

VOLUME REDUCTION BY CRYSTALLIZATION OF LOW-LEVEL RADIOACTIVE WASTES

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ABSTRACT

Low level radioactive wastes containing boric acid, borax, or sodium sulfate, with radioactive contaminants, are generated during the operation of nuclear power plants. These wastes require disposal, and as such, it is economically and environmentally desirable to reduce their volume. Crystallization was examined in the laboratory as a means of accomplishing this. The crystallizer was operated in both of two modes: evaporative cooling and total evaporation. A 12 wt% boric acid waste feed was concentrated to a 40 to 45 wt% slurry in both modes of operation. Using pure boric acid, a slurry containing over 60 wt% was obtained. An 18.5 wt% borax waste feed was concentrated to 50 wt% in the total evaporative mode and 70 wt% in the evaporatively cooled mode. A 22 wt% sodium sulfate feed was concentrated to a 78 wt% slurry in the total evaporative mode. For all of the feeds, this represents a 4- to 5-fold volume reduction by the crystallizer.

INTRODUCTION

Low-level radioactive wastes, generated during the normal operation of nuclear power plants, require storage and disposal in an environmentally acceptable manner. This requirement has made it necessary to develop an effective means for volume reduction and solidification of these low-level wastes. Westinghouse has responded to this need for the effective management of these wastes by developing a radwaste volume reduction/solidification system. This system makes use of a vacuum-cooled crystallizer to reduce the volume of waste, and a high speed, high shear cement solidification unit to encapsulate the waste. The resultant product, which is automatically packaged in waste disposal containers, is a homogenous, high strength solid containing

no free standing water. To develop such a system, laboratory tests were performed to obtain necessary design data, to generate operating parameters and experience, and to act as a data base for the full-scale system. The results of the tests conducted on the volume reduction portion of the system are presented here.

A bench-scale crystallizer was operated in both of two modes: evaporative cooling and total evaporative. The evaporative cooling mode is attractive because it can be operated at ambient temperature and requires no heat input, thus minimizing energy costs and the potential for line plugging should a shutdown occur. The total evaporative mode is advantageous in that it does not require a substantial decline in solubility with decreasing temperature to produce crystallization, so that sulfate wastes can be handled, and it does not return any waste stream to the power plant. The two modes were tested to make comparisons and to be able to deal with all types of waste likely to be generated from nuclear power plants. The waste can contain as its principal component boric acid (i.e., from pressurized water reactors), borax (i.e., neutralized boric acid), or sodium sulfate (i.e., from boiling water reactors). The crystallizer may have to handle any of these wastes and as such, crystallization studies were conducted on each waste type. Each crystallizer test examined various operating parameters: feed rates, recirculation rates, operating temperatures, and heat inputs. The operation of the crystallizer was found to be affected by both the mode of operation and the type of waste.

EXPERIMENTAL SYSTEM

The experimental system used for the total evaporative crystallization studies is shown in Fig. 1. In this mode, the system operation consists of pumping the hot feed into the recirculation stream which is then heated in the heat exchanger. In order to maintain the desired crystallizer operating temperature, heat input into the recirculation stream must be balanced by the evaporation rate in the crystallizer. The evaporation rate in turn determines the feed rate. The increase in concentration caused by the evaporation results in crystallization. The heat input into the system cannot be so great as to result in a temperature rise which causes boiling in the recirculation line. The system has a total liquid volume of approximately 7 gallons (26.5 liters).

In the evaporative cooling system, shown in Fig. 2, the heat exchanger is no longer needed and an overflow line and tank are added. System operation consists of feeding hot radwastes into the cooler recirculation line. Cooling of the crystallizer re-

