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HYDROTHERMAL CEMENTS FOR USE IN THE COMPLETION OF GEOTHERMAL WELLS

FINAL REPORT

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ABSTRACT

A research program to develop an improved cement for use in high-temperature geothermal wells was carried out. The report describes the work involved in the selection and evaluation of an aluminum hydroxide-cured cement from the SwRI family of hydrothermal cements for this use. The physical testing program is described; the topics discussed include placement ability, compressive and bond strengths, permeability to water, compatibility to drilling muds, corrosion properties, and thermal properties.

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EXECUTIVE SUMMARY

Specific formulations from a family of hydrothermal cements previously developed at SwRI* have been identified which appear to offer unique properties for geothermal well cementing. These cements are distinctly different from portland-type cements. They contain no calcium silicates and, rather than forming a crystalline hydrate, cure by an endothermic conversion of totally inorganic reagents into amorphous polymers of essentially silicon oxide and polysilicic acids. The hydrothermal cement is supplied as a dry blend of reagents and fillers in a "ready mix" formulation which is slurried with water (10 to 20% by weight) in the manner common to portland cement. Mixing and placement can be accomplished with conventional cementing equipment.

The cement has unique curing properties which offer specific advantages for use in geothermal or other high-temperature cement placement. These include:

1. Set is delayed until a specific threshold temperature is reached. Below this temperature, the cement slurry remains fluid or pumpable indefinitely. The threshold temperature may be varied by formulation; specific formulations are developed for activation temperatures from 66° to 316°C (150° to 600°F). This property allows the cement to be placed at the formation temperature without artificial cooling of the well and without the danger of a flash set.
2. The cure is endothermic, with heat supplied from the formation. Temperatures above the threshold or activation temperature accelerate the curing rate. Total cure time is important from the standpoint of avoiding excessive dilution of the cement slurry at any cement-water interface.
3. The cement cures with almost no shrinkage which assures good mechanical bonding to both casing and formation.
4. The cement chemically bonds to both metals and minerals with high shear bond strength, often in excess of the tensile strength of the cement. This chemical bonding is regenerative with time and temperature, i.e., the bond reheals after being broken. This is due to migration of certain cement constituents to the interface and chemical-physical bonding to the metal or mineral surface.
5. In previous work, these cements have been field tested using conventional mixing and pumping equipment for the cementing of deep gas wells in Texas and New Mexico.

* U.S. Patent No. 3,990,903, Issued Nov. 9, 1976.

The cured cement also demonstrates very good physical properties and environmental resistance. These include:

1. Compressive strengths obtained after 24-hr. cures exceeded the 6.9 MPa (1000 psi) requirement of the RFP, with strengths of 20 to 50 MPa (2900 to 7250 psi) obtained after longer cures.

2. Adhesion shear bond strengths to steel over 345 kPa (50 psi) and up to 8 MPa (1160 psi). The RFP suggested 69 kPa (10 psi) as a minimum requirement.

3. Stable in all environments up to 600°C (1112°F), once cured. This includes all formulations, cured at any presently known geothermal temperature and condition. This report includes data up to 400°C (752°F).

4. The cured cements are compatible with a wide range of drilling muds. In general, the cement is resistant to chemicals including concentrated acids, sulfates, and carbonates, with the exception of hydrofluoric acid.

5. The hydrothermal cements are noncorrosive to steel and, being slightly caustic with a bond coating of silica to the steel surface, can inhibit corrosion.

6. The permeability of hydrothermal cement cured at 200°C (392°F) or less is well below 0.1 millidarcy when measured with water at 551 kPa (80 psi) pressure difference. For specimens cured at higher temperatures, the permeability was much greater and extremely variable, probably because of dehydration of the specimen during cure and a resulting open, non-monolithic structure.

7. Costs in early 1980 will be about 25¢ per pound FOB manufacturing plant for large amounts of the $\text{Al}(\text{OH})_3$ formulation.

Recommendations for future work with these hydrothermal cements include:

1. Long-term exposure tests in a geothermal environment. Longest laboratory tests were 28 days.

2. Additional measurements of effect of formulation on thermophysical properties.

3. Effect of thermal cycling on physical and mechanical properties.

4. Development of better experimental consistometric measurements at temperatures above 300°C (572°F).

5. Improvement in permeability of the cements when cured at high temperatures. This may involve better understanding of the cure cycle and its relation to the permeability specimen and test procedure. The apparent dehydration of the permeability specimens cured at high temperatures should not occur in bulk specimens.

6. Additional study is needed to adapt the rheology of the hydrothermal cements to specific field mixing equipment, particularly jet mixers. The delay time for fluidization of the dry mix must be modified or accommodated in the mixing process.

I. INTRODUCTION

In October 1977, Southwest Research Institute (SwRI) began a research program to develop an improved cement for use in high-temperature geothermal wells. This report describes the research carried out during the two-year period under contract to Brookhaven National Laboratory. The work involved the selection of one or more candidates from the SwRI family of hydrothermal cements and optimization of the formulations for use in geothermal wells up to 400°C (752°F). The SwRI hydrothermal cements are a family of cements initially developed at the Institute to withstand the high temperatures associated with nuclear stimulation of gas-well production. These initial cements, patented in 1976,* were subsequently field tested successfully in several deep gas wells in Texas and New Mexico with bottom-hole temperatures to 165°C (329°F). The cements are formulated by mixing a dry powder with a low water ratio (10 to 20% by weight). They set by the formation of an amorphous polymer structure and, therefore, are quite distinct in structure and properties from portland cements. The set is temperature and time dependent, with formulations available which initiate cure at various critical temperatures. Pumping time and cure time can be adjusted to satisfy down-hole temperature profiles. The cement slurry remains pumpable indefinitely at temperatures below its initiation threshold. After cure the cements are stable to temperatures on the order of 600°C (1112°F) and have excellent strength and chemical resistance.

These general characteristics would appear to make the hydrothermal cements well suited for cementing of the very hot regions in geothermal wells. The present study, therefore, was initiated to select formulations most suitable for geothermal applications on the basis of their ability to satisfy physical property requirements, including:

1. Compressive strength, > 6,894 kPa (1000 psi) 24 hours after placement.
2. Permeability to water, < 0.1 millidarcy.
3. Bond strength to steel casing, > 69 kPa (10 psi).
4. Stability, no significant reduction in strength or increase in permeability after prolonged exposure at 400°C (~750°F) to 25% brine solutions, flashing brine, or dry steam.
5. Placement ability, capable of 3 to 4 hr retardation at expected placement temperatures.
6. Compatibility of the cement with drilling mud.
7. Non-corrosive to steel well casing.

* U.S. Patent No. 3,990,903, Issued November 9, 1976.

In order to determine the general and specific requirements for a reliable high-temperature well-cementing material, a review and evaluation was made of significant published information pertaining to high-temperature cements and the specific requirements for geothermal well cementing.

II. LITERATURE REVIEW AND EVALUATION

Titles and abstracts of some 3,000 references pertaining to geothermal-, oil-, and gas-well cements, hydrothermal cements, and well-completion methods were examined during the program. Some of these references date back at least to 1900, and many of them are also referenced in several of the listed books. Of all the thousands of titles, only 78 were considered pertinent to this program, and copies were obtained for review. The review and evaluation of the literature has been described below in several categories.

A. General Information

The cementing of casing in any well, whether for producing hydrocarbons or for production of geothermal steam, is almost a universal practice. A number of geothermal wells are produced open-hole. However, as use of geothermal steam power increases and more and more production wells are drilled, cementing of at least some of the hole will be required. As the temperatures of the producing zones increase to above 250°C (482°F) and eventually to as high as 400°C (752°F), completion of the well will require that the casing be effectively cemented to the formation. In the very high-temperature geothermal wells and deep geopressured wells, it will be mandatory to have production strings cemented to withstand high temperatures, high pressures, and highly corrosive fluids existing under these conditions.

As an aid to those not familiar with well-completion and -cementing techniques and problems, the following literature survey was made. Much of the oil- and gas-well technology is applicable to geothermal well completions.

If an overview of the whole field of geothermal energy is desired, a number of documents have been published which provide the information. A book edited by Kruger and Ott¹ gives some information on just about every phase of geothermal power. However, there is nothing in this book on the completion of wells. A source document of the National Technical Information Service by Smith² provides a continuing bibliography of all government-sponsored research on geothermal energy. One of the most ambitious documents is the comprehensive ERDA bibliography on geothermal resources³ which contains 5,476 citations of foreign and domestic research reports, journal articles, patents, conference proceedings, and books concerned with the exploration and exploitation of geothermal resources. The coverage dates back as far as useful references could be obtained and extends through June 1976. This is a valuable addition to the geothermal library.

Various volumes of proceedings^{4,5} and workshops⁶ cover a wide range of subject matter on geothermal energy, including the various geological sciences, drilling and production technology, energy utilization, environmental engineering, economics, and law. Many foreign authors are included, who give some information concerning geothermal developments in Italy, Mexico, Iceland, and other important areas. Armstead⁷ has brought together a number of excellent articles on geothermal energy.

B. Cements

The cementing of the geothermal well may be the most important operation in the completion process. Surface casing must be cemented in order to seal off and protect freshwater formations, provide an anchor for surface equipment, and give support at the surface for the deeper strings of casing. Intermediate strings of casing are cemented in order to seal off abnormal pressure formations effectively, isolate incompetent formations which would cause excessive sloughing unless supported by casing and cement, and shut off zones of lost circulation to prevent migration of fluids or steam to thief zones. Cement also effectively protects the casing from corrosive environments, notably corrosive fluids.

The cementing programs used in geothermal wells are usually similar to those used in deep oil or gas wells with high bottom-hole temperatures. An estimate has been made by Jet Propulsion Laboratory⁸ indicating a need for about 5,000 production and 2,000 reinjection wells to provide a national goal of 20,000 MW (26.8MHP) of electrical power by 1985. If these wells require about 183m (600 ft) of very high-temperature cementing, an estimated 150 sacks of special cement would be used for each well. Total cement requirements for the 7,000 wells, with an average depth of 1524m (5,000 ft), would be well over 12 million sacks. Volumes were calculated from theoretical rheology of an average hole, according to Graham.⁹

The American Society for Testing Materials (ASTM) had adopted specifications for ten different types of portland cements.¹⁰ However, these do not adequately define the properties required in oil and gas, or geothermal, wells. Therefore, the American Petroleum Institute (API) has established specifications for nine classes of oil-well cement.¹¹ These specifications have been accepted for cements used in geothermal wells; they do not specify portland cement, but they do specify the chemical requirements for each type of cement.

Working with well cements requires some knowledge of the nomenclature. API has defined the most commonly used terms associated with oil-well cementing,¹² also applicable to geothermal-well cementing.

For testing of oil- and geothermal-well cements and cement additives, the standard is the API RP 10B.¹³ Within the sections on each test, many of the ASTM standard tests are used. The purpose of this publication is to define the mandatory tests in Paragraph 2.6 of Specification 10A, and the nonmandatory tests for evaluating the physical properties of cement. New cement test schedules are issued as deeper and hotter wells are drilled.

A brief but comprehensive overview of cements and well cementing has been written by Parker, Clement, and Beirute in an eight-part series on basic cementing. The series includes sections on cement manufacture,¹⁴ specialty cements,¹⁵ additives and their application,¹⁶ slurry design,¹⁷ how to cement casing,¹⁸ squeezing and plugging,¹⁹ cementing calculations,²⁰ and auxiliary equipment and materials.²¹

A similar overview of the cementing of wells is given in an eight-part series by Suman and Ellis. This series includes articles on basic functions of cement,²² casing handling and inspection,²³ cement slurry chemistry and use of additives,²⁴ displacement mechanics and rheology,²⁵ guidelines for down-hole equipment and primary cementing techniques,²⁶ liner cementing, techniques and problems of pumping and placing cement,²⁷ special cementing such as plugging, squeezing, and tubingless completions,²⁸ and methods for evaluating primary cementing effectiveness.²⁹ These two series are both timely and excellent summaries of the whole spectrum of well cementing.

Portland cements, modified with various additives, make up the bulk of presently used geothermal-well cements. Recently, a number of new, non-portland cements have been developed and give promise of being good high-temperature cements.

Aldrich³⁰ describes an API Class G cement mixed with an additive to give a foamed cellular cement. He claims it has practical compressive strength, high or low permeability depending on porosity, and it has a future where light densities are required.

Cigni et al.³¹ discuss the cements used in Italian geothermal fields where temperatures up to 300°C (572°F) have been encountered. Problems caused by thermal conditions are found mostly in the lower string of cemented casing. The authors report reasonable success with a mix of 100 parts portland, 40 parts silica flour and retarders. They mention some test variances caused by using simulated conditions not totally representative of true down-hole conditions.

Clark et al.³² discuss tests made on a Class H cement developed by removing fines from the cement powder. This cement shows an increased thickening time which makes the slurry useful for high-temperature well cementing. The slurries showed high compressive strength, low permeability, and acceptable free-water loss.

As part of the DOE/Brookhaven research program to find good high-temperature cements, Eilers et al.³³ report on the development of geothermal-well completion systems. The authors gathered information from companies experienced in geothermal-well cementing concerning problems to be expected and cement requirements. The report also describes Dowell's current high-temperature cement research.

Kalousek and Chaw³⁴ discuss research relating some of the indicated low strengths of hot-well cements to the lime/silica ratio and the amount of alumina. Optimum compositions and ratios were presented. Six hydrated calcium silicates were found as potential binders in the study. The effects of alumina, ranging from beneficial to deleterious, were determined.

Kukacka et al.³⁵ have been involved in a long-term research program to determine the state-of-the-art and the potential for new geothermal-well cementing materials. Also, they are engaged in selecting and evaluating polymer cements. Contracts for the development of high-temperature inorganic materials have been awarded to five research organizations. This research encompasses almost every conceivable cement system.

Mallow and Dean³⁶ presented novel hydrothermal cements consisting of alkali metal silicates, polyvalent metal ions, siliceous fillers, and a hydratable silica source. These cements have a large number of unique chemical and physical properties. Of particular importance is the ability to retain their mobility and pumpability at high temperatures, up to 218°C (424°F) and increments of that, according to the recipe.

