

PHOSPHATE MANAGEMENT: FY2010 RESULTS OF PHOSPHATE PRECIPITATION TESTS

March 2011

Savannah River National Laboratory
Savannah River Nuclear Solutions
Aiken, SC 29808

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LIST OF ACRONYMS

DOE	Department of Energy
DI	De-ionized Water
ESP	Environmental Simulation Program
HLW	High Level Waste
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
PNNL	Pacific Northwest National Laboratory
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
WSU	Washington State University
WTP	Waste Treatment Plant
XRD	X-ray Diffraction

SUMMARY

The Phosphate Management program seeks to develop treatment options for caustic phosphate solutions resulting from the caustic leaching of the bismuth phosphate sludge. The SRNL subtask investigated the precipitation of phosphate salts from caustic solutions through addition of fluoride and by crystallization. The scoping tests examined the: precipitation of phosphate by the addition of sodium fluoride to form the sodium fluorophosphate double salt, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$, crystallization of phosphate by reducing the temperature of saturated phosphate solutions, and combinations of precipitation and crystallization. A simplified leachate simulant was used in the study produced by dissolving sodium phosphate in 1 M to 3.5 M sodium hydroxide solutions.

The results show that all three processes; precipitation with sodium fluoride, crystallization, and combined precipitation/crystallization can be effective for removing large amounts of phosphate from solution. The combined process of precipitation/crystallization showed >90% removal of phosphate at all hydroxide concentrations when cooling a non-saturated phosphate solution from 65 °C to 25 °C. Based on the measured solubility of sodium phosphate, pH adjustment/caustic addition will also remove large amounts of phosphate from solution (>80%). For all three processes, the phosphate concentration in the caustic solution must be managed to keep the phosphate from becoming too concentrated and thereby potentially forming a solid mass of sodium phosphate after an effective phosphate removal process.

1.0 INTRODUCTION

The Hanford Waste Treatment Plant (WTP), scheduled for startup in 2019, will treat and immobilize Hanford tank waste. As a result of uncertainties in the ability of the WTP to process all of the tank wastes within the expected plant lifetime, supplemental processes are being pursued by the Department of Energy (DOE) that treat waste outside the WTP and could potentially accelerate cleanup efforts. The bismuth phosphate waste stream at Hanford, containing high concentrations of phosphate, poses a significant challenge for the WTP due to limited ability of the high level waste (HLW) glass to incorporate phosphate. Caustic leaching can be used to remove the phosphate from the bismuth phosphate sludge.¹ The caustic leachate waste stream could potentially be treated outside the WTP removing a significant fraction of the phosphate in the tank waste from WTP processing.

The Phosphate Management program seeks to develop treatment options for these caustic phosphate solutions resulting from the caustic leaching of the bismuth phosphate sludge. The program consists of a number of sub-tasks carried out by three laboratories; the Pacific Northwest National Laboratory (PNNL), the Savannah River National Laboratory (SRNL), and Washington State University (WSU).² The SRNL subtask investigated the precipitation of phosphate salts from caustic solutions through precipitation and crystallization.³ The general approach employed in the scoping task included: precipitation of phosphate by the addition of sodium fluoride to form the sodium fluorophosphate double salt, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$, crystallization of phosphate by reducing the temperature of saturated phosphate solutions, and combinations of precipitation and crystallization. A simplified leachate simulant was used in the study produced by dissolving sodium phosphate in sodium hydroxide solutions. The sodium hydroxide solutions ranged from 1 M to 3.5 M. This report details the results for these scoping experiments. A report describing the subtasks conducted by PNNL was recently issued.⁴

2.0 EXPERIMENTAL METHODS, MATERIALS, AND EQUIPMENT

2.1 SIMULANT PREPARATION

Stock solutions of 1.0 M, 1.5 M, 2.0 M, 2.5 M, 3.0 M, and 3.5 M NaOH were prepared by dissolving the required mass of NaOH pellets in a portion of de-ionized water (DI) in volumetric flasks. After dissolution was complete, additional DI water was added to the calibration line on the volumetric flask. The solutions were analyzed by titration for base equivalents and Inductively-Coupled Plasma Emission Spectroscopy (ICP-ES) for sodium concentration. These NaOH stock solutions were used for all subsequent phosphate solution preparations.

Saturated phosphate solutions were prepared at 25 °C and 65 °C in each NaOH stock solution by adding excess $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ solids to a bottle containing the NaOH stock solution. The bottles were placed in a temperature-controlled incubator shaker oven (Innova Models 4230 from New Brunswick Scientific) at the required temperature and agitated continuously at 250 RPM. All solutions were allowed to equilibrate for a minimum of 24 hours. The saturated phosphate solutions were filtered at temperature through a 0.45 μm nylon filter. Aliquots of the saturated phosphate solutions were diluted at temperature in either DI water or 1.0 M nitric acid for analysis of phosphate ion by Ion Chromatography (IC) and phosphorus and sodium by ICP-ES.

Additionally, a set of phosphate solutions were prepared at 65 °C with each of the NaOH stock solutions with phosphate concentrations somewhat less than one-half the saturated concentration for use in crystallization tests.

2.2 PRECIPITATION TEST METHOD

The precipitation tests using NaF to precipitate phosphate were conducted on 25 °C saturated phosphate solutions. A bottle was prepared with a known amount of the saturated phosphate solution and NaF solids were added in the required amount to give a molar ratio of either 1.25:1 or 3.75:1 fluoride to phosphorus. The bottle was placed in a temperature-controlled incubator shaker oven at 25 °C and agitated continuously at 250 RPM. The mixture was allowed to equilibrate for a minimum of 24 hours. The solutions were then filtered through a 0.45 μm nylon filter and the solids allowed to air dry at room temperature. Samples of the filtrate were prepared by dilution in either DI water or 1.0 M nitric acid for analysis of phosphate ion by IC and phosphorus and sodium by ICP-ES. Samples of the air-dried solids were analyzed by X-Ray Diffraction (XRD).

2.3 CRYSTALLIZATION TEST METHOD

Filtered solutions of the 25 °C saturated phosphate solutions and the 65 °C saturated and non-saturated phosphate solutions were cooled to 0 °C and 25 °C respectively to promote crystallization of the sodium phosphate. In both cases a small volume of the solution was placed in a capped polyethylene bottle and then cooled to the appropriate temperature. The 25 °C saturated phosphate solutions were cooled in an ice bath to approximately 0 °C while the 65 °C non-saturated phosphate solutions were allowed to cool to room temperature (~25 °C). The crystallized solids were removed by filtration at temperature through a 0.45 µm nylon filter and allowed to air dry overnight at room temperature. Samples of the filtrate were prepared by dilution at temperature in either DI water or 1.0 M nitric acid for analysis of phosphate ion by IC and phosphorus and sodium by ICP-ES. Samples of the air-dried solids were analyzed by XRD.

2.4 COMBINED PRECIPITATION/CRYSTALLIZATION TEST METHOD

The combined precipitation/crystallization tests using NaF to precipitate phosphate were conducted on the 25 °C saturated phosphate solutions and the 65 °C non-saturated phosphate solutions. A bottle was prepared with a known amount of the phosphate solution and NaF solids were added in the required amount to give a molar ratio of ~1:1 fluoride to phosphorus. The bottle was placed in a temperature-controlled incubator shaker oven at 25 °C or 65 °C as required and agitated continuously at 250 RPM. The solutions were agitated at temperature for a minimum of 24 hours. The 25 °C saturated phosphate solutions were cooled in an ice bath to approximately 0 °C, while the 65 °C non-saturated phosphate solutions were allowed to cool to room temperature (~25 °C). The solutions were then filtered through a 0.45 µm nylon filter and the solids allowed to air dry at room temperature. Samples of the filtrate were prepared by dilution at temperature in either DI water or 1.0 M nitric acid for analysis of phosphate ion by IC and phosphorus and sodium by ICP-ES.

