Report on

Argonne's Modeling Capabilities for Developing Candidate Deep Well Cements - Development of Berlinite-Based Deep Well Cement

Arun. S. Wagh
Energy Technology Division
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439, USA

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Cementing Solutions, Inc.
Attn: Fred Sabins

Houston, TX

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Summary

In the earlier reports to the Sponsor, we modeled the solubility of less than sparsely soluble oxides and predicted possibility of forming deep well cements using reaction between aluminum oxide and phosphoric acid solution. Based on these theoretical results, we conducted experimental investigations and have now demonstrated that aluminum phosphate (berlinite) cement can be formed for wells at temperature ≥ 300 °F (150 °C). The slurry consists of calcined alumina (corundum) and phosphoric acid solution in which aluminum hydroxide is used to accelerate the reaction. Depending on the content of the hydroxide, the pumping time can be varied between 5-7 hours. Initially, the slurry is very thin and gives a very small Bc and hence can be pumped very easily. The hardening occurs when the temperature reaches 300 °F (150 °C). The resulting hard product has a compressive strength of ≈700 psi. The X-ray diffraction pattern indicates that the resulting hard product consists of alumina and berlinite.

I. Introduction

Aluminum oxides are found in many forms. The important ones are, calcined alumina (Al_2O_3), aluminum hydroxide $Al(OH)_3$, bohmite ($AlO{\cdot}OH$, or $Al_2O_3{\cdot}H_2O$), and gibbsite ($Al_2O_3{\cdot}3H_2O$). In addition to the pure phases given above, alumina is also found in natural soils such as kaolin (clay) and bauxite and these may also be used to produce cements.

Alumina phases dissolve in aqueous acid solution of phosphoric acid and react with the phosphate ions to form phosphate cements. Therefore the dissolution characteristics of alumina phases are very important. Since alumina phases have very low solubility, they do not form cements at room temperature, but when heated, their solubility increases and they dissolve and form cements.

Table 1 reproduced from Report 1 gives the temperature of maximum solubility of alumina phases. Because these temperatures of deep wells, i.e., in the range of 250 – 350 °F, they are most suitable for deep and hot wells.

Table 1. Temperature (°F) of maximum solubility for alumina phases

Alumina $AlO_{3/2}$	Hydroxide $Al(OH)_3$	Bohmite $AlOOH$	Gibbsite $AlO_{3/2}{\cdot}3/2H_2O$
223	239	270	338

Once they dissolve in the acid solution, they will react with the phosphate ions to form phosphates. A typical reaction with alumina is given below.

$$Al_2O_3 + 2H_3(PO_4) + H_2O \rightarrow 2AlPO_4{\cdot}2H_2O. \qquad (1)$$

$AlPO_4{\cdot}2H_2O$ is a hydrated phase of aluminum phosphate called variscite. In addition to the variscite, other phases are also reported in the literature, such as wavellite ($Al_3[PO_4]_2[OH]_3{\cdot}5H_2O$). If the same reaction is conducted in dry air, we form the anhydrous phase $AlPO_4$ called berlinite. Earlier studies [1] have shown that this reaction occurs at 150 °C (300 °F) which is also within the range of a downhole temperature of a deep well. Therefore it is likely that the reaction given by Eq. (1) may also occur in an aqueous environment in a deep well at this temperature to form cement with hydrated phosphate phases.

During the period of this report, we tested ithis dea and found that it is possible to produce high temperature oil well cement using reaction between alumina and phosphoric acid. Details are given below.

Raw Materials and Test Procedure for Thickening Time

Table 2 gives details of the materials used in this study. Alumina was from Argonne's inventory, while aluminum hydroxide and phosphoric acid were purchased commercially.

The stoichiometry of the reaction, i.e. the ratio of alumina and phosphoric acid needed to form this cement is given by Eq. (1). For each pound of Al_2O_3 one needs 1.85 pound of H_3PO_4. In practice, however, phosphoric acid is available in a diluted form, typically 85 wt.% or 70 wt.% concentrated solution. In the field, however, it is more convenient to use this acid in a more diluted form of 50 wt.%. For this reason, we used 50 wt.% dilute phosphoric acid solution in our study.

