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Initiation Temperature for Runaway Tri-n-butyl Phosphate/Nitric Acid Reaction[#]

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ABSTRACT

In a review of the safety basis for solvent extraction processes at the U.S. Department of Energy's Savannah River Site, a question was raised concerning the safety margin associated with a postulated accident involving a runaway tri-n-butyl phosphate (TBP)/nitric acid reaction due to the inadvertent heating of a tank. The safety margin was based on studies that showed that the maximum temperature would not exceed 128°C, as compared to 130°C, the minimum initiation temperature for runaway reaction established in the 1950s following damaging incidents at the Savannah River and Hanford Sites. The reviewers were concerned that the minimum initiation temperature was not conservative since data for solutions containing 20 wt% dissolved solids showed initiation temperatures at or below 130°C, and process solutions normally contain some dissolved solids.

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To address the safety concern, the initiation temperature for runaway reaction was measured as functions of the nitric acid and dissolved solids concentrations using a Reactive System Screening Tool™. The thermal stability studies showed a gradual decrease in the initiation temperature with increasing nitric acid concentration due to the increase in the available oxidant. Temperatures measured using solutions containing dissolved solids showed a small dependence on the salt concentration due to a salting-out effect and decreased linearly with the amount of nitric acid extracted by the TBP. The data illustrated that initiation temperatures measured in the 1950s using TBP contacted with nitric acid solutions containing 20 wt% dissolved solids were 10 to 15°C below predicted values; thus, the margin of safety is much larger than indicated by the previous work.

Key Words: Tri-n-butyl phosphate (TBP); Run away TBP/nitric acid reaction; Solvent extraction; Nuclear fuel reprocessing.

INTRODUCTION

During a review of the solvent extraction safety basis for the H-Canyon Facility at the Savannah River Site (SRS), Defense Nuclear Facility Safety Board (DNFSB) staff members, who have U.S. Department of Energy (DOE) oversite responsibilities, questioned the margin of safety associated with a postulated tri-n-butyl phosphate (TBP)/nitric acid runaway reaction due to the inadvertent heating of a canyon tank. The margin of safety was based on studies[1] that showed the maximum temperature would not exceed 128°C, compared to the minimum initiation temperature for a runaway reaction (greater than 130°C) measured by Colven[2] in the mid 1950s following damaging incidents at the Savannah River[3] and Hanford Sites. Colven measured the initiation temperature as a function of nitric acid concentration for 0 and 20 wt% dissolved solids (Fig. 1). The DNFSB staff members were concerned that data for 0 wt% dissolved solids were not conservative, given the facts that Colven's data for 20 wt% dissolved solids showed initiation temperatures below 130°C, and H-Canyon process solutions normally contained a small amount of dissolved solids.

To address the DNFSB safety concern, the initiation temperature for a runaway TBP/nitric acid reaction was measured as functions of the nitric acid and dissolved metal nitrate salt concentrations of the aqueous phase in equilibrium with pure TBP. Only the organic phase was used in the experiments due to the cooling mechanism provided by water, nitric acid, and volatile components produced by the degradation of TBP. Smith et al.[4] showed that the forced evaporation of volatile components by noncondensible

