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PRESENT STATUS OF THE INVESTIGATION OF
AQUEOUS SOLUTIONS SUITABLE FOR USE
IN A THORIUM BREEDER BLANKET

M. H. Lietzke
W. L. Marshall



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M H Lietzke and W L Marshall

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Present Status of the Investigation of Aqueous Solutions Suitable for Use
in a Thorium Breeder Blanket.

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Abstract

The present report summarizes the work that has been done in the search for an aqueous solution suitable for use in a thorium breeder blanket. Some of the work has been previously reported in H R P and Chemistry Division Quarterly Reports, but data concerning the basic nitrate system and the phosphate-nitrate system are reported here for the first time. It has been felt desirable to summarize all the work in this report so that an overall-picture may be had of the exploratory work that has been done to date

Thorium Nitrate-Water System

The system thorium nitrate-water has been studied by Templeton⁽¹⁾ from 20° C to 160° C and by Marshall, Gill, and Secoy⁽²⁾ from 20° C to 211° C. Above 130° C nitrogen oxides are liberated and basic thorium oxide is precipitated. However, in a closed system the vapor phase appears to equilibrate with the liquid phase, and the system in this form does not show precipitation until a temperature of about 230° C is reached for systems containing 80-90% thorium nitrate by weight. The experimental data indicate that a solution of thorium nitrate containing 1000 g Th/l will be stable in the temperature range 120° C to 230° C and that solutions containing lower concentrations of thorium will be stable from room temperature to the 100-230° C range.

Effect of Excess Nitric Acid on the Thorium Nitrate-Water Systems

Marshall and Secoy⁽³⁾ investigated the effectiveness of excess nitric acid in preventing hydrolysis of thorium nitrate solutions at high temperatures. Solutions with NO₃/Th ratios of 3.95, 5.47, and 6.65 were prepared in concentrations that varied from 20 to 400 g Th/l. The first mole of excess nitrate caused the greatest elevation in precipitation temperature, while the vapor phase coloration was much greater per unit change of nitrate after the initial four moles were added to the thorium. Crystalline solids appeared in the concentrated regions, the composition of which may have corresponded to acid salts. The crystalline compounds were reversible in solubility over the time of the experiments as contrasted to the apparent irreversibility in the solubility of the hydrolysis products. Solutions containing 400 g Th/l with NO₃/Th ratios of 5.47 and 6.65 were stable to temperatures between 300 and 340° C.

Effect of Excess Base on the Thorium Nitrate-Water System

A series of experiments was performed by Lietzke and Marshall to determine whether solutions in which the thorium had been partially hydrolyzed would be stable at higher temperatures. The partial hydrolysis was accomplished in two ways (1) by the addition of LiOH to a stoichiometric thorium nitrate solution, and (2) by precipitating thorium hydroxide and dissolving the precipitate in less than the stoichiometric amount of nitric acid.

Table 1 shows the results obtained with thorium nitrate solutions that had been partially hydrolyzed by the addition of LiOH. The effect of fluoride both on the partially hydrolyzed and on the stoichiometric thorium nitrate solutions is also shown. The rate of heating in each case was 2.5° C/min.

Table 1

Precipitation Temperatures of Thorium Nitrate Solutions to Which Lithium Hydroxide and Lithium Fluoride Have Been Added.

Thorium Concentration	NO ₃ ⁻ /Th	OH ⁻ /Th	F ⁻ /Th	Observations
400 g Th/l	4	1.8	0	Cloudy at 210° C, abundant ppt at 238° C.
	4	1.8	1	Abundant ppt. between 180° and 188° C
	4	1	1	Ppt at 225° C.
	4	0	1	Some particles at 260° C, much cloudiness at 264° C.
	4	0	1.8	Cloudy ppt at 248° C.

None of the precipitates redissolved upon cooling to room temperature.

The second method of preparing partially hydrolyzed thorium nitrate solution consisted in precipitating thorium hydroxide from diluted aliquots of thorium nitrate solution by saturation with ammonia gas. The thorium hydroxide was washed by centrifugation and decantation, then dissolved in sufficient concentrated nitric acid to give a NO_3/Th ratio of 2.2. The thorium concentration was varied from 200 g Th/l to 1000 g Th/l. Table 2 summarizes the data obtained upon heating these solutions at temperatures of 70° C and 80° C.

Table 2

Precipitation Temperatures of Thorium Nitrate Solutions With a Hydroxyl

Number of 18

Thorium Concentration	Temp. ° C.	Observations
200 g/l	70	No ppt. in 24 hrs.
	80	Ppt. after 3 hrs
400 g/l	70	Ppt. in 24 hrs.
530 g/l	70	No ppt in 24 hrs.
	80	Cloudy after 3 hrs. Ppt after 24 hrs.
800 g/l	70	No ppt. in 24 hrs.
	80	Cloudy after 24 hrs Ppt after 48 hrs.
1000 g/l	70	Ppt after 1½ hrs.

In all cases the precipitates did not redissolve upon cooling to room temperature. When HF was added to the solutions to give a F/Th ratio of 1.0 precipitation occurred upon standing at room temperature. The precipitate would not redissolve upon heating.

ThO₂-H₃PO₄-H₂O System

The marked solubility of ThO₂ or Th₃(PO₄) in concentrated phosphoric acid and the low neutron cross-section of phosphorus favor the consideration of the ThO₂-H₃PO₄ system as a possible breeder blanket solution⁽⁴⁾. Although apparently stable phosphate solutions containing up to 1100 g Th/l with PO₄/Th ratios of 5 to 7 could be prepared, the high viscosities of these solutions leave considerable doubt as to their applicability. However, solutions containing a PO₄/Th ratio of 10 with a total Th concentration of 400 g/l are stable at 250°-300° C and have a viscosity little higher than that of concentrated phosphoric acid.