Table 2. Raw material description and compositions

Material	Supplier	Characteristics
Alumina (Al_2O_3)	Argonne inventory	Calcined, average particle size was 2-3 μm (see Fig. 1 for detailed particle size distribution)
Aluminum hydroxide ($Al(OH)_3$)	Aluchem Corporation	Product no. AC 30 AN, Average particle size was 13 μm (see Fig. 2 for detailed size distribution). We suspect the powder has significant amount of amorphous aluminum hydroxide that helps rapid reaction.
Phosphoric acid ($H_3(PO_4)$)	Mallinkrodt	85 wt.% concentrated. It was diluted to 45-50 wt.%.

As mentioned in Report 1, the solubility of alumina even in phosphoric acid is very low. As a result, when cement is formed, it is only the surface of individual particles of alumina that reacts with phosphoric acid. Therefore, it is necessary to provide a large surface area for sufficient alumina to react with phosphoric acid solution. For this reason, we increased the amount of alumina in our test and used at 2-5 times that of the stoichiometric proportion.

The powders (calcined alumina + aluminum hydroxide) were first mixed thoroughly and the phosphoric acid solution was added and mixed in the Hobart mixer for 20 minutes. Then the slurry was poured into the slurry cup and tested for thickening time in the consistometer. After the consistency reached 70Bc the slurry was transferred into the syringes. These syringes were immersed in water in the consistometer slurry cup and were cured at 300 °F and 320 °F.

