ADVANCED HIGH TEMPERATURE CO_2-RESISTANT LIGHTWEIGHT CEMENTS

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KEYWORDS

calcium aluminate cements, phosphate containing compounds, flyash, acid-based 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 using conventional technology. 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 DOE/OGT sponsorship organized and conducted a 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 is 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, increase permeability, and corrosion on the outside surface of the well casing. Cement failures attributed to CO_2 are occurring in less than 5 yr, 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. Design criteria established by industry and ranked in order of importance are as follows: 1) compatible with conventional field placement technologies, 2) carbonation rate $<5\%$ after 1 yr in brine at 300°C containing 500 ppm CO_2, 3) compressive strength >5 MPa at 24 hr age, and 4) slurry density <1.2g/cc. Other important characteristics needed are: 1) life expectancy 20 yr, 2) pumpability of ~ 4 hr at >100°C, 3) bond strength to steel >70 KPa, and 4) H_2O permeability <0.1 m Darcy.

As of December 1996, several cement formulations that meet many of the design criteria have been identified. Based upon laboratory evaluations performed at BNL and by our industrial collaborators Halliburton and Unocal, one has tentatively been selected for use in a well completion currently scheduled for July 1997.

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 1.2 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, >70 KPa.
- Water permeability, <0.1m Darcy.

Expected Outcomes

Attainment of the project objectives will result in the following:

- 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 consists of 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 1 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 the most promising formulation are being 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 to develop cementing materials produced by acid-base reactions between calcium aluminate cements and phosphate-containing compounds was continued. Several candidate systems were evaluated. Studies of the cementing phases formed, microstructure developed, carbonation rate, and changes in strength and permeability after exposure to CO_2 solutions at 300° were completed. A cement formulation based upon Na_2O, CaO, Al_2O_3, SiO_2, P_2O_5, and H_2O appeared the most promising, and it yields results that meet the property and cost criteria necessary for use as a well completion material. As a result, it was tentatively selected for use in a full-scale test to be performed in FY1997. The cement formulation consists of 23.7 wt% Class F flyash; 15.8 wt% calcium aluminate cement, 31.4 wt% of a 40 wt% sodium metaphosphate solution, and 29.1 wt% Al_2O_3. The latter is in the form of lightweight, hollow ceramic micropheres. This formulation has a slurry density of approximately 1.2 g/cc, and after hydrothermal curing forms a strong, CO_2-resistant cement. As an example, autoclave exposure for 120 days to a 4 wt% Na_2CO_3 solution at 300° produced no evidence of carbonation or strength retrogression. In contrast, class G cement that is conventionally used for geothermal well completions, was severely deteriorated.

FUTURE PLANS

The BNL research phase of the activity to identify reaction paths leading to superior cementing formulations will be completed in FY1997. Specific topics will include: 1) evaluation of the effects of SiO_2 contaminants in Al_2O_3-enriched microspheres on the properties of sodium metaphosphate-modified flyash/calcium aluminate blended cement lightweight systems, 2) characterization of sludge/flyash blended cements, and 3) autoclave studies to measure the long-term durability of the cured lightweight formulations to carbonation in high CO_2 content hydrothermal environments. On-going cooperative work with Halliburton and Unocal to perform engineering-scale placement tests, economic evaluations and downhole exposures in high CO_2 brines will be continued.

INDUSTRY INTERESTS AND TECHNOLOGY TRANSFER

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

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