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Dynamic retarder exchange as a trigger for Portland cement hydration

Xueyu Pang, Pinmanee Boontheung, Peter J. Boul *

Halliburton, 3000 N Sam Houston Pkwy E, Houston, TX 77032, USA

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ABSTRACT

A series of NMR and isothermal calorimetry tests were conducted to depict a retarder exchange mechanism whereby a powerful organophosphonate retarder (nitrilotris(methylene) triphosphonate, or NTMP) is replaced by a much weaker phosphate retarder (sodium hexametaphosphate, or SHMP). The retardation of cement hydration by NTMP is believed to be primarily attributed to the dissolution of calcium from the cement and the subsequent precipitation of a layered calcium phosphonate that binds to the surface of the cement grains and strongly inhibits further hydration. The test results from this study show that the addition of SHMP helps to dissolve the precipitated calcium phosphonate and thus removes the strong retardation effect of NTMP. The proposed retarder exchange mechanism may be employed to develop cement systems with a controlled setting behavior.

1. Introduction

Hydraulic cements have been used as building materials for millennia. The Greeks used volcanic ash, finely ground, with lime and sand to produce a building material with good strength and water resistance properties. The Romans also used hydraulic cements to build some of the great civil structures still standing today. The technology behind these calcium silicate materials was lost for hundreds of years through the dark ages and it was not until the mid-1840s that Portland cement was redefined as a calcium silicate cement by William Aspdin [1].

Portland cement is an indispensable material in the oil field [2]. In drilling for oil, after a hole is drilled in the ground to the appropriate depth, a metal pipe (referred to as the casing) is placed in the wellbore. The inside of this casing is where the oil extracted from the well is channeled up to the surface. The annular volume between the outside of the casing and the formation is sealed to help ensure that the well maintains zonal isolation. Zonal isolation is the exclusion of undesirable fluids such as water or gas of one zone of the well from oil in a producing zone. Portland cement is often used as the sealant to establish zonal isolation in oil wells. Oil well grade Portland cement is a specialized kind of Portland cement designed to tolerate the harsh downhole environment up to 9000 m below the surface [3] and temperatures up to 650 °F [4].

Despite the complexity of the material, Portland cement can be tailored to meet the different challenging environments encountered in the oil field. Chemical additives are used to impart a number of different desirable properties into cement. Oil well cements can be adjusted for their rheologies, densities, hydration kinetics, and mechanical properties to name a few aspects. The choice of additive depends on many different factors including the temperature and pressure within the well, the geological formations, the length of the well, along with the presence of water, oil, or gas throughout the well.

Among the different types of additives are retarders and accelerators. These additives serve to control the time required for the cement to set. The amount of time that the cement is required to be flowable and pumpable into the well varies depending on the well size, temperature, pressure and the location (depth) within the well to which the cement is to be placed. The use of retarders and accelerators in cement slurries is often essential to the cement slurry design specific to those conditions demanded by the well.

There are a wide variety of different kinds of retarders used in oil well cementing to control the setting time of the cement. Examples of different retarders include organic phosphonates, phosphates, borates, saccharides, and lignosulfonates, to name a few. The different kinds of retarders are often observed to display quite different mechanisms for retarding cement slurries. The four different mechanisms for the retardation of cement that are now widely accepted are (1) calcium complexation, (2) the precipitation of a semipermeable layer on the cement grains, (3) direct surface adsorption of the retarder onto the clinker phase(s), and (4) nucleate poisoning of C–S–H and portlandite [5].

The complexation of calcium is an important mechanism for the retardation of cements by saccharides and a number of other retarding cement additives. The strong calcium chelation by alpha and beta hydroxycarboxylic acids, EDTA (ethylenediaminetetraacetic acid), and saccharides is thought to be the reason for their effectiveness in retarding the hydration of cement [6]. Calcium complexation prevents

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* Corresponding author.
E-mail address: Peter.Boul@halliburton.com (P.J. Boul).

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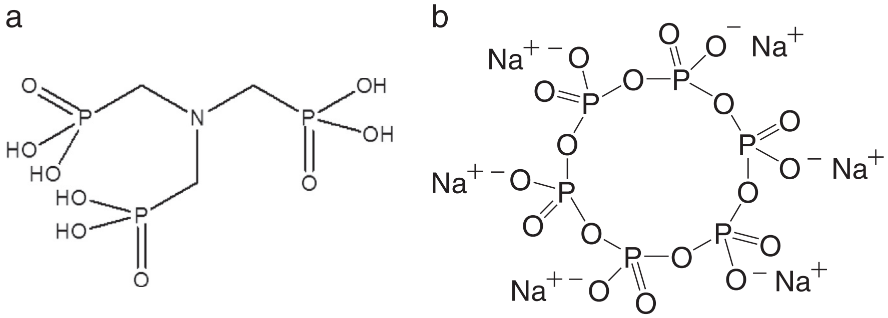

Fig. 1. The chemical structures of (a) nitrilotris(methylene)triphosphonic acid (H_6NTMP) and (b) sodium hexametaphosphate (SHMP).

the formation of portlandite in cement and prevents the nucleation of C–S–H. Phosphates are also believed to retard cement in this way [7].

