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Phosphate Solidification Of Caustic Process Solution Waste

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May 1972

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PHOSPHATE SOLIDIFICATION
OF CAUSTIC PROCESS SOLUTION WASTE

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ABSTRACT

A process for solidifying concentrated high-salt process solution waste with phosphoric acid is investigated on a laboratory-scale. Discussion of the proposed application of this process is presented, as well as the tests and results used to establish the parameters for solidification candidates. Synthetic high-salt caustic wastes are used to accumulate data on the kinetics of the reaction. The product is postulated to be the chemical complex

or a derivative thereof. Quality of the product is directly related to wt% water, total sodium molarity, and the amount of monovalent sodium salt present in the waste candidate.

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PHOSPHATE SOLIDIFICATION OF CAUSTIC PROCESS SOLUTION WASTE

INTRODUCTION

The Atlantic Richfield Hanford Company as a prime contractor for the Atomic Energy Commission has long been concerned with the responsibility for effective control of radioactive waste solutions generated in the reprocessing of nuclear fuel elements. Our experiences in the control and disposal of these wastes are of general interest as the use of nuclear reactors increases^[1] to supply the necessary power for modern communities and industry.

Efforts toward effective control and disposal of quantities of waste from reprocessing fuel elements has resulted in a variety of different concepts and practices. At Hanford these wastes were stored in underground, concrete tanks lined with mild steel. To prevent corrosion of the mild steel liners, acid waste solutions were converted to caustic waste (pH 8 or greater) with sodium hydroxide prior to storage.

In 1964 with the implementation of the In-Tank Solidification (ITS) program, efforts were directed toward containing the wastes in an immobile salt of reduced volume. In simple concept, ITS boils off the water and leaves the tanks filled with a cake of solid salt, thus reducing the volume of waste and creating an immobile waste-form for storage.

However processing experience has indicated that as concentration of these waste proceeds, the bottom cooling tanks behave as a large fractional crystallizer. This results in

the recycled mother liquor becoming enriched with the more soluble compounds--namely, sodium hydroxide, sodium nitrate, and sodium aluminate. Because of inherent limitations in thermodynamics, boil-off rates and bottoms concentration in the evaporator system decreased rapidly as the caustic level increased. When operation limits were reached, the tanks contained a mother liquor or concentrated bottoms, and salt cake with interstitial bottoms concentrate.^[2]

SUMMARY AND CONCLUSIONS

The addition of phosphoric acid to concentrated high-salt caustic waste produces complex trisodium orthophosphate hydrate. The reaction occurs at a sodium-to-phosphate mole ratio of 3.12:1 of the available sodium, that associated with OH^- or AlO_2^- . The amount of water present in the solidification feed must be no greater than 7 to 8 wt% excess of water of hydration when the stoichiometric amount of phosphoric acid is reacted with the available sodium. A smaller percentage of water is retained in solids derived from low caustic-high monobasic salt concentrations.

EXPERIMENTAL

The mobility of concentrated bottoms liquid in the tanks is very undesirable. While techniques for the removal of this liquid are being developed, the solidification of these concentrated liquid wastes is the current and real problem. Proposed methods of solidifying concentrated bottoms include the following:

- Cooling.
- Additional evaporation.

- Acid neutralization/re-evaporation.
- Solidification by chemical addition.

In this report the solidification by a minimal chemical addition is considered.

Essentially, concentrated bottoms liquor contains sodium compounds of aluminate, hydroxide, nitrate, and nitrite. The amounts of each constituent in Tank 103-BY are shown in Table I. Laboratory tests indicate that neutralization-reconcentration using different mineral acids and acid salts results in very little gain in total volume reduction, about 30% solidification, and slightly improved thermodynamics with the most efficient mineral acid.^[3] However, during the testing of mineral acids for neutralization/reconcentration, the discovery that the addition of phosphoric acid to a concentrated waste (Figure 1) produces significant quantities of solids presents a new concept of terminal bottom concentrated solidification.

