

SETTING TIME AND WORKABILITY OF MAGNESIUM PHOSPHATE CERAMICS SLURRY

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Abstract

In the nuclear industry, low and intermediate-level radioactive liquid wastes are often processed using methods that involve solidification. One of the most commonly used methods employs Ordinary Portland Cement (OPC) as a binder. While OPC is both versatile and inexpensive, there are alternatives that are used in certain instances where the use of OPC is not appropriate. As one of those alternatives, Magnesium Potassium Phosphate (MKP) Ceramics have found their niche applications in treating most difficult wastes such as salts, ashes, liquids, and sludge.

A key characteristic of the formation of MKP is its setting time, defined as the length of time between mixing of the ingredients and solidification of the MKP, during which the slurry is capable of being poured into molds, where solidification is desired to take place. A method of direct, real-time measurement of the torque experienced by the slurry mixing system (hence the viscosity of the slurry) was developed to monitor the setting behavior (e.g., setting time) of the slurry, and to provide a means of predicting the workability limit of a slurry. The effects of pH, additives (such as boric acid) and the composition of surrogate waste on MKP setting behavior were also examined using the method. It was found that the addition of 1.5 wt% boric acid was capable of extending the setting time by as much as 20 times, relative to the case without any boric acid addition in the pH of range of approximately 2 to 5.

1. Introduction

Various routine operations in the nuclear industry generate liquid wastes that contain both chemical and radiological contaminants. It is a common industry practice to solidify these radwaste liquids in order to reduce the risk to the environment (e.g. by leakage), and to allow for safe interim storage in either above-ground shielded storage containers, or below-ground bunkers. Methods such as cementation (using Ordinary Portland Cement (OPC)) and bituminization are frequently used for the solidification process [1] [2].

This paper examines the use of another method for solidifying liquid wastes, which involves the application of phosphate ceramics technology. While there are many types of materials that fall into the phosphate ceramics category, the one that is the subject of this study is a magnesium potassium phosphate. It is formed by a relatively simple exothermic chemical reaction that takes place when magnesium oxide (magnesia), monobasic potassium phosphate and water are combined:



In the above reaction, the water may be supplied as a constituent of the aqueous waste. In this situation, Magnesium Potassium Phosphate (MKP) ceramic immobilizes wastes by a combination of (1) chemical stabilization, by incorporation of some of the soluble waste components into the solidified lattice, (2) physical microencapsulation and (3) macroencapsulation [3]. The hydrated magnesium potassium phosphate, including the waste components encapsulated within it, is isomorphic with the mineral struvite. It can attain compressive strengths of 10 to 12 MPa, which are significantly higher than the US NRC land disposal requirement of 3.4 MPa for cement-based waste forms [4]. Phosphate ceramics also have excellent resistance to the leaching of chemical and radionuclide species [5] [6]. Additional features that make the application of phosphate ceramic technology attractive for waste solidification include its abilities to operate over a wide range of pH values (4 to 13) of the waste and to allow high waste loadings (up to 70 wt.% with nitrates), often exceeding those achievable using OPC [3] [6].

In the MKP system, the exothermic reaction ($\Delta H = -368$ kJ/mol [3]) between the acid phosphate and base magnesia is rapid, with typical setting times as low as a few minutes. This is significantly faster than the typical setting times for OPC, which are on the order of 2 to 8 hours [7]. Because longer setting times are more conducive to handling of the material, several methods have been explored to delay the setting times of MKP. These include the incorporation of set retarding agents such as boric acid (BA) [8], the use of less reactive magnesia (made by using larger particle sizes and/or higher calcination temperatures to prepare the magnesia), the use of different magnesia to phosphate ratios [9] [10] [11] and varying of the liquid-to-solid ratios [12].

