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CORROSION AND STABILITY TESTS ON CHEMICAL POISONS
IN HIGH-TEMPERATURE WATER

by

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CORROSION AND STABILITY TESTS ON CHEMICAL POISONS IN HIGH-TEMPERATURE WATER

by

C. R. Breden and Alma Abers

ABSTRACT

Corrosion-stability tests have been made in static autoclaves at 500 and 600F on solutions of compounds having high neutron cross sections to evaluate their usefulness for shutdown purposes.¹

The only compound tested which appeared to be completely stable in 600F water was boric acid. Limited corrosion data did not show it to cause excessive corrosion of zirconium or stainless steel.

I. INTRODUCTION

The possibility of reactor control by use of chemical poisons dissolved in the water in the core is a subject of considerable interest to reactor designers. Chemical poisons refer here to chemical compounds of high neutron cross section, capable, in sufficient amounts, of poisoning the reactor.

A further specification was that the poison should be of such nature that it can be eliminated from the reactor, if desired, and the reactor used again. From the chemical standpoint this means that the poison (1) should not cause excessive corrosion of the reactor parts, and (2) should be sufficiently stable so it cannot deposit or plate out in the core where it could permanently poison the reactor.

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The number of chemical elements, and possibly available isotopes, whose cross section is high enough to be of interest is quite limited.

Those which have been considered are listed below with their respective thermal neutron cross sections.

<u>Element or Isotope</u>	<u>Thermal Neutron Cross Section, barns</u>
Gd	36,000
Sm	10,000
Cd	3,100
Li ⁶	950
B	750

Various compounds containing these elements were investigated to study their chemical stability and corrosive action on zirconium and AISI Type 347 stainless steel in water at 500 or 600F.

The results of these investigations, carried out under static conditions without irradiation, comprise the basis of this report.

The investigation was carried out in 3 chronological phases: (1) corrosion tests with visual observation to evaluate the thermal stability of the solution; (2) corrosion tests with chemical analysis to evaluate the thermal stability of the solution; and (3) stability tests using the spectrophotometer to follow changes.

The work reported covers the period April, 1950 to July, 1952.

II. TEST EQUIPMENT AND PROCEDURE

A. Equipment and Method

Stability-corrosion tests on the various solutions were run in static autoclaves at 600F, and later a few at 500F, for periods of two weeks or a month. Samples of machined Grade A crystal bar zirconium and machined Type 347 stainless steel, both in the form of cylinders, were included in the autoclaves so that the corrosion rate could be calculated from the weight change. In some of the earliest experiments small sections of crystal bar zirconium were tested without machining except in the cut ends. In these tests no stainless steel samples were included. Sealing of the autoclaves was accomplished by means of a copper gasket. Most of the solutions showed some decomposition after two weeks, and further testing was discontinued.

The autoclaves were Type 347 stainless steel with a capacity of approximately 100 ml. The autoclaves were cleaned periodically with a mixture of nitric and hydrofluoric acids, and washed thoroughly with distilled water. After each run, the autoclave was filled with 10% nitric acid and allowed to stand overnight; then it was washed well and rinsed with distilled water.

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The test samples were also cleaned by immersing in a mixture of hydrofluoric and nitric acids, followed by thorough washing in distilled water. When the samples were reinserted for retest they were washed with water, degreased with acetone or trichloroethylene, and rinsed thoroughly with distilled water.

At the start of each test, 50 ml of the chemical solution were charged into the autoclave. For air-saturated testing, the autoclave was then sealed off and placed in a furnace maintained at a temperature of 600F. For the degassed conditions the charged autoclave was covered loosely with its top, and by means of heating with a hand torch, steam was expelled for a period of several minutes; then the top was tightened in place. One analysis of water prepared in this manner showed that 1.6 ml oxygen was present; therefore, it should be recognized that test solutions designated as degassed probably contained a small amount of oxygen. At the end of the test the corrosion samples were rinsed in distilled water, dried, and weighed to determine weight changes.