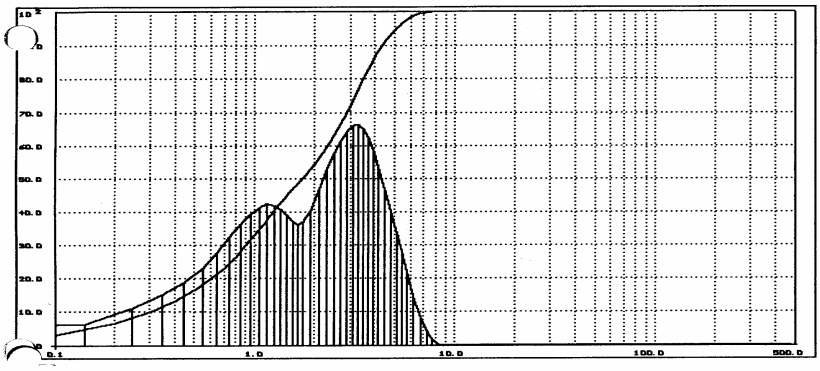

Figure 1. Particle size distribution of alumina used in this project

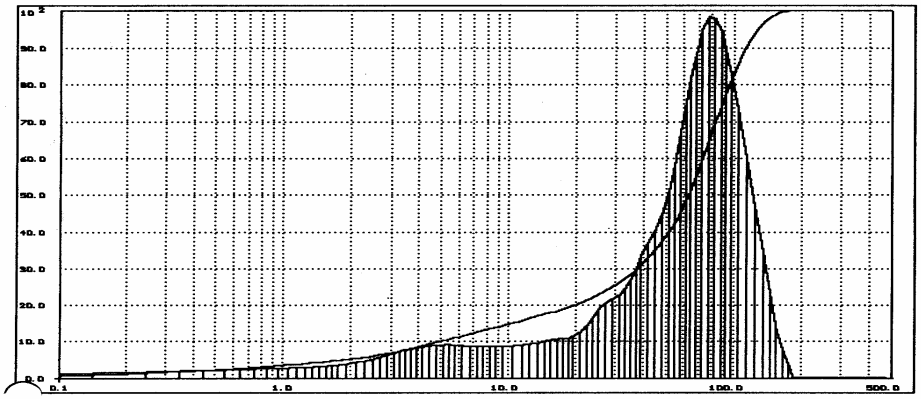

Figure 2. particle size distribution of aluminum hydroxide used in this study

Consistency and Thickening Time

The composition that satisfied all the basic requirements of oil well cement, such as, low initial consistency (< 30 Bc) for easy pumping, and sufficient pumping time are given in Table 3. When the composition did not contain aluminum hydroxide, the slurry remained thin and the test was terminated after 8 hours. This may be because, even the maximum solubility of alumina at 250 °F, is not sufficiently large to set the mixture within 3-5 hours. Therefore it is necessary to accelerate the reaction. We found that it is possible to accelerate the reaction by adding aluminum hydroxide in a small proportion. When this was done, the slurry reacted within hours and thickened. This may be seen in the third and fourth column in Table 3. An addition of 46g of aluminum hydroxide to 1000 g of alumina thickened the slurry in 4 hours (third column in Table 3). Similarly, addition of 23g of aluminum hydroxide to 1000g of alumina provided a thickening time of 6 hours at the pumping temperature of 300 °F (fourth column in Table 3). Thus, aluminum hydroxide acts like an accelerator and may be used in different proportions to provide the desired pumping time.

Table 3. Formulation at BHCT 250 °F and 300 °F

Components	Testing parameters		
	T=250°F, P=13285 psi	T=250°F, P=13285 psi	T=300°F, P=16650 psi
Calcined alumina (g)	1000	1000	1000
Aluminum hydroxide (g)	0	46	23
Boric acid (g)	0	10g	10g
45% H_3PO_4 Solution (ml)	500	500	500

Pumping Time	> 8h	4 Hrs	6 Hrs
Consistency 15-30 mins (Bc)	30	30	10

Figures 3 and 4 show the slurry characteristics at the pumping temperatures of 250 °F and 300 °F. The initial Bc at 250 and 300 °F are 30 and 10 Bc. The higher consistency at 250 °F is mainly because of the higher amount of aluminum hydroxide. It is therefore possible to reduce the initial Bc by lowering the amount of aluminum hydroxide and increasing the pumping time.

The sufficiently low numbers of Bc indicate that the slurry may be pumped easily. The Bc remains constant over most of the pumping period and then the slurry exhibits "right angle set" characteristics, where the Bc increases rapidly. Thus, the aluminum phosphate cement is likely to exhibit a very low permeability matrix that sets with a sufficient speed to prevent major gas intrusion.

In normal Portland cement systems often the increase in the consistency is accompanied by an increase in the temperature because of the exothermic cement hydration reactions. In aluminum phosphate system, however, no increase in the temperature was detected.