An important characteristic in the solidification of liquid wastes, particularly when this is done on an industrial scale, is the length of time taken for the initial slurry (formed by mixing the constituents) to solidify. It is a common practice in liquid waste solidification to use a mixing vessel to combine and thoroughly mix the ingredients, then to transfer the mixture to molds, in which the final solidified monoliths will form and attain their full mechanical strength [13]. In the case of cementation using OPC, the time scale for hardening of the solidified waste monoliths is typically on the order of several hours. The solidification of OPC monoliths is a gradual and continuous process, which is characterized by terms such as "initial" and "final" set. Initial set time is defined as the time taken (after initial of mixing of the ingredients) for the mixture to stiffen to a consistency where it can no longer be poured or otherwise transferred. Final set time is defined as the time taken for the material to become a completely rigid solid. These characteristics are usually measured using such methods as the Vicat measurement [14] or the Gillmore method [15], which use a needle that penetrates into the waste matrix a fixed distance (under a specified force) in the case of initial set, or cannot penetrate, in the case of final set. These methods are not applicable in the case of phosphate ceramics for two main reasons. First, phosphate ceramics typically set in a time scale that is too short for the limited time resolution of either of the needle-based methods to give reliable measurements (usually more than 30 min). Second, phosphate ceramics typically do not solidify in a gradual manner, so that even if solidification did occur after several hours, an "initial setting" phenomenon could not be defined.

More importantly, in the oilfield, thickening time is used to characterize the behavior of cement slurry and to determine whether the slurry remains pumpable. It is measured with a consistometer in which torque is applied to a spring-loaded paddle to cement slurry in a slurry cup rotating at 150 min⁻¹. The apparatus is calibrated to a standard output in Bearden Consistency units (Bc), which is a scale from 1 to 100, where generally difficult pumping is thought to begin at 50 Bc, with a complete set at 100 Bc [16]. This range of values (50~100 Bc) is commonly used to determine the safe

pumping time for the cement slurry. However, this device would not be appropriate for direct real-time monitoring of slurry because it handles an aliquot of test sample.

The methods for monitoring setting or thickening times described above do not appear to be suitable in terms of controlling either the transfer of MKP material from mixing vessels to molds or storage containers in industrial-scale processes, or the mixing time for in-situ solidification. Thus, this study attempts to establish a new method for real-time monitoring of the setting or thickening behavior of phosphate ceramics slurry and for investigating the effect of pH, additives (such as boric acid) and the composition of surrogate waste on MKP setting behavior.

2. Experimental

2.1 Preparation of Samples

The magnesia used in making the phosphate ceramic materials was a dead-burned, milled powder, supplied by Martin Marietta Magnesia Specialties LLC. The particular grade chosen was identified as MagChem P98, pulverized, which has a nominal composition of MgO, 98.0%, CaO, 0.95%, SiO₂, 0.7%, Al₂O₃, 0.19% and Fe₂O₃, 0.15%. The particle size distribution of the magnesia was 100% < 16 mesh, 99.8% < 30 mesh, 98% < 50 mesh, 91% < 100 mesh, 75% < 200 mesh and 60% < 325 mesh. The monobasic potassium phosphate was supplied by Sigma-Aldrich Canada, as a 99% reagent grade chemical. Boric acid (BA, reagent grade, 99.9%) was supplied by Fisher Scientific. Ferric ammonium citrate (reagent grade) was supplied by Sigma-Aldrich Chemical. Standard silicone oils from Brookfield Engineering Inc. were used for calibrating the viscosity versus torque measurements made on a Brookfield R/S+ viscometer.

A liquid waste surrogate was also prepared for use in the testing of various phosphate ceramic formulations. The surrogate represents a typical liquid feed stream in the Waste Treatment Centre (WTC) located at Canadian Nuclear Laboratories' Chalk River Laboratories site. The composition of the WTC waste surrogate is given in Table 1.

The key non-radiological species in the WTC concentrated waste that need to be considered are Cl⁻, Na⁺, nitrite/nitrate, SO₄²⁻ and organics. On the basis of the data from 2009 to 2013, the WTC concentrated waste contains key beta/gamma emitting radionuclides such as ⁶⁰Co and ¹³⁷Cs. The surrogate WTC waste was formulated on the basis of the average concentration of the non-radiological species in the concentrated liquid waste processed at the WTC during the 2009-2013 periods, as shown in Table 1. In addition, the key radiological species were simulated by their non-radioactive counterparts (i.e., Co and Cs).

In order to prepare phosphate ceramic samples, weighed aliquots of the dry powders (magnesia and potassium phosphate) were thoroughly mixed before being combined with the liquid components (water or WTC waste surrogate). In all of the tests, 15.1 wt% MgO, 51.0 wt% KH₂PO₄ and 33.9 wt% liquid (either water or WTC surrogate) were used. In tests where either boric acid and/or ferric ammonium citrate were used in the formulation, the required amounts of boric acid and the chemicals for pH adjustment (e.g., H₃PO₄ and NaOH) were dissolved in the water or liquid waste surrogate prior to mixing it with the dry powders.