Maravilla³⁷ presented laboratory data to show that a unique hydrothermal setting cement can be used as manufactured--without the addition of high-temperature retarders--to cement oil and gas wells (and geothermal) where bottom-hole static temperature is in the range of 125° to 160°C (257° to 320°F). Retarders and other additives can be used to extend that range. This cement is composed of a binder, quartz sand, and calcium hydroxide. The binder is beta dicalcium silicate, one of the main mineral constituents of portland cement. It is considered an API Class J cement with good physical performance statistics.

Tschirley³⁸ discussed problems encountered in deep, hot wells with bottom-hole temperatures of 260°C (500°F) and above. Laboratory tests proved that interface thickening of high-density-oil muds and cements can be prevented by using the proper spacer fluid and circulating to cool down the bottom section of the well before cementing.

C. Effects of Temperature and Pressure

Field engineers and others who handle cementing for present-day wells are responsible for one of the most critical phases of well completion. It has never been so important from the standpoint of safety, environmental protection, and economics to insist that the best available technology be applied.

One of the most important factors controlling the chemical reaction, and the resultant performance, of a cementing composition is the temperature to which it is exposed. Tragesser and Parker³⁹ outlined in 1972 the many problems to be encountered in deep hot, or just hot, wells. Accurate field measurements of well temperatures are a requirement when cementing wells.

Temperature and pressure were recognized as the primary problems in deep and ultrahot wells. Phillips and Sykes⁴⁰ and Holmes and Swift⁴¹ recognized these problems and suggested methods which can improve well cementing under high-temperature conditions. It is suggested that 425°C (797°F) may be the highest temperature to be expected, even under abnormal geothermal gradients. Except for very deep wells, i.e., > 6098m (>20,000 ft), most geothermal wells usually have a lower-than-normal pressure gradient.

Beyond the problems encountered with high temperatures controlling the setting of the cement, variable formation temperatures above the producing zone may have to be reckoned with. McNitt⁴² suggests that temperature logs be run before cementing so that the variations will be known. So-called cold zones may actually be so cold that they inhibit the cement from setting.

Bottom-hole temperature in an oil well is the most important factor affecting the choice of oil-well cement according to Shell and Tragesser.⁴³ This is also true of geothermal wells. Temperature information is also useful in other phases of drilling, completing, and producing wells. This paper presents the results of the gathering of such temperatures by a task group of the API Committee on Standardization of Oil-Well Cements.

Boone⁴⁴ discusses effective cementing and analyzes the effect of hydrostatic pressure of cement and mud on the cementing operation. If internal pressure is maintained on the casing during cement cure, the casing may pull away from the cement when pressure is released.

D. Strength of Cement (Compressive and Bond)

Adequate cement strength has been commented on in many of the previous references. In this section, several papers will be mentioned which are concerned specifically with the compressive and bond strengths of well cements.

Boone⁴⁵ discusses the loading of cement by hydrostatic forces. Many cementing failures are caused by not taking into account the various pressures working on the cement during curing. He suggests that the cement have a compressive strength equal to the maximum anticipated differential pressure between the original formation pressure, in a zone above or below, and the minimum pressure reached in producing the reservoir.

Smith⁴⁶ suggests that the minimum compressive strength required for proper operation of a well is about 3500 kPa (507 psi).

Fertl et al.⁴⁷ review cement bond logs from the standpoint of how they are interpreted and what information is obtainable with them. They discuss pitfalls, misinterpreted logs, and proper techniques to use. If used properly, the logs are a valuable tool for evaluating the bond of the cement to both the casing and the formation.

E. Porosity, Permeability, and Stability of Cements

These factors are dealt with in many of the previous references. Cook and Cunningham⁴⁸ stress that recent studies have illustrated the need for filtrate-loss-controlled cementing slurries to help prevent fluid leakage following primary and liner cementing. Christian et al.⁴⁹ also show that fluid-loss additives are important for controlling or preventing gas/fluids migration.

The stability of cements under actual well conditions is discussed by Beirute and Tragesser.⁵⁰ The expansive and shrinkage characteristics of well cements under actual well conditions of temperature and pressure have been measured by a highly sensitive device especially developed for the purpose. It was learned that some cements first shrink during the initial set of the cement.

F. Cementing Methods

Cementing methods are numerous and variable. Each well will be cemented according to the well conditioning, depth, temperature, pressure, mud system, and other requirements. Determination of a particular cement and method should be chosen with great care and after consideration of all available knowledge of the existing conditions.

Graham⁹ gives a well-written account of a rheology-balanced cementing method with many mud and cement curves and formulas for predicting the combinations of cement flow factors, pumping rates, etc. best suited to the well-cementing job. One of the best books on well cementing, by Smith,⁴⁶ presents a composite review of the technical literature on well cementing. Basic principles, materials, and techniques of cementing are reviewed and illustrated.

After selection of the system and method, a spacer fluid is usually placed ahead of the cement. It is most important to insure the cleanest possible conditions of the surfaces to be cemented. Matsuo⁵¹ suggests that a low filter-cake mud system be maintained to avoid severe cleaning problems. Beirute,⁵² Carney,⁵³⁻⁵⁵ Clark and Carter,⁵⁶ and Garvin and Slagle⁵⁷ discuss a number of spacer fluids which may be used under various conditions.

Beirute's paper deals with the problem of formation damage and use of his spacer system to clean the casing and well-bore surfaces to provide the best cement bond strength. Carney describes the development of several spacer fluids that are compatible with the cement slurries. Clark and Carter describe a test facility for determining the forces available and involved in displacing the mud with a cement slurry. Garvin and Slagle discuss tests conducted in model well-bores to determine the influence of relative mud-cement weights and yield values upon displacement efficiency.

Braunlich⁵⁸ discusses several well-completion techniques used by the oil industry. Three main stages in the well-completion operations are featured: cementing, perforating, and stimulation.

Running and cementing deep liners are explained by Lindsey.^{59,60} It is important that good clean-out procedures are closely followed. Significant components used in setting the liners are described and illustrated.

Poblano⁶¹ describes a computer method for calculating the proper type of cement and additives required for a particular cement job. Computers are utilized to consider the effects of many variables on the displacement efficiency of casing slurries. A flow chart of the program used is provided. Its logic is to test first for the turbulent flow method, then the laminar

flow, and, finally, the stage method. Results of over 50 cementing jobs were good.

G. Cement Failures and Repairs

There are many reasons for cementing casing in the well-bore. Among the most important are: (1) to provide vertical and radial support to the casing string; (2) to permit control of the well if further drilling is done; (3) to protect the casing from corrosion; (4) to isolate porous formations to prevent migration of fluids and gases; and (5) to facilitate selective well treatment.

Problems encountered during and after primary cementations generally can be traced back to an incomplete displacement of the drilling fluids by the cement slurry. The result is an inadequate annular seal due to lack of bonding to both the casing and the formation. After cementing is complete, a cement bond log or temperature survey should be run. If gaps are found between casing and formation or casing and hardened cement in a critical zone, squeeze cementing should be considered. Where high pressure and temperature exist, casing failures can occur where incomplete cementing has been found. Murphy⁶² describes several techniques for re-cement jobs in zones of faulty primary cementing.

At Cerro Prieto, Mexico, failures were observed in all wells where a single casing was used both as production casing and as mechanical support of the bore-hole walls.⁶³ Construction deficiencies and the use of standard portland cement aggravated the problems and increased the number of collapses and fractures. Factors which, together with thermal effects, caused problems are:

1. Reservoir temperature levels from 250° to 345°C (482° to 653°F).
2. Faulty well-drilling features, frozen casings, cement channeling, and use of only one casing for wall support and production, as mentioned above.
3. Failures caused by incrustations, corrosion, collapses, fractures of cement, sand invasion, and loss of control.

Repairs were usually made by injecting grout at 2756 to 4134 kPa (400 to 600 psi) in collapsed or channeled cement. Casing had to be cemented along the total length using modified Type G cement with silica and perlite.

High-strength steel casings had to be used to withstand the tensile stresses, compressive stresses, and collapsing pressures, which were much greater than in oil or gas wells because of the thermal effect.

It is necessary to make a thorough study of well conditions in order to achieve satisfactory squeeze cementing jobs, according to Boone.⁶⁴ Squeeze cementing is a complex combination of fracturing, filtration rate, bonding, cement strength, and chemistry.

Rike⁶⁵ discusses the use of squeeze cementing to exclude water, gas, or oil from the producing formation, repair of casing or pipe failure, and repair of a faulty primary cement job. His paper describes the low-pressure squeeze, extenders and fluid-loss control, retarders, etc., as well as special cement systems.

H. Drilling Geothermal Wells

The methods used in drilling and completing geothermal wells are not too much different from those used for conventional oil wells. The differences between drilling a geothermal well and an oil well are discussed by Cromling.⁶⁶ The high temperatures associated with geothermal wells affect the circulating system and the cementing procedures, as well as the design of casing and drilling string. These unique problems must be coped with along with those normally encountered. This paper describes drilling in the Geysers area and the Imperial Valley.

Cromling's second article⁶⁷ duplicates much of the above, while adding a few notes concerning the use of blow-out preventers on geothermal wells.

Matsuo⁵¹ gives a good report on drilling for geothermal steam and hot water. He rates drilling rigs, and discusses methods and mud systems, cementing of wells, and numerous other facets of geothermal well drilling and completion.

To complete this section, several documents on drilling fluids are included. The Bureau of Mines has made an extensive literature survey on geothermal-well drilling-fluid technology.⁶⁸ This paper describes the composition, properties, and problems encountered with drilling fluids of various formulations used at the important geothermal areas of the world.

API Bulletin D-11⁶⁹ is a glossary of drilling-fluid and associated terms, and API Bulletin D-4 reports on the effects of drilling-mud additives on oil-well cements.⁷⁰

I. Miscellaneous

There are a great many more references available concerning geothermal wells, including those on the drilling of wells, mechanics of geothermal fluids or steam, and various aspects of well completion, especially if one goes back prior to 1970. Most of the references included in this report contain bibliographies or reference lists ranging from several to more than 50 articles, many of them pre-1970.

The following are some of the miscellaneous articles of interest. Although not directly related to geothermal cements and cementing, they are concerned with some of the problems found in the geothermal environment and they provide general information on the deep geopressured zones which will be produced in the future.

An Assessment of Geothermal Resources⁷¹ lists many of the geothermal areas of the U.S. by various characteristics.

DePuy et al.⁷² and Kukacka et al.⁷³ are concerned with research on polymer-concrete composites for energy-related systems, materials that are needed for handling hot brine and steam. Thermal and physical properties of these materials are being studied.

The last five articles and documents reviewed, which are concerned with geopressured geothermal resources, are by Bebout and Gregory,⁷⁴ Dorfman and Deller,⁷⁵ Howard et al.,⁷⁶ Swanson et al.,⁷⁷ and Wilson et al.⁷⁸

Most down-hole equipment for use on both conventional oil wells and geothermal wells is efficient to about 260°C (500°F). We are developing new cements for use at higher temperatures, and new materials will be required to put the cement down into the hole. Steels used in drilling and producing oil and gas wells are also used in geothermal wells. These steels may lose much of their strength when exposed to temperatures in excess of 260°C (500°F). The thermal expansion of steel is much greater than that of cement at these temperatures. Several strings of casings are usually required in geothermal wells to control formation fluids and to prevent excessive loss of formation into the well-bore. Cementing in most very hot geothermal wells must be from the surface to the producing formation and, in the future, in the hot production zone. Therefore, new materials will be needed that are compatible with the high temperatures.

III. FORMULATION OF HYDROTHERMAL CEMENTS

A. General

In response to the need of oil and gas producers for cements adaptable to deep hot-well environments capable of withstanding not only geothermal temperatures but the thermal overburden of nuclear stimulation, a family of hydrothermally curable cements was developed at Southwest Research Institute. These cement mixtures upon addition of water retain their mobility and pumpability at less than the threshold activation temperatures that initiate the cure for indefinite periods of time. The activation temperature is distinctly different among the three basic systems which are designated as 65°, 110°, and 220°C (149°, 230°, and 428°F) formulations. The 65°C formulation, for example, remains pumpable for indefinite periods of time at temperatures below 65°C. While curing is initiated at 65°C (149°F), several hours are required before a significant change in rheology is induced. As the temperature is elevated, the rate of cure increases proportionately, obeying second-order reaction kinetics. The three basic recipes allow the selection of a suitable system for a broad range of down-hole temperatures assuring a trouble-free placement of the cement without danger of flash setting before the cement is pumped into position. The cure is endothermic and is triggered by the heat supplied by the surrounding formation. We have increased the useful range of the SwRI cements to 316°C (600°F) and higher during the course of this program.

These novel cements contain no portland or modified portland cements and their mechanism of cure is totally different, as will be noted in the discussion below. Portland cements owe their unique character to the formation of calcium silicate hydrate crystals by the solution, hydration, and crystallization of clinker particles. Portland is manufactured by the calcination and conversion of limestone, clay, and silica with related elements such as aluminum, iron, and sulfur in judicious proportions. This anhydrous mineral, upon exposure to water, partially dissolves, gels, and finally crystallizes to give a matrix of interlocking crystals contributing to the strength and stability of the product. The crystal hydrates are, however, subject to thermal retrogression and chemical attack by acids and many salts. This vulnerability, combined with tendencies to flash set and undergo shrinkage during cure, can limit the utility of portland cements in certain critical geothermal applications.

The SWRI cements are distinctively different, containing no calcium silicates and, rather than forming a crystalline hydrate, cure by an endothermic conversion of reagents into amorphous polymers of essentially silicon oxide and polysilicic acids. The reagents consist of a blend of naturally occurring mineral fillers, soluble alkali metal silicate, and polyvalent metal oxides and hydroxides. Substitution of the metal oxide changes the temperature of activation of the cement. These unique cements were made possible by the development of a new class of alkali metal silicates in the form of spray-dried hydrate powders. These powders have unique physical and chemical properties manifested by their fluidization of low-water content slurries and the rate and nature of their chemical reaction with polyvalent metal salts.