B. Analytical Methods

Chemical stability may best be determined by measuring the extent of hydrolysis of the chemical compounds under the conditions of the test. The most convenient method of ascertaining any hydrolysis is the measurement of the pH of the solution before and after each test. While this method cannot be used to calculate qualitatively the extent of hydrolysis, it will indicate any change. The pH and the resistivity were the only quantitative data collected on the first few groups of test solutions. Resistivity is significant for fairly concentrated or highly ionized solutions, but for compounds, such as boric acid, which have an initially high resistivity the measurement at the conclusion of the run is insignificant. Distilled water, resistivity about 500,000 ohm-cm, when heated alone in the test autoclaves for a period of two weeks, will drop to a specific resistance of about 10,000 ohm-cm, depending upon the previous history of the autoclave and various other factors.

The lack of reproducibility in the numerical data collected during the first few months of testing, and the lack of information regarding the cause of some of the visual changes observed, indicated that direct analytical information on the poisoning element would be desirable and much more conclusive. Accordingly, later tests of solutions at 600F were followed by a chemical analysis for the poisoning element in the untested and in the tested solution.

The analytical procedures for boron, cadmium and the rare earths are given in Appendix A. No attempt was made to analyze for lithium, as it was thought that the isotope Li^6 represented the poorest possibility, and standardization of an analytical method would have required considerable time.

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III. RESULTS

The results of the corrosion-stability tests are tabulated in Appendix C according to chemical composition as follows:

<u>Composition</u>	<u>Table</u>
Lithium salts	II
Boric acid solutions	III
Cadmium salts	IV
Rare earth salts	V

A. Lithium Salts

The lithium salts were run first because they were more readily available with a variety of anions. In most cases, zirconium alone was tested.

1. Lithium Chloride (LiCl)

Lithium chloride for two weeks at 600F did not cause much weight change in the samples tested, but at least in one instance a white oxide film was reported. Higher weight change occurred with longer exposure. The black residue noted gave a positive test for iron, resulting probably from the corrosion of the stainless steel autoclave. Both Experiments 9 and 10 showed a weight increase after two weeks, and a weight loss after additional testing.

2. Lithium Nitrate (LiNO₃)

Lithium nitrate produced considerably less corrosion than the lithium chloride. In general, yellow solutions resulted after the test; at first the color was attributed to the leaching of iron from the stainless steel autoclave, since almost all solutions gave a positive test for iron at the end of the test period. However, it has been found that the yellow color is often present under oxidizing conditions and is due to the presence of chromate ion leached from the stainless steel.

Experiments 11 and 12 showed a slight white film on the zirconium after two weeks and a small weight increase after the first two periods but no weight change after the third and fourth periods. None of the samples showed weight losses at any time.

3. Lithium Sulfate (Li₂SO₄·H₂O)

Lithium sulfate showed good corrosion behavior with respect to zirconium. Traces of white film were found in some cases, but, as with the nitrate, weight gains were characteristic of the first two periods followed

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by no weight change in the second two periods. No precipitate formation and no change in color of the solution were observed. The greatest change noted was in the drop in pH, which may be indicative of partial hydrolysis.

4. Lithium Metaborate (LiBO_2)

Lithium metaborate appeared to cause less corrosion of the zirconium than any of the lithium salts tested. The pH change was very slight during test, but a more noticeable change was in the resistivity which increased, probably due to increased hydrolysis at high temperature to form boric acid which is only slightly ionized.

In the ten-week test, tightly adhering orange crystals were found on the zirconium. These crystals have not been identified.

5. Lithium Tetraborate ($\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$)

Lithium tetraborate is more difficult to evaluate since the solubility at room temperature was below the concentration added, resulting in deposition of the salts on cooling. The weight changes of the washed samples, however, indicate a low rate of corrosion for the first two periods. The changes in pH and resistivity were similar to those for LiBO_2 but the actual pH values were considerably lower.