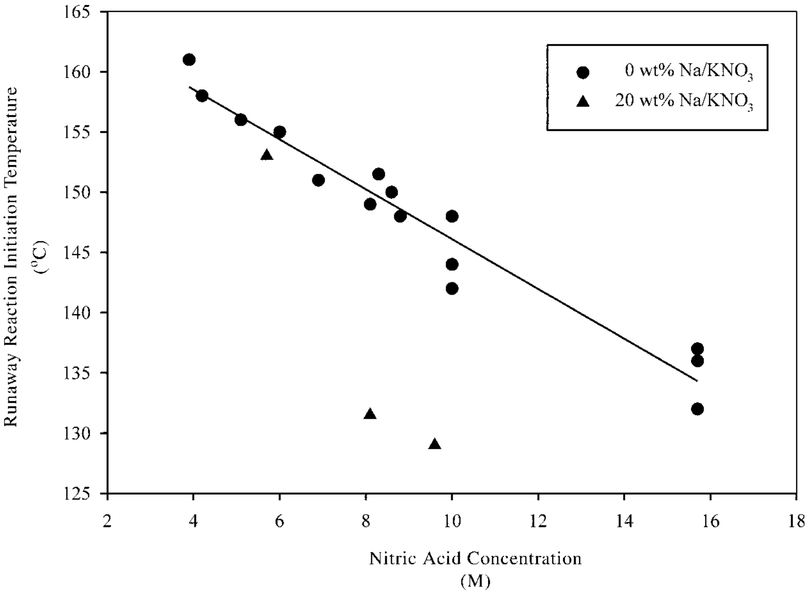

Figure 1. Colven data—initiation temperature for runaway TBP/nitric acid reaction.

product gases during the oxidation of TBP degradation products resulted in a cooling mechanism that more than balanced the heat from oxidation. As long as the TBP was in contact with an aqueous phase, water, the main coolant in the organic phase, was replenished by interfacial mixing by gas produced from oxidation in the aqueous phase. The results from Smith's experiments were applied to canyon evaporator operation just after shutdown when nitric acid-soluble organic material would be present in the aqueous phase to generate the bubbling required for mixing; however, Laurinat et al.[1] showed that mixing in a canyon tank during inadvertent steam heating was sufficient to replenish water extracted by TBP and a runaway reaction would not occur.

The dissolved solids used by Colven to measure the runaway reaction initiation temperatures were either sodium or potassium nitrate ($NaNO_3$ or KNO_3) or a combination of the two salts.[2] In the current work, aluminum nitrate ($Al(NO_3)_3$) was selected as the dissolved metal nitrate salt for the majority of the experiments for its ability to increase the extraction of nitric acid by a "salting-out effect." When a salting agent is added to the aqueous phase, extraction of nitric acid is enhanced by a combination of effects. The higher concentration of nitrate anions improves extraction by mass action. The activity of the nitric acid also increases due to complexation of water by aluminum, which then becomes unavailable as "free solvent."[5] The effectiveness of $Al(NO_3)_3$ as a salting agent should be better than the monovalent cations based on the size of the hydrated ion and known hydration number (6 vs 4 for $NaNO_3$ and KNO_3).[6,7] Thompson[6] demonstrated that $Al(NO_3)_3$ was a much better salting agent than $NaNO_3$ for nitric acid and selected lanthanide and actinide elements.

EXPERIMENTAL

Solution Preparation

Reagent-grade TBP, nitric acid, and $Al(NO_3)_3$, $NaNO_3$, and KNO_3 salts were used to prepare the solutions for the runaway reaction experiments. The concentration and density of the nominally 70 wt% nitric acid were measured to ensure that accurate dilutions were made during the preparation of the aqueous phase solutions. The TBP was prepared by contacting one volume (12 mL) of organic solution with five volumes (60 mL) of aqueous solution to maximize extraction of nitric acid. Only slight differences between the initial and equilibrium nitric acid concentrations would be expected because of the small organic to aqueous phase ratio. The aqueous solutions were prepared by transferring the desired mass of the metal nitrate salt to a beaker. The desired masses of deionized water and nitric acid were then added in succession. The mass of nitric acid required to prepare the solutions was calculated using nitric acid densities reported by Davis et al.[8] and the measured concentration of the starting reagent. Following the addition of all reagents, the metal nitrate salts were dissolved by stirring with a magnetic stir bar. For aqueous solutions containing metal nitrate salt concentrations approaching the solubility limit, it was necessary to gently heat the solution to obtain complete dissolution within a convenient time. The aqueous and organic phases were mixed for 2 minutes using a small separatory funnel and allowed to settle for 5 minutes prior to separation.