Table 1: Chemical Composition of the WTC Concentrated Liquid Waste Surrogate

Chemical	Concentration (mol/L)	Mass (g/L)
NaCl	0.136	7.956
Na ₂ SO ₄	0.015	2.130
NaNO ₃	0.341	29.985
CsNO ₃	0.008	1.560
Co(NO ₃) ₂ •6H ₂ O	0.003	0.873
Mg(NO ₃) ₂ •6H ₂ O	0.010	2.560
Al ₂ (SO ₄) ₃	0.0013	0.445
CaSO ₄ •2H ₂ O	0.014	2.409
Ferric Ammonium Citrate	0.005	1.310
Total Na	0.507	11.661
Total NO₃	0.375	23.498
Total SO₄	0.033	3.158

2.2 Mixing and Viscosity Measurement

The MKP slurries should not harden so quickly that the transfer to molds is prevented, but also should not harden too slowly, in order to prevent potential phase separation within the matrix before it completely solidifies. In this study, three different methods of measuring setting times (and the approach to setting) were considered: (1) visual inspection, which gives the observer a good qualitative sense of the process, but would not be suitable for industrial implementation, nor is it sufficiently accurate on a laboratory scale; (2) measurement of the temperature rise of the MKP slurry, which would be caused by the exothermic acid-base reaction; and (3) direct measurement of the viscosity of the MKP slurry during mixing, until it approaches the setting point.

The slurry was constantly stirred until it stiffened to a point at which stirring became difficult. To avoid any motor damage, the stirrer motor was designed to stop automatically when the torque exceeded a value of 50 mN·m and a slurry viscosity of 8000 cP was reached. Therefore, the setting time of a MKP slurry is reported as the time taken for the slurry to reach the viscosity of 8000 cP from the addition of dry powder to the liquid.

For mixing of the powders and liquid and formation of homogeneous slurry, a Brookfield R/S+ viscometer was selected with a paddle (5 cm × 5 cm) and 250-mL Nalgene beaker, as shown in Figure 1. This device not only served as the means of mixing, but also allowed for the simultaneous in-situ measurement of the torque experienced by the rotor.



Figure 1 Rheometer and Paddle Used for MKP Slurry Mixing and Viscosity Measurement.

The individual batches of phosphate ceramic had volumes of approximately 150 mL and total masses of 200 g. For each phosphate ceramic sample, the viscosity measurement was conducted at a rotor speed of 189 min^{-1} . During the mixing of the ingredients, the temperature was continuously monitored by a type K thermocouple placed in contact with the slurry and recorded at 7 second intervals, using a data acquisition system.

Phosphate ceramic batches contained the same quantities of magnesia, potassium phosphate and water (or WTC surrogate liquid). The stoichiometric (1:1:5) ratios of MgO to KH_2PO_4 to H_2O was used. In the case of the formulations made with the WTC surrogate, the same volumes of liquid were used, thus a slightly substoichiometric quantity (by approximately 3 wt%) of water was actually supplied. A range of setting times was examined in this study by producing a variety of phosphate ceramic-solidified specimens under predetermined conditions, including pH values ranging from approximately 2 to 12 and the addition of boric acid at different concentrations up to 1.5 wt%.

3. Results and Discussion

3.1 New Method of Real-time Viscosity Measurement for Monitoring Setting Behaviour

At a constant rotational speed of 189 min^{-1} , using standard silicone fluids of 10, 100, 1000 and 5000 cP ($1 \text{ cP} = 0.01 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$), a linear relationship between torque and viscosity was observed (Figure 2). This was used for calibrating the viscometer. For monitoring the workability status of MKP slurry using the viscosity measurement, this study introduced two custom terms: the stiffening onset time, which was reported as the time taken for the mixtures from the addition of dry powder to the liquid, i.e., time zero, to reaching a viscosity of 300 cP, and the setting time, which was reported as the time taken for the mixtures to reach a viscosity of 8000 cP from the addition of dry powder to the liquid.