3.0 RESULTS AND DISCUSSION

3.1 ANALYSIS OF SIMULANT SOLUTIONS

Table 3-1 shows the results of the analysis of the sodium hydroxide stock solutions. The hydroxide concentrations in the stock solutions were all within 5% of the targeted concentration. The phosphate solubilities in Tables 3-2 and 3-3 indicate a large dependence on temperature and hydroxide concentration. The data is shown graphically in Figures 3-1 and 3-2. In the 25 °C data set, the phosphate solubility drops almost an order of magnitude in moving from a 1.0 M to 3.5 M hydroxide solution. This indicates that pH adjustment/caustic addition can be used to effectively remove phosphate from solution. The 65 °C data also shows a strong dependence on pH with the phosphate solubility dropping ~50% with a change from 1.0 M to 3.5 M hydroxide solution. A temperature of 65 °C is the practical limit for using the $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ solids as the phosphate source since the solids melt at 73 °C. The melted solids are miscible with the sodium hydroxide solutions giving the appearance that the solids dissolved into solution well beyond the solubility limit at temperatures above the melting point.

3.2 RESULTS OF THE PRECIPITATION AND CRYSTALLIZATION TESTS

Tables 3-5 and 3-6 contain the results of the tests using sodium fluoride to precipitate the phosphate as the sodium fluorophosphate double salt, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$. The data in Table 3-5 shows the results from the addition of 1.25 moles of NaF per mole of phosphate to 25 °C saturated phosphate solutions. The sodium fluoride precipitation using approximately a 1:1 ratio of fluoride to phosphorus is effective at removing phosphate from solutions with lower hydroxide concentrations. However, as the hydroxide concentration increases the effectiveness rapidly diminishes likely due to the low solubility of phosphate at higher hydroxide concentrations. Table 3-6 shows the results of the precipitation using a molar ratio of 3.75:1 fluoride to phosphorus. The effectiveness of the precipitation was much higher with more NaF added to the saturated phosphate solutions. Even in the solutions with higher sodium hydroxide concentrations more than half of the phosphate was removed from solution. The data for the precipitation tests is shown graphically in Figure 3-3. The point at 2.0 M hydroxide for the 3.75:1 molar ratio appears to be anomalously low probably resulting from analytical error.

The precipitates from the NaF precipitation tests were in all cases highly crystalline, quick settling, and easily filtered from the solution. Figure 3-6 shows the XRD of the solids from the NaF precipitation of the phosphate saturated 1.0 M hydroxide solution using a molar ratio of approximately 1:1 fluoride to phosphorus. The only crystalline phase identified was the sodium fluorophosphate double salt, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$. The XRD in Figure 3-7 shows the same sodium fluorophosphate double salt, $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ along with two sodium carbonate phases for the precipitation of the phosphate saturated 3.5 M hydroxide solution

using a molar ratio of approximately 4:1 fluoride to phosphorus. The carbonate likely results from contamination present in the sodium hydroxide reagent or from absorption of carbon dioxide from the air.

The analytical results from the crystallization of the 25 °C saturated phosphate solutions are shown in Table 3-7. After cooling the solutions to ~0 °C in an ice bath a slushy crystalline product formed throughout the solution. The slushy product was pourable from the bottle and the solids were easily filtered through a 0.45 µm nylon filter. Approximately 75% of the phosphate was removed from solution at all six hydroxide concentrations. The XRD of the solids recovered through filtration, shown in Figures 3-8 and 3-9, consisted of hydrated sodium phosphate phases with one sodium carbonate phase being observed for the crystallization of the phosphate saturated 3.5 M hydroxide solution.

Crystallization of the 65 °C saturated phosphate solutions, by allowing the solutions to cool to room temperature (~25 °C), quickly resulted in the formation of a solid mass inside the bottle with no visible free liquid. These solutions were not analyzed due to the expected difficulty with processing and handling the product on a large scale. As a result, less concentrated phosphate solutions were made with phosphate concentrations somewhat less than one-half of the 65 °C saturated concentrations. After removing these 65 °C non-saturated solutions from the oven, no solids formed after cooling to ~25 °C. The solutions remained stable for greater than 24 hours with no sign of crystallization. Only after a small seed crystal was added to the bottle did any solids crystallize from the solution. As soon as the seed crystal touched the surface of the solution, a network of crystals could be seen growing throughout the solution over the course of ~15 minutes. Seed crystals of both $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$ were found to promote the crystallization. Interestingly, hematite, kaolin, and simulated sludge solids had no effect in promoting the crystallization. The end product of the crystallization appeared somewhat gel-like with some free liquid visible when the bottle was tilted to the side. The gel-like mass could be broken apart by moderate mixing with a spatula and the solids slowly settled to the bottom of the bottle. The solids were easily filtered through a 0.45 µm nylon filter. The crystallization was fairly effective, removing ~70-80% of the phosphate from solution with the exception of the 1.0 M hydroxide solution that showed only ~60% removal. The results of the crystallization tests at both temperatures are shown graphically in Figure 3-4.

Combining the NaF precipitation with subsequent cooling to promote further crystallization of phosphate solids produced mixed results as regards to phosphate removal from the solutions. For the 25 °C saturated phosphate solutions, the combined process removed slightly more phosphate from solution than the NaF precipitation process by itself, but removed less phosphate than the crystallization process alone. Table 3-9 shows the analytical results from the combined precipitation/crystallization of the 25 °C saturated phosphate solutions. In the combined process, the NaF was added to the saturated phosphate solution first and allowed to equilibrate followed by cooling. Possibly, the NaF precipitation reduced the phosphate concentration in solution sufficiently so that further phosphate removal through crystallization was inhibited. However, the combined precipitation/crystallization

process produced higher phosphate removal from the 65 °C non-saturated phosphate solutions than either the NaF precipitation or the crystallization processes alone. In all six solutions, slightly more than 90% of the phosphate was removed from solution. The results for both of the precipitation/crystallization tests are shown graphically in Figure 3-5.

3.3 THERMODYNAMIC MODELING OF THE PHOSPHATE TESTS

A thermodynamic model was developed in OLI Systems Inc, Environmental Simulation Program (ESP), version 8.1 to aid in experimental design. In this application, the absolute accuracy of the model is not as important as the ability of the software to correctly predict trends in the underlying chemistry. The model contained two sequential Mix blocks with the first block combining a sodium hydroxide solution stream with a solids only stream of hydrated sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$). The output of this first Mix block became an input to the second Mix block. The second Mix block allowed addition of a solids only sodium fluoride stream to the output from the first Mix block. Either block allows adjustment of the temperature to study the effect of increasing or decreasing temperatures on the solutions.

Modeling results for the solubility predictions of sodium phosphate in caustic solutions are included in the graphs of Figures 3-1 and 3-2. The PUBLIC database of ESP contains Na_3PO_4 , $\text{Na}_3\text{PO}_4 \cdot 1\text{H}_2\text{O}$, $\text{Na}_3\text{PO}_4 \cdot 6\text{H}_2\text{O}$, and $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$ as sources of sodium phosphate. The dodecahydrate used in the experiments was not available. Both Na_3PO_4 and $\text{Na}_3\text{PO}_4 \cdot 8\text{H}_2\text{O}$ were used in the modeling with very minor (<10%) differences observed in the results. As can be seen in the figures, the absolute accuracy of the model predictions are not very close to the measured values; however, the trends in phosphate solubility with respect to temperature and hydroxide concentration are consistent with the experimental data. The modeling results correctly indicate that manipulation of temperature and hydroxide concentration can be used to effectively remove a large fraction of phosphate salts from solution.