6. Lithium Hydroxide (LiOH)

The samples tested in lithium hydroxide showed very high weight increases, presumably due to the orange crystals deposited. It is of interest to note that the orange crystals observed, as well as those reported in the tests on LiBO_2 , appear to be associated with high pH.

B. Boric Acid Solutions

A complete listing of the boric acid test data are given in Table III, Appendix C. It will be noticed that the average weight change for zirconium in Experiments 19, 20, 47 and 48 is very low, and there are no visual changes in the solutions reported. The small increase in pH and the decrease in resistivity are probably due to a slight neutralizing reaction between the boric acid and the metal or an impurity, resulting in a compound more highly ionized than boric acid. These results appeared so promising that longer (10 weeks) tests were run (Experiments 85 and 86), and both zirconium and stainless steel samples were exposed. Under these conditions the zirconium showed evidence of slightly more corrosion than in the previous tests. The stainless steel showed slightly more corrosion than was usually produced by water alone, but there was no visual evidence of solution decomposition. The lack of consistency between the appearance of the zirconium in the 10-week tests as compared with the shorter tests is believed to be due to sample variations.

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Experiments 106-1 through 109-1 represent mixtures of lithium metaborate or tetraborate with boric acid to study the effect of pH. At pH values of 8.3 and 8.6 the weight change for zirconium appeared to be rather high. For stainless steel the weight changes were very low, excluding the sample from an autoclave that leaked. There was no consistent difference between aerated and degassed solutions.

The nitric acid Experiments 110-1 and 111-1 were run as part of the spectrophotometric studies to be described later. In spite of the low pH (1.6-6.4), the weight changes were not excessive. The oxidizing nature of nitric acid is undoubtedly an important factor in maintaining a protective oxide film.

The function served by lithium hydroxide in the remaining boric acid solutions listed in Table III is that of adjustment of the pH of the solution, which is important when attempting dissolution of the boric acid in as large quantities as possible for storage use. The higher pH favors increased solubility. Addition of lithium hydroxide to boric acid gives a resultant mixture of meta- and tetraborate compounds, so that these mixtures actually present no new data. Latimer and Hildebrand¹ make the following statement:

"In water solution, the ortho acid acts as a weak monobasic acid, i.e., its reactions are those of the meta acid, HBO_2 Upon the addition of hydroxide to the ortho acid the equilibrium, $2 \text{BO}_2^- + 2 \text{HBO}_2 = \text{H}_2\text{O} + \text{B}_4\text{O}_7^-$, is established, the equilibrium constant being about 10^3 ."

Therefore, mixtures of lithium hydroxide and boric acid correspond to some proportional mixture of boric acid, lithium metaborate, and lithium tetraborate. All of these had been tested previously as individual runs.

Experiments 112-1 through 117-1 represent duplicates of 3 slightly different ratios of lithium hydroxide and boric acid, resulting in solutions whose pH's were 8.8, 8.2, and 7.6. The weight changes in the zirconium are not excessive, but they are not consistent, even between duplicates, 3 out of 6 being negative.

¹W. M. Latimer, J. H. Hildebrand, "Reference Book of Inorganic Chemistry" (Rev. ed.; New York: Macmillan Co., 1940), pp. 83-84.

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Considering each pair, Experiments 112-1 and 113-1, with pH 8.8, showed the highest consistent weight change. In general, the appearance of the zirconium samples was good, except for Experiment 112-1 which exhibited some pitting, and for Experiment 114-1 which showed a deposit. The stainless steel samples, except for Experiment 112-1, showed consistent weight losses. The amount was small, however, and the appearance of the samples was good. The consistent presence of chromate in the solution after test, however, indicates definite attack of the stainless steel, confirming the consistent weight losses. As mentioned previously, the appearance of chromate in solution appears to be associated with an oxidizing condition.