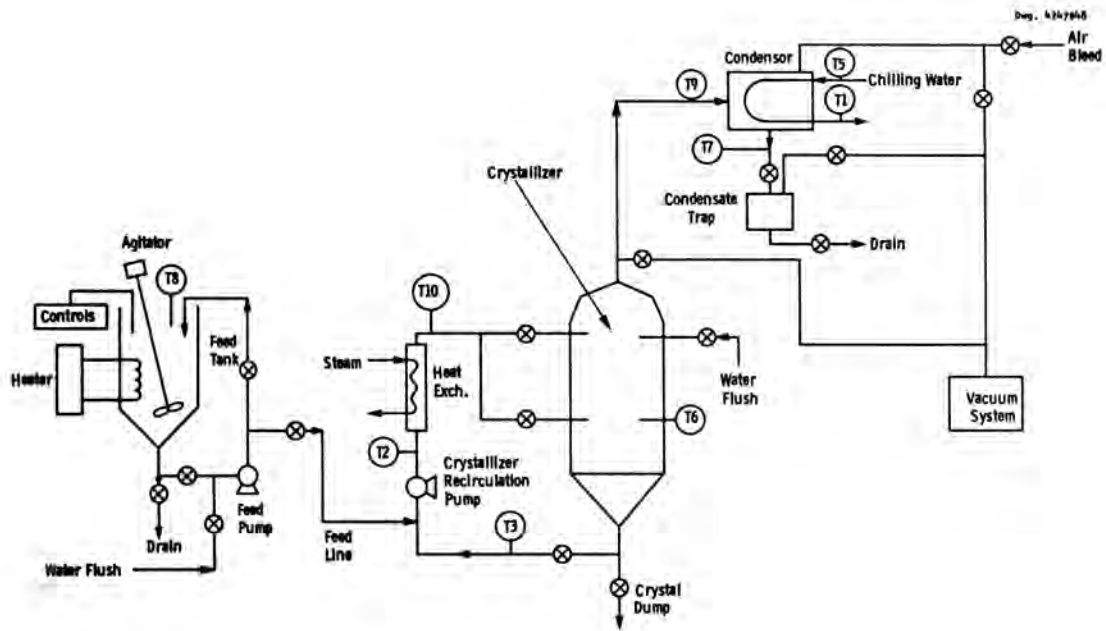


Fig. 1. Experimental total evaporative crystallizer flow sheet.

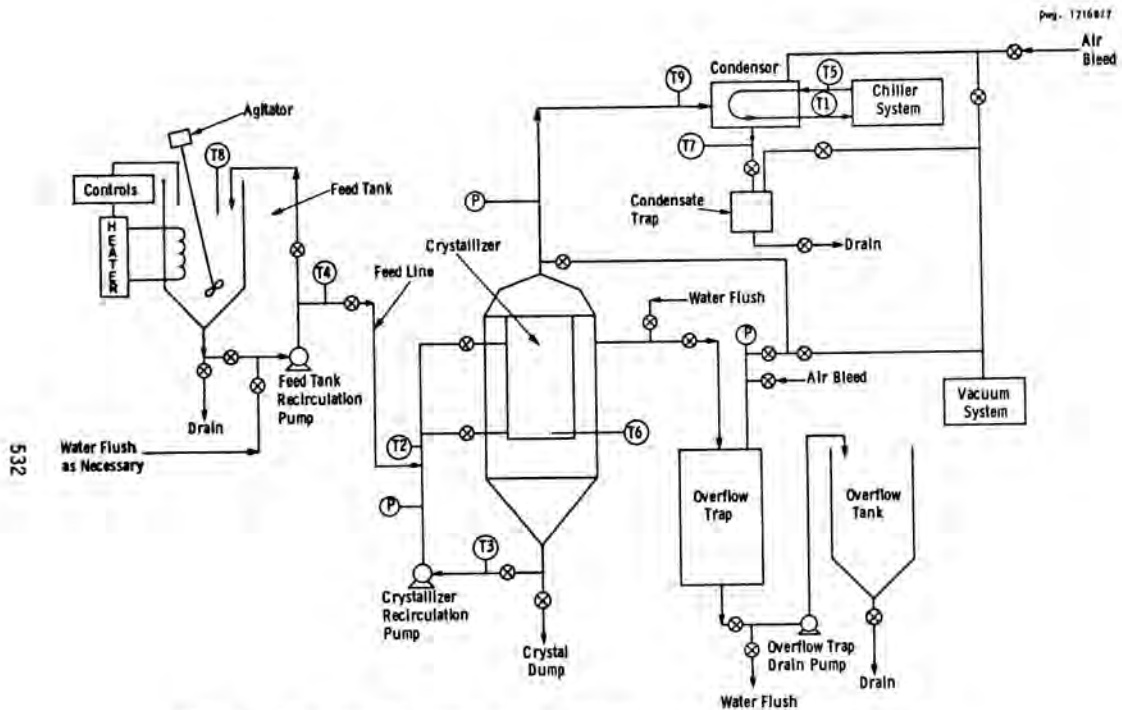


Fig. 2. Experimental evaporative cooling crystallization flow sheet.

quires operation under a high process vacuum and boiling away a small fraction of the water. This cooling action causes the waste in the feed stream to crystallize, and the crystals to grow. The feed rate must not be too high. Otherwise, this causes a large temperature rise, which produces boiling in the recirculation lines.