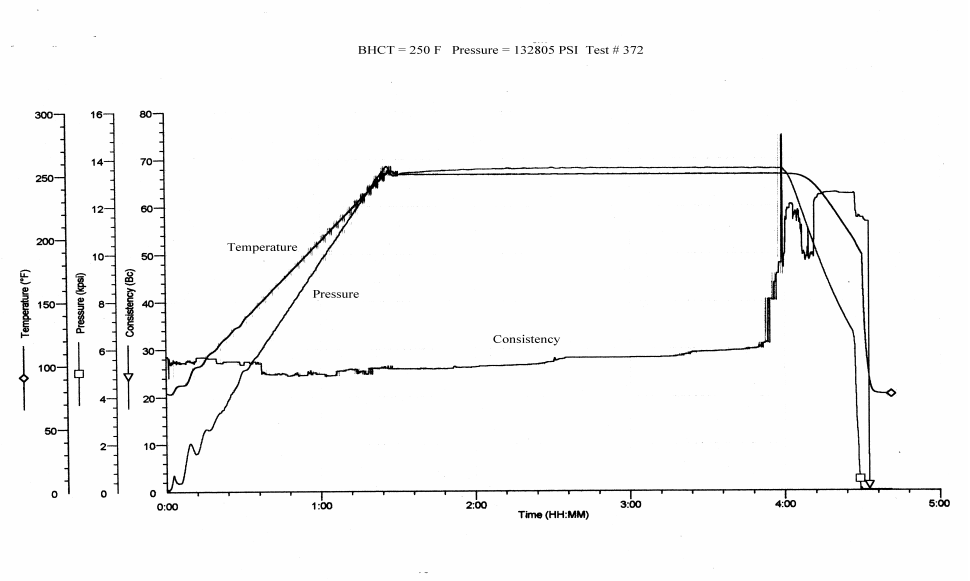

Figure 3. Pressure and temperature vs. consistency graph at 250 °F and 13285 psi

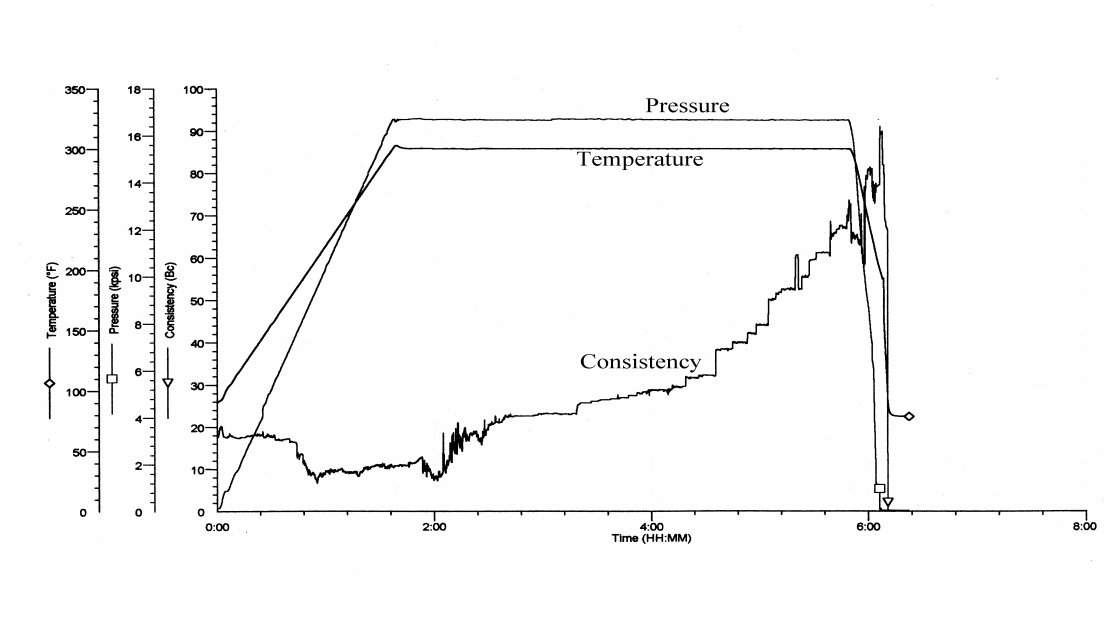

Figure 4. Pressure and temperature vs. consistency graph at 300F 16650 PSI

Physical Properties of the Set Product

Table 4 provides the physical properties of the hardened product formed by the slurry that was pumped at 250 °F, and cured at 3000 °F and 3000 psi for 30 h. The density of this cement is nearly the same as that of neat Portland cement, which is 2.4 g/cm^3. The slurry had a density of 2.46 g/ml, which implies that there has been a slight expansion of 4% during setting. This slight expansion allows the cement to be a nice seal as it will not produce any annular space between casing and the formation.

The open porosity was measured by water immersion method. An open porosity of 1.15 is sufficiently small to make this material and impermeable seal.

The compressive strength is higher than minimum strength of 500 psi required for oil well cements. In our opinion, this strength needs to be enhanced and more work is needed in this direction. However,

the samples were hard enough to be handled and it is likely that longer curing may provide better strengths. This needs to be tested systematically.