TABLE I
ANALYSIS OF TANK 103-BY

Na	10.28M
Al	2.30M
NO ₃	2.06M
NO ₂	1.11M
TAD	6.9M
H ₂ O	48 wt%

In early experiments the observation that different synthetic wastes produce varying degrees of solidification was assumed to be a function of the individual chemical composition of each synthetic. However, chemical analysis of the solids shows the same composition as the concentrated bottoms with the addition of phosphate. There is an indication,

FIGURE 1

SOLIDS PRODUCED BY THE ADDITION OF DIFFERENT MINERAL ACIDS TO A SYNTHETIC CAUSTIC HIGH-SALT WASTE

as shown in Table II, that during the addition of phosphoric acid the sodium concentration in the liquid phase decreases significantly before the aluminum precipitates.

TABLE II
ANALYSIS OF A SECOND STAGE WASTE EVAPORATION
DURING NEUTRALIZATION BY PHOSPHATE SOLIDIFICATION

<u>Mole Ratio</u> <u>Na:1M PO₄</u>	<u>pH</u>	<u>% Solids</u>	<u>Na</u>	<u>Al</u>
-	-	-	8.42	0.35
9.86	13.2	56.0	7.16	0.40
4.92	13.0	93.0	7.61	0.385
3.34	11.05	95.5	6.91	0.111
2.50	9.75	68.5	6.99	0.024
1.99	9.25	67.0	7.34	0.012
1.67	7.45	59.0	6.28	0.008

Solidification curves of extremely high caustic sodium salt waste as used in Figure 1 show that total solidification has a direct relationship on the amount of phosphoric acid added. Later solidification curves (Figure 2) of low-caustic, high-salt waste indicate that there is a definite sodium-to-phosphate mole ratio of 3:1 if it is assumed that monovalent sodium salts do not react with the phosphate in an alkaline media.

Microscopic studies of the crystals are used primarily to determine the size of crystalline product. However, the two micrographs in Figure 3 show the structure to be octagonal crystals. X-Ray diffraction patterns confirm the presence of a hydrated phosphate and show strong diffraction patterns of sodium nitrate.

Water analyses of the salt cake vary from 52.4 to 55.8 wt% (Table III) indicating that the amount of water in the salt cake corresponds closely in range to the waters of hydration of $H_3PO_4 \cdot 10H_2O$ and $H_3PO_4 \cdot 12H_2O$.

FIGURE 2
SOLIDIFICATION CURVES OF WASTE
SHOWING THAT MAXIMUM SOLIDS OCCUR AT A
SODIUM-TO-PHOSPHATE MOLE RATIO OF 3.12:1

FIGURE 3

PHOTOMICROGRAPHS OF SOLIDIFIED SYNTHETIC WASTE
SHOWING RANGE IN CRYSTAL SIZE AND SHAPE

[B is enlargement of central left portion of A]

TABLE III

Wt % H₂O OF DIFFERENT SOLIDIFIED SYNTHETIC WASTES
DETERMINED BY WEIGHT LOSS WHEN IGNITED TO 110 °C

<u>Sample Preparation</u>	<u>% H₂O</u>
Vacuum-drained	55.8
Air-dried	53.7
Solid as formed	52.4

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA), Figure 4, confirm the water content of the solids and show that the waters of hydration release at 100 °C, again correlating closely to sodium orthophosphate.

To assess the effect of H₂O on solidification by phosphate addition, a 106-BY synthetic (Table IV) with a total sodium molarity of 8.1 and a water content of 61.3 wt% is used to make up three other solutions by dilution and evaporation.

