Crystallization of Sodium Phosphate Dodecahydrate and Re-crystallization to Natrophosphate in Simulated Hanford Nuclear Waste.-16188

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ABSTRACT

The nuclear waste at the Hanford site near Richland, WA, has large concentrations of phosphate in the form of the phosphate ion, sodium phosphate dodecahydrate $(Na_3PO_4.12H_2O.(1/4)NaOH)$ and natrophosphate $(Na_7F(PO_4)_3.19H_2O)$. Sodium phosphate dodecahydrate can form a gel and natrophosphate can crystallize large particles, complicating the processing of slurries of both salts. The gel is regarded as more problematic, so natrophosphate has historically been crystallized to prevent phosphate gelling. This study determined if natrophosphate crystals can grow to large size in short time periods (a few weeks), time periods relevant to short process shutdowns. Solutions of NaOH and $NaAl(OH)_4$ were blended at different ratios with stock solutions containing NaOH, NaF, and Na_3PO_4 at 50 °C. The mixtures were allowed to cool to 22 °C, and the crystal growth was monitored by Polarized Light Microscopy (PLM) for 17 days. Four of the six blends investigated gelled rapidly due to $Na_3PO_4.12H_2O.(1/4)NaOH$ precipitation. The gel slowly dissipated over time as the solids recrystallized into natrophosphate. In one case, the natrophosphate reached sizes of greater than 1000 microns in diameter in just 4 days. This rapid gelling and crystallization kinetics is important to engineers trying to manage nuclear wastes high in phosphates. Hanford tank farm engineers are developing sampling plans to support temperature and process control strategies for preventing the formation of solid phosphates. They are also developing methods of suspending large natrophosphate crystals.

INTRODUCTION

The 56 million gallons of High-level nuclear waste at that Hanford site near Richland, WA, in the U.S.A. has substantial amounts of phosphate (Hill et al., 2011). The waste is immersed in a highly concentrated electrolyte solution, sodium being the dominant cation. Consequently, sodium phosphate salts have often precipitated from solution (Warrant and Cooke, 2003). The composition of Hanford waste is highly variable (Agnew, 1998; Hill et al., 2011), and the salt that forms depends on the composition of the waste (Warrant and Cooke, 2003).

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Sodium phosphate dodecahydrate ($Na_3PO_4.12H_2O.(1/4)NaOH$) is a needle-shaped crystal at the microscopic level, but bundles of those needles behave macroscopically like a gel (Mattigod et al., 2008). Phosphate gels have been implicated in line plugging incidents at the Hanford site, include lines that had to be abandoned because the plug could not be removed (Lagos and Roelant, 2013). Consequently, the conditions that form sodium phosphate gels are of interest. Natrophosphate ($Na_7F(PO_4)_3.19H_2O$) has been observed to form instead of sodium phosphate dodecahydrate in Hanford waste solutions (Reynolds et al., 2013; 2014). Consequently, gelling can be prevented by mixing high phosphate waste with high fluoride waste to form natrophosphate instead of the dodecahydrate.

In addition to the native sodium phosphate in the waste, phosphate also occurs as transition metal phosphates (Lumetta et al., 2009). These metal phosphate's are decomposed during caustic leaching of the waste, providing additional sodium phosphate that can re-precipitate downstream of filtration systems (Beam et al., 1998; McGinnis et al., 1999; Russell et al., 2010; Lumetta et al., 2009;). Precipitation of sodium phosphate from solution concomitantly removes dissolved uranium (Oji et al., 2010).

Natrophosphate forms octagon shaped crystals that do not gel but can grow to large particle size (Thorpe, 1872). Reynolds et al. (2012; 2013; 2014) report natrophosphate crystals between 25 and 250 microns in diameter. The present authors have unpublished observations of natrophosphate crystals with diameters measured in centimeters. Indeed, the first natrophosphate crystal reported in the literature by Thorpe (1872) was described as "being several centimeters in diameter". Natrophosphate can precipitate during blending of waste streams. The large size of natrophosphate may limit the ability to transport it with conventional waste slurry processing technology. Indeed, natrophosphate has been observed in Hanford waste tank heels, left behind with slurry handling equipment (Callaway 2013a;b; Cooke et al., 2013). It is not clear how long it takes for large natrophosphate crystals to grow.