The dry mix of hydrothermal cement thus consists of the inert fillers (e.g., sand and silica flour), the spray-dried silicate powders (Britesil), anhydrous sodium silicate, and a selected metal oxide or hydroxide curing agent. When the dry mix is blended with the optimum amount of water, which varies from 10 to 20% of the total mixture, a 2- to 3-minute induction period follows in which the alkali silicate powder hydrates and, until it does, the mixture remains very dry in appearance. With the dissolving of the silicate, the mixture spontaneously liquefies and becomes fluid. Until that time, no pouring or pumping is possible. This finite delay for fluidization during mixing is not a problem during batch mixing, but may require some adaptation for the cement to be used with continuous "jet mixing" devices.

Once fluidized, the aqueous mixture remains fluid indefinitely at temperatures below its activation threshold. Upon application of heat above this threshold, the alkali metal silicates are converted to high molecular weight, amorphous silicate moieties by the substitution of monovalent alkali metals by polyvalent metals in a repeating chain of alternating silica-polyvalent metal units. The polymerization reaction is endothermic, and the cement cures and sets with almost no shrinkage.

The temperature regions defined as activation thresholds mark the thermal regions at which the curing agent begins to exhibit ionic, reactive character. At or slightly above this temperature, the reaction proceeds very slowly, requiring several days to achieve substantial strength. With increased heating, the reactions accelerate. It is necessary to make the

cement selection in conformance with requirements such as pumping time, optimum curing rate, and the expected environment with which the slurry must interface. When cured or firmly set, the hydrothermal cements withstand prolonged exposure to acids, brine, heat, and moisture, usually increasing in mechanical strength with time.

B. High-Temperature Formulations

The basic formulation of SwRI hydrothermal cement systems for use at temperatures from about 70°C (158°F) to over 260°C (500°F) are listed in Table 1. It can be seen that there are only small differences from formulation to formulation in the relative amounts of the various ingredients. It should also be noted that the class of polyvalent metal salt is critical to the kinetics of the cement curing. The reactivity of aluminum oxide, hydroxides, and hydrates varies greatly with their source and structure. Amphoteric aluminum hydroxide prepared by controlled hydrolysis of sodium aluminate is greatly different in activation temperature and reactivity with alkali silicates from hydrated alumina or anhydrous calcined alumina. The commercially available stable aluminum hydroxides and hydrated aluminas are adequate for this cement technology. Sources and types of the preferred reagents are listed in Table 2. The dry materials are blended and stored in a conventional manner, similar to that used for portland cements, and mixed with water when needed.

Table 1
SwRI Hydrothermal Cement Formulations

Ingredients	Formulation, parts by weight				
	#1 at 66°C (151°F)	#2 at 204°C (399°F)	#3 at 260°C (500°F)	#4 at 260°C (500°F)	#5 at 260°C (500°F)
Silica sand	50	50	50	50	50
Silica flour	25	25	25	25	25
Britesil	10	10	10	10	10
Anhydrous sodium silicate	10	10	10	10	10
Al(OH) ₃		7			
La ₂ O ₃			5		
ZnO	5				
ZrO				7	
LaCO ₃					10
La(OH) ₃					10
H ₂ O	18	18	18	18	18
Total Parts	118	120	118	120	133

Table 2
Types and Sources of Ingredients

Material	Type and source
Silica sand	-2- + 60 mesh
Silica flour	-200: 100%
	-325: 80%
Britesil C24	2.4/1 ($\text{SiO}_2/\text{Na}_2\text{O}$), 18% water, spray-dried micro-spheres (-100 mesh)
Anhydrous Sodium Silicate	3.22/1 ($\text{SiO}_2/\text{Na}_2\text{O}$), glass powder, -325 mesh
$\text{Al}(\text{OH})_3$	RH-31f hydrated alumina, Reynolds Aluminum Company
Al_2O_3	RC-20 calcined alumina, Reynolds Aluminum Company
ZnO	XX60, New Jersey Zinc
ZrO	Zirconia, -325 mesh, National Lead
LaCO_3	Cake, -325 mesh, Molycorp
$\text{La}(\text{OH})_3$	Lanthanum hydroxide, -325 mesh, Molycorp
La_2O_3	Lanthanum oxide, -325 mesh, Molycorp

The process of optimizing the formulations involved precise variations of each ingredient, in the amounts blended and choice of class of silicate and metal oxide employed. Use of different ratios of sodium silicate will increase or decrease the reactivity. Use of other zinc salts, for instance zinc carbonate or hydroxide, prepared with each different silicate will exhibit varied reactivities. The stoichiometries of the various formulations were thus empirically determined on the basis of final product properties.

Excesses of the silicates can reduce the dimensional stability of the hardened cement. Further, excesses of the polyvalent metal oxides may reduce or inhibit adhesion of the cement to interfaced surfaces. Under optimum hydrothermal conditions a recipe designed for it will perform admirably. However, under the conditions encountered in geothermal wells, a recipe needs to be designed for a minimum cure temperature and optimum pumpability characteristics for the worst conditions encountered.

With this in mind, we extended our optimization procedures to find the "optimum formulation" for use at over 316°C (600°F). In Table 1, formulations #3 and #5 appeared to be the best and were pumpable for over 3 hours at this temperature. After 48 hours at 260°C (500°F), they were both in the gel state.

The final optimization procedure produced several candidates for a cement useful at temperatures over 316°C (600°F) and at least to 400°C (752°F). Table 3 gives the formulations for these selections. The aluminum hydroxide (#60 series) cement is the selection sent to National Bureau of Standards for verification of properties.

Table 3
SwRI Hydrothermal Cement Formulations
for Use at 316°C (600°F) and Higher

Ingredients (by weight)	Specimen series					
	#60	#70	#80	#90	#100	#110
Silica sand		50			50	
Silica flour	50	25	50	50	25	50
Britesil	10	10	10	10	10	10
Anhydrous sodium silicate	10	5	10	10	5	10
Bentonite	0.5	3	0.5	0.5	3	0.5
Al(OH) ₃	7					
Al ₂ O ₃		5				
TiO ₂					8	
ZrO ₂			7			
La(OH) ₂						7
LaO ₂				7		
H ₂ O	23	18	23	23	20	23

Appendix A gives a listing of the large number of formulations which were tested before the basic mixes described were chosen.

C. Mechanism of Cure

The reactions of hydrothermal cement formulations under conditions of elevated temperature and pressure where dilution and dehydration are avoided have been studied by x-ray diffraction. The zinc oxide and aluminum hydroxide curing systems have received the principal amount of study, and each will be reviewed herein.

1. Zinc Oxide Curing Recipe. Formulations comprising sodium silicates of 2.4/1 (SiO₂/Na₂O) ratio as a soluble hydrate powder together with anhydrous sodium silicate of 3.2/1 ratio are extended with silica flour and quartz sand. The grade of zinc oxide was selected on the basis of particle size to give a stable room temperature slurry with several weeks of shelf life before any change is observed in rheology. Slurries containing about 16 to 17% water by weight achieve viscosities suitable for pumping and measure approximately 1000 to 5000 cps by Brookfield viscometry. They are thixotropic slurries, and so their viscosity is shear dependent.

As the slurry is heated under restraining pressure to prevent evaporation, a sequence of reactions occurs which may be identified by sampling at varied time/temperature intervals. The slurry contains detectable amounts of sodium zincate, zinc oxide, zinc silicate (Zn₂SiO₄), and the quartz filler after one hour of autoclave exposure at 120°C (248°F). After about four hours, only traces of zinc silicate or sodium zincate are detectable. After eight hours, the only crystalline species observed are

zinc oxide and quartz. After twelve hours, the mass is extremely hard, with no visible shrinkage or free liquid apparent. Specimens are found to be alkaline (ph 10+), strong [over 20,000 kPa (2,900 psi) compressive strength in twelve hours], and strongly bonded to metal [shear bond of over 3400 kPa (494 psi) measured after twelve hours, and about 7500 kPa (1088 psi) in one week].

It is believed that sodium silicate solutions, upon heating in the presence of zinc oxide, undergo a variety of reactions including the generation of zinc hydroxides and sodium zincates with the resulting release of silicic acid under alkaline conditions. It is probable that the reaction of silicic acid monomer with hydroxide ions causes an expansion in the coordination numbers of silicon from 4 to 6, and this complex then reacts with another molecule of silicic acid as shown in Fig. 1 below, ultimately growing to polysilicic acid or silicon oxide polymer. Zinc hydroxide and sodium zincate may enter into the polymerization at any stage intermittently or regularly depending upon activation levels, accessibility, and mass effects. All components of the binder appear amorphous. The zinc silicate evident in the early stages does not reappear after the mass has attained significant rigidity, nor does sodium zincate persist or reoccur even after 14 days at 120°, 200°, or 300°C (248°, 392°, or 572°F).

Figure 1. Proposed Curing Mechanism for the Basic Zinc Oxide Formulation

Under certain conditions such as evaporation during heating, crystals of sodium silicate (ortho and meta) have been observed by SEM-microprobe analysis.

2. Aluminum Hydroxide Curing Recipe. Formulations comprising the same ingredients as discussed above with zinc oxide are employed; however, aluminum hydroxide is substituted for zinc oxide at concentrations determined empirically by hydrothermal curing and physical/mechanical testing of samples. The mechanism of curing with aluminum hydroxide is analogous to the chemistry of the production of aluminosilicate catalysts produced for cracking petroleum by the oil industry. Tamele⁷⁹ has shown that the condensation of SiOH groups on silica gel with AlOH groups leads to the formation of strong acid sites which are primarily responsible for the activity of the aluminosilicate cracking catalyst, widely used in the oil industry.

It is assumed that a sodium ion exchange occurs between acidic aluminum hydrogel and sodium silicate to produce first sodium aluminate and silicic acid followed by the generation of aluminum salts of silicic acid and polysilicic acids following a scenario similar to that depicted in Figure 1. In this system, however, trivalent aluminum coordinates with four oxygen atoms as it unites with silicic acid producing a negatively charged alumina siloxane structure as in Fig. 2.

Figure 2. Proposed Curing Mechanism for the Aluminum Hydroxide Formulations

Lowenstein⁸⁰ has formulated certain rules that may govern the linking together of tetrahedra which are occupied by silicon and of tetrahedra and octahedra which are occupied by aluminum. The distribution of such tetrahedra in a crystal is not entirely random, and it is likely that the same will be found to be true in the case of amorphous aluminosilicates:

a. Whenever two tetrahedra are lined by one oxygen bridge, the center of only one of these can be occupied by aluminum; the other center must be occupied by silicon or another small ion of electrovalence four or more, for example, phosphorous.

b. Whenever two aluminum ions are neighbors to the same oxygen anion, at least one of them must have a coordination number greater than 4, such as 5 or 6, toward oxygen. These rules explain the maximum substitution of 50% of the silicon in three-dimensional frameworks and plane networks of tetrahedra by aluminum. For 50% substitution, rigorous alternation between silicon and aluminum tetrahedra becomes necessary.

When aluminosilicates are produced in the presence of high concentrations of alkali metals, each ion of aluminum plus 3 takes up one sodium ion and one mole of water. Since all the sodium ions in the gel are exchangeable, the aluminum atoms which are the exchange sites must be near or at the surface of the gel. The inherently strong acid character of aluminum silicate gels favors the continued interaction with sodium silicate, the formation of polysilicic acids, and the chain interaction of polysilicates with aluminosilicate such that the strategically located aluminum ions readily shift their coordination from 6 to 4. Empirically, it has proved most effective to minimize the concentration of aluminum hydroxide and promote a high degree of silicic acid polymerization and a low level of aluminum substitution. At a stoichiometry of 1:1 of soluble silicate to aluminum hydroxide, the residue of unreacted aluminum hydroxide is overbearing to the matrix, depositing out and migrating to the surfaces and cement-metal interfaces. When the molar ratio of silicate to aluminum is slightly greater than one, the matrix is permeated with the excess alkali silicate and the aluminum hydroxide is more completely substituted. This provides a cement/steel interface with a greater distribution of alkali silicate and a strong chemical bond with regenerative properties. The preferred binder for a hydrothermal cement with adhesive regenerative properties is

The silicon oxide components may occur in monomeric or polymeric states within the above structure, most likely occurring as both forms.

While stoichiometry is relevant to optimum results, considerable latitudes are allowable, depending upon the ultimate application and property requirements of the cement. For application in the range of 125° to 260°C (257° to 500°F) the recipe can tolerate broad ranges of reagent concentrations, i.e., from 10 to 20% alkali silicate versus 4 to 8% of the aluminum hydroxide. In a typical recipe, comprising 10% anhydrous sodium silicate with 10% hydrated spray-dried powder, excellent strength is obtained with from 4 to 7% aluminum hydroxide (all weight percent basis total recipe composition). As the service temperature is increased, the permeability of the cured cement begins to increase because of dehydration of residual alkali silicate hydrogels as well as breakdown of silanol groups in the polysilicic acid and aluminosilicate polymers. By trimming the reagents to approximate the state of total conversion of alkali silicate and complete reaction of all aluminum ions, the permeability at temperatures above 260°C (500°F) should be less than 0.1 millidarcy. This approach to ideal stoichiometry may sacrifice bond regeneration in the hottest region of a hot deep well application, but this is compensated for in the upper cooler regions where thermal influences are less intense and the reaction deviates from complete to less-than-complete with respect to silanol dehydration and general condensation.

D. General Properties of Cured Cements

Physical property evaluations are discussed in the next section. However, certain properties of the cements related to their chemistry will be presented here. An essential feature of these cements for geothermal well cementing is their ability to be placed down-hole at the formation temperature. Formulations are selected to allow ample pumping time before gelation or thickening occurs. By placing the cement at the equilibrium temperature of the well, artificial cooling of the well is not necessary and subsequent problems associated with differential expansion of the casing, cement, and formation are avoided. Such problems include disbonding and/or crushing of the cement by thermal expansion of the casing.

The rate of set of the hydrothermal cement is controlled by its composition and the temperature. While a flash set should be avoided, too long a set time may allow for dilution of the slurry by formation waters and thereby degradation of strength at the interface. This may not be a problem when the overall height or mass of cement is large so that surface or interface effects are confined to a small percentage of the cement volume.