A series of experiments was performed⁽⁵⁾ in an effort to lower the viscosity of the thorium phosphate solutions containing the PO₄/Th ratios of 5 to 7 without at the same time decreasing the thorium concentration. It was found that some concentrated hydrofluoric acid can be added to the concentrated H₃PO₄ mixture but that precipitation occurs before any significant improvement in properties becomes evident, dissolving ThF₄ in H₃PO₄ appears to give a similarly viscous mixture at PO₄/Th ratio of 5. Solutions in H₂PO₃F seem to act similarly to those in H₃PO₄ with no improvement in solubility or viscosity. Adding H₂SO₄ to H₃PO₄-Th₃(PO₄)₄ mixtures lowers the solubility under otherwise similar conditions and appears to offer no advantages.

The ThO₂-H₃PO₄-HNO₃ System

Table 3 summarizes data obtained by Marshall in a study of the thorium-phosphate-nitrate system.

Table 3

Thermal Phase Stability of the ThO₂-H₃PO₄-HNO₃ System

Molarity H ₃ PO ₄	Molarity HNO ₃	Molarity ThO ₂	Mole Ratio Th/PO ₄ /NO ₃	After 1 1/2 weeks at 125-150° C
5.0	5.0	5.0	1/1/1	Completely solid (white)
5.0	5.0	2.5	1/2/2	" " "
5.0	5.0	1.67	1/3/3	Ca 95% " "
10.0	5.0	5.0	1/1/2	Completely " "
10.0	5.0	2.5	1/2/4	Ca. 60% " "
10.0	5.0	1.67	1/3/6	Ca 1% " "
7.5	2.5	2.5	1/1/3	Completely " "
7.5	2.5	1.25	1/2/6	Ca. 90% " "

From the data in Table 3 it appears that the ThO₂-H₃PO₄-HNO₃ system is stable at elevated temperatures only in the presence of concentrated H₃PO₄. In all cases the precipitates did not redissolve upon cooling to room temperature

Thorium Systems Involving SO₄⁼ and F⁻(5)

Preliminary results on dissolving Th(OH)₄ in an HF-H₂SO₄ mixture, containing one HF and one and one half H₂SO₄ molecules per molecule of Th(OH)₄ indicated a "solubility" of about 200 g Th/l. (There was evidence for the presence of a colloid.) Immediate dissolution occurred followed by slow precipitation. Changing the F⁻/SO₄⁼/Th(IV) ratios while maintaining stoichiometric neutrality showed no improvement in solubility. It was also found to be impossible to prepare similar solutions containing higher concentrations of thorium (400 and 600 g Th/l). The pH of all the supernatant solutions indicated that some

hydrolysis occurred during the precipitation. A solution made up to contain 50 g Th/l as the nitrate plus one mole of HF, one of HNO₃, and one and one half of H₂SO₄ per mole of thorium showed some precipitation on standing a few days. No hydrolysis would be expected to occur in this solution.

Thorium Systems Involving SO₄⁼, SeO₄⁼, Li⁺, and Mg⁺⁺.

A large number of exploratory tests with various combinations of thorium sulfate or thorium selenate with lithium and magnesium salts of the same anions have indicated

(1) The addition of the lithium or magnesium salt increases the solubility of the thorium salt at 25° C but not to a very great extent. The maximum amount of thorium that can be kept in solution is of the order of 100-150 g Th/l.

(2) In all cases thorium selenate is more soluble than the sulfate, but not sufficiently more so to compensate for the higher neutron cross-section of selenium.

(3) At temperatures above 100° C the solubility of the Th salts decrease rapidly. The formation of precipitates and their dissolution at room temperature are both slow. There is a strong possibility that the "solutions" at 25° C are actually metastable and that, in time, much of the thorium would precipitate.

(4) At 43° C a solution of thorium sulfate may be prepared containing 19 g Th/1000 g H₂O. This is the maximum solubility of thorium sulfate in water.

Conclusions

(1) Of the systems investigated only two, the $\text{Th}(\text{NO}_3)_4$ + excess HNO_3 and the $\text{Th}_3(\text{PO}_4)_4$ + H_3PO_4 with a PO_4/Th ratio of 10, have both the necessary thermal stability and desirably low viscosity.

(2) From the standpoint of neutron capture cross-section the $\text{Th}_3(\text{PO}_4)_3$ - H_3PO_4 system is perhaps satisfactory. In the case of the $\text{Th}(\text{NO}_3)_4$ system separated N^{15} isotope would have to be used.

(3) There is no present evidence that corrosion in the nitrate system would be intolerable. However, the phosphate system attacks both Ti and Zr at relatively low temperatures and no satisfactory container is yet known for this system. A more thorough study of the corrosion properties of the solutions should be made.

(4) The radiation decomposition of nitrate (including the products formed under varying conditions) appears to be the most important unknown concerning the nitrate system. A preliminary experiment by Bidwell of Los Alamos using a uranyl phosphate - H_3PO_4 solution containing enriched U^{235} in the LITR showed no gross decomposition of phosphate ion.

(5) Whenever hydrolytic phenomena seem to be responsible for precipitation in thorium systems the time factor is very important. Solutions which seem to be stable at higher temperatures on short time heating usually show precipitation upon being held at much lower temperatures for a longer period of time.

(6) On the basis of the rather extensive survey that has been made it seems unlikely that any thorium systems other than the two mentioned will be found that satisfy both the thermal stability and low neutron capture cross-section requirements. However this statement cannot be made with certainty unless a thorough phase study is made of some of the systems investigated.

Dawson u. 1

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