The modeling results for the NaF precipitation were not plotted in the corresponding figures since the model predicted only ~25% of the phosphate could be removed from all of the hydroxide solutions regardless of the quantity of sodium fluoride added. The measured values from the experiments in Figure 3-3 show much higher phosphate removal and a clear difference between adding ~1:1 versus a ~4:1 ratio of fluoride to phosphorus. The modeling of the crystallization tests consistently showed phosphorus removal of $\geq 90\%$ for all solutions for the 25 °C to 0 °C temperature change and the 65 °C to 25 °C change. The actual results of the crystallization tests were not quite that high as can be seen in Figure 3-4.

Table 3-1. Analysis of Sodium Hydroxide Stock Solutions

Targeted NaOH Concentration (M)	Measured NaOH Concentration (M)	Measured Density (g/ml)
1.0	0.955	1.050
1.5	1.504	1.074
2.0	1.976	1.091
2.5	2.462	1.105
3.0	2.953	1.126
3.5	3.536	1.142

Table 3-2. Analysis of 25 °C Saturated Phosphate Solutions

Nominal NaOH Concentration (M)	Measured NaOH Concentration (M)	Measured PO₄ Concentration (M)
1.0	0.955	0.219
1.5	1.504	0.135
2.0	1.976	0.081
2.5	2.462	0.057
3.0	2.953	0.045
3.5	3.536	0.037

Table 3-3. Analysis of 65 °C Saturated Phosphate Solutions

Nominal NaOH Concentration (M)	Measured NaOH Concentration (M)	Measured PO₄ Concentration (M)
1.0	0.955	2.267
1.5	1.504	1.969
2.0	1.976	1.679
2.5	2.462	1.588
3.0	2.953	1.436
3.5	3.536	1.203

Table 3-4. Analysis of 65 °C Non-Saturated Phosphate Solutions Used for Testing

Nominal NaOH Concentration (M)	Measured NaOH Concentration (M)	Measured PO₄ Concentration (M)
1.0	0.955	0.734
1.5	1.504	0.600
2.0	1.976	0.496
2.5	2.462	0.342
3.0	2.953	0.261
3.5	3.536	0.174

Table 3-5. Phosphate Precipitation of 25 °C Saturated Phosphate Solutions at Various NaOH Concentrations using 1.25 Moles of Sodium Fluoride per Mole of Phosphate

Initial NaOH Concentration (M)	Initial PO₄ Concentration (M)	Final PO₄ Concentration (M)	Percent of PO₄ Removed from Solution
0.955	0.219	0.069	68.5%
1.504	0.135	0.056	58.8%
1.976	0.081	0.046	43.7%
2.462	0.057	0.039	32.6%
2.953	0.045	0.032	28.1%
3.536	0.037	0.027	25.2%

Table 3-6. Phosphate Precipitation of 25 °C Saturated Phosphate Solutions at Various NaOH Concentrations using 3.75 Moles of Sodium Fluoride per Mole of Phosphate

Initial NaOH Concentration (M)	Initial PO₄ Concentration (M)	Final PO₄ Concentration (M)	Percent of PO₄ Removed from Solution
0.955	0.219	0.033	84.8%
1.504	0.135	0.029	78.5%
1.976	0.081	0.046	42.8%
2.462	0.057	0.023	60.3%
2.953	0.045	0.019	58.0%
3.536	0.037	0.016	56.6%

Table 3-7. Phosphate Crystallization of 25 °C Saturated Phosphate Solutions at Various NaOH Concentrations by Cooling to ~0 °C in Ice Water

Initial NaOH Concentration (M)	Initial PO₄ Concentration (M)	Final PO₄ Concentration (M)	Percent of PO₄ Removed from Solution
0.955	0.219	0.056	74.3%
1.504	0.135	0.034	75.1%
1.976	0.081	0.022	72.7%
2.462	0.057	0.015	73.5%
2.953	0.045	0.011	75.1%
3.536	0.037	0.009	75.7%

Table 3-8. Phosphate Crystallization of 65 °C Non-Saturated Phosphate Solutions at Various NaOH Concentrations by Cooling to ~25 °C

Initial NaOH Concentration (M)	Initial PO₄ Concentration (M)	Final PO₄ Concentration (M)	Percent of PO₄ Removed from Solution
0.955	0.734	0.280	61.9%
1.504	0.600	0.165	72.5%
1.976	0.496	0.107	78.5%
2.462	0.342	0.076	77.8%
2.953	0.261	0.056	78.4%
3.536	0.174	0.045	73.9%

Table 3-9. Phosphate Precipitation of 25 °C Saturated Phosphate Solutions at Various NaOH Concentrations using 1.25 Moles of Sodium Fluoride per Mole of Phosphate and Cooling to ~0 °C in Ice Water

Initial NaOH Concentration (M)	Initial PO₄ Concentration (M)	Final PO₄ Concentration (M)	Percent of PO₄ Removed from Solution
0.955	0.219	0.060	72.7%
1.504	0.135	0.039	71.0%
1.976	0.081	0.050	38.4%
2.462	0.057	0.025	56.6%
2.953	0.045	0.025	43.4%
3.536	0.037	0.019	48.9%

Table 3-10. Phosphate Precipitation of 65 °C Non-Saturated Phosphate Solutions at Various NaOH Concentrations using 1.10 Moles of Sodium Fluoride per Mole of Phosphate and Cooling to ~25 °C

Initial NaOH Concentration (M)	Initial PO₄ Concentration (M)	Final PO₄ Concentration (M)	Percent of PO₄ Removed from Solution
0.955	0.734	0.066	91.1%
1.504	0.600	0.050	91.7%
1.976	0.496	0.043	91.3%
2.462	0.342	0.026	92.3%
2.953	0.261	0.024	90.9%
3.536	0.174	0.015	91.1%