The composition of the simulated waste feeds used in both modes of operation are given in Table I. The contaminant composition of the waste is based on the analysis of actual waste streams. This "average" feed composition is hopefully of value in identifying operational characteristics which can be related to any specific feed. Of course, it would be of value to test an actual feed of interest, and, thus, accurately determine the process parameters.

RESULTS

Boric Acid Tests

The results of the crystallization tests are presented in Table II. In the 4 tests performed with boric acid in the evaporative cooling mode, slurries were produced which contained an average of 44.9 wt% boric acid (\pm a standard deviation of 3.0). In the total evaporative mode, the 4 tests resulted in slurries containing about 42.7 wt% boric acid (\pm a standard deviation of 4.0). Thus, the two modes of operation produced essentially the same weight percent slurries. This represents a 4- to 5-fold volume reduction by the crystallizer. It should be noted that in earlier tests performed with pure boric acid feed, slurries were produced which contained over 60 wt% boric acid. The presence of contaminants thus affects the slurries produced.

The total evaporative mode allowed for greater crystal accumulation (23 vs 17 vol%), which results in a greater volume of feed being processed and a longer residence time for crystal growth. The boric acid crystal growth rates and crystal characteristics were similar in both modes of operation. The waste crystals produced were pinkish-white, flake-like, and "fluffy" (see Fig. 3); unlike the white, regular, round, hard crystals produced from the pure boric acid feed solutions (see Fig. 4).

Foaming was found to be a potential problem if excessive oil (0.2 wt%) was present in the feed. The presence of phosphates in the feed was also thought to add to the foaming problem. Foaming is undesirable because it prevents adequate settling rates and proper slurry drainage from the crystallizer. Antifoaming agents are present in the crystallizer feed of most power plants. Hence,

TABLE I
Simulated Waste Compositions

| Element/ Compound | Boric Acid Feed wt% | Borax Feed wt% | Sodium Sulfate Feed wt% |
|----------------------|------------------------|-------------------|-------------------------------|
| Boric Acid | 12.0 | - | - |
| Borax | - | 18.5 | - |
| Sodium Sulfate | - | - | 22.0 |
| PO_4^{-3} | 0.15 | 0.15 | 0.15 |
| Ca | 0.10 | 0.10 | 0.10 |
| K | 0.30 | 0.30 | 0.30 |
| Sr | 0.01 | 0.01 | 0.01 |
| Cs | 0.01 | 0.01 | 0.01 |
| Co | 0.01 | 0.01 | 0.01 |
| Na | 1.30 | 1.30 | 7.1 |
| Cl | 2.23 | 2.23 | 2.23 |
| Li | 0.01 | 0.01 | 0.01 |
| SiO_2^{-2} | 0.10 | 0.10 | 0.10 |

TABLE II

Summary of Radwaste Crystallization Studies

| Waste Feed | Mode Of Operation | No. Of Tests | Average Wt% In Settled Slurry | Maximum Crystal Accumulation (Volume %) |
|----------------|---------------------|--------------|--------------------------------------------|-----------------------------------------|
| Boric Acid | Evaporative Cooling | 5 | 44.9 wt% Boric Acid ($\pm 3.0\%$) | 16.8 vol% |
| Boric Acid | Total Evaporative | 4 | 42.7 wt% Boric Acid ($\pm 4.0\%$) | 23.0 vol% |
| Borax | Evaporative Cooling | 3 | 70.1 wt% Borax ($\pm 3.4\%$) | 20.7 vol% |
| Borax | Total Evaporative | 2 | 50.5 wt% Borax ($\pm 1.0\%$) | 25.3 vol% |
| Sodium Sulfate | Total Evaporative | 3 | 78.0 wt% Sodium Sulfate ($\pm 4.0\%$) | 39.4 vol% |