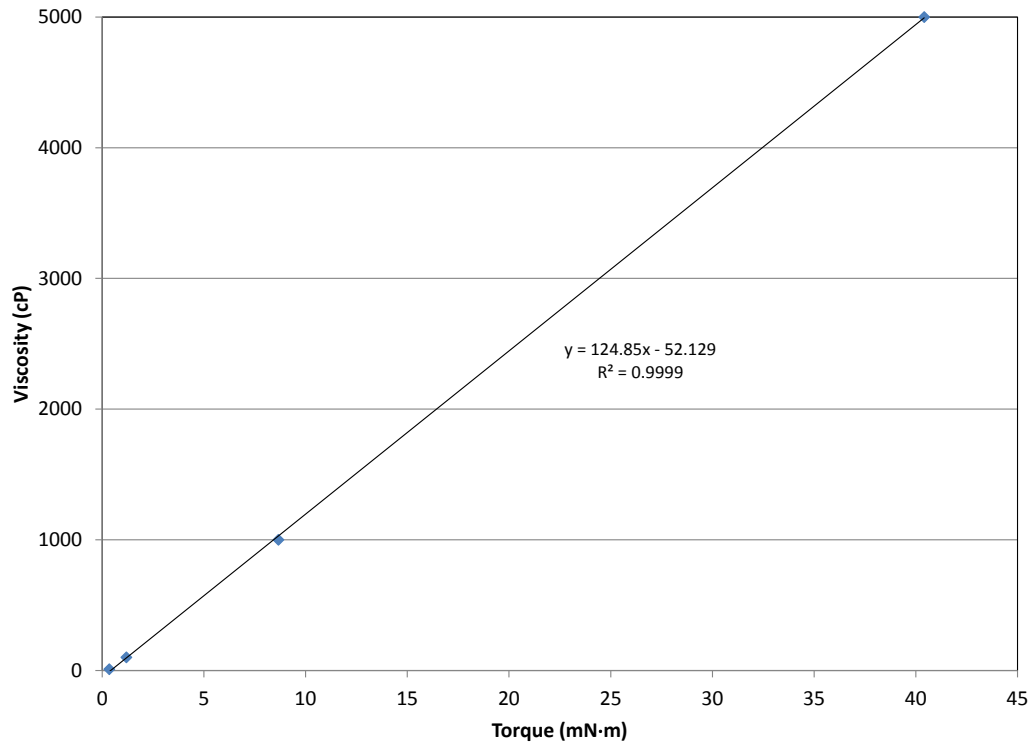


Figure 2: Relationship between torque and viscosity at rotational speed 189 min^{-1}