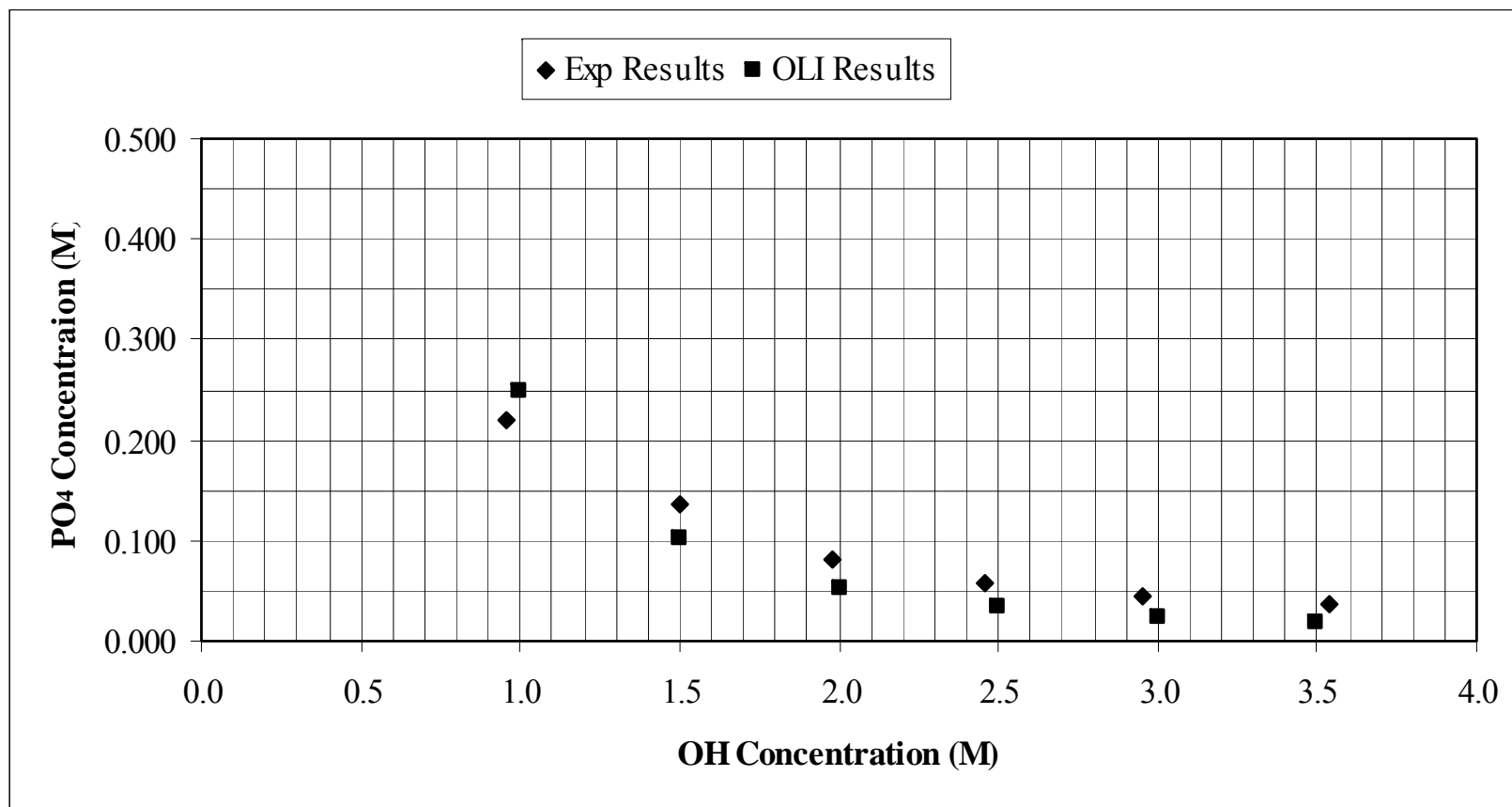


Figure 3-1. Measured Saturated Sodium Phosphate Concentration in NaOH Solutions at 25 °C compared with OLI Modeling Results.

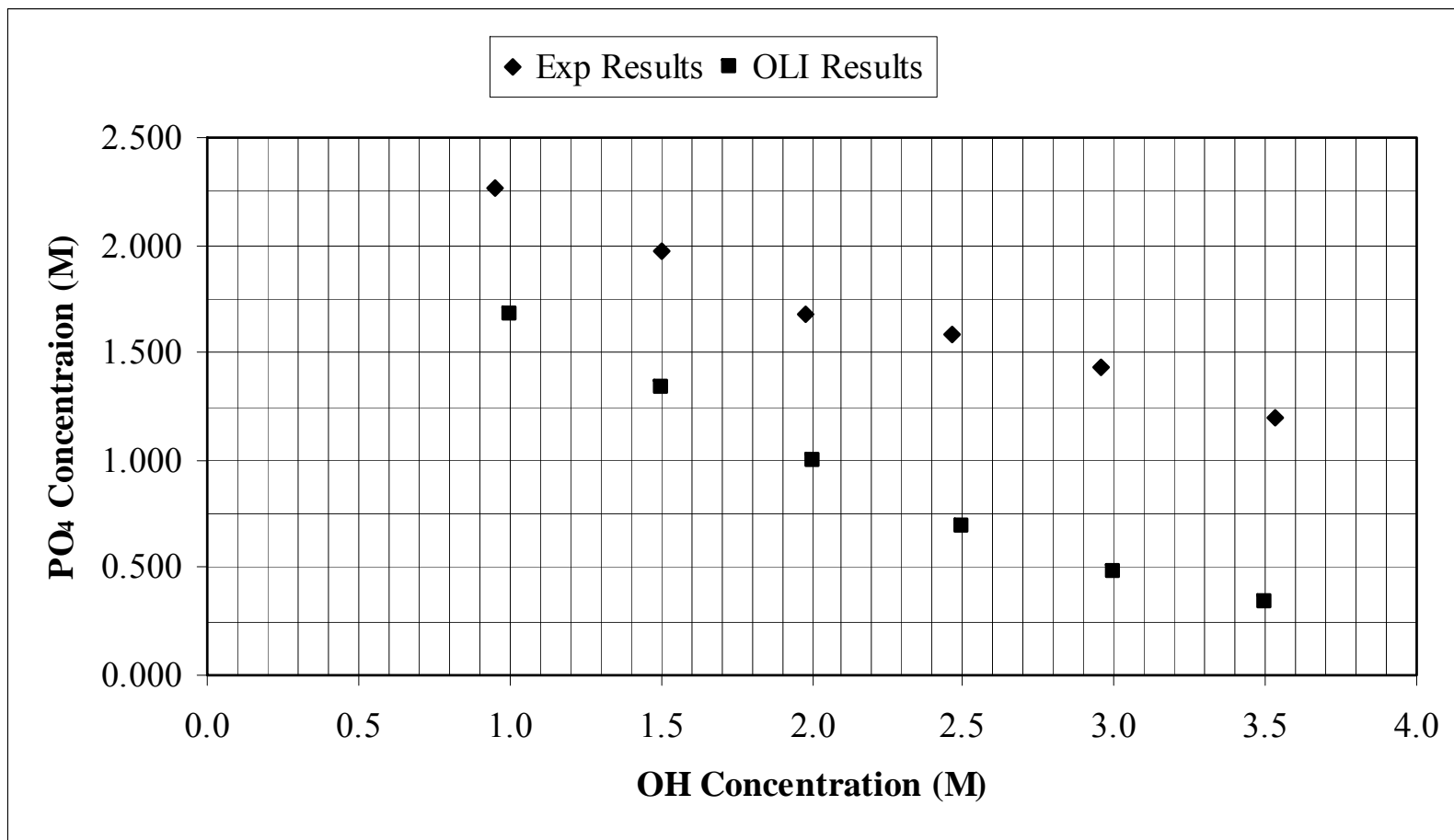


Figure 3-2. Measured Saturated Sodium Phosphate Concentration in NaOH Solutions at 65 °C compared with OLI Modeling Results.

