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ADVANCED HIGH TEMPERATURE CO_2-RESISTANT LIGHTWEIGHT CEMENTS

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KEYWORDS

calcium aluminate cements, phosphate containing compounds, flyash, acid-base reactions, mechanical properties, carbonation, lightweight, pumpable, well completions

PROJECT BACKGROUND AND STATUS

The quality of the cementing phase of a geothermal well completion often establishes the life expectancy of the well. Improperly designed cement jobs can result in blow-outs and casing corrosion or collapse. In addition to the need for cements which, upon curing, yield the necessary physical, mechanical and chemical characteristics, their slurry precursors must have rheological properties that permit placement. Low slurry densities (~1.2 g/cc) are desirable to minimize the frequency of lost circulation episodes when attempts are made to cement in weak unconsolidated rock zones with very fragile gradients.

During the period 1978-84, BNL under Department of Energy (DOE) Geothermal Division sponsorship organized and conducted an R&D program to develop and test advanced normal weight cement formulations. This international effort coordinated through the American Petroleum Institute, which involved universities, private industry and government laboratories, culminated in the field testing under downhole flowing brine conditions of several cement formulations cured *in-situ*. The CO_2 content in this well was low, therefore carbonation resistance was not evaluated. The results from this effort currently serve as the basis for the selection of cements used for geothermal well completions throughout the world. All of the cement slurries evaluated that had densities <1.6 g/cc failed to meet the test criteria, thereby identifying a research goal that based upon recent work, appears attainable.

A more recently identified problem that is severely reducing well life, and has increased costs and environmental concerns, is cement deterioration due to alkali metal catalyzed reactions between CO_2-containing brines and the calcium silicate hydrate (CSH) compounds and calcium hydroxide present in conventional well cements. In the former, reactions between Na and K in the brines and CSH phases lead to the formation of substituted CSH compounds such as pectolite and reyerite, both of which are susceptible to carbonation. Leaching of the resulting $CaCO_3$ and $Ca(HCO_3)_2$ leads to rapid reductions in strength, increased permeability, and corrosion on the outside surfaces of the well casing. Cement failures attributed to CO_2 are occurring in less than 5 years, and in one case, resulted in a collapsed well casing within 90 days. Solving these materials problems, which could seriously constrain the development of the world's geothermal resources, is the goal of the current cement research activity.

As of December 1995, several cement formulations that meet many of the design criteria have been identified. Laboratory characterizations are underway. Industrial collaborators (Halliburton Services and Unocal) have been identified and they are participating in ongoing engineering-scale tests and downhole evaluations.

PROJECT OBJECTIVES

The objective of the project is to develop and field test lightweight, low-cost, CO_2- resistant, non-portland based cementitious materials that can be used for geothermal well completions.

Technical Objectives

Design criteria for the cements being developed in this program are as follows:

- Slurry density, approximately 1.3 g/cc.
- Pumpability, 4 hr at 100°C.
- Carbonation rate, <5% after 1 yr in brine at 300°C containing 500 ppm CO_2.
- Compressive strength, >5 MPa at 24 hr age.
- Bond strength to steel, >0.07 MPa.
- Water permeability, <0.1 m Darcy.

Expected Outcomes

- Decreased costs for well completions due to reductions in lost circulation control episodes.
- Increased well life to >20 yr.
- Reduced environmental concerns regarding blow-outs.
- Permit development of higher temperature, higher CO_2 content brines.

APPROACH

The project is organized into five phases: 1) fundamental cement research, 2) mix design, 3) property characterization, 4) placement technology, and 5) downhole evaluations. Phases 4 and 5 are conducted as cost-shared efforts with industry to insure the practicability of the materials and technology transfer.

Phase I consists of fundamental work to synthesize non-portland cement-based materials and to elucidate the interactions that occur between them and a number of lightweight inorganic and organic microsphere fillers. State-of-the-art surface science analytical techniques are used in all parts of this phase. Phase 2 consists of the development of cement-filler mixtures and curing conditions to yield the desired properties. In Phase 3, the mechanical, physical and chemical resistance characteristics of promising formulations are determined before and after autoclave exposures to CO_2-containing hydrothermal fluids. The technical feasibility for use of the cement slurries in well completions using conventional placement technology is determined in Phase 4. This work includes the selection of retarding admixtures to extend pumpability, and verification of this by the performance of consistometer testing in accordance with American Petroleum Institute standards. Industrial assistance in the selection of retarders is contributed by a well service company. In Phase 5, which is a cost-shared activity with a well service company and a well owner, the ability to mix and place the cements on a large-scale is verified, and the long-term durability of samples cured in and exposed to downhole geothermal environments is determined.