The hydrothermal cement slurry may be delivered to the well bottom by conventional means but should be separated from conventional cement slurries, if employed before or after the hydrothermal cement, using a few barrels of water or mud. The cement is compatible with most drilling muds and additives commonly employed in the oil and gas industry. The few exceptions include alcohols, ketones, and other water-miscible organic solvents which could abstract moisture from the lean cement slurry and

cause thickening. Acids and acid salts will also induce thickening and, hence, should be "spaced" by water or mud. Field tests of a SwRI hydrothermal cement are described in the April 1975 issue of The Pipeliner published by El Paso Natural Gas Company.⁸¹

Another feature of the hydrothermal cement which makes it attractive for well cementing is its high shear bond strength to both metals and minerals. Mechanical bonding is enhanced by the nonshrinking property of the cement on cure. In addition, chemical bonding occurs also, and it has been shown that this chemical bond is regenerative. The presence of unreacted hydrous sodium silicate glass in the matrix contributes to rehealing of broken shear bonds. Any unreacted alkali silicate capable of migration to the cement-metal, or cement-formation, interface may react with the metal or mineral surface to form silicates of the metal or mineral, providing a chemical-physical bridge between the two faces. This pseudo-autogenesis has been demonstrated both in the laboratory and in the field. The field tests comprised bond logging of cemented casing before and after perforation of the casing with a later bond log performed to assess the state of adhesion after several subsequent days. Both laboratory shear bond specimens and the gas-well casing logs revealed a rehealing of sheared faces after a few days under hydrothermal conditions. In many cases, the interfacial shear strength may exceed the tensile strength of the cement.

IV. PHYSICAL PROPERTIES EVALUATION

The following tests were made on the various cement formulations to evaluate their physical properties:

1. Placement Ability. The thickening time of the several formulations was determined by pressure-temperature consistometric testing. A high-temperature thickening time test chamber was fabricated to simulate the API RP10B recommended equipment but which would be capable of temperatures to 400°C (752°F).

2. Compressive Strength. This test was similar to that specified in ASTM C109, Standard Method of Test for Compressive Strength of Hydraulic Cement Mortars. Some modifications were necessary when testing small round specimens. Compressive strength tests were made on specimens removed from the curing process or aging after periods of from 1 day to 28 days.

3. Bond Strength. A test was developed to determine the shear bond strength by use of small steel cylinders filled with cement and containing a center pin. The shear bond is measured by forcing the pin out of the cured cement using an Instron Testing Machine.

4. Permeability to Water. Tests were made in a cement permeameter essentially as described in API Bulletin RP10B, Section 9, Permeability Test. Specimens were cast in steel molds, cured, and tested at room temperature.

5. Compatibility with Drilling Mud. A series of tests were made using typical drilling muds containing the various additives which might be encountered in drilling a geothermal well. Cement specimens were exposed to these slurries under simulated down-hole conditions.

6. Corrosion Properties. Tests were made to determine the effects of the SwRI cement on well casing.

7. Coefficient of Thermal Expansion. The linear coefficient of thermal expansion was determined in accordance with ASTM C531, Shrinkage and Coefficient of Thermal Expansion of Chemical-Resistant Mortars.

8. Elastic Moduli. A test of the flexural strength and modulus of elasticity in flexure was determined.

9. Thermal Conductivity and Specific Heat. These properties were determined for one of the cement formulations.

Curing and aging of our specimens have been done under simulated down-hole geothermal conditions which provide a realistic and severe test of a cement to be used for completing a well with a bottom-hole temperature of 316°C (600°F) and higher. We have not precured or preset the specimens at a lower temperature and then exposed them to the high heat for long-term aging. For other materials, it may be possible to cool the well down to 150°C (302°F) or lower for periods of an hour or more, which would allow casing to be cemented without a flash set, or with few pumping problems. A cement with a high compressive strength would be required to withstand the force of the expanding casing upon reheating to the static bottom temperature.

The long-term exposure of our specimens for periods greater than 7 days at 316° and 400°C (600° and 752°F) has been in an environment of static steam and artificial brine. Enough liquid is placed in the autoclave to provide a fully saturated vapor condition at the final exposure temperature. This usually amounts to only 20 or 30 ml (0.676 or 1.015 oz) of water in the 1-liter (1.057 qt) autoclave loaded with specimens. The brine solution used is a synthetic, simulating the "average" brine at the Mesa geothermal field, as shown in Table 4.

Table 4
Dissolved Solids Content of 5 East Mesa Wells, ppm

Component	5-1A	5-1B	5-1C	6-1A	6-1B	Composite average
SiO ₂	201	130	130	128	220	162
Na	593	798	798	9,000	5,130	3,264
K	29	49	49	1,047	632	281
Ca	16	46	46	896	389	279
Mg	2	4	4	15	22	9
Cl	454	825	825	15,870	9,014	5,398
SO ₄	102	169	196	192	20	136
HCO ₃	331	705	717	126	305	437

A. Placement Ability

The thickening time of oil-well cements is normally tested by use of the Chandler Consistometer. This is gauged by the length of time it takes the cement to reach 100 standard API units of consistency (Bearden, Bc units) as recommended by API RP10B. The Chandler unit at SwRI is capable of only 204°C (400°F) although it can be pressurized to 172 MPa (25,000 psi). We, therefore, modified an Autoclave Engineering, Inc., stainless steel autoclave for use as a consistometer up to 400°C (752°F) and 36.5 MPa (5294 psi).

The heating unit is controlled automatically, reading both the heater temperature and the cement temperature inside. A stirring paddle is brought through the head using water-cooled Teflon seals. The stirrer is turned by a motor which is variable to turn the paddle from 1 to 500 rpm. Connected to the stirring rod outside the autoclave are strain gages which electronically convert torque into consistency of the slurry. The consistency measured in this manner can be roughly translated into the API units by calibration with a slurry of known thickening time. Table 5 gives the results of thickening time tests indicating the placement ability of that slurry. Figure 3 shows the effect of temperature on thickening time of the various SwRI cements.

Table 5
Results of Thickening Time Tests

Activator used	Lowest activation temperature, °C(°F)	Hours to 100 units consistency
ZnO ₂	60(140)	6
	90(194)	2
	120(248)	3/4
Al(OH) ₃	204(400)	4
	218(424)	3
	232(450)	5
	260(500)	8
Al ₂ O ₃		(48 - gel only)
ZrO ₂	218(424)	7
	260(500)	6
ZrCO ₃		(48 - gel only)
	260(500)	?
La ₂ O ₃		(Hard in 48)
	260(500)	2
ZrO ₂	330(626)	2
	340(644)	1
Al ₂ O ₃ (with minus 60 mesh silica sand)	400(752)	2

Figure 3. Effect of Temperature on Thickening Time of Various SwRI Cements at Down-Hole Pressure, Typically 17m 225 kPa (2,499 psi)

B. Compressive Strength Tests

Various formulations of the SwRI hydrothermal cements were cured in steam and/or brine and the compressive strength was then determined. The ASTM C109, Standard Method of Test for Compressive Strength of Hydraulic Cement Mortars, was followed for making the tests. After curing and exposure for periods of time varying up to 28 days, the specimens were removed from the high-temperature and -pressure facility and tested at room temperature.

Strength tests were made using a Model No. 977 Instron Load Cell Testing Machine calibrated with standards traceable to NBS. The maximum load available on this machine is 44,537 N (10,000 lb). For a greater load, we used a calibrated Forney FT-40-DR Compression Testing Machine capable of providing a maximum load of 1,113,435 N (250,000 lb). The ram speed during testing was 0.5 mm/min (0.02 in/min); compressive strength S_c was calculated by the standard formula, $S_c = 4F/\pi D^2$, where F = fracture force applied and D = diameter of specimen.

For many of the strength tests the specimens were obtained by placing the cement in a small curing cell 0.025 m (1 in.) in diameter by 0.102 m (4 in.) long. These cells were made from rigid copper tubing, capped at the bottom, filled with cement, capped at the top, and placed in the autoclave at the required temperature and conditions for thermal aging. The caps were not sealed tightly, but were open enough to allow the steam and/or brine to contact the cement. After curing, the specimen was removed by cutting away the copper tubing.

Other specimens were cured in glass test tubes with a stopper placed in the top. Also used were short pieces of Pyrex glass tubing, sealed at the bottom, filled with cement, and stoppered for curing. It was found that at curing temperatures $>316^\circ\text{C}$ (600°F), the cement and glass reacted to form an intermediate form of sodium borosilicate between the glass and the cement. These specimens were very hard and strong.

At the lower temperatures, regular 0.051 x 0.051 m (2-inch) cubes were made for testing using three-unit cube molds. These could be used at temperatures up to 150°C (302°F). Table 6 gives the compressive strength test results for the various specimens cured at temperatures up to 260°C (500°F) in saturated steam. Table 7 gives the estimated range of one-day compressive and bond strengths for aluminum hydroxide cement at 316°C (600°F). Table 8 gives the test results for the SwRI formulations cured at 316° and 400°C (600° and 752°F).

Table 6
Compressive Strengths of Various SwRI Formulations
Cured at Lower Temperatures

Specimen	Curing		Curing time days	Compressive strength kPa(psi)
	condition	temperature °C(°F)		
ZnO	S.S.*	120(248)	1	>20,670(3000)
	S.S.	100(212)	5	18,465(2678)
	S.S.	218(424)	7	26,180(3797)
	S.S.	218(424)	14	34,865(5057)
	S.S.	218(424)	28	37,480(5436)
Al(OH) ₃	S.S.	120(248)	1	14,560(2111)
	S.S.	120(248)	5	18,430(2673)
	S.S.	204(400)	1	20,210(2931)
	S.S.	204(400)	3	21,360(3098)
	B.L.	260(500)	3	>20,670(3000)
Al [Al(OH) ₃]	S.S.	260(500)	1	21,718(3150)
	S.S.	260(500)	7	15,847(2298)
A2 "	S.S.	260(500)	7	16,605(2408)
A3 "	B.L.	260(500)	7	19,361(2808)
A4 "	B.L.	260(500)	7	16,949(2458)
Al ₂ O ₃	S.S.	260(500)	2 gel - no tests	
	S.S.	260(500)	7	>20,670(3000)
ZrO	S.S.	260(500)	2 gel - no tests	
ZrCO ₃	S.S.	260(500)	2	>20,670(3000)
Z1 (ZrO ₂)	S.S.	260(500)	7	47,680(6916)
Z2	S.S.	260(500)	7	48,060(6971)
Z3	S.S.	260(500)	7	39,962(5796)
Z4	S.S.	260(500)	7	43,751(6346)

* S.S. = saturated steam
B.L. = brine

Table 7
Estimated Range Compressive and Bond Strengths

Activating agent	Curing		Time days	Strength, kPa(psi)	
	condition	temperature °C(°F)		compressive	bond
Al(OH) ₃	S.S.*	316(600)	1	17,235(2500)	1896(275)
Al(OH) ₃	S.S.	316(600)	1	24,129(3500)	2068(300)

* S.S. = saturated steam

Table 8
Compressive Strengths of SwRI Formulations Cured at Higher Temperatures

Specimen No.	Activating agent	Curing condition	temperature °C(°F)	Curing time days	Compressive strength kPa(psi)
60	Al(OH) ₃	S.S. [†]	316(600)	28	23,495(3408)
70	Al ₂ O ₃	S.S.	316(600)	28	28,634(4153)
80	ZrO ₂	S.S.	316(600)	14	25,148(3647)
90	LaO ₂	S.S.	316(600)	28	8,268(1199)
100	TiO ₂	S.S.	316(600)	14	12,677(1838)
110*	La(OH) ₂	S.S.	316(600)	14	5,842(847)
601A	Al(OH) ₃	S.S.	316(600)	15	33,864(4912)
601B	Al(OH) ₃	S.S.	316(600)	15	21,524(3122)
601C	Al(OH) ₃	S.S.	316(600)	15	22,654(3286)
601D	Al(OH) ₃	S.S.	316(600)	15	20,105(2916)
601E	Al(OH) ₃	S.S.	316(600)	15	33,981(4929)
601F	Al(OH) ₃	S.S.	316(600)	15	34,553(5012)
602A	Al(OH) ₃	B.L.	316(600)	14	28,889(4190)
602B	Al(OH) ₃	B.L.	316(600)	14	21,806(3163)
602C	Al(OH) ₃	B.L.	316(600)	14	19,567(2838)
602D	Al(OH) ₃	S.S.	316(600)	14	25,933(3761)
602E	Al(OH) ₃	S.S.	316(600)	14	31,721(4601)
602F	Al(OH) ₃	S.S.	316(600)	14	35,118(5093)
603A	Al(OH) ₃	B.V.	316(600)	28	38,976(5653)
603B	Al(OH) ₃	S.S.	316(600)	28	34,835(5052)
603C	Al(OH) ₃	S.S.	316(600)	28	26,175(3796)
603D	Al(OH) ₃	S.S.	316(600)	28	34,711(5034)
603E	Al(OH) ₃	S.S.	316(600)	28	41,160(5970)
603F	Al(OH) ₃	B.L.	316(600)	28	29,454(4272)
604A**	Al ₂ O ₃	S.S.	400(752)	7	3,169(459)
604B	Al ₂ O ₃	S.S.	400(752)	7	2,232(323)
604C	Al ₂ O ₃	S.S.	400(752)	7	4,044(586)
604D	Al ₂ O ₃	S.S.	400(752)	7	5,815(843)
604E	Al ₂ O ₃	S.S.	400(752)	7	8,281(1201)
612A	Al(OH) ₃	S.S.	316(600)	28	37,378(5421)
612B	Al(OH) ₃	S.S.	316(600)	28	38,928(5646)
612C	Al(OH) ₃	S.S.	316(600)	28	38,618(5601)
613A	Al(OH) ₃	S.S.	400(752)	28	48,023(6965)
613B	Al(OH) ₃	S.S.	400(752)	28	42,821(6211)
613C	Al(OH) ₃	S.S.	400(752)	28	44,316(6428)
614A	Al(OH) ₃	B.L.	400(752)	28	40,513(5876)
614B	Al(OH) ₃	B.L.	400(752)	28	46,438(6736)
614C	Al(OH) ₃	B.L.	400(752)	28	47,678(6915)

* Cement was not sufficiently cured after 14 days in autoclave.