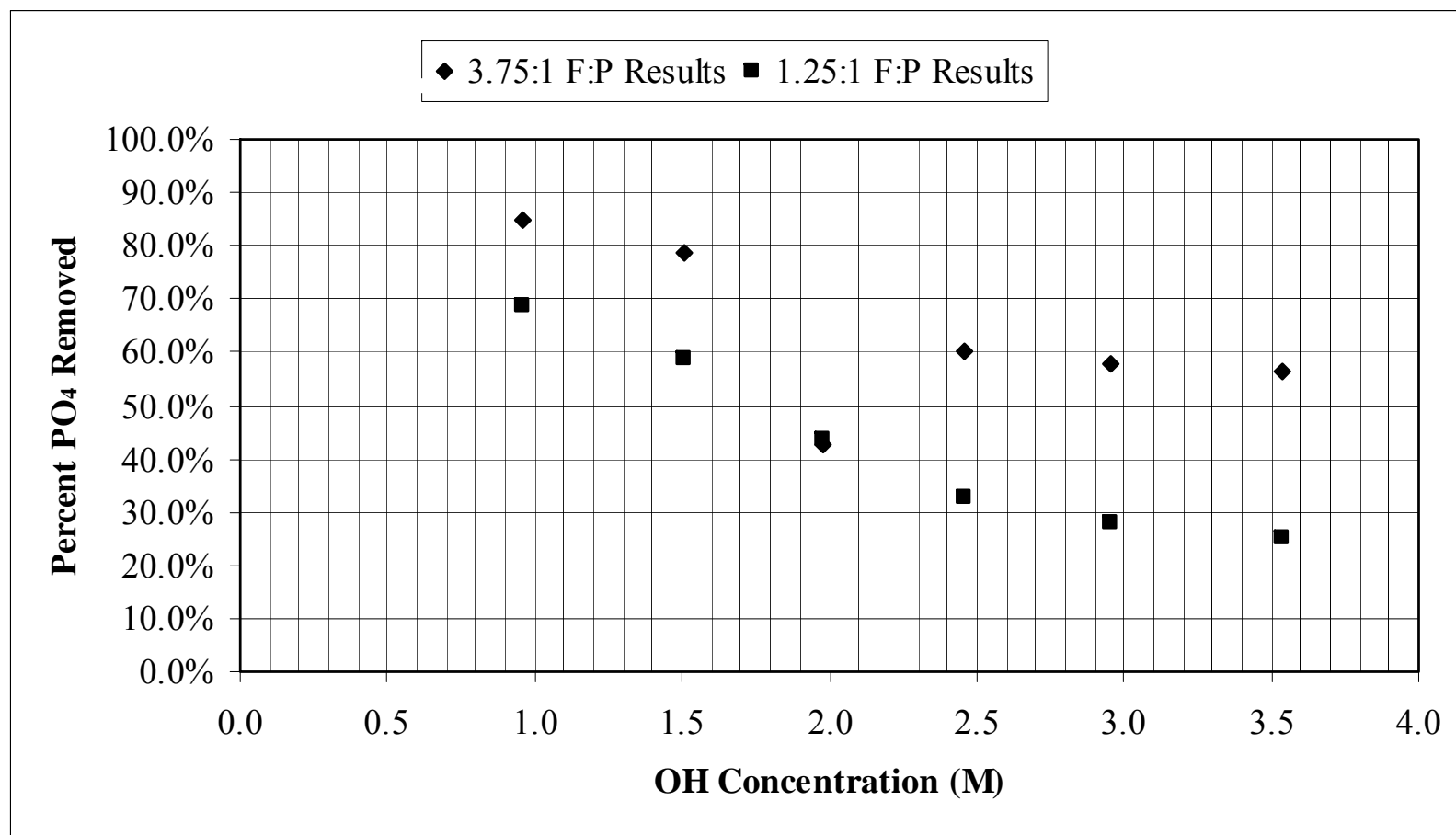


Figure 3-3. Phosphate Precipitation of a 25 °C Saturated Phosphate Solutions at Various NaOH Concentrations using 3.75 or 1.25 Moles of Sodium Fluoride per Mole of Phosphate

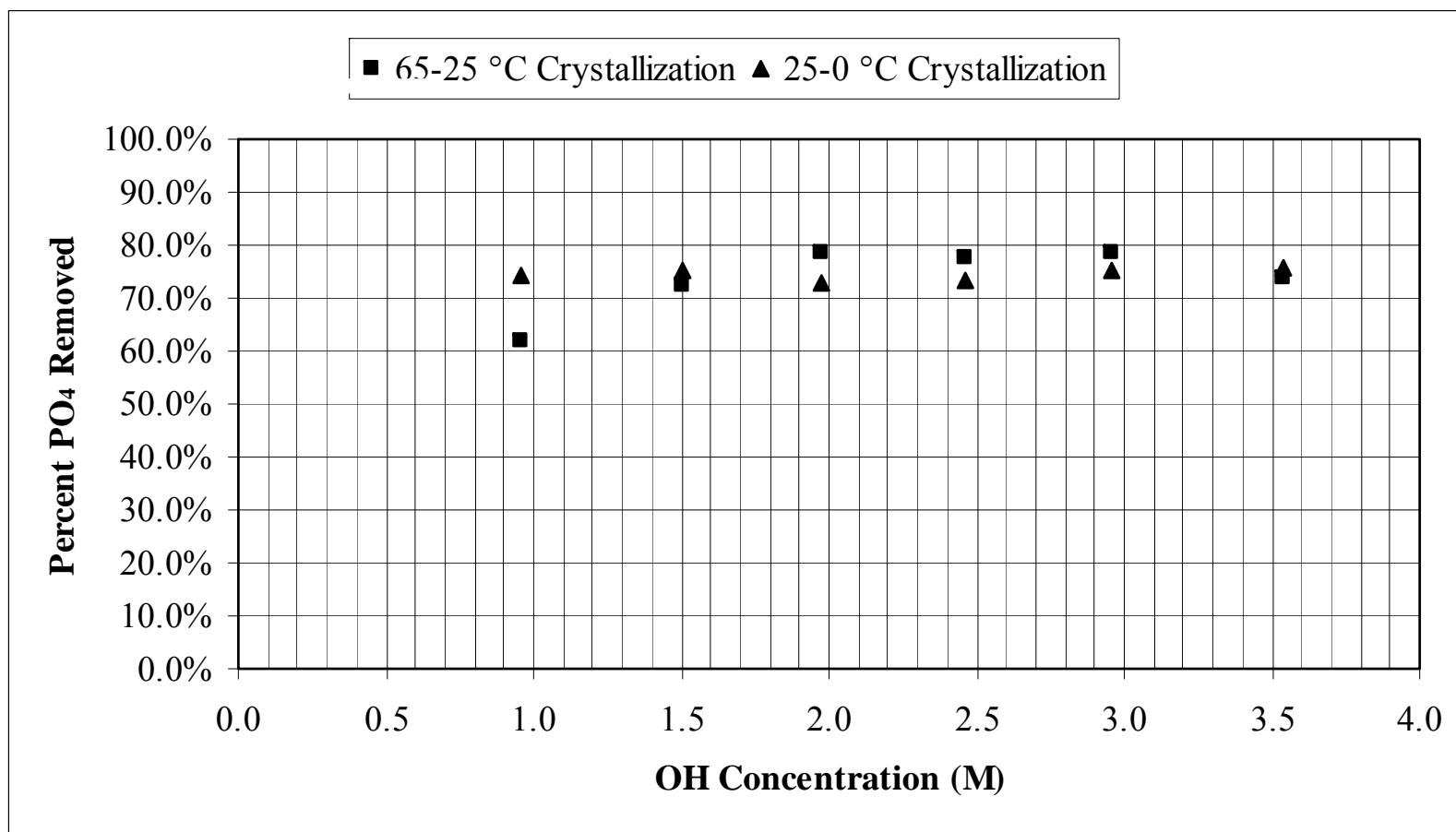


Figure 3-4. Crystallization of Sodium Phosphate from NaOH Solutions at 25 °C Cooled to 0 °C and 65 °C Cooled to 25 °C.

