PERMAFROST CEMENTING PROCESS
13 Claims, 9 Drawing Figs.

ABSTRACT: This specification discloses methods of treating wells drilled into the earth. These methods are particularly applicable for cementing behind casing located in wells drilled through permafrost zones. In carrying out these methods, slurries of calcium aluminate cement, clays selected from the group of bentonite, attapulgite and mixtures thereof, and water are formed and placed in the wells to be treated.
PERMAFROST CEMENTING PROCESS

BACKGROUND OF THE INVENTION

This invention relates to calcium aluminate cements and in particular to the use in wells of mixtures of calcium aluminate cement, clays and water.

Oil well cementing practices have been used in completing wells drilled into the earth since at least the early 1900's and oil well cements have been standardized by the American Petroleum Institute (API). In this standardization, the term "oil well cement" refers to Portland cement.

Various additives have been used in Portland cements to affect the properties thereof. For example, in U.S. Pat. No. 2,582,459 to Richard A. Salatih, bentonite and a soluble salt of a sulfonic acid are added to Portland cement to produce an oil well cement which has low mechanical strength and will not shatter under high impact. In U.S. Pat. No. 3,197,317 to Freeman D. Patchen, attapulgite is added to Portland cement slurries for use in oil well cementing to reduce the density of the slurries. In U.S. Pat. No. 3,227,213 to Dwight K. Smith, bentonite or attapulgite is prehydrated and then mixed with hydraulic cement of the character of Portland to form a slurry having a much higher yield than a slurry utilizing dry bentonite.

Calcium aluminate cements have not been in general use for cementing wells. However, they have proved to be ideal for use in thermal recovery wells and in particular when fine silica sand and ground firebrick are used as an admix. They have also been shown by laboratory and field experience to be usable in areas where permafrost problems exist, for example, on the North Slope of Alaska and Northern Canada. (Petroleum Engineer, Sept. 1966, pp. 64-66, "High Alumina Cement Solves Permafrost Cementing Problems," D. L. Stude) Stude gives data obtained in a model built to simulate conditions on the North Slope of tests of neat Ciment Fondu (calcium aluminia cement) and 50:50 mixtures of Ciment Fondu and fly ash which indicate that calcium aluminate cements are to be preferred over Portland cements for use in permafrost zones.

However, certain problems associated with calcium aluminate cements are pointed out by J. S. Dier in "New Ideas Solve Permafrost Drilling/Cementing Problems," WORLD OIL, May 1969: "High alumina cement was not considered when certain specified wells were drilled through the permafrost because of cost, normal slurry yielding characteristics and their sensitivity to contaminants."

As described in U.S. Pat. No. 3,226,240 to Michael S. Crowley, calcium aluminate cements are prepared by calcining and melting a mixture of limestone and alumina. For the "pure" calcium aluminate, the limestone is a chemical grade of at least about 97 percent purity, and the alumina is Bayer alumina of at least about 99 percent purity. After calcination, the calcium aluminate is quenched and pulverized. "Lumnite" and "Ciment Fondu" are examples of sintered types which contain alumina up to 43 percent (see The Condensed Chemical Dictionary, Sixth Edition, Reinhold Publishing Corporation).

SUMMARY OF THE INVENTION

In accordance with the present invention there are provided new and improved techniques for cementing wells penetrating the earth. A cement slurry is formed comprising calcium aluminate cement, clay selected from the group consisting of bentonite, attapulgite, or mixtures thereof, wherein the clay is present in an amount no greater than 6 percent by weight based on cement and water in an amount of at least 2.0 gallons per percent of clay in excess of the amount of water required to form a pumpable slurry of calcium aluminate cement, and the slurry is pumped into the well and allowed to set. In a preferred embodiment of the invention the clay is present in an amount of no greater than 3 percent by weight based on the cement. The clay is comprised of a mixture of bentonite and attapulgite wherein the ratios of bentonite to attapulgite vary within the range of 2 to 3 and 1 to 1.