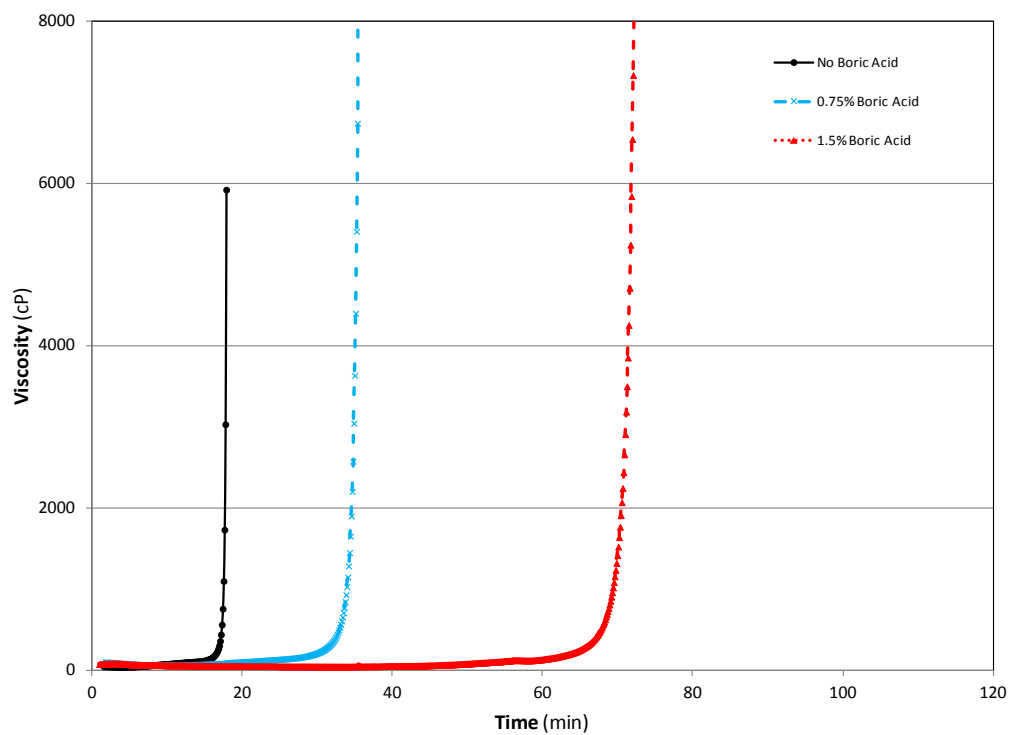


Figure 3: Viscosity Behavior of MKP Formulations

Regardless of the length of setting time, all the rheograms had the same characteristic shape, as shown in Figure 3. This was characterized by an induction or dormant period of mixing at low viscosity, followed by a sudden increase in torque or viscosity until the stirrer motor was stopped and fluidity of the slurry was essentially lost. The implication of this behavior is that direct in-situ monitoring of the slurry viscosity could be used as an industrial practice to control the mixing when a batch of material needs to be transferred to molds for the solidification to finalize. For example, prior to the stiffening onset time (at or below the viscosity of 300 cP), the slurry should be poured or transferred to a storage container, since the viscosity is dramatically increased in less than 5 minutes in most cases after this point.

3.2 Setting Behaviour of MKP Slurry

An entire set of test results for the phosphate ceramic formulations, i.e., observations of the stiffening onset time, setting time and the setting temperature, are shown in Table 2. Test conditions are also listed, including the quantities of waste surrogate and additives, the pH of the liquid before solidification.

Table 2: Effects of pH and Additives on the Setting Behavior of MKP Samples

Test Number	Liquid Used	pH ⁽¹⁾	Boric Acid Added (wt%)	Stiffening Onset Time ⁽²⁾ (min)	Setting Time ⁽²⁾ (min)	Setting Temp. ⁽²⁾ (°C)	Number of Repeats
1	Water	7.0	-	16 ± 4	18 ± 0.3	51 ± 2	4
2		5.6	0.75	32 ± 0.1	35 ± 0.1	45 ± 0.4	2
3		4.6	1.5	60 ± 10	69 ± 10	41 ± 3	3
4		1.9	-	25 ± 5	27 ± 7	49 ± 4	4
5		1.9	-	230	266	30	1
6		12.1	-	29 ± 3	34 ± 4	43 ± 2	2
7		11.9	1.5	29 ± 2	32 ± 3	46 ± 1	4
8	WTC	6.1	-	24 ± 0.8	28 ± 1	44.6 ± 0.2	2
9	Surrogate	3.1	0.75	460	643	22	1

¹ the pH was adjusted with the addition of H₃PO₄ or NaOH

² each result includes the averages and standard deviations calculated from the measured data of replicates (except for tests 5 and 9, in which cases only one sample was fabricated for each test)

Figure 4 summarizes the setting time (shown in bars) and the setting temperature (shown in lines) for the MKP formulations tested. Two to four replicates were made for each test. As shown in Figure 4, the boric acid addition delayed the setting time of the MKP formulations by a factor of 4 to 20. However, for the high pH solution, the effect of the boric acid addition was negligible.