Table 4. Physical properties of the set cement

Properties	Measured value
Density of the set cement (g/cm^3)	2.36
Open porosity (vol.%)	1.15
Compressive strength (psi)	694

Effect of Aluminum Hydroxide on Pumping Time

The pumping time is found to be sensitive to the amount of aluminum hydroxide in the slurry. To investigate this feature, consistometer tests were run with different proportions of aluminum hydroxide content in the slurry. Figure 5 shows the variation of the thickening time at 250 °F as a function of aluminum hydroxide content for every 100 g of alumina. Similarly, Table 4 shows the effect of aluminum hydroxide on the thickening time at 300 °F. As the hydroxide content is increased, the thickening time decreases. It can be seen from the figure, a reduction of 15g increases the pumping time from 2 hrs to 4 hrs. Similarly at BHCT 300 °F a decrease of 23g increases the pumping time from 2hrs to 6hrs. This is because the amorphous aluminum hydroxide provides additional nucleation sites for the reaction and hence the reaction proceeds faster.

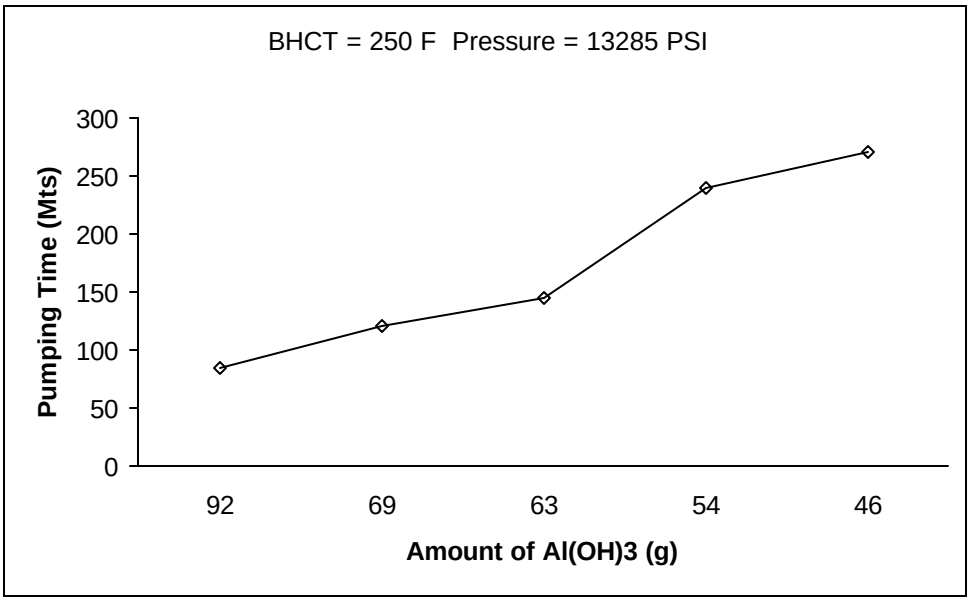

Figure 5. Effect of amorphous aluminum hydroxide on pumping time

Table 5. Effect of $Al(OH)_3$ on pumping time at 300F and 16650 psi

Amount of $Al(OH)_3$	Pumping time
46g	2 hrs
23g	6 hrs

Effect of Pressure on Pumping Time

In portland cement system, an increase in pressure accelerates the setting reactions and decreases the thickening time [2]. Our theoretical analyses show that the effect of pressure on thickening of aluminum phosphate system is negligible [3]. To test this, we tested the composition given in Table 4 at 13,285 and 16,650 psi respectively. The results are given in the same Table.