The invention is particularly useful in cementing behind casing in wells penetrating a permafrost zone. By employing this technique in such wells there is provided a body of cement in the well formed from a slurry of calcium aluminate cement and clay selected from the group consisting of attapulgite and mixtures of attapulgite and bentonite, wherein said clay is present in an amount no greater than 6 percent by weight based on cement.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a wellbore penetrating a permafrost zone of the earth which illustrates the placing of a cement slurry in the annulus between the casing and the permafrost zone.

FIG. 2 is a cross-sectional view of a wellbore penetrating a permafrost zone of the earth which illustrates a cement slurry surrounding the casing and heat being applied indirectly to the slurry.

FIG. 3 is a plot which illustrates that the heat of hydration of a neat calcium aluminate cement slurry will maintain the slurry at a sufficiently high temperature such that it will set under permafrost conditions.

FIG. 4 is a plot, similar to FIG. 3, which illustrates that the heat of hydration of a calcium aluminate cement slurry by the addition of water and clay thereto.

FIG. 5 is a plot which illustrates the effect upon the compressive strength in 24 hours at 32°F. of the addition of various ratios of bentonite/attapulgite to a calcium aluminate cement slurry containing 79.2 weight percent of water based on cement.

FIG. 7 is a plot which illustrates the false set characteristics and thickening times at 40°F. of two calcium aluminate cement slurries, on containing 1.5 percent bentonite and the other containing 0.75 percent bentonite and 0.75 percent attapulgite, where each slurry contains 9.4 gallons of water per 94-pound sack of cement.

FIG. 8 is a plot which illustrates the effect of various ratios of attapulgite/bentonite on the false set characteristics of calcium aluminate slurries containing 1.5 percent clay. FIG. 9 is a plot which illustrates the false set characteristics and thickening times at 40°F. of two calcium aluminate slurries, on containing 1.5 percent prehydrated bentonite and the other containing 0.75 percent prehydrated bentonite and 0.75 percent attapulgite where each slurry contains 10.8 gallons of water per 94-pound sack of cement.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

I have discovered that calcium aluminate cement slurries can be tailored to give improved results in permafrost zones. This tailoring reduces the rate of hydration of calcium aluminate cement to desired rates for use in permafrost zones.

Broadly, this tailoring is done by adding calcium aluminate cement to a designated amount and clay selected from the group of bentonite and attapulgite and mixtures thereof. These slurries though particularly useful under permafrost conditions are also useful for treating higher temperature wells. However, for simplicity, this invention is described by making reference to its use under permafrost conditions.

Severe problems have been encountered in drilling and completing wells drilled through frozen formations, referred to as permafrost, found in the northern areas of Canada and Alaska and particularly along the North Slope of Alaska. Permafrost zones are comprised of strata of earth that exist at subfreezing temperatures generally considered to be within the range of 15°F. to 27°F. The permafrost zones which give the most problems in drilling and completing wells are those unconsolidated sands and gravels which contain ice as the continuous phase of the matrix. Such zones, if thawed, tend to flow or cave away producing excessive hole enlargement. Thus, in permafrost cementing the cement slurry must have unique properties. Its heat of hydration should be high enough to keep the slurry from freezing while it sets, but not so high as to melt the permafrost during the setting period. If the heat of
hydration of the slurry is too low or if it is released too slowly the slurry freezes and never sets satisfactorily. However, if the heat of hydration of the slurry is too high or is released too rapidly or early in the setting process the permafrost is thawed.

For setting well casing through permafrost zones by one embodiment of this invention, a slurry is formed of calcium aluminate cement, clay selected from the group consisting of bentonite, attapulgite and mixtures thereof in amounts of no greater than 6 percent by weight based on cement, and water in an amount of at least 2.0 gallons per percent clay in excess of the amount of water required to form a pumpable slurry of calcium aluminate and the slurry is pumped into the well and allowed to set.