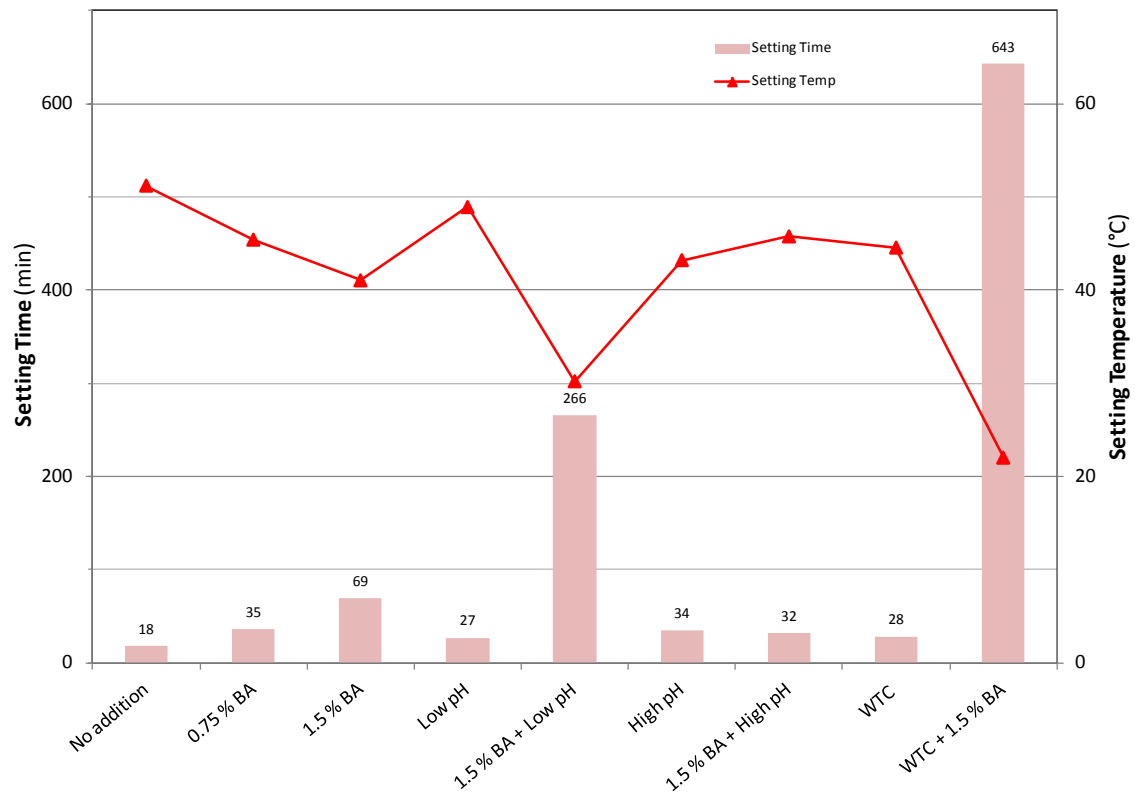


Figure 4: Effects of pH and Composition on the Setting Behavior of MKP Samples

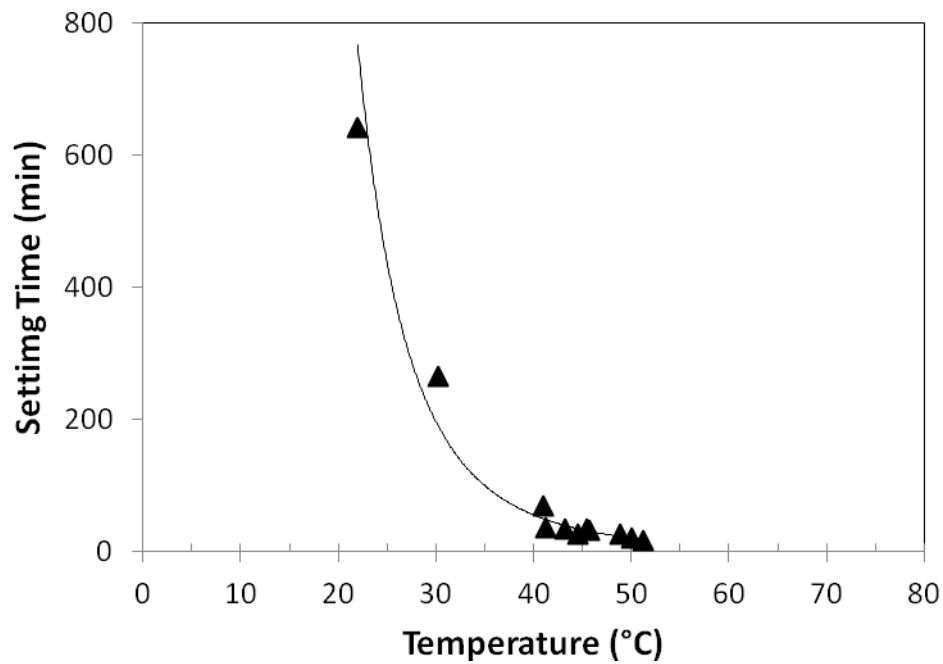


Figure 5: Correlation of MKP Setting Time with Setting Temperature

An inverse relationship between setting time and setting temperature was observed from the data of the entire set of the tests (Figure 5). The setting temperatures in the tests ranged between 41 and 51°C, except for the two formulations (containing the 1.5 wt% boric acid) that had longer setting times in excess of 200 minutes (Figure 5 and Table 2).