RSST Operation

The initiation temperatures for runaway TBP/nitric acid reactions were measured using a Reactive System Screening Tool™ (RSST™) manufactured by Fauske and Associates, Inc.[9] The RSST™ is a nearly adiabatic calorimeter equipped with temperature and pressure sensors to allow real-time data monitoring and acquisition. A well-insulated, 10-mL test cell was fitted with a small heater, which allowed heating the contents at a controlled rate. The test cell is normally sealed within a high-pressure containment vessel that serves as both a pressure simulator and a safety vessel; however, the TBP/nitric acid experiments were performed by sealing the safety vessel at atmospheric pressure before heating. To perform an experiment, a 10-mL aliquot of TBP previously equilibrated with a nitric acid solution was transferred to a new test cell. A small magnetic stirrer was added to the cell to provide stirring during the experiment. The RSST™ control system was programmed to increase the temperature of the TBP at nominally 1°C/minute. The runaway reaction initiation temperature was determined by monitoring the temperature of the TBP and pressure of the RSST™ safety vessel as a function of time. The experiments were terminated when the temperature of the TBP reached 200°C by turning off the cell heater.

RESULTS AND DISCUSSION

Thermal stability experiments were performed at 0, 5, 10, and 20 wt% dissolved solids ($Al(NO_3)_3$, $NaNO_3$, and KNO_3) using nitric acid concentrations ranging from 4 to 15 M. The runaway reaction initiation temperature for the experiments was defined by the time period when a rapid increase in the pressure of the RSST™ safety vessel was initially seen. The procedure for defining the initiation temperature is illustrated on Fig. 2. Using the pressure profile of the safety vessel (i.e., pressure vs time data), the time of the initial pressure spike was noted. However, due to uncertainties in establishing the exact point of initiation, the time was generally defined as a 1-minute interval. The initiation temperature was then determined from the corresponding temperature vs time data. In most experiments, the 1-minute interval in which the initial pressure spike occurred corresponded to a range of temperatures due to the excessive self-heating of the TBP. When this behavior was seen, the average of the temperature range was designated the runaway reaction initiation temperature. Data from the experiments are summarized in Table 1.

To compare the initiation temperatures for a runaway TBP/nitric acid reaction measured by Colven and the data presented in Table 1, the initiation temperature as functions of nitric acid and dissolved solids concentrations for both data sets are plotted in Fig. 3. Only the linear regression line for the Colven data at 0 wt% dissolved solids is shown to facilitate the comparison. Inspection of the data shows that there is good agreement between both data sets at 0 wt% dissolved solids with the initiation temperature gradually decreasing with increasing nitric acid concentration. The decrease in the

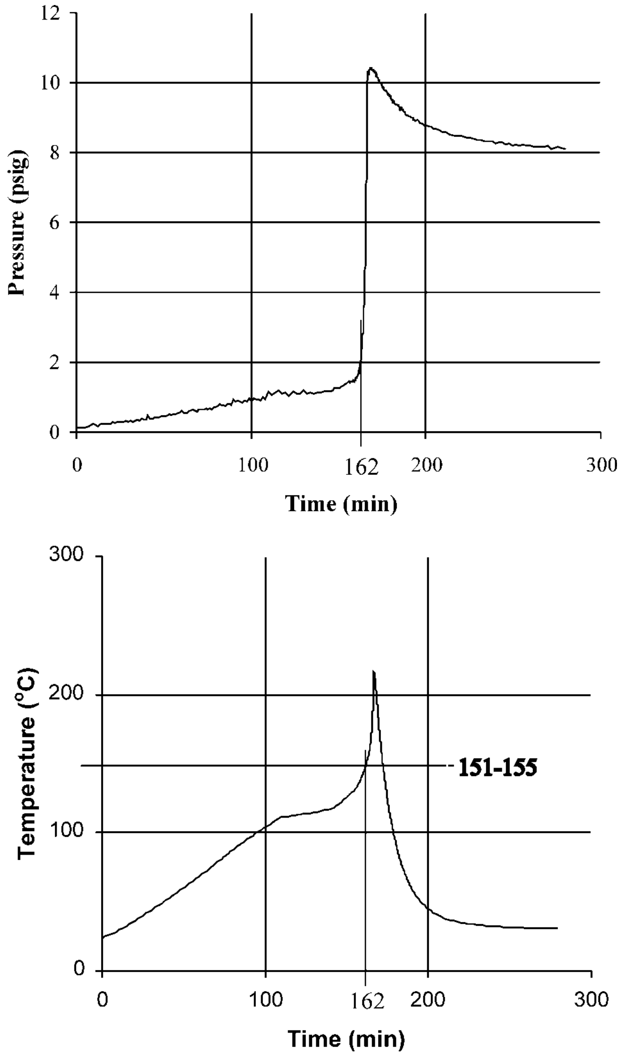

Figure 2. Defining the initiation temperature for a runaway TBP/nitric acid reaction (Run No. TBP 0/8-3).