TABLE IV
COMPOSITION OF 106-BY

NaAlO ₂	2.M
NaNO ₂	1.M
NaNO ₃	2.M
NaOH	3.1M

Volume percent solids are determined on each adjusted feed with selected mole ratios of sodium-to-phosphate. Interstitial liquids are removed by pressing the cooled mixture under 28 psi of static pressure. Figure 5 shows that total solidification does not occur in the wastes containing greater than 60 wt% H₂O. The wastes containing 50 wt% H₂O or less demonstrate complete solidification under the conditions tested.

RESULTS AND DISCUSSION

From the experiments above we discern (1) that solids are produced on a sodium-to-phosphate mole ratio of 3:1; and (2) that total solidification is a function of the wt% H₂O in the waste. In a scholarly work, Bell^[4] states that trisodium phosphate compounds containing more than 8 H₂O are not simple hydrates, but hydrated complexes

FIGURE 5
SOLIDIFICATION OF DIFFERENT H_2O
CONTENT 106-BY SYNTHETICS

which always contain the sodium salt of a monobasic acid or sodium hydroxide. These complexes are of two types and can be represented by the following formulas:

where $N = 1$ or 2 , Y is a monobasic anion, and $X = 18$ or 19 and

where $N = 4$ to 7 , $X = 11$ or 12 , and Y is a monobasic anion OH , NO_2 , NO_3 , or AlO_3 . Later work by Wendrow and Kobe^[5] shows a sodium-to-phosphate mole ratio of 3.21 when $N = 5$ and 3.12 when $N = 7$ in formula (2).

Considering the composition of synthetic 106-BY in Table IV or the actual waste analysis in Table I as it might apply to formula (2), the following hydrated complexes of trisodium orthophosphate may be present:

Complex	Melting Point
	°C
$5(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O})\text{NaOH}$	74
$7(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O})\text{NaOH}$	70
$4(\text{Na}_3\text{PO}_4 \cdot 11\text{H}_2\text{O})\text{NaNO}_2$	72
$7(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O})\text{NaNO}_3$	-
$7(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O})\text{NaNO}_3$	60
$7(\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O})\text{NaAlO}_2$	-

Relating the information above to solidification of caustic salt waste, we would expect the following reaction:

When phosphoric acid is first added, it reacts primarily with the free caustic, forming trisodium orthophosphate. The heat of reaction raises the temperature of the slurry to approximately 90 °C. At this temperature the trisodium phosphate is present as the hexa- or octahydrates. In addition, some local precipitation of $\text{Al}(\text{OH})_3$ occurs. As the slurry cools, the

complex hydrates form, taking on additional waters of hydration. The loss of water into the complex hydrates results in a solution supersaturated with NaNO_3 , NaNO_2 , and NaAlO_2 which also begin to crystallize.

Solidification by phosphate addition is dependent on the amount of water present in the bottoms concentrate. The solidification of a solution containing total reactable sodium can be expressed by the formula

The formula for 85% H_3PO_4 is shown as $(\text{H}_3\text{PO}_4 \cdot 0.96\text{H}_2\text{O})$. In this formula the amount of water is equal to 53.5 wt% of the waste solution. Actual caustic salt waste as shown in Table I can be represented by the formula

if it is assumed that NaAlO_2 is capable of reacting with phosphoric acid in a manner similar to NaOH . The 7.11 moles of available sodium are the difference between total sodium molarity and the molarity of nitrate plus nitrite $[10.28 - (2.06 + 1.11)]$.

By using the ratio of 1 mole phosphate to 3.12 moles of available sodium, 2.28 moles of phosphate react with the 7.11 moles of available sodium. The reaction is shown in formula (5).

Because of the high monobasic salt content, only about three-fourths of the water in formula (2) is tied up in the hydrated trisodium phosphate complex. However, the neutralization of 103-BY as shown in Figure 4 indicates that total solidification occurred.

This difference between experimental observations and

theoretical mechanisms has to be explained as interstitial liquid retention by adhesion and Van der Waal's forces. Experiments show that commercial grade trisodium orthophosphate retains about 6 wt% water when pressed under 28 psi static pressure.

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