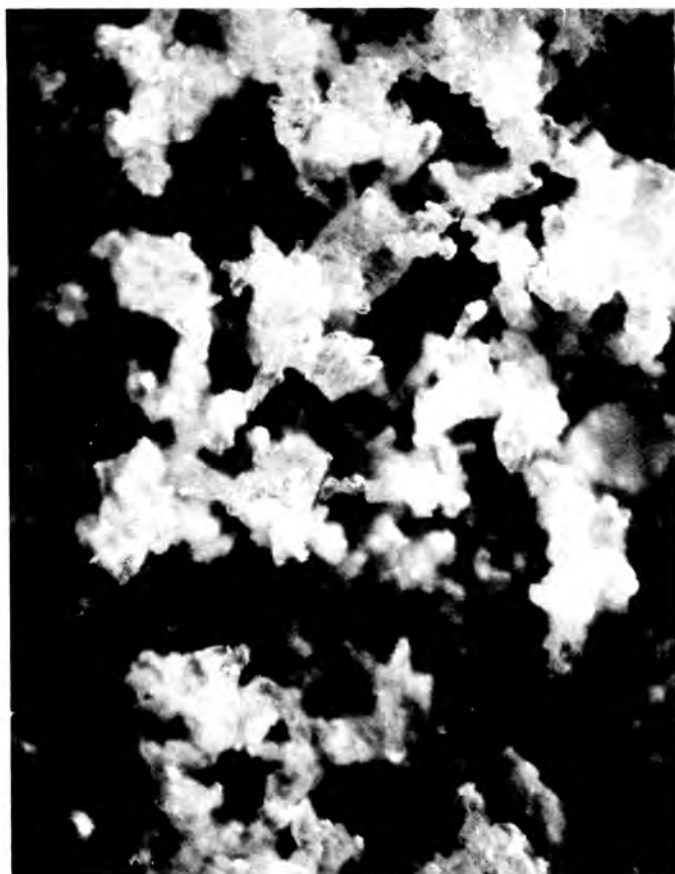


Fig. 3 — Crystals produced from waste boric acid feed,
(x100)

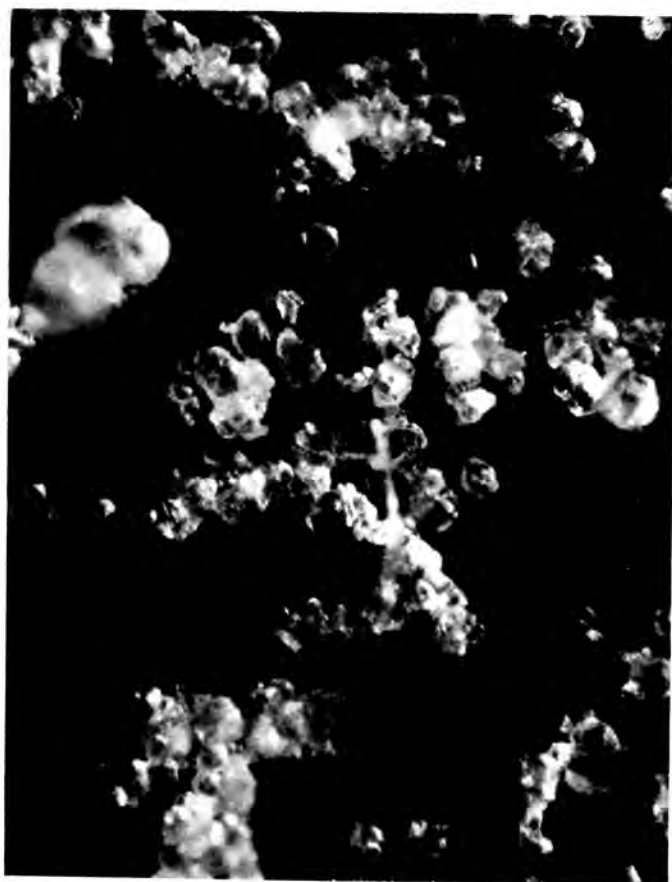


Fig. 4 – Crystals formed from pure boric acid feed, (x100)

foaming is not expected to affect full-scale crystallizer operation using actual feed solutions. No experimental tests were conducted using antifoaming agents because the formulations are plant-site specific.