Table 1. Runaway reaction initiation temperatures.

	Aqueous				
Run number	Nitric acid (M)	$Al(NO_3)_3$ (wt%)	Organic nitric acid (M)	Initiation temperature range (°C)	Average initiation temperature (°C)
TBP 0/4-3[a]	4.00	0	2.33	155–159	157
TBP 0/8-2[a]	8.00	0	3.37	149–152	150
TBP 0/8-3[b]	8.00	0	3.08	151–155	153
TBP 0/10-1	10.00	0	3.51	143–145	144
TBP 0/12-1	12.00	0	4.15	139	139
TBP 0/13-1	13.00	0	4.53	141–143	142
TBP 0/14-1	14.00	0	4.83	137	139
TBP 0/15-2[a]	14.99	0	5.78	139	139
TBP 0/15-3[a]	15.00	0	5.79	134–140	137
TBP 5/4-7[a]	4.00	5.00	2.33	155–159	157
TBP 5/4-8	4.00	5.00	2.37	153–156	154
TBP 5/6-2	6.00	5.00	2.83	149–152	150
TBP 5/8-1[a]	8.00	5.00	3.37	145–147	146
TBP 5/8-2[c]	8.00	5.02	3.21	147–149	148
TBP 5/10-1[a]	10.00	5.00	3.82	143	143
TBP 5/12-3[a]	11.99	5.00	4.37	139	139
TBP 5/12-4[a,d]	12.00	5.01	4.37	139–140	139
TBP 10/4-1	4.00	10.01	2.48	151–154	152
TBP 10/4-2[e]	4.00	10.00	2.06	155–156	155
TBP 10/6-1	6.00	10.01	2.97	148–151	149
TBP 10/8-1	8.00	10.01	3.43	146–148	147
TBP 10/8-2[c]	8.00	10.01	3.27	147	147
TBP 10/9-1	8.99	10.01	3.67	147–149	148
TBP 10/10-1	10.00	10.00	3.89	145–147	146
TBP 10/10-2	10.00	10.00	3.89	145–147	146
TBP 20/4-1[a]	4.00	20.00	2.76	147–150	148
TBP 20/4-2	4.00	19.99	2.81	154–158	156
TBP 20/6-1[a]	6.00	20.00	3.14	148–150	149
TBP 20/6-2	6.00	20.00	3.08	151–154	152
TBP 20/6-3	6.00	19.99	3.23	146–149	147
TBP 20/7-1	7.00	20.00	3.43	139–140	139
TBP 20/7-3	7.00	20.00	3.62	149–151	150
TBP 20/7-4	7.00	20.00	3.48	146–150	148
TBP 20/8-1[a]	8.00	20.00	3.70	146–149	147

[a] Estimated organic phase nitric acid concentration.

[b] Two-phase experiment.

[c] $NaNO_3$ used as dissolved solid.

[d] Three-phase experiment.

[e] KNO_3 used as dissolved solid.

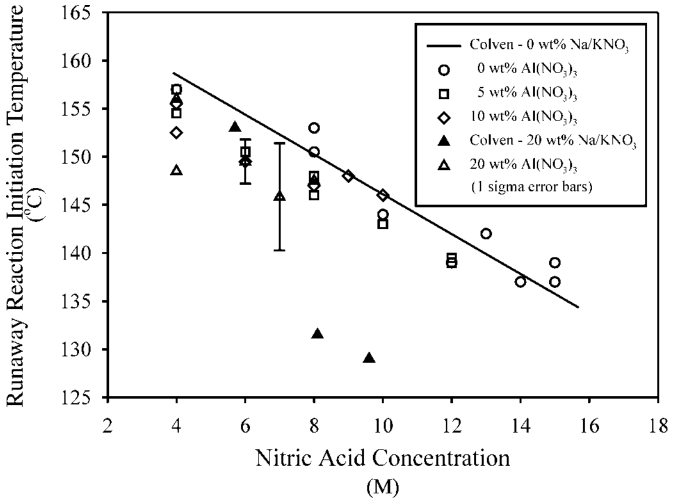

Figure 3. Effect of acid concentration and solids content on the initiation temperature for a runaway TBP/nitric acid reaction.