** Series 604A thru 604E were not sufficiently cured after 7 days in autoclave.

[†] S.S. = saturated steam

B.L. = brine

B.V. = brine vapor

C. Bond Strength Tests

Shear bond tests were made on the SwRI formulations to determine the effective bond strength to steel casing. The tests were made using specimens of cement cured in steel cylinders. Several sizes and types of cylinders were used, depending mostly on the curing and aging temperatures. The largest of these were 0.76 m (3 in.) inside diameter and 0.76 m (3 in.) high with a 0.25 m (1-in.)-steel pin centered by use of a machined base plate. Another type was similar but was 0.35 m (1.375 in.) inside diameter by 0.51 m (2-in.)-long, with a .013 m (0.5-in.)-steel pin centered with a base plate. The steel cylinders were machined from regular ungalvanized pipe stock. No attempt was made to polish the inside of the pipe. The steel center pins were polished to a near-mirror finish using 600-grit paper.

The cement slurry was poured into these molds, capped loosely, and the entire cylinder placed in an autoclave to be cured for periods up to 28 days. Curing conditions are included in Table 9. After the aging period, the molds were taken from the autoclave and the end plates removed. The shear bond was then measured by forcing the pin out of the cement and cylinder using an Instron test machine. Because of the polished pin, the cement almost always sheared away from it first. The bond strength was calculated by use of the formula $S = F/\pi DL$, where S = shear bond strength, kPa; F = maximum force required to displace the pin, lb; D = diameter of steel pin, in.; and L = length of cement steel interface, in. Shear bond strength test results are shown in Table 9.

D. Permeability to Water

Permeability tests were made on a large number of SwRI hydrothermal cement formulations. These tests were made with a cement permeameter similar to that described in the American Petroleum Institute (API) Method RP10B, Section 9. Specimens were made by pouring the cement mix into the round steel mold, capping top and bottom, and then placing the mold in the autoclave for curing. After curing at up to 400°C (752°F) in saturated steam and/or artificial brine, the mold with specimen was placed in the permeameter for testing.

The permeability of a porous material is given by the volume of flow of a fluid during unit time through a volume of the material having unit cross-sectional area and unit thickness when unit pressure difference exists between the ends. The formula for this determination is given as

$$K = 14,700 \frac{Q\mu L}{AP}$$

where

- K = permeability in millidarcys;
- Q = flow rate in milliliters/second;
- μ = water viscosity in centipoise;
- L = length of sample in centimeters;
- A = cross-sectional area of sample in cm²;
- P = differential pressure in psi for above.

Table 9
Shear Bond Strengths

Specimen	Active agent	Curing conditions @ °C(°F)	Curing time days	Bond strength kPa(psi)
B1	ZnO	S.S.* 100(212)	6	7,560(1096)
B2	ZnO	S.S. 218(424)	3	8,270(1199)
B3	ZnO	S.S. 218(424)	7	9,650(1399)
C1	Al ₂ O ₃	S.S. 218(424)	3	7,580(1099)
Z6	ZrO ₂	S.S. 218(424)	3	345(50)
Z6	ZrO ₂	S.S. 218(424)	14	8,610(1248)
Z1	ZrO ₂	S.S. 260(500)	7	7,925(1149)
Z2	ZrO ₂	S.S. 260(500)	7	8,060(1169)
Z3	ZrO ₂	S.S. 260(500)	7	7,060(1024)
Z4	ZrO ₂	B.V. 260(500)	7	7,580(1099)
A1	Al(OH) ₃	S.S. 260(500)	7	3,305(479)
A2	Al(OH) ₃	S.S. 260(500)	7	3,270(474)
A3	Al(OH) ₃	B.V. 260(500)	7	3,580(519)
A4	Al(OH) ₃	B.V. 260(500)	7	3,410(494)
6010A	Al(OH) ₃	S.S. 316(600)	7	2,720(395)
6020A	Al(OH) ₃	S.S. 316(600)	15	7,380(1070)
6020B	Al(OH) ₃	S.S. 316(600)	15	4,415(640)
6030A	Al(OH) ₃	S.S. 400(752)	14	2,720(394)
6030B	Al(OH) ₃	S.S. 400(752)	14	14,760(2140)
6040A	Al(OH) ₃	S.S. 316(600)	28	16,700(2422)
6040B	Al(OH) ₃	S.S. 316(600)	28	2,780(403)
60	Al(OH) ₃	S.S. 316(600)	28	5,650(819)
70	Al ₂ O ₃	S.S. 316(600)	28	10,270(1489)
80	ZrO ₂	S.S. 316(600)	14	8,750(1269)
90	LaO ₂	S.S. 316(600)	28	4,340(629)
100	TiO ₂	S.S. 316(600)	14	5,510(799)
110	La(OH) ₂	S.S. 316(600)	14	**

* S.S. = saturated steam
B.V. = brine vapor

** Cement did not harden sufficiently in 14 days.

Earlier tests showed that the basic SwRI cements, cured at temperatures below 200°C (392°F), had permeabilities below 0.1 millidarcys. However, at the higher temperatures the permeability was found to be extremely variable. Routine permeability tests were made on the basic high-temperature formulation containing aluminum hydroxide as the activator. Some variations were used in the mix design, usually in the amount of anhydrous sodium silicate, or by the addition of other materials, in an attempt to decrease the permeability. Table 10 shows the results of these tests. Note the excellent results with specimens 9A and 9B cured at 150°C (302°F).

Table 10
Permeability to Water

Notes on formulations	Cure temp. °C(°F)	Cure time days	Permeability, md [at P-275 kPa (40 psi)]
# 1 : Cement reacted w/spacers	316(600)	2	100
2 : "	316(600)	8	200
3 : "	316(600)	8	100
4 : Bonded well to steel	316(600)	2	100
5 : Partly broken in top	316(600)	2	100
6 : Bonded well to steel	316(600)	14	200
7A: Reduced anhyd. sod. sil.	316(600)	7	80
7B: "	316(600)	7	60
8 : Add ASA and pyrophos.	316(600)	6	200
9A: Decr. sand - incr. silica flour	150(302)	1	0.01
9B: "			0.005 } 551 kPa
10A: Add ZnO	316(600)	5	200
10B: Normal mix	316(600)	5	193
10C: Add Al ₂ O ₃	316(600)	5	Not set
10D: Add ZrO ₂	316(600)	5	Not set
11A: ZnO subst. for Al(OH) ₃	316(600)	7	Leakage at wall
11B: Add ZnO	316(600)	7	1 ml/sec
11C: ZrO ₂ subst for Al(OH) ₃	316(600)	7	Not set
12A: Add ZnO and bentonite	316(600)	4	14
12B: "	316(600)	4	19
12C: "	316(600)	4	17
13 : Average of 3 additions (12A,B,C)	400(752)	3	15
14 : ZrO ₂ and bentonite additions	400(752)	4	Not set

Further attempts were made to modify the Al(OH)₃ formulation to give less than 0.1 millidarcy permeability after curing and aging at 316° and 400°C (600° and 752°F). The recipes given in Table 11 were designed for this purpose and samples were made, cured, and tested, with the results shown in Table 12. It can be seen that the best specimens were still too permeable by a factor of 10. These same formulations have high compressive and bond strengths, however.

Scanning electron microscopy was used in an attempt to determine the cause of the low- and high-permeability anomalies. Figure 4 compares two of these, one precured at 200°C (392°F) and then aged at 316°C (600°F) in saturated steam, and the other cured in saturated steam at 316°C (600°F). The dehydration of specimen 1645-S in the lower photograph is very evident. An extremely low permeability may become an absolute requirement only in a few geothermal wells. However, we will continue to try various additions and modifications to the Al(OH)₃ formulation in an attempt to bring the porosity down to an acceptable figure for use where required.

Table 11
Formulations for Permeability Tests

Ingredients*	Specimen series										
	G	H	I	J	K	L	M	N	O	P	Q
Sand	40	40	40	40	50	50	50	50	50	50	50
Silica flour	35	35	35	35	25	5	10		30	30	30
Britesil	8	10	8	8	10	10	10	10	10	10	10
Anhydrous sodium silicate	2	2	2	5	5	5	5	5			5
Bentonite	1.5	1.5	1.5	1.5	2	2	2	1	1	2	2
Al(OH) ₃	4	4	5	5	5	5	3	3	5	5	5
CaCO ₃						25					
ZnO	1	1			1	1	1	1			
Calcined kaolin								15			
Wollastonite							15	10			
Borosilicate glass										10	6
Water	16	16	17	16.5	19	18	18	19	16	18	18

* Ingredients are given in parts by weight.

Table 12
Permeability to Water

Formulation	Cure temp.* °C(°F)	Cure press. kPa(psi)	Cure time days	Permeability, md **
G	316(600)	8,270(1200)	17	17
H	316(600)	8,270(1200)	17	105
I	316(600)	8,270(1200)	17	223
J	316(600)	8,270(1200)	17	47
K	400(752)	13,100(1900)	20	1.5
L	400(752)	13,100(1900)	20	25
M	400(752)	13,100(1900)	20	3.2
N	400(752)	13,100(1900)	20	4.5
K	400(752)	12,400(1800)	28	1.7
L	400(752)	12,400(1800)	28	33
M	400(752)	12,400(1800)	28	1.8
N	400(752)	12,400(1800)	28	7.3
O	316(600)	8,960(1300)	7	76
P	316(600)	8,960(1300)	7	146
Q	316(600)	8,960(1300)	7	462

* Cured in saturated steam

** Average of 3 measurements.

2-1698-S

1500X

Specimen cured in saturated steam at 200°C (392°F), then aged in brine vapor at 316°C (600°F) for 14 days. Permeability = 0.05 md at 551 kPa (80 psi)

2-1645-S

1500X

Specimen cured at 316°C (600°F) for 14 days in saturated steam and brine. Permeability = 200 md at 551 kPa (80 psi).

Figure 4. Scanning Electron Microscope Photomicrograph of Al(OH)_3 Recipes Aged in Steam

E. Compatibility with Drilling Muds

A series of tests were made to determine the compatibility of the SwRI cements with several types of drilling fluids commonly used in drilling wells, and a large number of drilling mud additives. The mud systems were made up in laboratory batches and included effective high-temperature [250°C (482°F)] types. The primary type used was made up with bentonite, 8-9%; blended lignosulfonate compounds, 4-5%; sodium hydroxide, 0.1%, to raise pH to about 9.4; and water with one or more of the additives.

Twenty-four additives were tested by placing cured specimens of the zinc oxide, aluminum hydroxide, and zirconia recipes in an autoclave with a typical drilling mud containing the particular additive. The results are shown in Table 13. In the evaluation system given in the Table, we have used the following notations:

1. C = Compatibility has been confirmed by actual test with this agent.
2. AC = Compatibility has been deduced by previous experience with these classes of agents and the cement constituents.
3. I = Incompatibility determined by actual test with this agent.
4. NR = Not recommended as interface to hydrothermal cement except in very dilute concentrations.

There are many more additives and probably a half dozen different drilling mud formulations which could have been checked. However, we believe that the results are sufficient to show that only a few mud additives are incompatible with our cements. These are the amines, some phosphates, and an extremely high or low pH, and then only when the cement is in the slurry form. Once set, there are only a few chemicals that will affect them, such as hydrofluoric acid.

F. Corrosion Properties

The corrosive or noncorrosive qualities of the SwRI hydrothermal cement formulations were tested using steel-well-casing coupons coated with, and submerged in, the cements. Coupons were withdrawn from the test at intervals of two months. Curing and aging were done in artificial brine and steam at temperatures from 150° to 400°C (302° to 752°F).

No corrosive effects have been evidenced at any temperature. At a pH >5, carbon steel has an estimated life of about 15 years. If the pH is reduced to 4, carbon steel has a life of only about two years. The SwRI hydrothermal cement recipes are caustic, with a pH >7. This would indicate that the casing would last more than 15 years. Further, the SwRI cements produce a protective bond coating of silica on the steel surface which in fact inhibits corrosion.

A test comparable to ANSI/ASTM Test Method C876-77, Half Cell Potentials of Reinforcing Steel in Concrete, with some modifications, was attempted but was rejected. Temperatures of the test cells could not be over about 60°C (140°F) and, because of the dielectric properties of the cured cement, there was not an acceptable electrical circuit.

Steel nipples used for curing recipes at 400°C (752°F) and the steel rings used for curing the cement for permeation tests have shown no corrosion after 28 days of aging in steam and brine.

Table 13
Compatibility of Drilling Mud and Additives
with SwRI Hydrothermal Cements

Product name	Description	Additions Kg/bbl(1b/bbl)	SwRI Rating
Amines	Corrosion inhibitors	0.91(2.0)	I
AQUAGEL	Sodium montmorillonite powder, nontoxic, S.G. 2.7	4.54-11.34(10-25)	C
Barite	BaSO ₄ - weighting agent	As required	C
BAROID	Barite, barium sulfate powder, BaSO ₄ , S.G. 4.2	22.68-40.82(50-90)	C
CARBONOX	Lignitic humic acid powder, nontoxic	0.23-15.88(0.5-35)	AC
Caustic soda	NaOH flake toxic	0.05- 1.36(0.1-3)	NR
Cellulose	Polyanionic	0.05- 1.36(0.1-3)	C
CC-16	Solubilized sodium salt of lignitic humic acid powder	0.23- 2.72(0.5-6)	AC
Clay	Organophilic	0.23- 3.18(0.5-7)	C
Guargum	Viscosifier	0.45- 2.27(1-5)	C
Gypsum	CaSO ₄ ·2H ₂ O powder, nontoxic	0.91- 2.72(2-6)	NR
Lime	Ca(OH) ₂ powder	0.45- 2.27(1-5)	NR
OMC	Oil Mud Conditioner	0.91- 1.81(2-4)	C
PETROTONE	Organophilic clay powder for use as oil mud suspending agent	0.23- 2.27(0.5-5)	C
Pyrophosphate	Sodium acid, as dispersant	0.05- 0.09(0.1-0.2)	NR
Q-BROXIN	Ferrochrome lignosulfonate powder	0.45- 9.07(1-20)	C
QUIK-GEL	High-yield bentonite	2.27- 4.54(5-10)	C
Salt	NaCl granular nontoxic	2.27-56.70(5-125)	C
Soda ash	Na ₂ CO ₃ powder	0.23- 0.91(0.5-2)	NR
Sodium chromite	Na ₂ CrO ₄ powder, toxic	0.05- 1.81(0.1-4)	NR
Starch	Filtrate reducer powder	0.91- 3.63(2-8)	C
Unknown	Organic thinners	0.23- 1.36(0.5-3)	C
Unknown	Surface active defoamer	0.005-0.05(0.01-0.1)	C
ZEOGEL	Attapulgit powder	4.53- 9.07(10-20)	C

G. Other Physical Properties

1. Thermal Conductivity and Specific Heat. Specimens of the $\text{Al}(\text{OH})_3$ -activated hydrothermal cement were cured and aged in steam for 28 days at 400°C (752°F) for the purpose of measuring thermal conductivity. The specimens were removed from the autoclave and tested in accordance with ASTM Test Method C177, Thermal Conductivity of Materials by Means of the Guarded Hot Plate.