As noted earlier, natrophosphate crystals with diameters greater than 200 microns are routinely observed in Hanford waste samples in our laboratory (Reynolds et al., 2012, 2013, 2014). The present study determined if natrophosphate can grow to this large size during a short time (several weeks), consistent with a pause during a transfer of wastes between tanks. During the study, it was discovered that sodium phosphate dodecahydrate can crystallize first and then re-crystallize into natrophosphate.

METHODS

The solutions investigated (Table I) were prepared by blending two types of stock solutions. One stock solution was made by dissolving technical grade sodium aluminate and sodium hydroxide in water. The second was prepared by dissolving sodium hydroxide, sodium phosphate, sodium fluoride in water.   The Hanford site is currently retrieving waste from older single shell tanks into newer tanks. Coarse gibbsite and natrophosphate are left behind in the heels (Callaway 2013a;b; Cooke et al., 2013). The first stock solution represents solutions generated from the dissolution of the gibbsite in the heels with sodium hydroxide (Herting et al., 2014), whereas the second represents solutions generated from the dissolution of natrophosphate heels in water. These stock solutions were blended together to make the starting solution composition listed in Table I for the six sets of experiments, and represents blends of stock solutions. Solutions one through three differed from each other in that they had progressively higher concentrations of aluminate and hydroxide. Solutions four through six also differed from each other in that they had progressively higher concentrations of aluminate and hydroxide. Samples 1-3 differed from samples 4-6 in that they had a different aluminate to hydroxide ratio. The stock solutions were prepared at 50 °C, but the solutions were allowed to cool to room temperature (22 °C) after the blends in Table I were prepared. The solutions were held room temperature (22 °) for 17 days, with small subsamples were taken periodically for Polarized Light Microscopy (PLM) analysis when crystals were observed visually, or at 17 days if they were not observed visually before then.

TABLE I. Initial concentrations (before salt crystallization) of anions in the blends and crystals identified. Sodium is the Charge-balancing cation.

Sample	Aluminate Molarity	Hydroxide Molarity	Phosphate Molarity	Fluoride Molarity	Solid Precipitated
1	0.1	1.33	0.2	0.1	None
2	0.2	2.00	0.2	0.1	p then d
3	0.4	2.67	0.2	0.1	p then d
4	0.1	0.67	0.2	0.1	d
5	0.2	1.33	0.2	0.1	p then d
6	0.4	2.00	0.2	0.1	p then d

p = Sodium Phosphate Dodecahydrate; d = Double Salt (Natrophosphate)

Sodium phosphate dodecahydrate and natrophosphate were identified by PLM (Olympus BX-51 polarizing microscope) per the method of Herting (1992). Sodium

phosphate dodecahydrate is readily distinguished from natrophosphate by differences in morphologies; natrophosphate forming an octagon and the hydrate forming a needle (Herting, 1992, Mason and Ashcraft, 1939). They also have a number of other optical differences that were used to distinguish them from other potential sodium phosphate phases (Herting 1992, Quimby, 1947).

RESULTS

Samples 2, 3, 5, and 6 gelled rapidly after the stock solutions were blended. The solids in the gels were confirmed to be sodium phosphate dodecahydrate by PLM, Figure 1 being an example micrograph from sample 5. Sodium phosphate dodecahydrate slurries are known to form gels (Lagos and Roelant, 2013; Mattigod et al., 2008).