initiation temperature is due to the increase in the available oxidant (nitric acid) extracted by the TBP. The minimum initiation temperature, 137°C, measured at 14 to 15 M nitric acid is consistent with the values (132 to 137°C) measured by Colven at nominally 15.7-M nitric acid. The initiation temperatures measured using TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% dissolved solids show a small dependence on the salt concentration due to the salting-out effect. From Fig. 3, it is also apparent that the initiation temperatures measured using solutions containing 20 wt% $Al(NO_3)_3$ exhibit much more scatter than the solutions containing 0, 5, or 10 wt% dissolved solids. In retrospect, it is possible that the mixing time was not sufficient to allow the nitric acid extraction to reach equilibrium due to the viscous nature of the high salt-containing solutions.

Correlation of Initiation Temperature with Extracted Nitric Acid Concentration

The decrease in the runaway reaction initiation temperature with increasing dissolved solids content is due to the increased extraction of nitric acid due to the salting-out effect. To illustrate this point, duplicate samples of the TBP used to perform a majority of the RSST™ experiments were analyzed for free acid to determine the amount of nitric acid which was extracted by the TBP (see Table 1). To obtain an estimate of the nitric acid extracted by the TBP used in experiments for which samples were not analyzed, a series of extractions was performed with TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% $Al(NO_3)_3$. Data from the extractions (Fig. 4) are consistent with the empirically smoothed data reported by Davis et al.[8] (for no dissolved solids).

From inspection of Fig. 4, it is seen that the addition of $Al(NO_3)_3$ to the various nitric acid solutions did not have a measurable effect on the concentration of nitric acid in the organic phase until the aqueous phase contained 20 wt% $Al(NO_3)_3$. This is surprising given the small decrease in the runway reaction initiation temperature observed for TBP contacted with nitric acid solutions containing 5 and 10 wt% $Al(NO_3)_3$. It is possible that the titration procedure was not sensitive enough to resolve the difference between the amount of nitric acid extracted from the aqueous phase below 20 wt% $Al(NO_3)_3$. Since the nitric acid concentrations for the TBP contacted with acid solutions containing 5 and 10 wt% $Al(NO_3)_3$ differed little from the data reported by Davis, the smoothed data were used to estimate the concentration of nitric acid in the TBP samples contacted with aqueous phases containing 0,

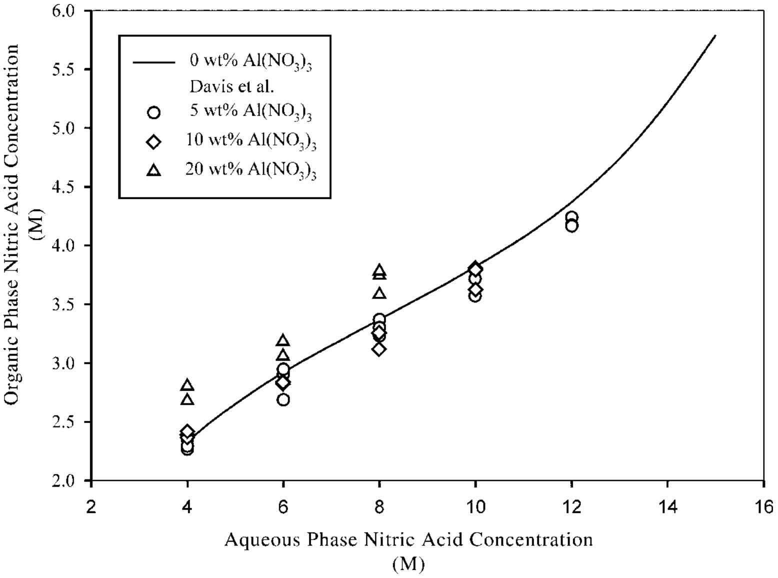

Figure 4. Extraction of nitric acid into pure TBP.