Normally the amount of water that is mixed with cement to form a slurry thereof is expressed in units of gallons per 94-pound sack of cement. The normal amount of water which is required to form a pumpable slurry of clay-free calcium aluminate cement is considered to be 5.2 gallons per 94-pound sack of cement, though less water can be used if a more viscous slurry is acceptable and more water can be used if a less viscous slurry which has poorer setting properties is acceptable. With the addition of clay to the cement slurry water in excess of the above 5.2 gallons per sack must be used if the viscosity or thickness of the slurry is to be maintained above equivalent to the pumpable clay-free slurry. I have found that an additional amount of water of at least 2 gallons per percent of cement must be used for each 1 percent of clay added. Thus, if 1 percent of clay or 0.94 pound of clay is added to 94 pounds of cement, then 7.2 gallons of water per sack are required rather than the 5.2 gallons required for a clay-free sack of cement. Furthermore in this specification and appended claims whenever the amount of water per percent of clay in excess of the amount of water required to form a pumpable slurry of calcium aluminate cement is called for, it is to be understood that this means the additional amount of water required per percent of clay for each 1 percent of clay.

Such a slurry of calcium aluminate cement, clay, and water will develop significant compressive strength in 8 to 12 hours at 32°F. The slurry may be maintained at 32°F, at the interface between the cement and the permafrost by tailoring the heat of hydration (primarily by varying the amount of water), controlling the temperature of the mixing water and applying external heat.

The slurry is then pumped in a conventional manner down the well and positioned around the casing. For example, the slurry may be pumped down the well through the casing between two moving plugs, as is illustrated in FIG. 1. Referring to FIG. 1, there is shown a borehole 1 which has been drilled into the permafrost 3. Casing 5 is positioned within the borehole and extends to approximately the bottom thereof. Guide shoe 7 is attached to the lower end of casing 5, and float collar 9 of located within casing 5 above guide shoe 7. Cement slurry 11 is shown partially displaced from casing 5 into annulus 13. Lower cement plug 15 is shown within casing 5 at float collar 9 and upper cement plug 17 is shown separating the upper portion of cement slurry 11 from displacement liquid 19 thereabove. Displacement liquid 19 is pumped down casing 5 displacing slurry 11 before plug 17 until the movement of plug 17 is stopped by float collar 9. The cement slurry 11 is then maintained within annulus 13 until it sets and bonds casing 5 to permafrost 3. As previously mentioned, in accordance with the preferred embodiment of this invention, cement slurry 11 is mixed at a temperature of approximately 40°F. to 45°F. and displaced down casing 5 by displacement liquid 19 which is also at a temperature of about 40°F. to 45°F. By thus placing slurry 11 within annulus 13, permafrost 3 is not thawed and the temperature of slurry 11 will normally be maintained by its heat of hydration at about 32°F. or at least at a sufficiently high temperature to set but not at such a high temperature as to cause thawing of the permafrost 3.

As illustrated in FIG. 2, cement slurry 11 is shown positioned around the lower portion of casing 5 and within the annulus 13 formed between the casing 5 and the wall of borehole 1. Under some conditions it may be desirable to apply heat indirectly to cement slurry 11 within annulus 13 until cement slurry 11 begins developing its heat of hydration. This heat may be supplied by circulating heated fluid within casing 5. For example, a drill string 21 may be lowered within casing 5 to approximately the location of float collar 9 and heated fluid 20 circulated down drill string 21 and back up annulus 23 formed between drill string 21 and casing 5. Generally this heated fluid 20 is at a temperature of about 40°F. to 45°F. However, fluids of other temperatures, for example, steam, may be circulated in this manner. The primary concern in supplying heat indirectly to cement slurry 11 within annulus 13 is to maintain the slurry at such a temperature, preferably about 32°F., so that permafrost 3 is not thawed during the setting of slurry 11. A body of cement bonding casing 5 to permafrost 3 is thus formed.

The fact that the temperature of a neat calcium aluminate cement slurry is maintained by its heat of hydration at a sufficiently high temperature such that it will set under permafrost conditions is shown by FIG. 3 which illustrates data presented in the aforementioned article by Studt. In FIG. 3 time in hours is plotted as the abscissa and temperature in degrees Fahrenheit as the ordinate. The curve of FIG. 3 is representative of the temperature at the interface of a neat calcium aluminate cement slurry and the permafrost zone as measured by a thermocouple located at the interface. As shown by the curve, a peak temperature of about 81°F. is reached at this interface. Such a high temperature causes undesirable thawing of the permafrost zone in the vicinity of the well. However, the slurry does set under these conditions.