In all cases the bulk gels eventually disappeared, though some sodium phosphate dodecahydrate crystals were still observed by PLM at day 17 in sample 6. PLM observations indicated that sodium phosphate dodecahydrate re-crystallized into natrophosphate. Figures 1 through 3 show the progression from sodium phosphate dodecahydrate to natrophosphate in sample 5. Inspecting these figures indicates that the sample was nearly entirely needle-shaped sodium phosphate dodecahydrate at day 1, which had partially transformed to natrophosphate octagons at day 4. The solids had completely re-crystallized to natrophosphate by day 17 (Figure 3). A similar progression was observed in samples 2, 3 and 6, though some needles were still present at 17 days in sample 6. No solids were observed at any time in sample 1. Sodium phosphate dodecahydrate was never observed in sample 4, but natrophosphate was observed by 4 days (Figure 4). Some natrophosphate crystals at four days observed in Sample 4 were already greater than 500 microns in diameter (Figure 4). The particles were not appreciably bigger at 17 days, however. A summary of the results are shown in Table I.

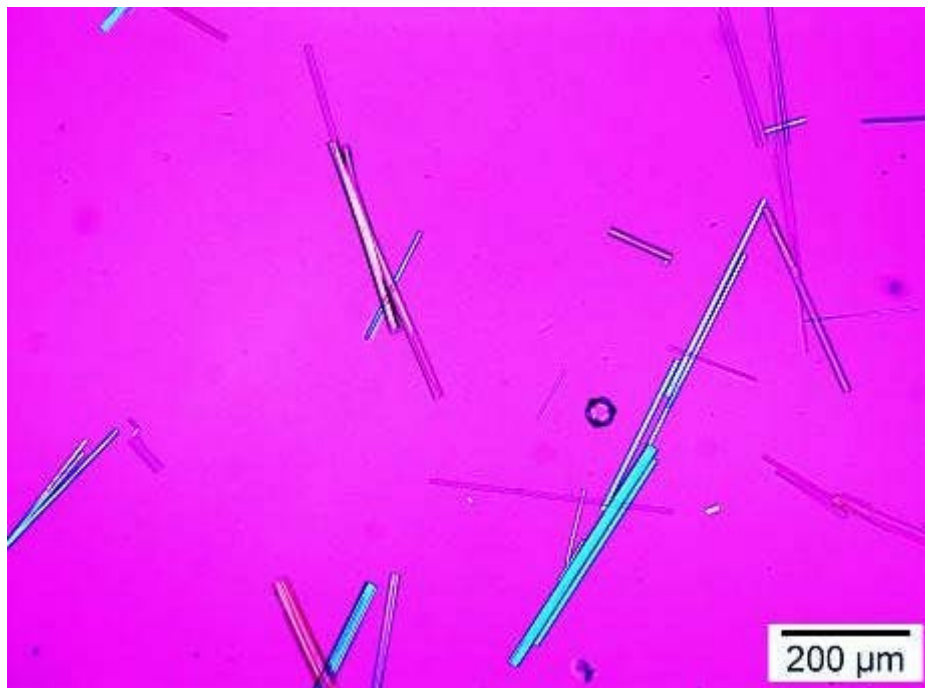Fig. 1. PLM Image of Sodium Phosphate Dodecahydrate Needles formed the First Day.