5, and 10 wt% dissolved solids. For experiments performed with an aqueous phase containing 20 wt% $Al(NO_3)_3$, the measured values were used to estimate the amount of extracted nitric acid. The estimated concentrations are summarized in Table 1.

The Davis data and the measured values for TBP contacted with an aqueous phase containing 20 wt% $Al(NO_3)_3$ were also used to estimate the concentration of nitric acid in the TBP samples used by Colven to measure the initiation temperature for a runaway TBP/nitric acid reaction. Data from Colven's experiments, including the estimated organic phase nitric acid concentration, are summarized in Table 2.

Data from Tables 1 and 2 were plotted in Fig. 5 to show the initiation temperature for a runaway TBP/nitric acid reaction as a function of the nitric acid concentration in the organic phase. From Fig. 5, a general

Table 2. Estimated organic phase nitric acid concentrations for Colven data.

Aqueous phase			
Nitric acid (M)	$Al(NO_3)_3$ (wt%)	Est. organic phase nitric acid (M)	Initiation temperature (°C)
3.9	0	2.294	161
4.2	0	2.398	158
5.1	0	2.678	156
6.0	0	2.920	155
6.9	0	3.128	151
8.1	0	3.392	149
8.3	0	3.436	151
8.6	0	3.502	150
8.8	0	3.546	148
10.0	0	3.700	142
10.0	0	3.700	144
10.0	0	3.700	148
15.7	0	N/A[a]	132
15.7	0	N/A[a]	136
15.7	0	N/A[a]	137
5.7	20	3.09	153
8.1	20	3.75[b]	131
9.6	20	N/A[a]	129

[a] Outside bounds of available data.
[b] Extrapolated value using data at 8-M nitric acid.

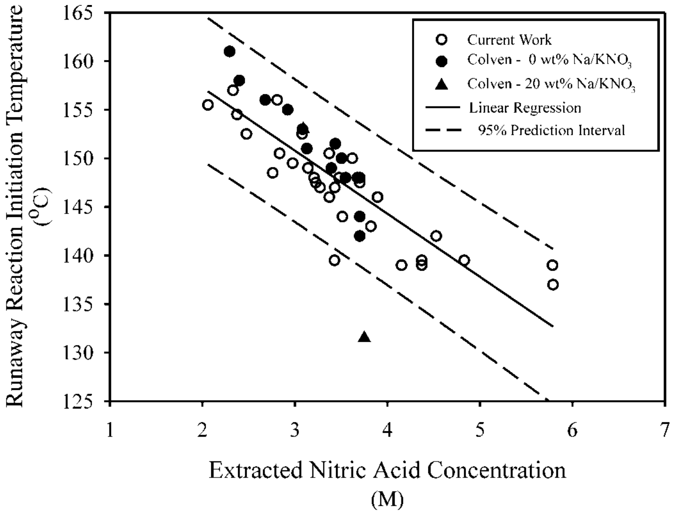

Figure 5. Correlation of runaway reaction initiation temperature with extracted nitric acid concentration.

linear decrease in the initiation temperature as the extracted nitric acid concentration increases is seen. This behavior is not unexpected. The initiation temperature should decrease as the amount of oxidant (nitric acid) increases. The higher nitric acid concentration permits a faster reaction (oxidation) rate at a lower temperature which reduces the temperature where runaway reaction occurs.

The data plotted in Fig. 5 also illustrate that the runaway reaction initiation temperatures measured by Colven using TBP contacted with an aqueous phase containing 8 to 10 M nitric acid and 20 wt% Na/KNO_3 are excessively low and inconsistent with the other data. An extrapolation of the data plotted in Fig. 4 was used to estimate the extracted nitric acid concentration for one of the two Colven data points (8.1 M nitric acid and 20 wt% Na/KNO_3). The measured initiation temperature for this experiment is approximately 15°C below the expected value based on the linear regression used to correlate the data. It falls outside the 95% prediction intervals given in the figure. One would also expect the initiation temperature for the Colven experiment performed using an aqueous phase nitric acid concentration of 9.6 M to be approximately 10°C higher based on the experimental data. Therefore, the margin of safety for the postulated accident involving inadvertent heating of a canyon tank is much larger than indicated by the previous work.