Bishop et al. [8] proposed a dissolution–precipitation mechanism to explain the retardation of Portland cement hydration by nitrilotris(methylene)triphosphonic acid (H_6NTMP). In this mechanism, calcium is first extracted from the surface of cement grains and then forms a transiently soluble complex with the chelating phosphonate. After a short period of time, the calcium phosphonate complex oligomerizes and precipitates, possibly as a layered sheetlike coating that binds to the surface of the cement grains. The insoluble polymeric calcium phosphonate precipitate is believed to retard both further dissolution of the anhydrous phase (by creating a barrier to water diffusion) and growth of the hydrates (by acting as a nucleation inhibitor) [8,9].

There are many conditions in cementing a well where there is considerable use in systems which respond to instructions from the operator. In particular, if a cement can be instructed when to set, the cost of operations at the well site can be reduced substantially. An example of the use of this kind of "set-on-demand" cement in the oil field is in a product known as LIQUID STONE®. The patent literature from the company that makes this material describes an extended life slurry system where a retarder such as sodium gluconate or calcium gluconate is used to produce a storable Portland or slagment cement slurry which can be activated at a later time (prior to pumping) with an activator such as sodium silicate [10]. In the concrete industry, ready-mix is a product which is designed to activate in a similar way. A strong phosphonate retarder, such as NTMP, is used in ready-mix to prevent concrete from setting. When the concrete set is desired, an accelerator (such as calcium nitrate) is added to set the concrete [11]. This allows the recycling of unused concrete at the end of a work day such that the left-over concrete can be used the next work-day or work-week.

In this work presented here, a storable cement slurry is described whereby activation occurs by replacing a strong retarder of Portland cement with a weak retarder. This slurry can exist in slurry form for an extended period of time (from 3 days to as much as a year) due to the effect of the strong retarder. The weaker retarder can be added to the cement slurry just prior to pumping the slurry down the well. In this way the cement is instructed to begin hydration as according to the hydration dynamics of the weaker retarder. Along these lines, a system has been developed which can hydrate on demand in response to a chemical stimulus (i.e. through the addition of the weaker retarder).

Table 1
Oxide composition of the cement by mass percentage.
(Na_2O and MgO values were determined by ICP while all other values were determined by XRF.)

Oxide	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO
Percent	0.11	1.59	3.13	21.75	2.88	0.15	64.45
Oxide	TiO_2	Mn_2O_3	Fe_2O_3	ZnO	SrO	LOI[a]	
Percent	0.23	0.07	4.66	0.03	0.09	0.86	

[a] Loss on ignition.

2. Materials and methods

2.1. Materials

Calcium hydroxide, deuterium oxide, sodium hexametaphosphate (SHMP) and H_6NTMP were purchased from Aldrich. H_6NTMP was provided as an aqueous solution with 50% active solids by mass and a density of 1.3 g/mL. Its dosage has been converted to the total solid content in the following discussions about mixture designs. The chemical structures of H_6NTMP and SHMP are presented in Fig. 1.

API Class H cement was obtained from Lafarge Co. (Joppa, IL plant). The oxide composition of the cement is determined by inductively coupled plasma emission spectrometry (ICP) and X-ray fluorescence spectroscopy (XRF) and the results are presented in Table 1. The phase compositions of the cement were estimated from the measured oxide composition using the Bogue calculation method [12] and powder X-ray diffraction with accompanying Rietveld refinement [13] (Table 2). The main phase compositions estimated by the two different methods agree very well with each other, except for the sulfate content. The results from the Bogue method, which agree with the chemical property data provided by the manufacturer, are probably more accurate here because they are based on an element analysis and sulfate is the only sulfur-containing phase in the composition. Rietveld method has been reported to be prone to overestimating the concentrations of materials that are present in small concentrations [13]. As the C_3A content of the cement is estimated to be between 0 and 0.43% of the total weight of the dry cement, the early hydration of this cement is expected to be dominated by C_3S.

2.2. NMR experiments

NMR experiments were conducted to study the interactions between calcium, NTMP and SHMP in solutions. Seven different

Table 2
Estimated main compound compositions (by mass percentage) of the cement.

Method	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	Free lime
Bogue	61.0	16.9	0.43	14.3	4.9	0.16
Rietveld	58.6	17.5	0	13.2	10.7[a]	–

[a] Sulfate content comprised both gypsum (2.4%) and anhydrite (8.3%).