Borax

The crystallization results using the waste borax feed are given in Table II. The slurries produced contained an average of 50.5 wt% borax (\pm a standard deviation of 1.0) in the 2 total evaporative mode tests performed, and 70.1 wt% (\pm a standard deviation of 3.4) in the 3 evaporatively cooled tests. The 70 wt% slurry represents a 4- to 5-fold waste volume reduction. The higher weight percent borax slurry obtainable in the evaporative cooling mode is due to the finer, and thus denser packing, crystals produced. As with boric acid, the total evaporative mode permitted greater crystal accumulation (25 vs 21 vol%). In both modes of operation, the crystal growth rates and crystal characteristics were approximately the same. The pink, fluffy particles produced were very similar in appearance to the waste boric acid crystals. Operating difficulties (i.e., plugging and pumping problems) were experienced at operating temperatures above 130°F (55°C). These problems were due to a change in the sodium borate hydration state upon cooling. As shown in Fig. 5, there is a conversion upon cooling of the tetrahydrate crystal to the decahydrate.

Sodium Sulfate

The sodium sulfate crystallization studies were only conducted in the total evaporative mode. Due to the relatively high solubility of sodium sulfate, shown in Fig. 6, it is not possible to crystallize sodium sulfate in the evaporative cooling mode at the practical operating temperatures of 80°F (27°C) or above. The slurry produced in the three total evaporative tests contained 78.0 wt% (\pm a standard deviation of 4.0) sodium sulfate which is approximately a 5-fold waste volume reduction. The slurry occupied a maximum of over 39 vol% in the crystallizer. The solubility and hydration characteristics of sodium sulfate, shown in Fig. 6, caused some operating difficulties. Due to its inverse solubility at temperatures greater than 90°F (32°C), scaling of the crystallizer's heat exchanger can occur. The log mean temperature differential between the recirculation solution and the steam heat of the exchanger has to be optimized to minimize this scaling problem. Also, the sodium sulfate forms a decahydrate upon cooling to below 90°F (32°C), thus taking up all available free water. The product turns rock-hard and is difficult to manage. These potential problems were anticipated and solved. Successful sodium sulfate crystallization was accomplished, and operating parameters discerned and optimized.