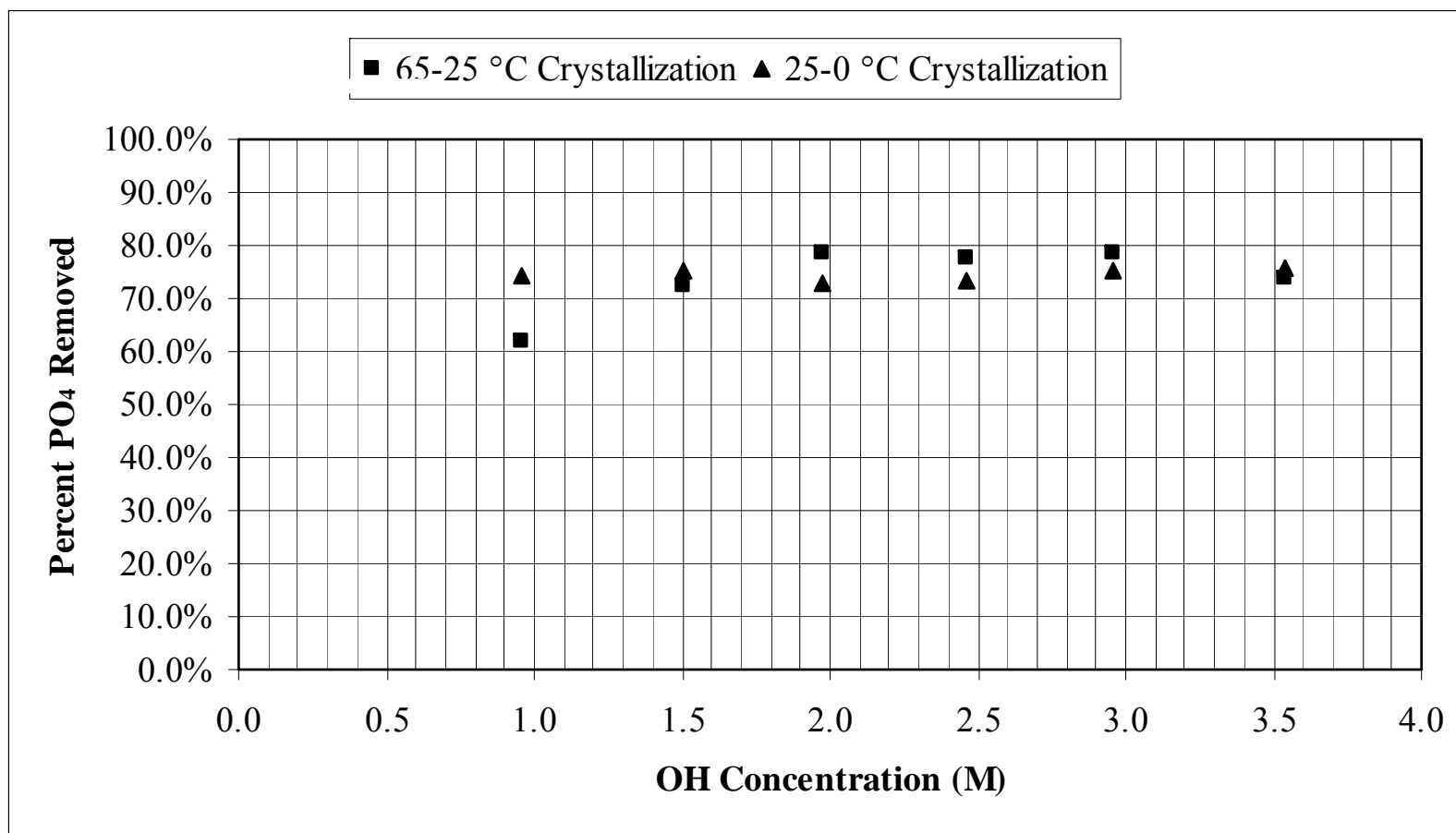


Figure 3-5. Combined Phosphate Precipitation/Crystallization of Phosphate Solutions at Various NaOH Concentrations using ~1 Mole of Sodium Fluoride per Mole of Phosphate.

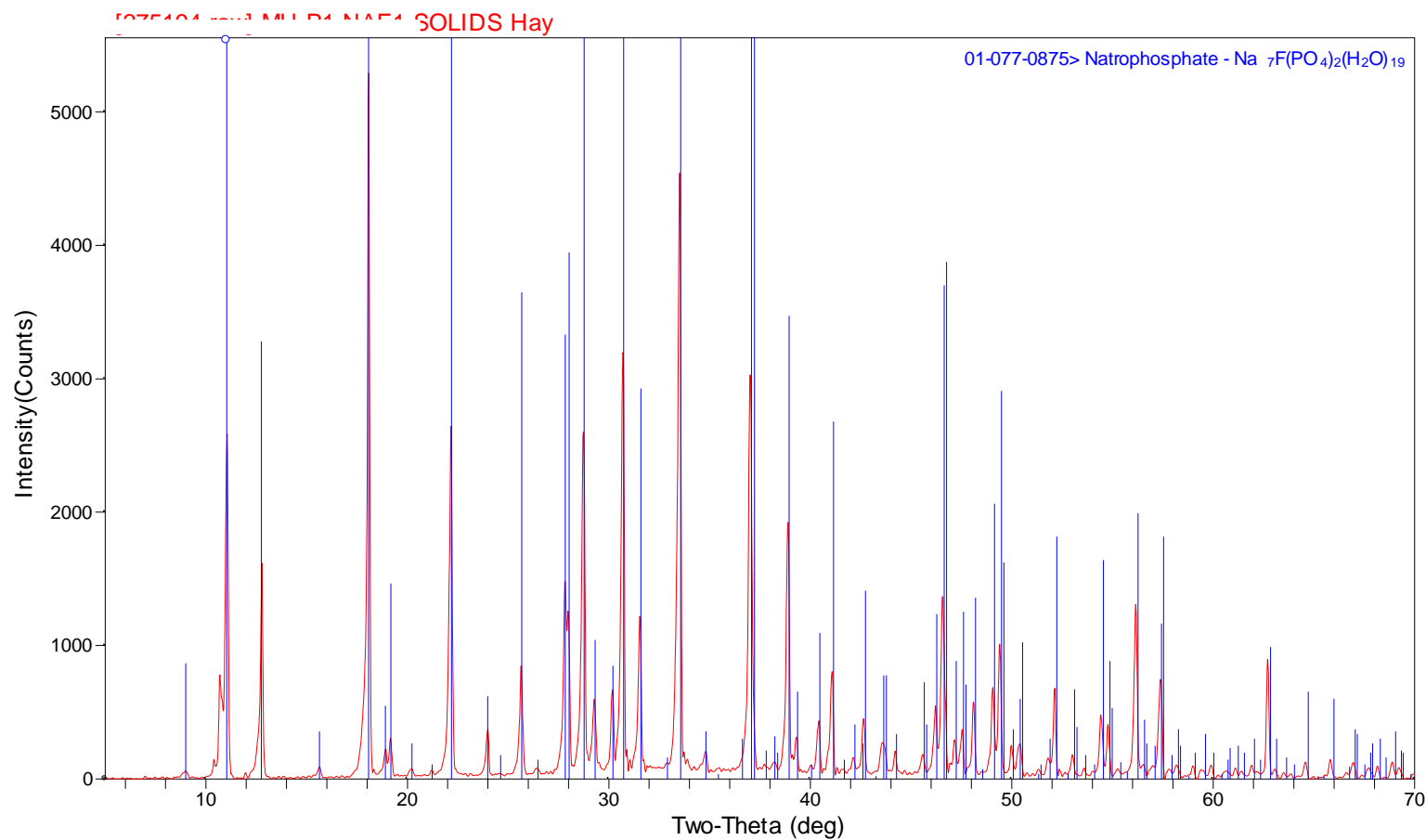


Figure 3-6. XRD of solids from the NaF precipitation (1.25:1 F:P) of a saturated phosphate solution in 1.0 M NaOH at 25 °C. Crystalline phases identified were Natrophosphate $\text{Na}_7\text{F}(\text{PO}_4)_2(\text{H}_2\text{O})_{19}$