The thermal conductivity was calculated from

$$\lambda = \frac{(q) (\Delta x)}{(A) (\Delta T)},$$

where λ = thermal conductivity, q = power dissipation in the main heater, Δx = total thickness of both test specimens, A = the metering surface area taken twice, and ΔT = total temperature difference across both specimens.

The results are shown in Table 14. The specimens were $180 \times 180 \times 25$ mm ($7.1 \times 7.1 \times 1$ in.), having a test density of 1855 kg/m^3 (116 lb/ft^3).

Table 14
Thermal Conductivity of SwRI $\text{Al}(\text{OH})_3$ Hydrothermal Cement

Temperature		Condition	Thermal conductivity	
$^\circ\text{C}$	$^\circ\text{F}$		$\text{W m}^{-1} \text{ }^\circ\text{K}^{-1}$	$\text{Btu in. h}^{-1} \text{ft}^{-2} \text{ }^\circ\text{F}^{-1}$
24	75	As received	1.77	12.3
24	75	Dried	1.70	11.8
250	482	Dried	1.30	9.0

2. Coefficient of Thermal Expansion. The linear coefficients of thermal expansion were determined for the SwRI hydrothermal cement according to ASTM Test Method C531-68, Shrinkage and Coefficient of Thermal Expansion of Chemical-Resistant Mortars, and the results are given in Table 15. All specimens were cured in saturated steam at 316°C (600°F) and a pressure of $8,270 \text{ kPa}$ (1200 psi).

Table 15

Specimen No.	Curing Temp./Press. 316°C (600°F) 8,270 kPa (1200 psi)	Shrinkage %	Linear coefficient of thermal expansion cm/cm per°C (in/in°F)
1A	7 days	0.014	
1B	"		1.78×10^{-5} (9.89×10^{-6})
2A	"	0.016	
2B	"		1.77×10^{-5} (9.83×10^{-6})
3A	14 days	0.016	
3B	"		1.80×10^{-5} (1.00×10^{-6})
4A	"	0.016	
4B	"		1.90×10^{-5} (1.06×10^{-6})
5	"		2.03×10^{-6} (1.13×10^{-6})

3. Elastic Properties. The flexural strength was measured on several specimens of the SwRI hydrothermal recipe containing $\text{Al}(\text{OH})_3$. These specimens were cured and aged in saturated steam at 316°C (600°F) and 8270 kPa (1200 psi) for periods up to 14 days. The testing was in accordance with ASTM Test Method C580-74, Flexural Strength and Modulus of Elasticity of Chemical-Resistant Mortars, Grouts, and Monolithic Surfacing. The results of these tests are given in Table 16. Each test "sample" represents the average of five similar specimens.

The specimens were cast into bars 1 in. square by 10 in. long and cured for periods up to 14 days at 316°C (600°F). Testing was done on an Instron Load Cell Testing Machine, using a 229 cm (9-in.) span and a center-of-the span loading nose. Deflection was measured automatically with the motion of the loading nose.

The flexural strength was calculated from the formula $S_f = 3PL/2bd^2$, where S_f = flexural stress in the specimens at midspan, P = load at break, L = span, b = width of beam tested, and d = depth of beam tested.

Table 16
Flexural Strength of SwRI Cements

Sample	Cure time days	Flexural strength MPa(psi)
1	14	9.06(1314)
2	14	9.47(1373)
3	1	9.3 (1348)
4	2	9.0 (1305)
5	14	9.1 (1319)
6	6	9.4 (1363)
7	4	9.3 (1348)
8	2	9.3 (1348)

V. CYCLICAL TESTS OF SwRI 150°C CEMENT

A. Hot Dry Rock Thermal Cycling Tests

A proposal was accepted for SwRI to perform certain tests on a 150°C (302°F) formulation for possible application in the remedial cementing of the injection well at Fenton Hill near Los Alamos, New Mexico. The program consisted primarily of a series of cyclical bond tests to try to simulate the cyclical conditions in the Hot Dry Rock (HDR) experimental well. Each cycle was about 48 hours long, cooling down from 200° to 35°C (392° to 95°F), followed by reheating to 200°C (392°F), etc. A complete test was on the basis of 1, 3, and 7 cycles. Tests were run at 34.4 MPa (4990 psi), equivalent to the HDR well bottom-hole pressure. At the end of each sequence of cycles, the specimens were removed from the autoclave for bond and compressive strength tests, and then replaced for the next sequence of thermal cycling.

Test specimens were of two types:

1. Pipe-in-pipe, or steel rod-in-pipe, with cement in the annulus between pipes.
2. Pipe-in-rock. This closely simulates the conditions down-hole with the three different thermal coefficients to deal with. We believe that the 8-in.-long sections which were used were sufficient for obtaining good bond strength data.

It was our intention to show that our hydrothermal cement would form an excellent bond to the casing and rocks with good bond strengths. If the casing were to shrink away from the SwRI cement, breaking the bond, then expand again with an increase in heat flux, the cement bond would "heal" and nearly regain its maximum strength within 24 to 48 hours.

The results of the tests for bond strength on pipe and rock specimens are shown in Table 17.

Table 17
Cyclical Shear Bond Tests

Specimen	Cycles	Strength, kPa(psi)
Pipe-in-rock	1	690(100)
	3	500(72)
	7	4820(699)
Pipe-in-rock	1	1295(187)
	3	900(130)
	7	7360(1067)
Steel-rod-in-pipe	1	590(85)
	3	650(94)
	7	not completed
	7	8560(1241)
	7	8670(1257)

Compressive strength tests were also made on the cement after exposure to the cyclical conditions. These specimens were removed at the end of the 1-, 3-, and 7-cycle sequences as in the above bond tests.

Compressive strength tests of specimens cured with the above bond test specimens were 2650 and 2300 kPa (384 and 333 psi) at the end of the 3 cycles. Measurements were not made after the first cycle. One specimen was tested at the end of the 7 cycles, with a strength of 22,000 kPa (3191 psi).

Along with the above thermal cycling tests, SwRI was asked to run curing tests at 80°, 100°, 125°, and 150°C (176°, 212°, 257°, and 302°F). This was prompted by the failure of the National Bureau of Standards (NBS) to obtain good curing properties on the SwRI 150°C (302°F) cement formulation containing zinc oxide as the activator. A decision was made by SwRI to switch to the use of a higher-temperature activation material, aluminum hydroxide. The NBS laboratory tests could not confirm that the $Al(OH)_3$ formulation cured properly nor had good mechanical properties.

However, the LASL HDR test well had recovered thermally to a maximum of only 150°C (302°F) at the bottom of the casing 2927 m (9600 ft) and not much more than about 130°C (266°F) at 2805-2866 m (9200- to 9400-ft) depths. It became evident that the aluminum hydroxide formulation, because of the lower test hole temperature, might not set for possibly a week or more. Therefore, the series of curing tests were made at each of the above temperatures. Samples of cement were pulled at the end of 72 hours and, if not properly cured, every two or three days until a good cure was obtained or it was determined that the cement would take too long, i.e., 14 days, to harden. Table 18 shows the results of this series of tests.

Table 18
Long-Term Curing at Low Temperatures

Temp., °C(°F)	Length of cure, days	Results
80(176)	12	Uncured, gelled
80(176)	15	Firm, but only partially cured
100(212)	12	Firm
100(212)	15	Hard, but not completely cured
125(257)	12	Hard cure - OK
150(302)	5	Hard cure - OK

On December 19, 1978, a meeting was held at LASL, G4 Division, Los Alamos, New Mexico. At this meeting, members from LASL, NBS (Washington), and SwRI discussed the above thermal cycling tests and the tests performed at NBS. Because of the difficulties in resolving differences in curing and bond tests, and other anomalous behavior, it was decided not to use the SwRI aluminum hydroxide formulation in the remedial cementing of the Fenton Hill test well.

The reasons for the anomalous behavior were associated with the inherent characteristics of the SwRI cement. In the following study, an attempt was made to understand and correct some of the problems which might arise with the use of these silica polymer cements. Although most, if not all, well cements will react in a similar fashion, the portland cements will usually be flash set in an attempt to avoid the mixing at the water interface. In regular oil-well cementing, the water is pushed ahead of the cement with a buffer. In spite of this, there is almost always a zone at the cement face which is intermixed with fluids.

B. Immersion Curing of Hydrothermal Cement Slurries

When an annulus between a casing and a formation is filled with a slow-curing hydrothermal cement slurry, and one end of the column is in direct contact with water, the hydrothermal cement will fail to attain typical strengths at the interface because of dilution by permeation of water into the cement slurry. The purpose of this experiment was to determine the approximate degree of penetration and the impact upon the strength of the cement by exposing a column of this cement to water at one interface of the column.

The SwRI hydrothermal cement was designed to allow maximum pumping time and to cure slowly in the heated zone. This virtue is countered by the prolonged vulnerability of the slurry to attack by water and the permeation of water into the slurry. To gauge the degree of penetration and attack, a 0.3 m (1-ft) length of 0.013 m (0.5-in.)-diam copper tubing was charged with slurry and placed under water in a 2.44 m (8-ft)-long autoclave. The autoclave was heated to 200°C (392°F) under 14-MPa (2031 psi) nitrogen pressure. The tubes were crimped on one end to prevent displacement of slurry and to simulate the down-hole effect of an open bottom/closed top situation with respect to water exposure. Two U-shaped tubes and two straight tubes were charged with slurry and, after four days' exposure to 200°C (392°F) at 14 MPa (2031 psi), the autoclave was cooled, vented, and the tubes recovered. The tubes were cut at 0.025 m (1-in.) intervals and the contents inspected.

The samples in all tubes were found to be very hard at the closed (crimped) end and progressively softened away from the closure toward the open end. The cement in the straight tubes was hard in the last three inches, softening thereafter by gradual degree toward the open end. The curved tubes, however, were found to contain very hard cement from the closed end to about the midpoint and then to become progressively weaker toward the open end. The cement slurries at the open ends were probably dried by exposure during cooling and venting and, hence, were firmer than the segments 0.025 m (1 in.) away from the opening. The softest point in the U-shaped tube was about 0.102 m (4 in.) into the open end followed progressively by a stronger mass inward as represented in the tabulation below.

<u>Position of sample</u>	<u>U-bend</u>	<u>Straight tube</u>	<u>U-bend</u>	<u>Straight tube</u>
.025m(1 in.) from closed end	Very hard	Very hard	Very hard	Very hard
.051m(2 in.) from closed end	Very hard	Very hard	Very hard	Very hard
.076m(3 in.) from closed end	Very hard	Firm	Very hard	Firm
.102m(4 in.) from closed end	Very hard	Medium	Very hard	Firm
.127m(5 in.) from closed end	Hard	Soft	Hard	Medium
.152m(6 in.) from closed end	Firm	Soft	Firm	Soft
.152m(6 in.) from open end	Firm	Soft	Firm	Soft
.127m(5 in.) from open end	Soft	Soft	Soft	Soft
.102m(4 in.) from open end	Soft	Soft	Soft	Soft
.076m(3 in.) from open end	Medium*	Medium*	Medium*	Medium*
.051m(2 in.) from open end	Firm*	Firm*	Firm*	Firm*
.025m(1 in.) from open end	Firm*	Firm*	Firm*	Firm*

* Probably due to drying rather than curing.

A similar test was conducted to generate recoverable specimens for compressive strength tests but it proved impossible to recover the cements from the metal and glass tubes in which they were cured. It was decided to machine Teflon stock to provide a heat-resistant plastic mold from which the specimens could be recovered. The results of these tests, after four days curing in saturated steam at 200°C/14 MPa (392°F/2031 psi) are shown below.

<u>Section of Tube</u>	<u>Sc</u>
Bottom 1 in. (closed end)	= 20 MPa (2901 psi)
2nd length	= 8 MPa (1160 psi)
3rd length	= 2.4 MPa (348 psi)
4th length	= too weak to measure
5th length	= too weak to measure
6th length	= too weak to measure
7th length	= too weak to measure
8th length	= too weak to measure
9th length	= too weak to measure
10th length	= too weak to measure
11th length	= too weak to measure
12th length	= too weak to measure

The conclusion reached from the above experiments is that slow-setting hydrothermal cements are permeated by surrounding waters especially under heat and pressure to the extent that a length of such slurry will be attacked and weakened by the environment. This was noted in the El Paso Gas Company well by bond logs which showed several feet of cement/water interface to be varied in strength. However, this interface represents a fraction of a percent of the total column height, the remainder of which was strongly bonded and well cured. The water in the El Paso test was a gel spacer used to displace standard portland cement slurry which comprised the upper annulus in the zone below 112°C (234°F) while the hydrothermal cement filled the remainder of the annulus to the bottom.

The hydrothermal cement formulation, containing Al(OH)_3 as the activator, can be obtained presently for a cost of approximately 25¢ per pound, in bulk quantities of 100,000 pounds or more.