I have found that cement slurries comprised of calcium aluminate cement, clay selected from the group consisting of bentonite and attapulgite and mixtures thereof, wherein the clay is present in an amount no greater than 6 percent by weight based on cement, and water in an amount of at least 2.0 gallons per percent of clay per 94-pound sack of cement in excess of the amount of water required to form a slurry of calcium aluminate cement, will set under permafrost conditions without thawing the permafrost. Further, the addition of these clays affects the other properties of the cement slurry, such as density, setting time, compressive strength, yield, and pumping time in a way which is either beneficial or acceptable for use in the completion of wells. A satisfactory amount of water to form a pumpable slurry of heat calcium aluminate cement is 5.2 gallons per 94-pound sack of cement. Thus, for example, if 3 percent clay is used then the amount of water required per sack of cement is at least 5.2+3x2, or 11.2 gallons.

Data was obtained in a permafrost model in order to clearly show the effects of tailoring the heat of hydration of a calcium aluminate cement for use in permafrost zones. FIG. 4 is a plot, similar to FIG. 3, of this data and can be compared to FIG. 3. The data of FIG. 4 is obtained by testing a slurry comprising calcium aluminate cement (Ciment Fondu), attapulgite in an amount of 1 percent by weight based on cement, bentonite in an amount of 2 percent by weight based on cement, and water in an amount of 80.5 percent by weight based on cement. As shown by the curve of FIG. 4, the temperature at the interface of the slurry and the permafrost zone during a time period in which the slurry sets reached a maximum of about 32°F. and remained at that temperature for about 11½ hours after which the temperature began to decrease. This represents an ideal condition because the slurry will set in less than 1½ hours at 32°F. and the permafrost in the vicinity of the well will not be thawed.

It is to be noted that the above slurry is quite thick and for practicable purposes is unpumpable. However, FIG. 4 illustrates the effect of tailoring of the heat of hydration by the addition of water such that the temperature of the slurry is maintained at 32°F. during the setting of the slurry. A pumpable slurry would be obtained without any significant effect upon the heat of hydration of the slurry by reducing the amount of clay so that the water present was equivalent to at least 2.0.
3,581,825

gallons per percent of clay in excess of the amount of water required to form a pumpable slurry of calcium aluminate cement.

The amount of water used in the slurries of this invention is determined as follows. The amount of water required to form a pumpable slurry of a cement is determined by the Halliburton Consistometer. Thus, 2.0 gallons of water per percent of clay is termed "minimum water." The so-called normal amount of water is 2.8 gallons per percent of clay which when added results in a slurry having a consistency of about 11 poises after 20 minutes of stirring as determined by use of the Halliburton Consistometer.

Thus, the minimum amount of water to be added to form a slurry of calcium aluminate cement, 1.125 percent bentonite by weight based on cement, and 0.375 percent attapulgite by weight based on cement is determined to be about 85 percent calculated as follows:

\[
\text{Amount of water per 94-pound sack of} \quad \frac{6.33}{35} \quad \text{pounds water/gal. water} \times 6.33 \quad = 43.3
\]

\[
\text{Minimum amount of water per} \quad \frac{3.33}{10} \quad \text{pounds water/gal. water} \quad \times 2.0 \quad \text{gallons water/gal. water} = 25.0
\]

\[
\text{1.5 cereal sacker cement} \quad = 68.3
\]

Thus, a minimum of 68.3 pounds of water is used per sack of cement with 1.125 percent clay, or expressed as percent:

68.3 pounds water/sack cement

94 pounds cement/sack cement

100 = 72.7% water is used in preparing the slurry.