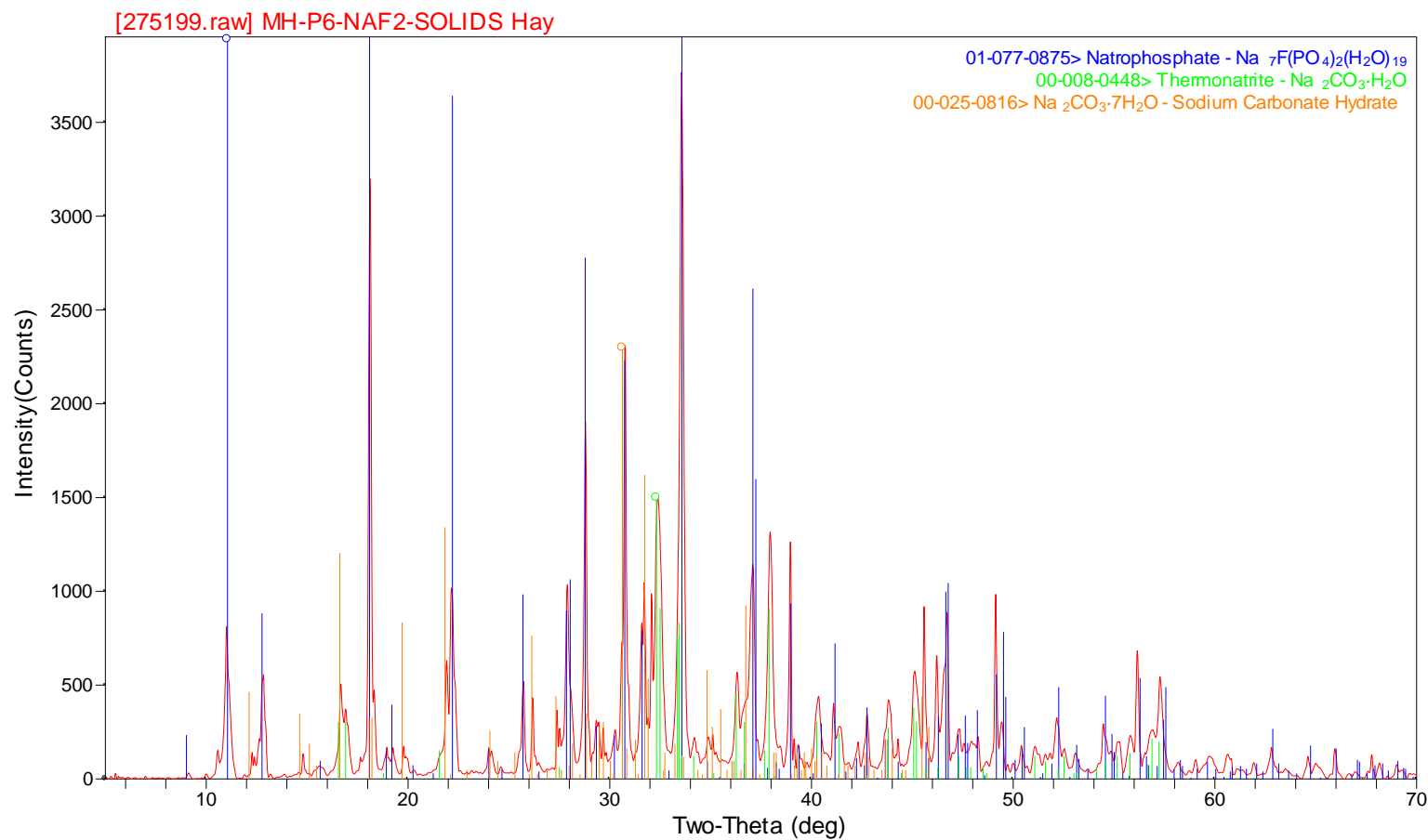


Figure 3-7. XRD of solids from the NaF precipitation (3.75:1 F:P) of a saturated phosphate solution in 3.5 M NaOH at 25 °C. Crystalline phases identified were Natrophosphate $\text{Na}_7\text{F}(\text{PO}_4)_2(\text{H}_2\text{O})_{19}$, Thermonatrite $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, and Sodium Carbonate Hydrate $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$