VI. REFERENCES

1. P. Kruger and C. Otte, Eds., Geothermal Energy, Stanford University Press, 360 pp., 1973.
2. M. F. Smith, Geothermal Energy, Volumes 1-3, National Technical Information Service, Springfield, VA (citations from NTIS Data Base, 1975 through 1977, various numbers).
3. ERDA, Geothermal Resources: Exploration and Exploitation. A Bibliography, ORNL TID-3354-R1, Technical Information Center, 636 pp., July 1976.
4. Proc. Symp. New Sources of Energy, 3 volumes, Rome, Italy, August 21-31, 1961.
5. Proc. 2nd Symp. Develop. and Use Geotherm. Resour., San Francisco, May 20-29, 1975, 3 volumes, UC-LBL, National Science Foundation, Washington, DC, Research Applied to National Needs, 1976.
6. Energy Technologies for the West: Geothermal, Energy from the Earth, Workshop, San Francisco, Sept. 21, 1976, ERDA, Washington, DC, 68 pp., 1976.
7. H. C. H. Armstead, Ed., Geothermal Energy: Review of Research and Development, Unesco Press, Paris, 186 pp., 1973.
8. Jet Propulsion Laboratory, Geothermal Energy Development Status: Pasadena, California, Status Report Geothermal Definition Project, Part 2, p. 5, Apr. 1975.
9. H. L. Graham, Rheology-balanced cementing improves primary success, Oil Gas J, pp. 53-9, Dec. 18, 1972.
10. ASTM C150: Standard Specification for Portland Cement, Book of ASTM Standards, Part 13, Philadelphia, 1977.
11. API Spec. 10A, Oil-Well Cements and Cement Additives, API Production Dept., 19th Ed., Am. Pet. Inst., Washington, Apr. 1977.
12. API Bull. 10C, Oil-Well Cement Nomenclature, API Production Dept., 2nd Ed., Am. Pet. Inst., Washington, Apr. 1969.
13. API RP 10B, Testing Oil-Well Cements and Cement Additives, API Production Dept., 20th Ed., Am. Pet. Inst., Washington, Apr. 1977.

14. P. Parker, C. Clement, and R. Beirute, Basic cementing - 1: Today's oil-well cements offer operators a variety of choices, Oil Gas J., pp. 59-63, Feb. 21, 1977.
15. P. Parker, C. Clement, and R. Beirute, Basic cementing - 2: Specialty cements can solve special problems, Oil Gas J., pp. 128-31, Feb. 28, 1977.
16. P. Parker, C. Clement, and R. Beirute, Basic cementing - 3: Additives tailor cement to individuals wells, Oil Gas J., pp. 54-8, Mar. 14, 1977.
17. P. Parker, C. Clement, and R. Beirute, Basic cementing - 4: Flow charts remove the guesswork from slurry design, Oil Gas J., pp. 59-63, Mar. 28, 1977.
18. P. Parker, C. Clement, and R. Beirute, Basic cementing - 5: Slurry and pumping guidelines smooth casing, Oil Gas J., pp. 54-9, Apr. 11, 1977.
19. P. Parker, C. Clement, and R. Beirute, Basic cementing - 6: Outline simplifies squeezing and plugging, Oil Gas J., pp. 108-13, Apr. 25, 1977.
20. P. Parker, C. Clement, and R. Beirute, Basic cementing - 6: Cementing calculations essential part of design stage of project, Oil Gas J., pp. 58-62, May 9, 1977.
21. P. Parker, C. Clement, and R. Beirute, Basic cementing - 8: Auxiliary cementing materials contribute to successful jobs, Oil Gas J., pp. 80-4, May 23, 1977.
22. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 1, World Oil, pp. 43-51, Mar. 1977.
23. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 2, World Oil, pp. 69-76, Apr. 5, 1977.
24. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 3, World Oil, pp. 48-57, May 1977.
25. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 4, World Oil, pp. 69-77, June 1977.
26. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 5, World Oil, pp. 117-25, July 1977.
27. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 6, World Oil, pp. 43-50, Aug. 1, 1977.
28. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 7, World Oil, pp. 87-95, Oct. 1977.
29. G. O. Suman and R. C. Ellis, Cementing oil and gas wells - Part 8, World Oil, pp. 79-92, Nov. 1977.

30. C. H. Aldrich and B. J. Mitchell, Strength, permeabilities, and porosity of oilwell foam cement, ASME Paper No. 75-Pet-10, Sept. 21-25 Mtg., 4 pp., 1975.
31. Ugo Cigni, F. Fabbri, and A. Giovannoni, Advancement in cementation techniques in the Italian geothermal wells, Proc. 2nd Symp. Develop. and Use of Geotherm. Resour., San Francisco, May 20-29, 1975, pp. 1471-82, 1976.
32. C. R. Clark, J. H. Steele, and J. L. Gidley, Coarse grind cement in oil-well cementing, Oil Gas J., pp. 50-3, Jan. 24, 1972.
33. L. H. Eilers et al., Development of geothermal well completion systems, Phase I Report, Dow Chemical U.S.A., Tulsa, OK, July-Sept., 1977.
34. G. L. Kalousek and S. Y. Chaw, Research on cements for geothermal and deep oil wells, Soc. Pet. Eng., AIME J., pp. 307-9, Dec. 1976.
35. L. E. Kukacka et al., Cementing of Geothermal Wells, Progress Reports 1-6 (April 1976 to Sept. 1977), BNL, Upton, NY.
36. W. A. Mallow and J. K. Dean, Nonshrinking heat and acid-resistant hydrothermal cements for use in oil and gas wells, ASME Paper No. 77-Pet-27, Energy Technol. Conf. and Exhibition, Houston, Sept. 18-22, 1977.
37. S. Maravilla, Hydrothermal setting cement for cementing ultradeep, hot wells, J. Pet. Technol., pp. 1087-94, Oct. 1974.
38. N. K. Tschirley, Cementing in oil muds, Pet. Eng., pp. 140, 142, 144, May 1975.
39. A. Tragesser and P. N. Parker, Using improved technology to obtain better cement jobs on deep, hot liners, J. Pet. Technol., pp. 1307-13, Nov. 1972.
40. J. N. Phillips and C. R. Sykes, Temperature, pressure, key hurdles ahead in ultradeep wells, Oil Gas J., pp. 66-70, 75, July 20, 1970.
41. C. S. Holmes and S. C. Swift, Calculation of circulating mud temperatures, J. Pet. Technol., pp. 670-4, June 1970.
42. J. R. McNitt, The role of geology and hydrology in geothermal exploration, Geothermal Energy, Unesco, Paris, pp. 33-40, 1973.
43. F. Shell and A. Tragesser, API is seeking more accurate bottom-hole temperatures, Oil Gas J., pp. 79-9, July 10, 1972.
44. D. E. Boone, Reduce failures by watching pressure effects and placement techniques, Oil Gas J., pp. 81-6, June 9, 1969.
45. D. E. Boone, Adequate cement strength. A must for drilling success - 1, Oil Gas J., pp. 72-6, May 26, 1969.

46. D. K. Smith, Cementing, AIME, Soc. Pet Eng. Monograph, Vol. 4, p. 184, New York, 1976.
47. W. H. Fertl, P. E. Pilkington, and J. B. Scott, Look at cement bond logs, J. Pet. Technol., pp. 607-17, June 1974.
48. C. Cook and W. C. Cunningham, Filtrate control - A key in successful cementing practices, Soc Pet Eng Reg. Mtg. on Oper. Pract. in Drill and Prod. Proc., Oklahoma City, Feb. 20-22, 1977.
49. W. W. Christian, J. Chatterji, and G. W. Ostroot, Gas leakage in primary cementing - a field study and laboratory investigation, J. Pet. Technol., pp. 1361-9, Nov. 1976.
50. R. Beirute and A. Tragesser, Expansive and shrinkage characteristics of cements under actual well conditions, J. Pet. Technol., pp. 905-9, Aug. 1973.
51. Keiji Matsuo, Drilling for geothermal steam and hot water, Geothermal Energy, Unesco, pp. 73-83, 1973.
52. R. M. Beirute, All purpose cement - mud spacer, 2nd Symp. Form Damage Control, Houston, Jan. 29-30, Paper SPE 5691, AIME, New York, 1976.
53. L. L. Carney, Cement spacer fluid, Symp. Form Damage Control, New Orleans, Feb. 7-8, 1974, Paper SPE 4784, AIME, New York, 1974.
54. L. L. Carney, Cement spacer fluid, J. Pet. Technol., pp. 856-8, Aug. 1974.
55. L. L. Carney, Single stage spacer for deep liner cementing, Pet. Eng., pp. 38, 40, June 1975.
56. C. R. Clark and L. Carter, Mud displacement with cement slurries, J. Pet. Technol., pp. 775-83, July 1973.
57. T. Garvin and K. A. Slagle, Scale-model displacement studies to predict flow behavior during cementing, J. Pet. Technol., pp. 1081-8, Sept. 1971.
58. F. H. Braunlich, Well completion--techniques and methods, Environ. Aspects Chem. Use Well-Drilling Oper., Conf. Proc., Houston, May 21-23, 1975, pp. 73-100, 1975.
59. H. E. Lindsey, Jr., Running and cementing deep well liners - (1, 2), World Oil, pp. 85-8, Nov. 1974; pp. 51-4, Dec. 1974.
60. H. E. Lindsey, Jr., Running and cementing deep well liners - 3, World Oil, pp. 103-4, 106, 108, Jan. 1975.
61. O. R. Poblano and R. A. Acuna, Pemex computer casing design, Pet. Eng., pp. 49-60, Apr. 1977.
62. W. C. Murphy, Squeeze cementing requires careful execution for proper remedial work, Oil Gas J., pp. 87-8, 90, 93-4, Feb. 16, 1976.

63. A. B. Dominguez and B. F. Vital, Repair and control of geothermal wells at Cerro Prieto, Baja, California, Mexico, Proc. 2nd U.N. Symp. Develop. and Use Geotherm. Resour., San Francisco, May 20-29, 1975, pp. 1483-95, 1976.
64. D. E. Boone, Success in squeeze cementing requires understanding, confidence - 3, Oil Gas J., pp. 95-8, June 30, 1969.
65. J. L. Rike, How to make squeeze cementing successful, Oil Gas J., pp. 58-64, July 1, 1974.
66. J. Cromling, Geothermal drilling in California, J. Pet. Technol., pp. 1033-8, Sept. 1973.
67. J. Cromling, How geothermal wells are drilled and completed, World Oil, pp. 42-5, Dec. 1973.
68. K. J. Liles, L. Y. Sadler, and A. H. Goode, Geothermal Well Drilling Fluid Technology: A Literature Survey, Bureau of Mines, Tuscaloosa, AL, Tuscaloosa Metallurgy Research Lab., 97 pp., Oct. 1976.
69. Glossary of Drilling-Fluid and Associated Terms, 1st Ed., API Bull. D-11, Washington, DC, Dec. 1965.
70. The Effects of Drilling - Mud Additives on Oil-Well Cements, Corrected Ed., API Bull. D-4, Washington, DC, Mar. 1963.
71. D. E. White and D. L. Williams, Eds., Assessment of Geothermal Resources of the United States, Geological Survey Circular 726, Washington, DC, 155 pp., 1975.
72. G. W. DePuy, L. E. Kukacka, A. Auskern, W. C. Cowan, P. Colombo, W. T. Lockman, A. J. Romano, W. G. Smoak, M. Steinberg, and F. E. Causey, Concrete-Polymer Materials Fifth Topical Report, BNL 50390, Dec. 1973.
73. L. E. Kukacka, T. Sugama, J. Fontana, W. Horn, and J. Amaro, Alternate Materials of Construction for Geothermal Applications, Progress Reports 1 through 13, Brookhaven National Laboratory, Apr. 1974 through June 1977.
74. D. G. Bebout and A. R. Gregory, Texas geothermal prospect slated to begin operations at Martin Ranch, Oil Gas J., Oct. 3, 1977.
75. M. H. Dorfman and R. W. Deller, Proc. 2nd Geopressured Geotherm. Energy Conf., Austin, TX, Feb. 23-25, 1976.
76. J. H. Howard, P. A. House, P. M. Johnson, D. Towse, and D. G. Bebout, Geology and Potential Uses of the Geopressure Resources of the Gulf Coast, University of California, Livermore, 23 pp., June 1976.
77. R. K. Swanson, P. Oetking, J. S. Osoba, and R. C. Hagens, Zones of the Upper Gulf Coast Based on a Study of Abnormally Pressured Gas Fields in South Texas, ERDA, Washington, 122 pp., Aug. 1976.

78. J. S. Wilson, B. P. Shepherd, and S. Kaufman, Analysis of the Potential Use of Geothermal Energy for Power Generation Along the Texas Gulf Coast, Dow Chemical Co., Freeport, TX, 69 pp., Oct. 15, 1975.
79. M. W. Tamele, Discussions Faraday Soc., No. 8, Heterogeneous Catalysis, pp. 270-4, 1950.
80. W. Lowenstein, Am. Mineral. 39, 92-6 (1950).
81. The Pipeliner, El Paso Nat. Gas Co., pp. 9-13, Apr. 1975.