The implication of a relationship between setting temperature and setting time, as well as the gradual increase in temperature as the MKP slurry begins to thicken is that temperature monitoring could be a useful industrial practice to control the mixing when a batch of material needs to be transferred to molds for the solidification to finalize.

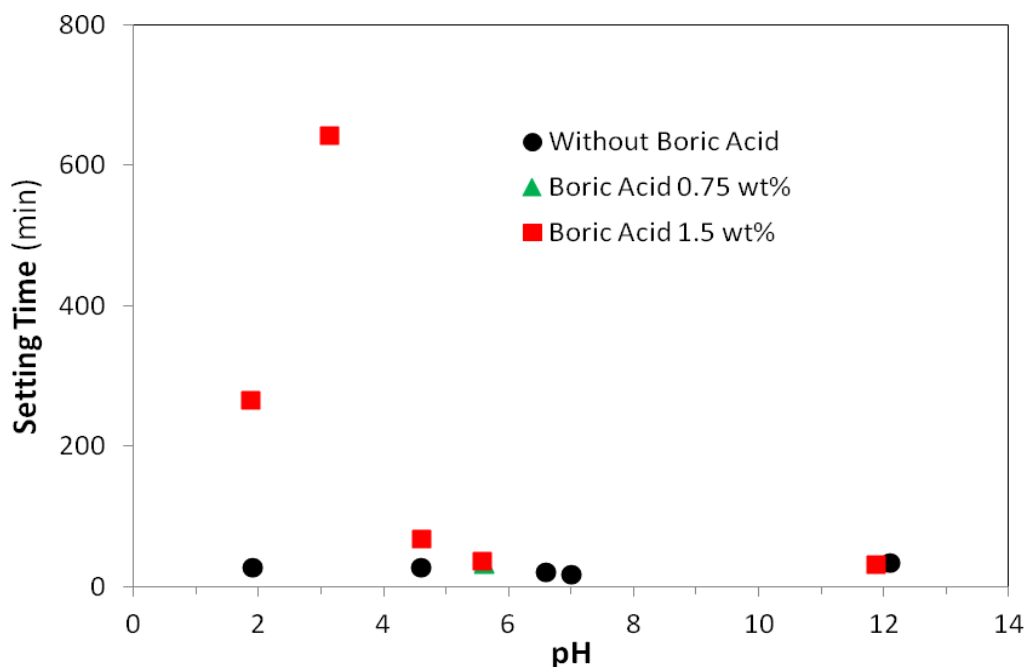


Figure 6: Influence of Solution pH on MKP Setting Behavior at Various Boric Acid Concentrations

Figure 6 shows the setting times as a function of the liquid pH, after pH adjustments and/or BA additions were completed, for the formulations given in Table 2.

It is clear that the effect of boric acid addition on delaying setting time was significant when waste liquids had pH values between approximately 2 and 5. That is, the addition of 1.5 wt% boric acid to formulations within this pH range increased the setting times by 4 to 20 times the values observed for the formulation without any boric acid addition. In one formulation at a pH of 5.6, with a lesser amount of 0.75 wt% boric acid, there was no significant change in setting time, relative to the corresponding formulation without any boric acid addition. This is reasonable on the basis of acid-base chemistry, which suggests that at pH values above 7, the boric acid would be essentially converted to sodium borate. The set retarding effect of boric acid, at similar levels to those reported in this study, has been reported in [3] [8] [10] [17]. In an analogous Struvite system (magnesium ammonium phosphate) [18], Sarkar demonstrated, using x-ray diffraction, that boric acid formed a polymeric coating on the MgO grains. This coating, which retarded dissolution of the MgO, was

found to have a "lünebergite" structure with the composition $\text{Mg}_2\text{B}_2(\text{PO}_4)_2(\text{OH})_6 \cdot 6\text{H}_2\text{O}$. It is apparent that a similar mechanism was observed to affect the MKP (potassium Struvite) system reported here.