When preparing the slurry for treatment of wells penetrating permafrost zones in accordance with an embodiment of this invention, mixing water at a temperature of about 40°F to 45°F is used and the slurry is displaced down the well by displacement liquid also at a temperature of about 40°F to 45°F. This allows the cement slurry to be mixed without incurring problems associated with freezing of the water or "false setting" of the cement slurry. Further, so placing the slurry adjacent the permafrost zone does not cause substantial thawing of the permafrost and allows sufficient time for the slurry to begin developing its heat of hydration which prevents freezing of the slurry.

| TABLE 1 | PROPERTIES OF CALCIUM ALUMINATE CEMENT SLURRIES CONTAINING GEL AND OR ATTAPULGITE |
|----------------------------------|---------|-----------------|-------------|---------|-----------------|------------|-----------------|-------------|---------|-----------------|-------------|
| Cement formulation used          | Mixing water | weight percent on cement | Slurry density, lb/gal | Yield, cu. ft./sack | Sack strength, p.s.i. at 30°F | Consistency after 30 min, Halliburton units | Water separation, cc/70 poises |
| Luminate                        | 46             | 69.2              | 7.81          | 14.0       | 1.83              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 1% gel            | 45.8           | 95.8              | 10.81         | 12.85      | 1.03              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 2% gel            | 120            | 156.2             | 18.00         | 12.85      | 2.23              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 3% gel            | 151.5          | 141.5             | 18.00         | 12.85      | 2.65              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 4% gel            | 69.2           | 69.2              | 7.81          | 14.0       | 1.83              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 1% gel and 1% attapulgite | 124.0      | 124.0             | 14.00         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 2% gel and 1% attapulgite | 69.8    | 69.8              | 10.81         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 3% gel and 1% attapulgite | 55.8   | 55.8              | 10.81         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Luminate Plus 4% gel and 1% attapulgite | 55.8   | 55.8              | 10.81         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu                     | 46             | 69.2              | 7.81          | 14.0       | 1.83              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 1% gel         | 45.8           | 95.8              | 10.81         | 12.85      | 1.03              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 2% gel         | 120            | 156.2             | 18.00         | 12.85      | 2.23              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 3% gel         | 151.5          | 141.5             | 18.00         | 12.85      | 2.65              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 4% gel         | 69.2           | 69.2              | 7.81          | 14.0       | 1.83              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 1% gel         | 124.0          | 124.0             | 14.00         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 2% gel         | 55.8           | 55.8              | 10.81         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 3% gel         | 55.8           | 55.8              | 10.81         | 12.85      | 2.37              | 94            | 455              | 17           | 0      | 0.0              | 0            |
| Ciment Fondu Plus 4% gel         | 163            | 163               | 15.30         | 11.35      | 2.97              | 94            | 455              | 17           | 0      | 0.0              | 0            |

Attapulgite is a clay which consists principally of the mineral attapulgite and is mined in the United States in southwestern Georgia and northwestern Florida. It is a hydrous, magnesium aluminum silicate whose crystalline structure is needlelike in shape.

Bentonite, commonly called gel, is a clay composed almost exclusively of the clay mineral sodium montmorillonite and is mined principally in Wyoming and South Dakota. It is a hydrous alumina silicate which has platelike-shaped crystalline structure.

I have carried out laboratory tests to demonstrate the applicability of this invention for use in cementing wells drilled through permafrost zones. Two trade brands of calcium aluminate cement, Ciment Fondu and Luminate, were used in carrying out these tests. The results of these tests are tabulated in TABLE 1 and presented in FIGS. 5 through 9.

FIG. 5 is a plot having an abscissa of bentonite content in weight percent based on cement and an ordinate of compressive strength in pounds per square inch in 24 hours at 32°F. This FIG. 5 illustrates the effect of the addition of bentonite to calcium aluminate cement on the compressive strength which is developed in 24 hours at 32°F. In fact, the calcium aluminate cement slurries water was used in an amount of 5.2 gallons per 94-pound sack of cement plus the normal amount of water for the various percentages of bentonite added, which normal amount was found to be about 2.8 gallons per percent of bentonite based on a 94-pound sack of cement, or, more precisely, the normal amount of water was found to be 2.8 gallons per percent of bentonite for the first 3 percent of clay. 2.6 gallons for the 4th and 5th percent of bentonite, and 2.2 gallons for the 6th percent of bentonite. In this test it is seen that the compressive strength of the set cement containing 14% percent bentonite is about 1,045 p.s.i. and this compressive strength decreases to about 40 p.s.i. for cement containing 5 percent bentonite. It is generally conceded to be good cementing practice to cement around the lower portion of a well with a cement which exhibit a compressive strength of at least 500 p.s.i. after 24 hours under the conditions existing in the well. However, cements having less strength than 500 p.s.i. may satisfactorily be used, particularly as lead cements for blocking off waterflows from upper formations. Satisfactory results as a lead cement can be obtained with cements which exhibit compressive strengths of as low as about 5 to 10 p.s.i. after 24 hours.