Table 6. Effect of pressure on pumping time

Composition	T=250 °F P= 13285 psi	T=250 °F P= 16650 psi
Calcined Alumina	1000g	1000g
$Al(OH)_3$	54g	54g
Boric Acid	10g	10g
45% H_3PO_4 Solution	500ml	500ml
Pumping Time	3 Hr 40 Mts	3 Hr 30 Mts

Phase Analysis of the Cement

To understand the composition of the cement formed in the consistometer, we conducted X-ray diffraction analysis of the product. The results are presented in Figure 6. Three distinct phases were observed. These are alumina, aluminum hydroxide and aluminum phosphate (berlinte). This implies that significant amount of alumina remains unreacted as expected in a system where excess alumina is added. We also find significant amount of aluminum hydroxide, which must have been formed by hydration of some of the alumina. Berlinte is the reaction product, which is the binder component of the mixture. We have not seen any hydrated phases of this binder such as wavelite, or variscite, but they may be amorphous phases and may not be detectable by the X-ray diffraction technique.

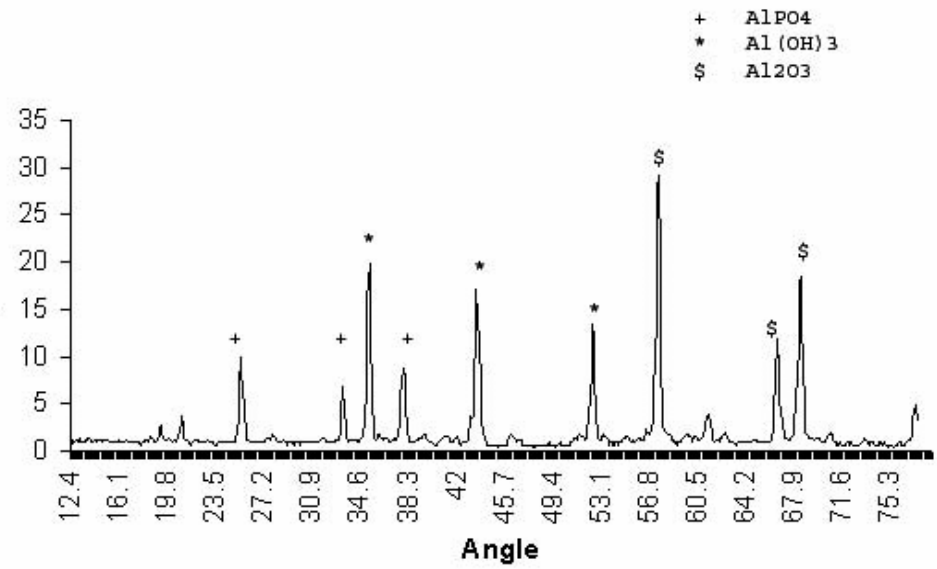

Figure 6. X–ray diffraction pattern of sample pumped at 250F and cured at 300F for 27 h.

Conclusions

The work reported here indicates that aluminum phosphate cement system may be a very good system for deep wells at temperatures >250 °F. It is formed by the reaction of aluminum oxide with phosphoric acid solution, in which a small amount of aluminum hydroxide is added for initial acceleration of the reaction. The resulting product is a mixture of alumina, aluminum hydroxide, and the

binder phase berlinite. The pumping time is > 3 hours, and it can be increased by adjusting the content of aluminum hydroxide in it. The compressive strength of the cement is ≈700 psi. This is not as high as one would expect in a good cementing system. The samples taken out of the consistometer used as a curing chamber looked hard, but they were cut with a diamond saw and it is likely that this step initiated flaws in the material and that led to lowered measured strength. It is likely that if the test is conducted in a proper curing chamber, we will obtain a better strength. This may be tested at the CSI facility.

References and Comments

1. Wagh, A. S., S. Grover and S. Y. Jeong, Chemically Bonded Phosphate Ceramics: II, Warm-Temperature Process for Alumina Ceramics, J. Am. Ceram. Soc., 86[11] (2003) 1845-49

2. Smith D. K., Cementing, SPE Monograph vol. 4 in Henry L Doherty Series, Society of Petroleum Engineers, New York (1990), p.43.

3. We have shown this with a lengthy theoretical analysis. Interested readers may contact the author for more details.