Report 2

Argonne's Modeling Capabilities for Developing Candidate Deep Well Cements - Thermodynamic Evaluation of Common Silicates and Aluminates*

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Summary

We investigated silicates and aluminates of calcium and magnesium as candidate materials for development of down hole cement for very deep wells. Magnesium aluminate appears to be such a material that can be used above 350 °F. Below that temperature we have already proposed aluminum phosphate cement. With these two together, we may be able to cover a very wide range of temperatures in the deep trek program.

I. Introduction

Recently, U.S. Department of Energy, through its National Energy Technology Laboratory (NETL) funded a project to Cementing Solutions, Inc., to develop novel cementing materials for deep oil and gas wells, where the temperature and pressures are > 250 °F and >15,000 psi. DOE also funded Argonne National Laboratory (ANL) to support this activity with its capabilities in identifying novel cement compositions. This is the second report submitted by ANL to CSI. In this report, we have evaluated calcium and magnesium aluminates and silicates and identified magnesium aluminate as a candidate cement for development of hot wells with temperatures
> 300 °F.

II. Silicates and Aluminates of Calcium and Magnesium

Silicates are one of the most common minerals in nature, and aluminates, though are not so common, are available as natural minerals or may be manufactured in an industrial plant. Table 1 provides a list of these minerals and their chemical formulae.

Table 1. Candidate minerals, chemical formulae and cement notation

Mineral	Chemical formula	Cement notation
Wollastonite	$CaSiO_3$	$CaO \bullet SiO_2$, or **C•S**
Magnesium silicate	$MgSiO_3$	$MgO \bullet SiO_2$, or **M•S**
Calcium aluminate	$CaAl_2O_4$	$CaO \bullet Al_2O_3$, or **C•A**
Magnesium aluminate	$MgAl_2O_4$	$MgO \bullet Al_2O_3$, or **M•A**

Among these four, wollastonite is very abundant and readily available in the commercial market. Magnesium silicate, though is not as abundant as wollastonite, is also available commercially. Calcium aluminate is sold as aluminate cement and hence is readily available, while magnesium aluminate, though not as common as other three, is still available with vendors such as Alfa Aeser. Because of the availability of these four, we have selected them for this study.

There exist other minerals such as 2**C•S,** or **C•2S**, 2**C•A** or **C•2A**, and similarly, 2**M•S**, or **M•2S**, and 2**M•A** or **M•2A**. These minerals are not easily available. They can be manufactured if needed, but our evaluation did not show any benefits of these minerals over the four listed in Table 1, and hence they were not pursued.

The first step in the evaluation of these minerals is to calculate the temperature of maximum solubility and compare that temperature with that of a well under consideration. The temperature can be calculated from the solubility reaction. Table 2 gives the solubility equation of these minerals.

Table 2. Solubility equations of minerals under consideration

Mineral	Solubility equation
Wollastonite	$CaSiO_3 + H_2O = Ca^{2+}(aq) + SiO_2 + 2OH^-$ ……(1)
Magnesium silicate	$MgSiO_3 + H_2O = Mg^{2+}(aq) + SiO_2 + 2OH^-$ ……(2)
Calcium aluminate	$CaAl_2O_4 + 4H_2O = Ca^{2+}(aq) + 2Al^{3+}(aq) + 8OH^-$ …(3)
Magnesium aluminate	$MgAl_2O_4 + 4H_2O = Mg^{2+}(aq) + 2Al^{3+}(aq) + 8OH^-$ …(4)

The formula that gives the maximum solubility temperature T_m in absolute scale is given by,

$$T_m = T_0 - DH\,(T_0)/DC_p. \qquad (1)$$

Here, DH and DC_p are respectively the net change in the enthalpy and specific heat calculated by using equations in Table 2, and T_0 = 298 K.

Table 3 gives the enthalpy (ΔH_0) and specific heat C_p for each of the components in the equations in Table 2. Using these numbers and Eq. (1), T_m is calculated and given in Table 4.

Table 3. Enthalpy and specific heats of components

Component	ΔH_0 (kJoules/mole)	C_p (Joules/mole/°C)
Wollastonite	-1634.94	85.19
Magnesium silicate	-1547.7	82.09
Calcium aluminate	-2324.08	120.68
Magnesium aluminate	-2299.32	115.94
SiO_2	-910.7	44.4
H_2O	-285.8	75.3
Ca^{2+}(aq)	-542.8	0.8
Mg^{2+}(aq)	-466.9	38.5
Al^{3+}(aq)	-531	38.1
OH^-	-230	-148.5

Table 4. Maximum solubility temperatures

Mineral	T_m (°F)	Well for which the cement can be used
Wollastonite	109	Shallow
Magnesium silicate	65	Shallow
Calcium aluminate	142	Medium depth
Magnesium aluminate	363	Very deep or geothermal

In Table 4, we have also indicated the well in which the cement of the particular mineral can be used. Note that, except for magnesium aluminate, other minerals have solubility temperatures corresponding to shallow or medium depth wells, while magnesium aluminate can form cement suitable for very deep or hot well. For the deep trek project, we conclude that magnesium aluminate cement would give ideal composition.

Sugama and his group reacted calcium aluminate cement with ammonium phosphate and developed cement for geothermal applications [1]. Their system consists of reacting calcium aluminate cement with ammonium phosphate solution. Unfortunately, such systems release ammonia during setting and form very porous cements with poor strength. We propose that with the temperatures calculated above, we should be able to react them above these temperatures with phosphoric acid solution and produce comparatively denser cements.

III. Proposed Cement Composition

The cement composition will consist of stoichiometric amount of magnesium aluminate and phosphoric acid solution. The stoichiometric equation that governs the cement formation is given below.

$$MgAl_2O_4 + 3H_3PO_4 = MgH\ PO_4 \bullet 3H_2O + 2AlPO_4 + H_2O \qquad (5)$$

The first term on the right hand side is called newberyite. Newberyite cements have been synthesized by us in the past by reacting magnesium oxide with magnesium dihydrogen phosphate [2]. The second term on the right hand side is aluminum phosphate or berlinite, which was again synthesized by us and has been discussed in Report 1 submitted to CSI last month. Thus, using magnesium aluminate cement, we can produce cement that is a blend of two cement phases, newberyite and berlinite.

Based on the molecular weight of each of the components on the left hand side of Eq. 5, we can arrive at the composition of the cement. If we use 50 wt.% concentrated phosphoric acid solution, ten pounds of magnesium aluminate will require 14 pounds of the solution. This should give good flowable slurry for testing.

IV. Path Forward

For a systematic development of the phosphate cement of magnesium aluminate, experimental investigations are needed to confirm the solubility temperature and predicted phosphate reactions. This may be done in the following tasks.

1) Conduct differential thermal analyses of the mixtures of magnesium aluminate and phosphoric acid solution,

2) produce cements by heating the slurry in oven and produce the set cement. Analyze it with X-ray diffraction analysis to understand the mineralogy, and confirm that stable cement is formed. Finally,

3) test the formulations in a consistometer according to American Petroleum Institute standards.

References

1. Sugama, T., and N. Carciello, Hydrothermally synthesized aluminum phosphate cements, Advances in Cement Research, vol. 5 [17] (1993) 31-40.

2. Wagh, A. S., and S. Jeong, Chemically Bonded Phosphate Ceramics: I. A Dissoluttion Model of Formation, J. American Ceramic Society, vol. 86 [11] (2003) 1838-1844.