrial corrosion protection coatings.



Figure 9: Thermite deployment tool: control and initiation module (left), reactive package (right) and full tool assembly downhole (center).

The control unit provides initiation logic control (in particular for autonomous operation with slickline systems) to ensure safe operation under specific conditions. For example, a countdown timer initiated by a sensed threshold temperature or pressure ensures the tool is sufficiently in the borehole to start the timed initiation sequence. The control unit also monitors the operation, recording the temperature of the environment above the reaction to verify successful reaction. In figure 10 are shown the components of the control unit, showing the inner electronics housing, the phase change surround (using low melt temperature alloy phase change material), insulation, and the outer unit packaging. This design has shown that it can control the electronics temperature to acceptable levels for up to 4 hours in 180°C well conditions



Figure 10: Control module, showing thermal management design and electronics assembly (right).

4.2 Planned field tests

Two near term field tests are planned for the expanding thermite tools. The first is an expanding bridge plug application in a steam-filled geothermal well. For this application a 5" diameter thermite package will be located at approximately 2300 ft. in the well, just below the bottom of the casing, and expand to fill an 8.5" open borehole (Figure 11). This ceramic platform will allow the operators to decommission the well by cementing only the upper section of the well, above the bridge plug. This field test is planned for summer 2019. Material development and testing is currently underway for this test. Full diameter reaction experiments have demonstrated that the desired expansion ratio can be achieved and the plug form held in place.

The second field test program will be conducted at a research mine in Colorado, in near surface hard rock and tailings. In that project, a number of 6" boreholes will be cored and multiple expanding plugs formed in each. In some of the holes the load-bearing capacity of the plugs will be measured by top-loading with the drill rig, while in others the plugs will be cored and the resulting 'screen' permeability measured.

Results of both of these field tests will be presented at the conference.



Figure 11: Field test configuration for expanding ceramic plug, steam-filled geothermal well (summer 2019).

5. New developments from oil and gas: hybrid thermite/low melt temperature alloy systems for well intervention and P&A

There is a great deal of interest by the oil and gas industry in integrating thermite and low melt temperature metal alloys to form very high performance seals and address complex well configurations, particularly offshore. Thermite offers a great deal of thermal energy in a small volume, useful when melting and mobilizing low melt temperature metal alloy (such as the bismuth/tin system) so it can flow into complex geometries and form seals. Thermite can also form the platform upon which the alloys will be cast. Bismuth-based alloys are particularly interesting in that they expand upon solidification (up to 3%), flow like water (viscosity of 2-4 cP), are extremely dense (aiding penetration into microannuli), and relatively corrosion resistant.

Olympic Research is partnering with isol8 Ltd. to develop a hybrid sealing technology targeted at such complex well completions (Figure 12). This system utilizes engineered thermite formulations and metal alloy systems to form seals in simple tube or casing (reservoir seals), single annulus, multiple annulus, and casing cement sheath repair/sealing. While the bulk of the near term applications are at temperatures below 150° C, thermite and alloy combinations are being designed to address >200°C applications, placing them in the realm of geothermal conditions.

6. Conclusions

This paper presents the concept and engineering development of expanding thermite-based ceramic features formed in wells for geothermal flow control and sealing applications. The systems use highly engineered thermite formulations, tailored to generate expanded pores and

yield foam-like products with specific porosity and permeability characteristics. The applications include formation of ceramic bridge plugs, flow control screens, and borehole stabilization/lost circulation control.



Figure 12: Application configurations of the isol8 Ltd. Fusion system, which integrates engineered thermite systems with low melt temperature metal alloys to seal complex well configurations.

Expanded thermite products are generated under well pressures through use of gas-generating additives, such as carbonate materials. We evaluated existing equation of state data for CO_2 , and projected its characteristics to the very high temperature regime typical of thermite reactions, and show that carbonates are in fact viable additives and will produce non-condensable pore-forming gas as predicted (in quantities reasonable for the reaction formulations). Further analysis also showed that the gaseous products will remain stable, with some degradation to a mix of CO and CO_2 , at these conditions, but the net effect of moles of gas generated remains the same.

At least as important as pore formation is the ability of the reaction products to retain and 'freeze' the pores in place, versus allowing them to float out of the product mass. We used the natural analog of volcanic magma properties to understand the conditions under which pores will be retained, specifically freezing point and fluid viscosity. These results are being compared to experimental observations to guide the thermite formulation development.

The engineering design of the system was presented, including both the control module (which initiates the reaction and monitors its operation) and the reactant package, a consumable aluminum housing that holds the thermite material in place during the reaction.

Two near term field tests are described, one in a steam-filled geothermal well, and the other a series of near surface, small scale experiments evaluating plug bond strength to open borehole

rock and the effective permeability of screens formed by the thermite system. The results of these field tests will be presented at the conference.

Lastly, recent developments in oil and gas sealing and isolation system are presented, that should be of interest to the geothermal community. These technologies integrate thermite heat sources and low melt temperature alloys to seal very complicated single- and multi-annulus well configurations, as well as cement sheaths behind casing. While most of these applications are below 150°C, the HP/HT applications are above 200°C and are being addressed with special alloy systems.

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REFERENCES

- Aref, H., and Vainchtein, D. L., 2000, The equation of state of a foam, Phys. Fluids 12(1), 23-28.
- Brian Boates, Amanuel M. Teweldeberhan, and Stanimir A. Bonev, Proceedings of the National Academy of Sciences, September 11, 2012 109 (37) 14808-14812
- Cashman, K.V., Mangan, M.T. and Newman, S., 1994, Surface degassing and modifications to vesicle size distributions in Kilauea basalt. J. Volcanol. Geotherm. Res. 61, 45-68.
- Fischer, S.H., Grubelich, M.C., Theoretical Energy Release of Thermites, Intermetallics, and Combustible Metals, Sandia National Laboratories report SAND99-1170C (1999).
- Lowry, W., Coates, K., Wohletz, K., Dunn, S., Duguid, A., Arnold, B., Patera, E., Groven, L., Ceramic Plugs for Deep Borehole Seals, Proceedings of the Waste Management Conference 2017 (2017).
- Mangan, M.T., Cashman, K.V., and Newman, S., 1993. Vesiculation of basaltic magma during eruption. Geol. 21, 157-160.Mizuta, T., Obata, M., and Egami, K., 1990, Morphology and distribution of vesicles in the Togawa andesitic lava. Kazan 2(35), 249-262.
- Proussevitch, A., Sahagian, D., and Kutolin, V., 1993, Stability of foams in silicate melts, J. Volcanol. Geotherm. Res. 59, 161-178.