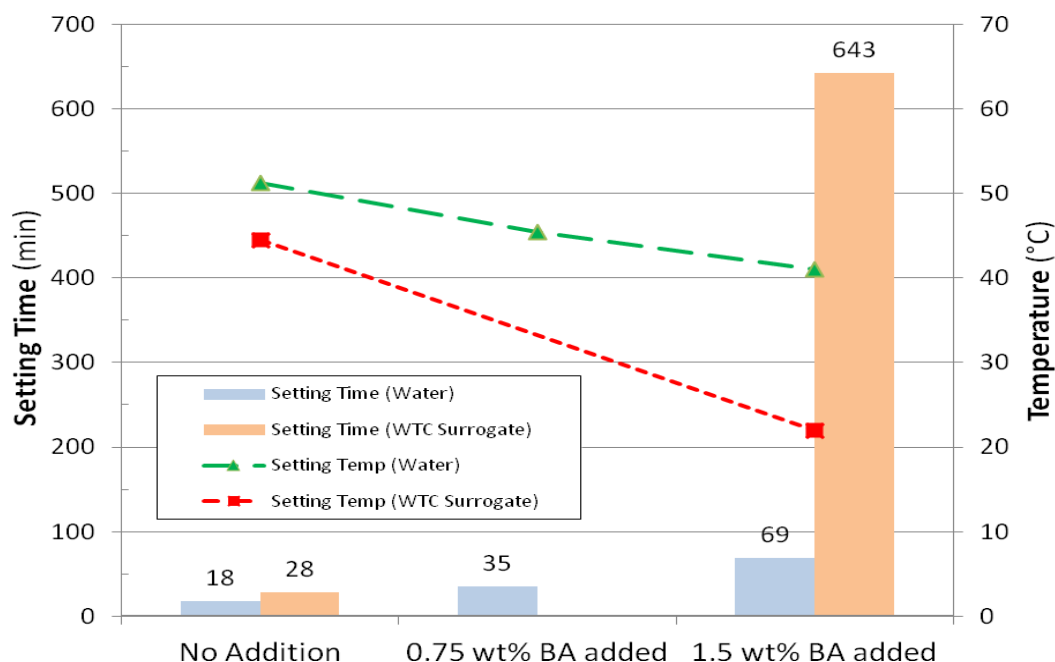


Figure 7: Effect of Boric Acid Addition on the Setting Time and Setting Temperature of MKP Formulations made with Water and WTC Surrogate Liquid

Figure 7 compares the setting times obtained for the MKP formulations with water and for the ones with the WTC surrogate, as the boric acid addition varied. Figure 7 shows the effect of boric acid addition on both the setting time and setting temperature of phosphate ceramics, in which water (shown in blue) and the WTC waste surrogate (shown in orange) were used as the solidifying liquid. With both liquids, the addition of boric acid retards the setting time. The effect of boric acid was much more pronounced with the WTC surrogate than with water. Without boric acid addition, the WTC surrogate showed a longer setting time than deionized water (28 vs. 18 minutes). However, when 1.5 wt% boric acid was added to WTC surrogate solution, the setting time was dramatically increased by approximately over 20 times, in comparison with the batch containing no boric acid.

4. Conclusions

A new method was established, based on the direct viscosity measurement while mixing phosphate ceramic slurries, for real-time monitoring of the setting or thickening behavior of phosphate ceramics slurry and for investigating the effect of pH, additives (such as boric acid) and the composition of surrogate waste on MKP setting behavior. This method provided a means of measuring the time required for the slurry to reach its limit of workability. In an industrial application, this capability would be used to indicate when MKP slurry should be transferred to storage containers for final solidification of the immobilized waste product.

It was demonstrated that adding up to 1.5 wt% boric acid can delay the setting time (relative to mixtures not containing this additive) by a factor of up to 20. However, this effect is restricted to feed conditions in which the adjusted pH is in the range of 2 to 5. An inverse correlation was observed between the temperatures of the MKP mixtures at their setting points, and their setting times. This suggests that setting temperature could be also used as a means of controlling phosphate ceramic waste immobilization process on a large scale.

5. References

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