As previously noted, the normal amount of water used in making these tests. There is a range of water referred to as minimum water to maximum water which may be used in mixing cement slurries. When minimum water is used, the resulting set cement exhibits a higher compressive strength than when either normal or maximum water is used. However, this increased compressive strength is attained at a sacrifice of yield (volume of cement slurry per sack of cement). Therefore, the curve of FIG. 5 would be shifted upward if the ce-
TABLE I: PROPERTIES OF CALCIUM ALUMINATE CEMENT SLURRIES CONTAINING GEL AND/OR ATTAPULGITE

<table>
<thead>
<tr>
<th>Cement formulation used</th>
<th>Mixing water</th>
<th>weight percent on cement</th>
<th>Slurry density, lb./gal.</th>
<th>Yield, cu. ft./ sack</th>
<th>Sock weight, lb./ sack</th>
<th>Compressive strength, p.s.i., in 24 hrs. at 32°F</th>
<th>Consistency after 20 min.</th>
<th>Water separation, er.</th>
<th>Halliburton units</th>
<th>Halliburton time at 40°F</th>
<th>Min. to start of set</th>
<th>Min. to 70% set</th>
<th>3 days at 32°F.</th>
<th>1 Average.</th>
</tr>
</thead>
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<tr>
<td></td>
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<td></td>
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<td>1,121</td>
<td>1.161</td>
<td>1.161</td>
<td>1.257</td>
<td>1.233</td>
<td>0.848</td>
<td>0.838</td>
<td>1.006</td>
<td>0.904</td>
</tr>
<tr>
<td>Plus 0.15% attapulgite and 1.37% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>55</td>
<td>134</td>
</tr>
<tr>
<td>Plus 0.35% attapulgite and 2.28% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>57</td>
<td>137</td>
</tr>
<tr>
<td>Plus 0.37% attapulgite and 1.13% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
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<td></td>
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<td></td>
<td>60</td>
<td>136</td>
</tr>
<tr>
<td>Plus 0.50% attapulgite and 0.90% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
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<td></td>
<td></td>
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<td></td>
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<td>62</td>
<td>138</td>
</tr>
<tr>
<td>Plus 0.7% attapulgite and 0.55% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
<td></td>
<td></td>
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<td></td>
<td>71</td>
<td>140</td>
</tr>
<tr>
<td>Plus 1.00% attapulgite and 0.50% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
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<td></td>
<td>81</td>
<td>143</td>
</tr>
<tr>
<td>Plus 1.00% attapulgite and 1.00% gel.</td>
<td>79.2</td>
<td>9.40</td>
<td>13.25</td>
<td>1.75</td>
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<td></td>
<td></td>
<td>116</td>
<td>300</td>
</tr>
<tr>
<td>Plus 1.2% attapulgite.</td>
<td>79.2</td>
<td>0.40</td>
<td>13.25</td>
<td>1.75</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>55</td>
<td>134</td>
</tr>
<tr>
<td>Plus 2% attapulgite.</td>
<td>79.2</td>
<td>0.40</td>
<td>13.25</td>
<td>1.75</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>57</td>
<td>137</td>
</tr>
<tr>
<td>Plus 2% prehydrated gel.</td>
<td>55.8</td>
<td>10.81</td>
<td>12.85</td>
<td>1.60</td>
<td></td>
<td></td>
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<td></td>
<td>89</td>
<td>206</td>
</tr>
<tr>
<td>Plus 1.5% prehydrated gel and 1.5% attapulgite.</td>
<td>55.8</td>
<td>10.81</td>
<td>12.85</td>
<td>1.60</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td>110</td>
<td>254</td>
</tr>
</tbody>
</table>