Fig. 2. PLM Images of Sodium Phosphate Dodecahydrate Needles and Natrophosphate Octagons at Four Days.
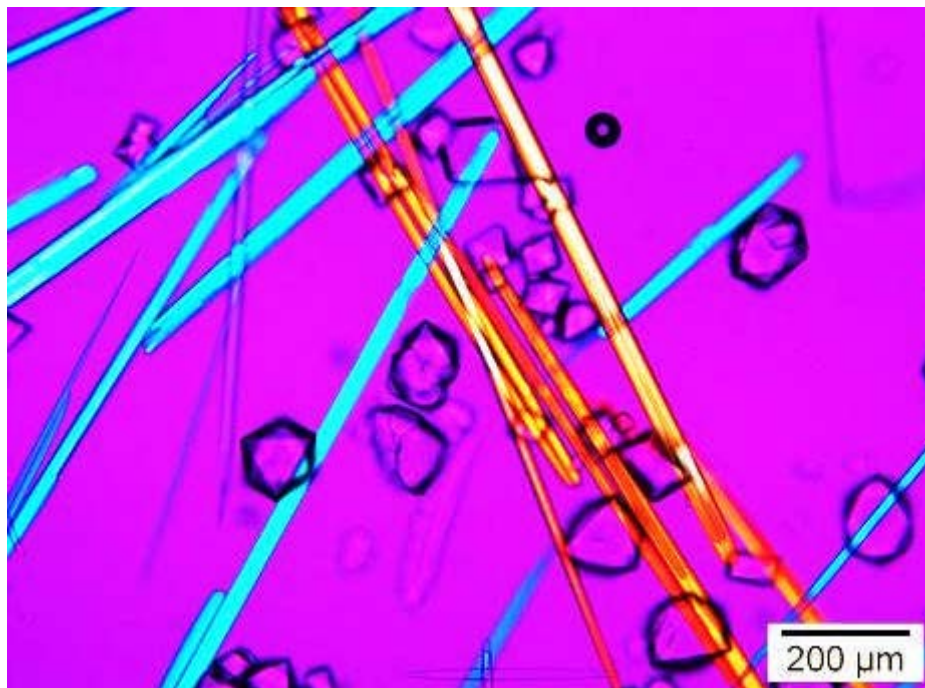
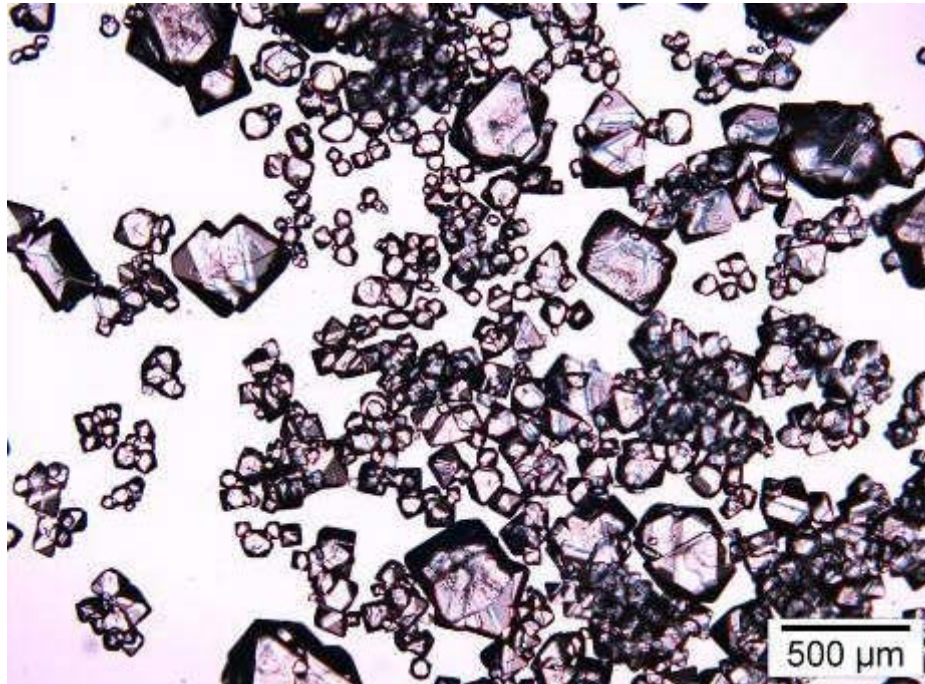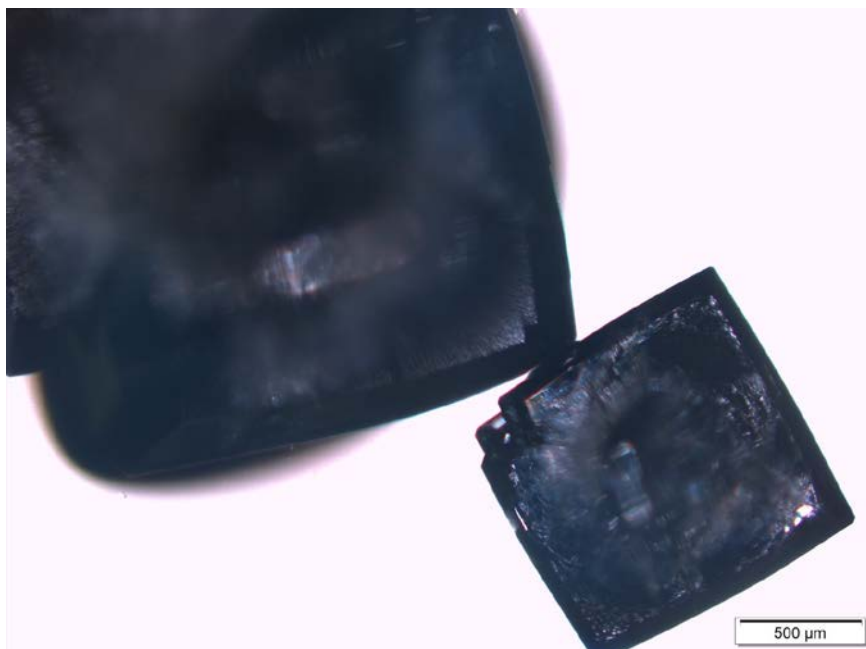Fig. 3. PLM Images of Natrophosphate Octagons at 17 Days