RESEARCH RESULTS

Cost-shared R&D between BNL, Halliburton Services and Unocal was continued. The results confirmed that materials that yield a cementing matrix produced by acid-base reactions between calcium aluminate cements and phosphate-containing compounds can be mixed with lightweight fillers to produce pumpable slurries with densities as low as ~1.1 g/cc. Upon curing for 20 hr in hydrothermal environments up to 300°C, high strength (>58 MPa), durable and CO_2- resistant cement pastes are produced. Measurements of the $CaCO_3$ concentrations after autoclave exposure to a 0. 05 Na_2CO_3 solution at 250°C for 120 days indicated values generally of <0.4 wt%. A conventional portland cement-based well completion material will form approximately 10 wt % $CaCO_3$ after only 7 days exposure to the same environment. Upon laboratory exposure to extremely harsh conditions (>1.5% CO_2, 300°C), some carbonation-induced decomposition of calcium phosphate cements was noted. It was also determined that the rate of carbonation obtained upon exposure to hot water containing CO_2 gas is essentially the same as that in Na_2CO_3- laden hot water. Experimentally, it is easier and safer to use the latter.

The incorporation of inorganic and organic microsphere fillers into the calcium phosphate cement matrix (CPC) produces a lightweight, moderate strength and highly durable cement. Aluminosilicate-based hollow microspheres, with a density of 0.67 g/cc and a particle size of 75 to 200 m, produced a low slurry density of approximately 1.3 g/cc and a compressive strength greater than 6.89 MPa. The slurry did not segregate after storage for 24 hr at 25°C due to chemical interactions between the microspheres and the cementing matrix formulation.

Although the calcium phosphate cements are extremely resistant to carbonation at CO_2 concentrations up to those present in geothermal fluids currently of interest, care must be taken to insure that reactions with filler materials are not induced. For example, data from well tests performed at a depth of 2440 meters on lightweight cements containing glass and ceramic microspheres indicated that both of these inorganic-based microspheres reacted chemically with the cement hydrates. These reactions resulted in the formation of numerous microcracks and subsequent strength loss. The fluid temperature and pressure for these tests were 257°C and 16.3 MPa, respectively. BNL laboratory data confirmed these downhole results. In the BNL studies, lightweight calcium phosphate cements containing mullite microspheres exhibited 70% reductions in strength after 6 mo autoclave exposure to a 0.05 M Na_2CO_3 solution at 250°C.

Chemically inert organic-type microspheres were found to be promising fillers for use with calcium phosphate cements to produce lightweight, CO_2- resistant cements. As an example, slurries containing hollow acrylonitrile microspheres had a density of 1 g/cc and produced a cured cement which upon autoclave exposure at 250°C for 6 mo. retained 73% of its initial strength. Optimization of this formulation is in progress.

Recent BNL studies have identified blast furnace slag and class F flyash combinations as promising cementing material additives. Since they both are industrial by-products, they are inexpensive. They are also highly reactive with $(NaPO_3)_n$ solutions and exhibit rapid hydration ratės. Preliminary BNL studies using high alumina cement/blended class F flyash cement mixtures modified with $(NaPO_3)_n$ solutions produced cements with compressive strengths >27 MPa after curing for 7 days at 300°C . The cost of this formulation is estimated to be 70% lower than that derived from $(NaPO_3)_n$ modified high alumina cement slurries. Studies of the phases formed, microstructure developed, carbonation rate, and changes in strength and permeability after long-term exposures to CO_2 solutions at 250°C have been started.

FUTURE PLANS

Fundamental and applied research leading to the identification of reaction paths yielding advanced high temperature lightweight CO_2-resistant cements will be continued. Promising materials will be characterized and then introduced into the cooperative program with the geothermal industry for scale-up and downhole evaluation.

INDUSTRY INTEREST AND TECHNOLOGY TRANSFER

Organization(s)	Type and Extent of Interest
Halliburton Services	Cement properties characterization, pumpability studies, economic evaluation.
Unocal	Field testing.

REFERENCES

Milestone, N. B., Sugama, T., and Carciello, N. Carbonation of geothermal grouts-part 2: CO_2 attack at 250°C. Cement and Conc. Res., 17, 37-46, (1987).

Sugama, T. and Carciello, N. Strength development in phosphate-bonded calcium aluminate cements. J. Am. Ceram. Soc., 74, pp. 1023-30, (1991).

Schlumberger, Dowell. Geothermal Cementing pp 4-5, (1993).

Sugama, T. and Carciello, N. Carbonation of calcium phosphate cements after long-term exposure to Na_2CO_3-laden water at 250°C. Cem. Concr. Res., 23, 1409 (1993).

Sugama, T. and Wetzel, E. Microsphere-filled lightweight calcium phosphate cements. BNL 48543, J. Mater. Sci., 29, 5165 (1994).

Sugama, T. and Carciello, N. Sodium phosphate-derived calcium phosphate cements. BNL 60195, Cem. Concr. Res., 25, 91 (1995).

Kukacka, L. E. and Sugama, T. Lightweight CO_2-resistant cements for geothermal well completions. Proc. of World Geothermal Congress 1995, May 18-31, 1995, Florence, Italy, Vol 2, 1439-44.

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