FIG. 7 is a presentation of data which illustrates the pumping and false set characteristics at 40°F. of two calcium aluminates cement slurries; one, curve A, containing 1.5 percent bentonite, and the other, curve B, containing 0.75 percent bentonite and 0.75 percent attapulgite. In this plot the abscissa is time in minutes in a Halliburton Consistometer at 40°F. and each ordinate is Halliburton Consistometer poises. The false set characteristics are identified by the initial part of the curve as indicated by D of curve A. For example, a slurry of Cement Fondu plus 1.5 percent bentonite, curve A, initially gives a consistency of 11 poises which almost immediately increases to 15 poises and then decreases to about 7 poises after 80 minutes and does not increase again to 11 poises until about 88 minutes. Thus, the slurry offers a high consistency initially and thereafter decreases to a minimum value before beginning to increase again as the slurry thickens with time. This high initial consistency, D, is what is referred to as false set and can under some conditions get so that the slurry cannot be pumped even though the slurry has not set. The calcium aluminates cement slurry containing a mixture of bentonite and attapulgite, curve B, exhibits only minimal or no false set characteristics. The initial consistency is about 4 poises and remains essentially constant for about the first 115 minutes at which time it begins to increase, but at a slower rate than shown by curve A. Thus, the pumping time for calcium aluminates cement slurry containing 1.5 percent bentonite at 40°F. is considered to be about 88 minutes whereas the pumping time of the slurry containing 0.75 percent bentonite and 0.75 percent attapulgite is considered to be 115 to 148 minutes. These pumping times are based upon the API mixing time which is the time required to reach 70 poises. It is seen that by blending the attapulgite and bentonite together the false set characteristics shown when bentonite alone is used are decreased and the pumping time is increased.

This reduction in the false set characteristics of calcium aluminates cement and bentonite produced by blending attapulgite with bentonite is further illustrated in FIG. 8, which is another plot similar to FIG. 7. Here, a total of 1.5 percent clay is used but the ratios of attapulgite to bentonite vary. The slurry of curve F contains 0.125 percent attapulgite and 1.375 percent bentonite and shows a false set characteristic J. The slurry of curve G contains 0.25 percent attapulgite and 1.25 percent bentonite and shows a false set characteristic K which is less than J of curve F. Likewise, the slurry of curve H has 0.375 percent attapulgite and 1.125 percent bentonite and shows false set characteristic L which is less than K of curve G. The slurry of curve I contains 0.75 percent attapulgite and 0.75 percent bentonite and for all practicable purposes can be considered to show no false set characteristic. Thus, FIG. 8.

ment had been mixed with minimum water and would be shifted downward if the cement had been mixed with maximum water. Likewise, a similar curve would be obtained if attapulgite had been used instead of bentonite. However, the attapulgite curve would be shifted downward since the addition of equivalent amounts of attapulgite rather than bentonite produces a set cement having less compressive strength. This is illustrated by FIG. 6 described below. Thus, it is seen that when clay selected from the group consisting of bentonite and attapulgite, and mixtures thereof, is added to calcium aluminates cement in an amount no greater than 6 percent by weight based on cement and allowed to set, a cement is formed having compressive strength which is satisfactory for oil well use. The upper ranges of the amount of clays added to the calcium aluminates cement are normally utilized when preparing a lead cement. Preferably, no greater amount than 3 percent by weight based on cement of bentonite or attapulgite or mixtures thereof are added to calcium aluminates cements, when the slurry is to be used for cementing around the lower portion of the casing to holding the casing in place. When these preferred amounts of not greater than 3 percent clay are added, a set cement is formed which exhibits a compressive strength of about 500 p.s.i. or greater in 24 hours at 32°F. which is completely satisfactory for permanent use.
clearly illustrates the improvement in false set characteristics of a calcium aluminate cement slurry which results from increasing the amount of attapulgite as compared to bentonite used in the slurry. A slurry containing either large amounts of attapulgite as compared to bentonite or attapulgite alone exhibits only minimal or no false set characteristics. This is highly desirable when the slurry is to be used under certain cementing conditions.