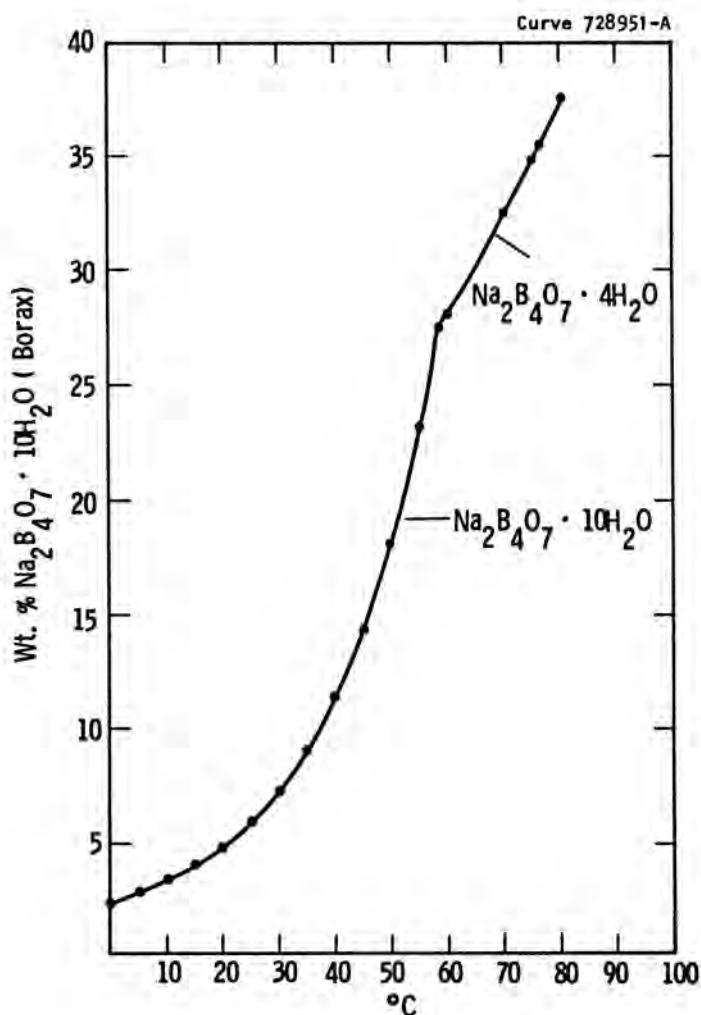


Fig. 5 — Solubility of borax as a function of temperature.

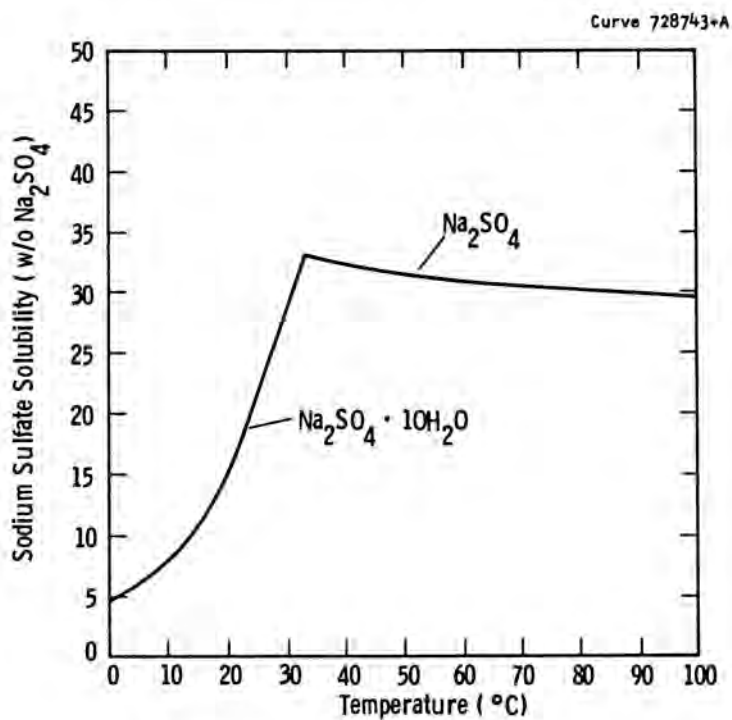


Fig. 6 — Sodium sulfate solubility as a function of temperature

DISCUSSION

The crystallization of sodium sulfate requires operating the system in the total evaporative mode, because this achieves crystallization by removing water and thus increasing the concentration. Unlike evaporative cooling, total evaporation does not need a low solubility at low temperatures, which sodium sulfate does not have. Total evaporation also has the advantages of allowing greater crystal accumulation and not returning any waste stream to the power plant. However, if the returning of an overflow waste stream to the plant is permissible, then evaporative cooling is the preferred mode of operation for boric acid and borax.

The evaporatively cooled mode of operation is preferred because it does not require heat input, which minimizes energy costs, and the low-temperature operation reduces the possibility of lines plugging. The high temperature required in the total evaporative mode can lead to operational difficulties. Fouling can occur on the colder vessel walls, and line blockages can form if the system has to be shut down and the solution cools in the line. In addition, the necessity of operating the borax system at below 130°F results in higher obtainable feed rates in the evaporatively cooled mode.

SUMMARY

The crystallization volume reduction system being marketed by Westinghouse has been successfully tested in the laboratory. The tests were used to identify desirable operating conditions and potential operating problems. The data generated from these tests have shown that various low-level wastes (i.e., boric acid, borax, and sodium sulfate) can be successfully crystallized and their disposal volume significantly reduced using this system. The crystallizer is thus a viable means for radwaste volume reduction. In order to deal with a range of streams (e.g., boric acid and sodium sulfate) the crystallizer should be capable of operating in both the evaporatively cooled and the total evaporative modes. It should be noted that the laboratory data obtained was used to design, construct, and successfully start up a full-scale system (~ 500 gallons, 1900 liters) which operated exactly as expected based on the laboratory tests performed.