Effect of Other Variables on Initiation Temperature

Several RSST™ experiments were performed to evaluate the effect of other variables (nitrate salt and number of phases) on the initiation temperature for a runaway TBP/nitric acid reaction. A baseline RSST™ experiment was also performed using pure TBP to ensure that no observed exothermic behavior was due to TBP thermal decomposition products. In this experiment (TBP 0/0-1), the TBP temperature increased at nominally 1°C/minute up to 200°C and no self-heating was observed.

Since the dissolved solids used by Colven to measure the initiation temperature for a runaway TBP/nitric acid reaction were either $NaNO_3$ or KNO_3, RSST™ experiments were performed for comparison using TBP contacted with nitric acid solutions containing both of these salts. Two experiments (TBP 5/8-2 and TBP 10/8-2) were performed using $NaNO_3$ and one (TBP 10/4-2) with KNO_3 as the dissolved solid. The runaway reaction initiation temperatures measured for these experiments were almost identical to the temperatures measured in experiments using the same nitric acid concentration and $Al(NO_3)_3$ as the dissolved solid (see Table 1). Based on these results, the observed salting effect of $Al(NO_3)_3$ was not significantly greater than the effect for $NaNO_3$ and KNO_3 at these concentrations of dissolved solids. It is likely that the enhanced salting effect was obscured by the accuracy of temperature and pressure measurements in the RSST™ containment vessel, which did not provide completely adiabatic conditions.

RSST™ experiments were also performed to evaluate the effect of additional phases (aqueous and solid) on the thermal behavior of the TBP samples. One experiment (TBP 0/8-3) was performed in which a 1-mL aliquot of the aqueous phase used to equilibrate the TBP was also added to the RSST™ test cell. The presence of the aqueous phase had little effect on the runaway reaction initiation temperature. The measured value was approximately the same (153 vs 150°C) as the temperature measured during an experiment (TBP 0/8-2) performed with just the organic phase contacted with an aqueous solution containing the same nitric acid and $Al(NO_3)_3$ concentrations. The only noticeable difference in thermal behavior was the extended time required to evaporate the aqueous phase prior to runaway reaction occurring.

A second experiment was performed in which organic and aqueous phases and a small amount of solid $Al(NO_3)_3$ were added to the RSST™ test cell. In this experiment (TBP 5/12-4), a single seed crystal was added to the separated aqueous phase following contact with TBP. The seeded solution was placed in an ice bath to promote crystallization. Within a few minutes, crystals had formed. The two-phase mixture was removed from the ice bath and allowed to return to room temperature. A 1-mL aliquot of the mixture, including solid $Al(NO_3)_3$ crystals, was added to the RSST™ test cell with the organic phase. The presence of the aqueous and solid $Al(NO_3)_3$ phases had no effect on the runaway reaction initiation temperature. The initiation temperature, 139°C, was the same as measured during an experiment (TBP 5/12-3) using the organic phase alone, which had been contacted with an aqueous solution containing the same concentrations of nitric acid and $Al(NO_3)_3$. Like the two-phase experiment, the only difference in the thermal behavior of the two experiments was the extended time required to evaporate the aqueous phase prior to initiation of the runaway reaction.

CONCLUSION

Small-scale experiments were used to investigate the thermal stability of TBP contacted with an aqueous phase containing 4 to 15 M nitric acid and 0 to 20 wt% dissolved solids. In these experiments, an RSST™ was used to measure the initiation temperature for a runaway TBP/nitric acid reaction. The initiation temperature was defined by the time and corresponding temperature when a rapid increase in pressure was initially seen. Initiation temperatures measured for TBP contacted with nitric acid solutions containing no dissolved solids were in good agreement with values measured by Colven, showing a gradual decrease in initiation temperature with increasing aqueous phase nitric acid concentration. The decrease in the initiation temperature is due to the increase in the available oxidant (nitric acid) extracted by the TBP. The initiation temperatures measured using TBP contacted with nitric acid solutions containing 5, 10, and 20 wt% dissolved solids showed a small dependence on the salt concentration. The slight lowering of the initiation temperature was due to the increased extraction of nitric acid from the salting-out effect of the dissolved solids.