FIG. 9 is another plot similar to FIGS. 7 and 8 but where prehydrated bentonite rather than dry bentonite is used. Curve P is a plot of data obtained by testing calcium aluminate cement containing 1.5 percent prehydrated bentonite, and curve Q is a plot of data obtained by testing calcium aluminate cement containing 0.75 percent prehydrated bentonite and 0.75 percent attapulgite. The prehydrated bentonite shows false set characteristics similar to dry bentonite. Also, the yield of prehydrated bentonite in calcium aluminate cement is about the same as the yield of dry bentonite in calcium aluminate cement, which is a vast distinction from Portland cement slurries where approximately 4 times as much dry bentonite must be used as prehydrated bentonite to obtain the same yield.

What I claim is:
1. In a process of treating a well penetrating the earth, the steps comprising:
   a. forming a cement slurry comprising calcium aluminate cement, clay selected from the group consisting of bentonite and attapulgite and mixtures thereof in an amount no greater than 6 percent by weight based on cement, and water in an amount of at least 2.0 gallons per each 1 percent of clay in excess of the amount of water required to form a pumpable slurry of clay-free calcium aluminate cement;
   b. introducing said cement slurry into said well; and
   c. allowing said cement slurry to set within said well.
2. The process of claim 1 wherein said clay is present in an amount no greater than 3 percent by weight based on cement.
3. The process of claim 1 wherein said clay is present in an amount no greater than 6 percent by weight based on cement.
4. The process of claim 1 wherein said clay is bentonite in an amount no greater than 6 percent by weight based on cement.
5. The process of claim 4 wherein said bentonite is present in an amount no greater than 3 percent by weight based on cement.
6. The process of claim 1 wherein said clay is attapulgite in an amount no greater than 6 percent by weight based on cement.
7. The process of claim 6 wherein said attapulgite is present in an amount no greater than 3 percent by weight based on cement.
8. In a process of treating a well penetrating a permafrost zone of the earth, the steps comprising:
   a. forming a cement slurry comprising a mixture of calcium aluminate cement, clay selected from the group consisting of bentonite and attapulgite and mixtures thereof wherein said clay is present in an amount of no greater than 6 percent by weight based on cement, and water in an amount of at least 2.0 gallons per each 1 percent of clay in excess of the amount of water required to form a pumpable slurry of calcium aluminate cement;
   b. positioning said slurry adjacent said permafrost zone; and
   c. allowing said slurry to set.
9. The process of claim 8 wherein said clay is a mixture of bentonite present in an amount of 1.125 percent by weight based on cement and attapulgite present in an amount of 0.375 percent by weight based on cement.
10. The process of claim 8 wherein the amounts of bentonite and attapulgite vary between the ratios of 2:1 and 5:1 bentonite to attapulgite.
11. In a well equipped with casing and penetrating a permafrost zone of the earth, a body of set cement surrounding said casing within said permafrost zone, said set cement being comprised of calcium aluminate cement and clay selected from the group consisting of attapulgite and mixtures of attapulgite and bentonite, wherein said clay is present in an amount of no greater than 6 percent by weight based on cement.
12. In a process of treating a well equipped with casing penetrating a permafrost zone of the earth, the steps comprising:
   a. forming a cement slurry comprising calcium aluminate cement, clay selected from the group comprising bentonite and attapulgite and mixtures thereof, wherein said clay is present in an amount of no greater than 6 percent by weight based on cement, and water at a temperature greater than 32°F through said well in indirect heat exchange with said cement slurry.
   b. pumping said slurry down said well;
   c. displacing said slurry from said well with a displacing liquid at a temperature of about 40°F to 45°F wherein said slurry is positioned intermediate said casing and said permafrost zone; and
   d. allowing said slurry to set therein.
13. The process of claim 12 further comprising prior to step (d) circulating fluid at a temperature greater than 32°F through said well in indirect heat exchange with said cement slurry.