Figure 4. Micrograph of Natrophosphate Particles from Sample 4 at Four Days.

DISCUSSION

Handling large natrophosphate crystals can be problematic with standard sluicing technology, as indicated by the natrophosphate that has been left by sluicing single shell tanks at Hanford (Callaway 2013a;b; Cooke et al., 2013). Nonetheless, natrophosphate crystals are not as problematic as bulk gelling caused by sodium phosphate dodecahydrate crystallization (Mattigod et al., 2008; Lagos and Roelant, 2013). One way to prevent gelling is to deliberately crystallize natrophosphate, as evidenced by the fact that the gels disappeared in this study when the dodecahydrate re-crystallized into natrophosphate. If the dodecahydrate crystallizes first kinetically, however, initial gelling may occur, as observed in samples 2, 3, 5, and 6. Thus, process engineers who are counting on the precipitation of natrophosphate to prevent bulk gelling need to be wary of the potential to initial crystallize the dodecahydrate.

As noted above, large natrophosphate crystals have been found to be left behind during Hanford single shell tank retrieval using sluicing (Callaway 2013a;b; Cooke et al., 2013). Sluicing is a type of jet retrieval where the solids are hosed into pump suction during retrieval. The waste had been in those tanks for decades, so natrophosphate had plenty of time to ripen to those large sizes. What has been unknown is how long it will take to grow to large size. An upset condition could leave natrophosphate in a transfer line. If the natrophosphate grew to large size during that time period, it may be difficult to re-suspend. The maximum particle size for re-suspension following an upset condition would depend on the particular situation, but it is reasonable safe to assume that anything less than 250 microns in diameter would be easily suspended with typical equipment used historically at Hanford. Figure 4 indicates that natrophosphate can grow to over 500 microns in diameter in a matter of days. This means that any upset condition that could cause natrophosphate to crystalize could have large particles in just four days. This rapid crystallization kinetics needs is being considered during the design of transport systems.

CONCLUSION

This study has determined that natrophosphate can grow to over 500 microns in size in as little as four days under some conditions. This means that it is possible to grow large crystals during short down periods the process is shut down. Sodium phosphate dodecahydrate, which forms gel-like slurries, was found to crystallize before natrophosphate in some cases. Process engineers counting on the crystallization of small natrophosphate crystals to prevent gelling will have to consider the potential large size of the crystals grown as well as the potential of gelling during the initial mixing of solutions.

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