To illustrate the effect of extracted nitric acid on the runaway reaction initiation temperature, the amount of acid extracted by the TBP was measured or estimated for the thermal stability experiments and the data reported by Colven. When the runaway reaction initiation temperature was plotted as a function of the extracted nitric acid concentration, the temperature decreased linearly with increasing concentration. A higher nitric acid concentration in the TBP resulted in a faster reaction (oxidation) rate at a lower temperature, which reduced the temperature where runaway reaction occurred. The correlation also illustrated that initiation temperatures measured by Colven using TBP contacted with an aqueous phase containing 8 to 10 M nitric acid and 20 wt% Na/KNO_3 were excessively low and inconsistent with this correlation. The measured initiation temperatures were 10 to 15°C below the expected values based on the linear regression used to correlate the data. Therefore, the margin of safety for the postulated accident involving inadvertent heating of a canyon tank is much larger than indicated by Colven's work.

A number of RSST™ experiments were performed to look at the effect of other variables (nitrate salt and number of phases) on the initiation temperature for a runaway TBP/nitric acid reaction. Experiments were performed in which the dissolved solids were changed from $Al(NO_3)_3$ to $NaNO_3$, or KNO_3. No significant effect on the initiation temperature was observed. RSST™ experiments were also performed to evaluate the effect of additional phases (aqueous and solid) on the thermal behavior of the TBP samples. Neither the presence of the aqueous phase originally used to contact the TBP nor a small amount of undissolved solids in the aqueous phase had a significant effect on the runaway reaction initiation temperature. The only noticeable difference in thermal behavior was the extended time required to evaporate the aqueous phase prior to initiation of the runaway reaction.

REFERENCES

1. Laurinat, J.E.; Hassan, N.M.; Rudisill, T.S.; Askew, N.M. *Analysis of Steam Heating of TBP/n-Paraffin/Nitric Acid Mixtures*; WSRC-TR-98-00171, Rev. 1; Westinghouse Savannah River Company: Aiken, SC, July 22, 1998.
2. Colven, T.J. Jr. *Nitric Acid Recovery Units Permissible Steam Pressure in Reboilers*; DPST-56-243; E. I. Du Pont de Nemours & Company: Aiken, SC, 1956, April 27.
3. Colven, T.J., Jr.; Nichols, G.M.; Siddall, T.H. Interim technical report. *TNX Evaporator Incident, January 12, 1953*; DP-25; E. I. du Pont de Nemours & Company: Aiken, SC, 1953, May 15.
4. Smith, J.R.; Cavin, W.S. *Isothermal Heat Measurements of TBP-Nitric Acid Solutions*; WSRC-TR-94-0540; Westinghouse Savannah River Company: Aiken, SC, 1994, December 16.
5. Morrison, G.H.; Freiser, H. *Solvent Extraction in Analytical Chemistry*; John Wiley & Sons, Inc.: New York, NY, 1957; 43–45.

6. Thompson, M.C. *Distribution of Selected Lanthanides and Actinides Between 30% TBP in n-Paraffin and Various Metal Nitrate Solutions*; DP-1336; E. I. du Pont de Nemours & Company: Aiken, SC, 1973, November.
7. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed.; John Wiley & Sons, Inc.: New York, NY, 1988; 132, see also 215.
8. Davis, W., Jr.; Mrochek, J.; Hardy, C.J. The system: tri-n-butyl phosphate (TBP)–nitric acid–water–I. J. Inorg. Nucl. Chem. **1966**, *28*, 2001–2014.
9. Creed, M.J.; Fauske, H.K. An easy inexpensive approach to the DIERS procedure. Chem. Eng. Prog. **1990**, *86* (3), 45–49.