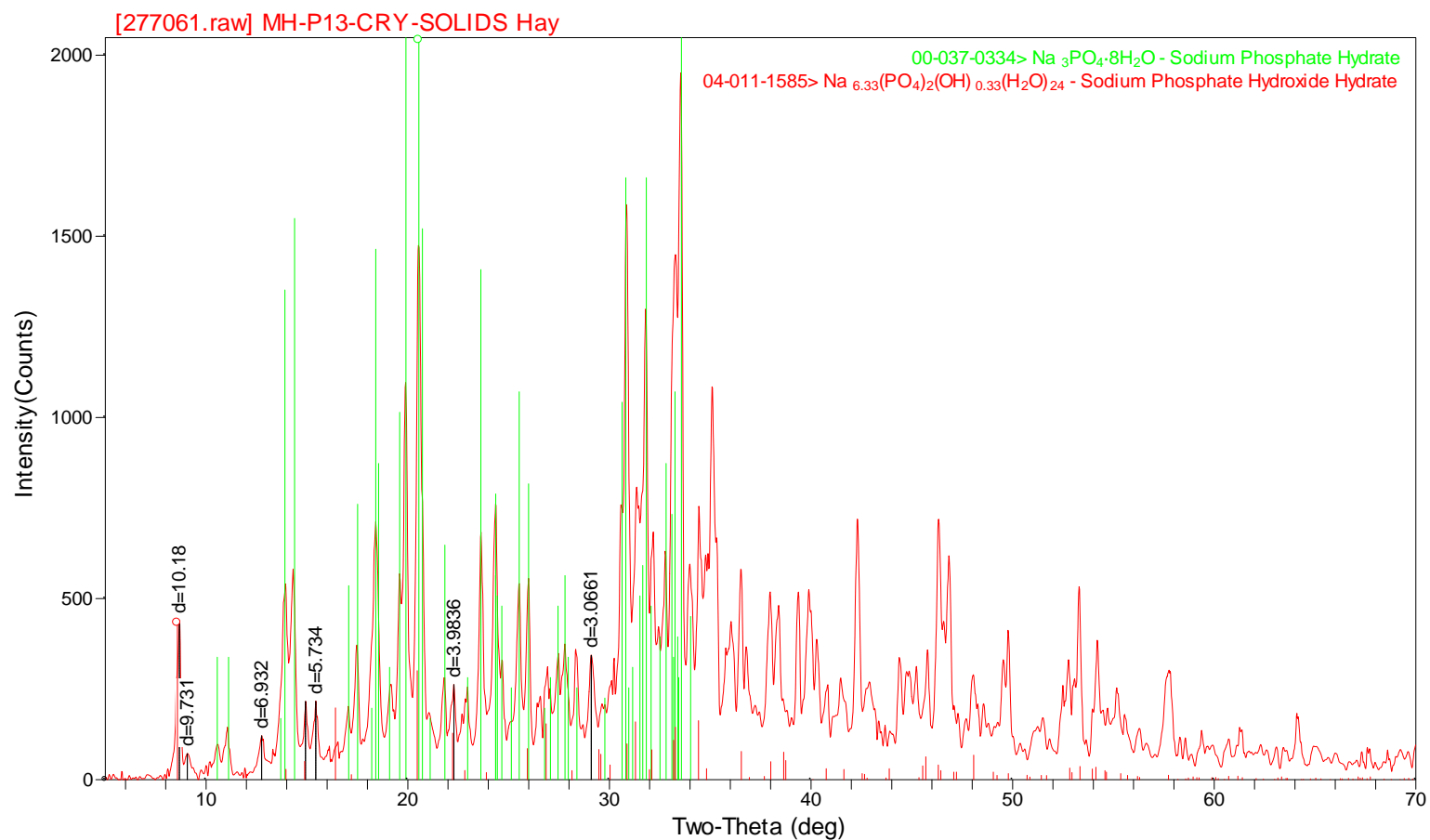


Figure 3-8. XRD of solids from the crystallization of a saturated phosphate solution in 1.0 M NaOH at 25 °C cooled to 0 °C. Crystalline phases identified were Sodium Phosphate Hydrate $\text{Na}_3(\text{PO}_4) \cdot 8\text{H}_2\text{O}$ and Sodium Phosphate Hydroxide Hydrate $\text{Na}_{6.33}(\text{PO}_4)_2(\text{OH})_{0.33}(\text{H}_2\text{O})_{24}$

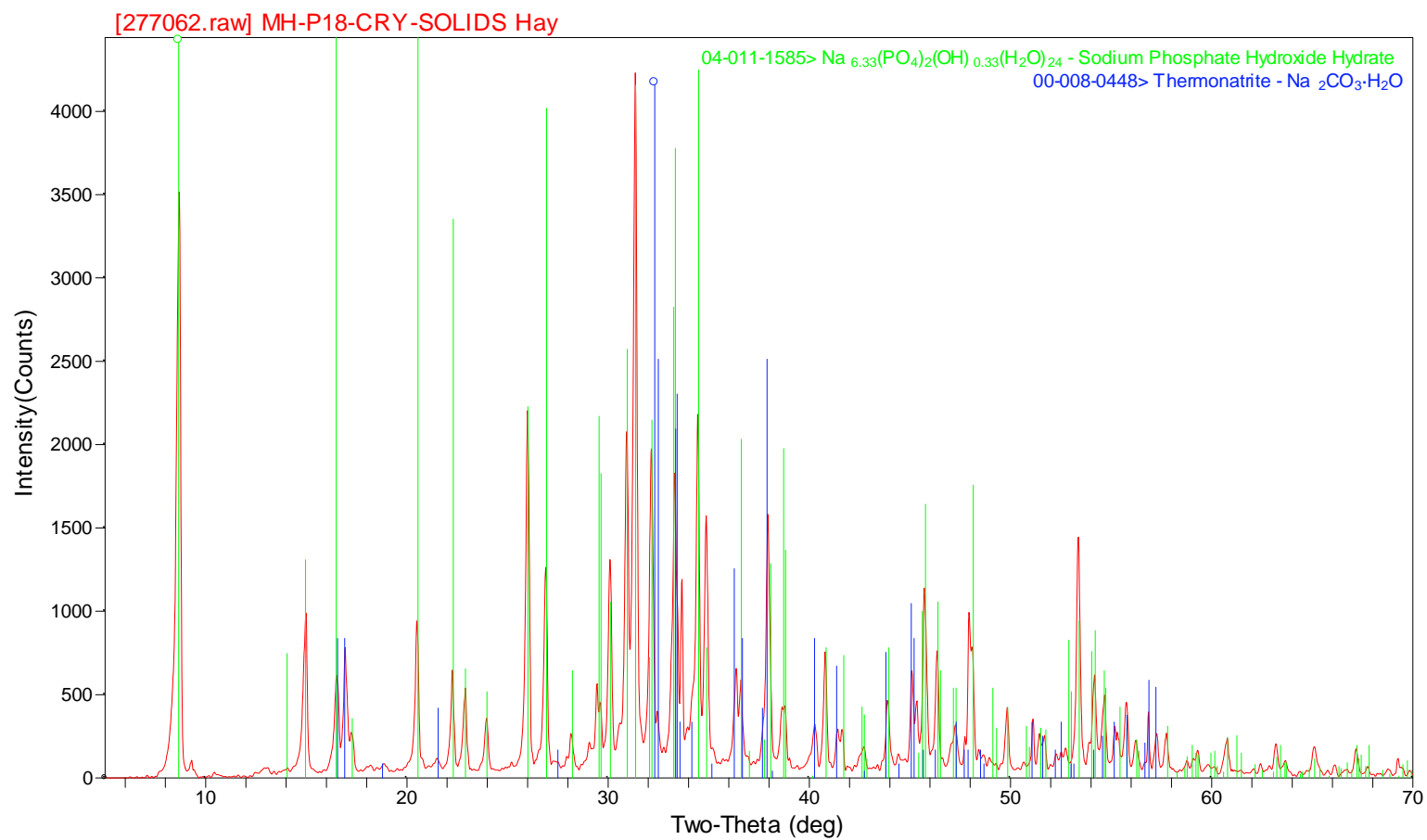


Figure 3-9. XRD of solids from the crystallization of a saturated phosphate solution in 3.5 M NaOH at 25 °C cooled to 0 °C. Crystalline phases identified were Sodium Phosphate Hydrate $\text{Na}_3(\text{PO}_4) \cdot 8\text{H}_2\text{O}$ and Themonatrite $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

4.0 CONCLUSIONS

The results show that all three processes; precipitation with sodium fluoride, crystallization, and combined precipitation/crystallization can be effective for removing large amounts of phosphate from solution. Based on the measured solubility of sodium phosphate, pH adjustment/caustic addition will also remove large amounts of phosphate from solution (>80%). The combined process of precipitation/crystallization showed >90% removal of phosphate at all hydroxide concentrations when cooling a non-saturated phosphate solution from 65 °C to 25 °C.

The sodium fluoride precipitation appears to be more effective at lower hydroxide concentrations in the phosphate solution and can be enhanced by cooling after the precipitation is complete to promote further crystallization under some conditions. The crystallization of phosphate from caustic solutions was found to be effective at removing large amounts of phosphate even from non-saturated phosphate solutions due to the large temperature dependence of the phosphate solubility. The crystallization process has the advantage that no additional chemicals need be added to the waste stream. The product of sodium phosphate crystallization has a highly networked crystalline structure that appears gel-like. However, the crystallization product appears to be relatively easy to break apart and settles to the bottom of the vessel.

For all three processes, the phosphate concentration in the caustic solution must be managed to keep the phosphate from becoming too concentrated. Solutions containing phosphate concentrations < 1-1.5 M can potentially lead to a solid mass of sodium phosphate after an effective phosphate removal process.

Additional study needs to be done with more complex/representative simulants to determine the effect of other dissolved species on the precipitation and crystallization processes. Reducing the hydroxide concentration of the phosphate solution (<1 M) should improve the effectiveness of NaF precipitation process. The potential processing issues of the somewhat gel-like crystallization product would require investigation in larger scale experiments to verify that the product can be easily mixed and transported through piping.

5.0 REFERENCES

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