APPENDIX A. LABORATORY FORMULATIONS

Sample No.	Sand (Grams)	Si Flour or Other (Grams)	SS Hydrate GR 87 & 89 (Grams)		SS Anh. (Grams)	SS 42 (Grams)	H ₂ O (Grams)	Gelling Agents & Others (Grams)
A	150	59 Fly Ash				50	8.0	5 SFS + 2.9 Na OH
B	150	50 Fly Ash				50	2.5	5 SFS
C	249.5	54 Fly Ash					46	1.2Ca(OH) ₂ + 90.8 Port. + 27 SMS
D	249.5	54 Fly Ash						1.2Ca(OH) ₂ + 90.8 Port. + 27 SMS
1	44	30 Fly Ash	9.1	87			17	4 SFS 3.0Ca(OH) ₂
2	44	30 Fly Ash	9.1	87			10	4 SFS
3	44	30 Fly Ash	9.1	87			20	4 SFS + 3.0Ca(OH) ₂
4	44	30 Fly Ash	11	87			20	4 SFS + 3Ca(OH) ₂
5	44	30 Fly Ash	9.1	87			20	4 SFS + 3Ca(OH) ₂
6	44	30 Fly Ash	9.1	87			25	4 SFS + 3Ca(OH) ₂
7	44	30 Fly Ash	11	87			25	4 SFS + 3Ca(OH) ₂
8	44	30 Fly Ash	11	87			25	5.5 SFS
9	44	30 Fly Ash	11	87			26	4 SFS
10	44	30 Fly Ash	9.1	87			17	4 SFS
11	44	30 Fly Ash	9.1	87			25	4 SFS
12	44	30 Fly Ash	9.1	87			17	4 SFS + 3Ca(OH) ₂
13	44	30 Fly Ash	9.1	87			25	4 SFS + 3Ca(OH) ₂
14	50	25 SiF	10	89			18	4 SFS
15	50	25 SiF	10	89			18	4 SFS + 15 Bentonite
16	50	25 SiF	10	89			17	5 SFS + .5 Bentonite
17	50	25 SiF	10	89			17	5 SFS + .5 Bentonite
18	50	25 SiF	10	89			17	5 SFS + .5 Bentonite
19	50	25 SiF	10	89			20	5 SFS + .5 Bentonite
20	50	25 SiF	10	89			17	5 SFS + .5 Bentonite
21	50	25 SiF	10	89			20	5 SFS + .5 Bentonite
22	50	25 SiF	10	89			17	6 SFS + .5 Bentonite
23	50	25 SiF	10	89			20	6 SFS + .5 Bentonite
24	50	25 SiF	10	89			23	6 SFS + .5 Bentonite
25	58	29 SiF	10	89			17	5 SFS
26	58	29 SiF	10	89			20	5 SFS
27	60	30 SiF	10	89			20	5 SFS + .5 Bentonite
28	50	25 SiF	11	89			20	5.5 SFS + .5 Bentonite
29	50	25 SiF	11	89			17	5.5 SFS + .5 Bentonite
30	58	29 SiF	11	89			20	5.5 SFS + .5 Bentonite
31	50	25 Dia-A	10	89			20	5 SFS + 0.5 Bentonite
32	50	12.5 SiF/ 12.5 Dia-A	10	89			20	5 SFS + 0.5 Bentonite

Sample No.	Sand (Grams)	Si Flour or Other (Grams)	SS Hydrate GR 87 & 89 (Grams)		SS Anh. (Grams)	SS 42 (Grams)	H ₂ O (Grams)	Gelling Agents & Others (Grams)
33	50	18.75 SiF/ 6.25 Dia-A	10	89			20	5 SFS + 0.5 Bentonite
34	50	6.25 SiF/ 18.75 Dia-A	10	89			20	5 SFS + 0.5 Bentonite
35	50	25 Dia-A	11	89			20	5.5 SFS + 0.5 Bentonite
36	30	12.5 SiF/ 12.5 Dia-A	11	89			20	5.5 SFS + 0.5 Bentonite
37	50	18.75 SiF/ 6.25 Dia-A	11	89			20	5.5 SFS + 0.5 Bentonite
38	50	6.25 SiF/ 18.75 Dia-A	11	89			20	5.5 SFS + 0.5 Bentonite
39	50	25 SiF	10	89			17	5 SFS + 0.5 Bentonite
40	50	25 SiF	10	89			20	5 SFS + 0.5 Bentonite
41	50	25 SiF	12	89			20	6 SFS + 0.5 Bentonite
42	50	25 SiF	12	89			17	6 SFS + 0.5 Bentonite
43	50	25 SiF	7	89			20	3.5 SFS + 0.5 Bentonite
44	50	25 SiF	8	89			20	4 SFS + 0.5 Bentonite
45	50	25 SiF	9	89			20	4.5 SFS + 0.5 Bentonite
46	50	25 SiF	10	89			20	5 SFS + 0.5 Bentonite
47	50	25 SiF	11	89			20	5.5 SFS + 0.5 Bentonite
48	50	25 SiF	12	89			20	6 SFS + 0.5 Bentonite
49	50	25 SiF	7	89			17	3.5 SFS + 0.5 Bentonite
50	50	25 SiF	8	89			17	4 SFS + 0.5 Bentonite
51	50	25 SiF	9	89			17	4.5 SFS + 0.5 Bentonite
52	50	25 SiF	10	89			17	5 SFS + 0.5 Bentonite
53	50	25 SiF	11	89			17	5.5 SFS + 0.5 Bentonite
54	50	25 SiF	12	89			17	6 SFS + 0.5 Bentonite
55	50	25 SiF				19	8	.5 ZnO
56	50	25 SiF				19	8	1 SFS + 4 ZnO
57	50	25 SiF				19	8	2 SFS + 3 ZnO
58	50	25 SiF				19	8	3 SFS + 2 ZnO
59	50	25 SiF				19	8	5 Zn ₃ (PO ₄) ₂
60	50	25 SiF				19	8	4 Dib. Ca H PO ₄
61	50	25 SiF	12	89	10		21	6 SFS
62	40	25 SiF	12	89	10		21	6 SFS
63	30	25 SiF			12		25	6 SFS + 0.5 Bentonite
64	50	25 SiF				19	8	5 ZnO

Sample No.	Sand (Grams)	Si Flour or Other (Grams)	SS Hydrate GR 87 & 89 (Grams)	SS Anh. (Grams)	SS 42 (Grams)	H ₂ O (Grams)	Gelling Agents & Others (Grams)
65	50	25 SiF	12	89	10	21	6 SFS
66	40	25 SiF	12	89	10	21	6 SFS
67	50	25 SiF				19	5 Dib. Ca HPO ₄
68	50	25 SiF	12	89		20	6 SFS
69	50	25 SiF			19	8	5 Zn ₃ (PO ₄) ₂
70	50	25 SiF			19	8	4 Dib. Ca HPO ₄
71	50	25 SiF			19	9.5	4 Trib. Ca HPO ₄
72	50	25 SiF	10 Kasil			20	3 SFS
73	50	25 SiF	4	89	10	20	6 SFS
74	50	25 SiF	4	89	10	22	6 Dib. Ca HPO ₄
75	50	25 SiF	12	89		22	7 Dib. Ca HPO ₄
76	50	25 SiF			19	8	6 Dib. Ca HPO ₄
77	50	25 SiF	10	89	10	21	8 SFS
78	50	25 SiF	10	89	10	23	8 SFS + 4Ca(OH) ₂
79	50	25 SiF	10	89	10	21	8 SFS + 4Ca(OH) ₂
80	50	25 SiF	10	89	10	21	8 SFS
81	50	25 SiF	10	89	10	21	8 SFS + 3Ca(OH) ₂
82	50	25 SiF	10	89	5	19	6 SFS + 4Ca(OH) ₂
83	50	25 SiF	10	87	10	19	8 SFS + 1 Drop 10% Sol CaCl
84	50	25 SiF	10	89	10	18	8 SFS + 11 Drop 10% Sol CaCl
85	50	25 SiF	10	89	10	22.5	1 SFS + 5 Dib. Ca HPO ₄ + 5 ZnO + 5Ca(OH) ₂
86	50	25 SiF	10	89	10	23.5	10 Dib. Ca HPO ₄ + 6 Dia M-Al + 5Ca(OH) ₂
87	50	25 SiF	10	89	10	22	10 Dib. Ca HPO ₄ + 5Ca(OH) ₂
88	50	25 SiF	10	89	5	19	5 Dib. Ca HPO ₄ + 5Ca(OH) ₂
89	50	25 SiF	10	89	6	19	1 SFS + 5 Dib. Ca HPO ₄ + 5Ca(OH) ₂
90	50	25 SiF				19	5 Dib. Ca HPO ₄
91	50	25 SiF				19	5 Dib. Ca HPO ₄ + 5Ca(OH) ₂
92	30	25 SiF				19	1 SFS + 5 Dib. Ca HPO ₄ + 5Ca(OH) ₂
93	50	25 SiF				19	5 Dib. Ca HPO ₄
94	50	25 SiF	10	89	10	22	1 SFS + 5 ZnO + 5 Dia-M-Al + 10Ca(OH) ₂
95	50	25 SiF	10		6	19	1 SFS + 3 Dib. Ca HPO ₄ + 5Ca(OH) ₂

Sample No.	Sand (Grams)	Si Flour or Other (Grams)	SS Hydrate GR 87 & 89 (Grams)	SS Anh. (Grams)	SS 42 (Grams)	H ₂ O (Grams)	Gelling Agents & Others (Grams)
96	50	25 SiF	10	6		19	1 SFS + 10Ca(OH) ₂
97	50	25 SiF	10	10		21.5	1 SFS + 6 Dia-M-Al + 10Ca(OH) ₂
98	50	25 SiF	10	10		20	1 SFS + 10Ca(OH) ₂
99	50	25 SiF	10	10	89	25	1 SFS + 10Ca(OH) ₂
100	50	25 SiF	10	10		20	1 SFS + 10Ca(OH) ₂
101	50	25 SiF	5			24	1 CaCl ₂ 10% Sol + 15 Ca(OH) ₂ + .5 Na OH
101B	50	25 SiF	10			19	1 SFS + .10Ca(OH) ₂
102	50	20 SiF	5	5		20.5	15Ca(OH) ₂
103	50	15 SiF	5	5		22	20Ca(OH) ₂ + .5 Na OH
104	50	25 SiF		5		21	10Ca(OH) ₂ + 2 Na OH
105	50	20 SiF	10			19	1 SFS + 15Ca(OH) ₂
106	50	15 SiF	10			23.3	25Ca(OH) ₂ + .5 Na OH
107	50	20 SiF	5	10		21	15Ca(OH) ₂
108	50	20 SiF	5	5		21	15Ca(OH) ₂ + .5 Na OH
109	50	25 SiF	10	10		20	1 SFS + 10Ca(OH) ₂
110	85	25 SiF				42	20Ca(OH) ₂
111	50	25 Vol Ash				37	20Ca(OH) ₂
112	50	25 SiF	10	10		20	1 SFS + 10Ca(OH) ₂
113-1	50	25 SiF	10	10		21	20 Al(OH) ₃ (Reagent)
113-2	50	25 SiF	10	10		21	20 Al(OH) ₃ (Reagent)
113-3	50	25 SiF	10	10		21	20 Al(OH) ₃ (Reagent)
113	50	25 SiF	10	10		21	20 Al(OH) ₃ (Reagent)
114	50	25 SiF	10	10		20	10 Mg(OH) ₂
115	50	25 SiF	10	10		20	10 ZnO
116	100	50 SiF	20	25		40	20 Colmanite G
117	50	25 SiF	10	10		20	10 Colmanite B
118	50	25 SiF	10	10		20	10CaCo ₃
119	100	50 SiF		11		48	25Ca(OH) ₂
120	100	50 SiF				48	25Ca(OH) ₂
121	80	25 SiF				20	10Ca(OH) ₂ + 1 Na OH
122A	50	25 SiF				0	27 CaCl SS Sol + 1 Na OH + 10Ca(OH) ₂
122B	50	25 SiF				9	15 CaCl SS Sol + 1 Na OH + 10Ca(OH) ₂

Sample No.	Sand (Grams)	Si Flour or Other (Grams)	SS Hydrate GR 87 & 89 (Grams)	SS Anh. (Grams)	SS 42 (Grams)	H ₂ O (Grams)	Gelling Agents & Others (Grams)
122C	50	25 SiF				14	10 CaCl SS Sol + 1 Na OH + 10Ca(OH) ₂
122D	50	25 SiF				18	5 CaCl SS Sol + 1 Na OH + 10Ca(OH) ₂
122E	50	25 SiF				22	0 CaCl SS Sol + 1 Na OH + 10Ca(OH) ₂
123	50	25 SiF	10	10		25	20 Calcined Aluminate Cement
130	200	100 SiF	40	40		82	80 Alumina
131	200	100 SiF	40	40		74	80 Al(OH) ₃
132	200	100 SiF	40	40		74	80 ZnO
132 Dup	200	100 SiF	40	40		74	80 ZnO
133	200	100 SiF	40	89	40	84	80 Al(OH) ₃
134	200	100 SiF	40	40		84	20 ZnO
135	200	100 SiF	40	40		98	80 Mg(OH) ₂
136	200	100 SiF	40	40		92	40 MgCO ₃
137	Titan Mix						
138	50	25 SiF				20	10Ca(OH) ₂ + 2 Na OH
139		75 SiF	10	10		40	20 Al Hydrate
140	50	25		10		26	10Ca(OH) ₂
141	50	25				22	5Ca(OH) ₂ + 10 ZnO + 2 Na OH
142		75 Fly Ash	10	10		44	20 Al Hydrate
143	50	25		3		23	10Ca(OH) ₂
144	50	25	10			23	10 MgCO ₃
145	50	25	10			23	10 MgCO ₃
146	50	25	10			20	10 Urea
147		40	10			25	20 Al (Rey)
148	50	25	10	10		17.5	10 ZnO
149	200	100				80	40Ca(OH) ₂
150	200	100	40	40		66	20 Al(OH) ₃

GLOSSARY OF TERMS

SiF or SF	=	Silica flour
Dia-A	=	Diamix A
Kasil	=	Potassium silicate (Philadelphia quartz)
Ca HPO ₄	=	Calcium phosphate - dibasic: Ca ₂ HPO ₄
SS anhyd.	=	Sodium silicate, anhydrous powder, 3.22/1 SiO ₂ /Na ₂ O ratio
SS hydr.	=	Hydrated powder Sodium silicate 2.4/1 ratio, 18% water
SS 42	=	Sodium silicate solution, Grade 42' Baume, 3.22/1 ratio ~ 39.3% solids
SFS	=	Sodium silicafluoride, powder
Colmanite	=	Mineral forms of calcium borate salts
SMS	=	Sodium metasilicate pentahydrate
Trib. Ca HPO ₄	=	Tribasic calcium phosphate: Ca ₃ (PO ₄) ₂
Al (Rey)	=	Reynolds Aluminum Co.: Al(OH) ₃
ZnO	=	Zinc oxide
Mg(OH) ₂	=	Magnesium hydroxide

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