The correlation between pH and the relative proportions of LiOH and H_3BO_3 , as determined by a titration experiment, was found to be as follows:

<u>pH</u>	<u>LiOH, moles</u>	<u>H_3BO_3, moles</u>
7.0	1	30
8.5	1	10
10.0	1	4

Experiments 118-1 through 120-1 were made with solutions corresponding to these 3 proportions, primarily to investigate changes in boric acid content during the test as determined by chemical analysis. Corrosion samples of zirconium and stainless steel were present for observation, but weight changes were not determined. The results showed that with solutions of pH 7 and 8.5 there was no change in boric acid content during the test. The solution of pH 10 did show a drop in the boric acid content. From the corrosion standpoint, the solution at pH 8.5 showed the greatest attack on both the zirconium, where the attack was in the form of tiny blisters and pits, and the stainless steel, where the surface had a dark dull film. These results, although too limited to warrant definite conclusions, suggest that the pH of 8.5 is more corrosive than pH 10 or pH 7 for both zirconium and stainless steel, at least when they are in the same solution. A correlation² of pH with the corrosion-erosion of steel shows a maximum point at pH 8 and minimum points at pH 6 and pH 10, respectively.

Although the mixture at pH 7 showed good stability with respect to change in boric acid content and low corrosive action, the presence of chromate ion in the solution leaves the desirability of this solution open to questions. If the oxygen content should be sufficiently low, this may not be a problem. The mixture at pH 10 does not apparently leach chromium from the stainless steel with the formation of chromates. It also seems to have a low corrosivity. However, according to the test data, it did not show good stability from the standpoint of boric acid content.

² J. M. Decker, H. A. Wagner, J. C. Marsh, "Corrosion-Erosion of Boiler Feed Pumps and Regulating Valves at Marysville, Second Test Program," Trans. ASME, 72, 19-26, (1950).

C. Cadmium Salts

Much importance has been attached to finding a suitable cadmium compound for use as a poison in the reactor since cadmium has, in effect, a positive temperature coefficient for neutron absorption in certain temperature ranges. Samarium, to a much less degree, also possesses this property but cadmium is more readily available in the form of salts and therefore deserved first effort.

The cadmium tests are summarized in Table IV, Appendix C. In the first series of tests, stability was judged solely on the basis of the appearance of the solution after testing. A cadmium chloride solution tested for two weeks at 600F contained a small amount of black residue which gave a positive test for iron. This material was probably magnetite.

Halides are corroding agents for stainless steel at high temperatures; therefore chloride solutions always contained some solid corrosion products at the end of two weeks. The chloride anion seemed to favor corrosion by production of Fe_3O_4 in the case of the lithium and cadmium salts, but the rare earth chlorides, to be described later, produced a red to orange precipitate containing Fe_2O_3 . Corrosion of zirconium in the chloride solutions appear to be negligible. The bromide, Experiment 126-1, showed an apparent increase in concentration after test, probably due to faulty analytical technique.

Solutions containing cadmium acetate (Experiment 28) resulted in a heavy percentage of decomposition of the salt, as judged by the amount of precipitate in solution and the marked increase in resistivity. Weight increases, probably due to deposition, were high. In regard to radiation stability, the only organic compounds to show any degree of stability are the aromatics; therefore no other aliphatic organic salts were tested.

Two-week tests with cadmium sulfate solutions at 600F yielded a clear solution with a small quantity of dirty yellow precipitate, which gave a positive test for iron and sulfur. The positive test for sulfur may be due to impurities in the cadmium sulfate as purchased. An analysis of Experiment 131-1 showed little change in concentration. The corrosion of the zirconium appeared to be low.

Cadmium nitrate was one of the first compounds to be tested. Visual inspection of the solution and exposed samples led to the conclusion that it was one of the best possibilities. A ten-week test was made during which time the test was interrupted at the end of 2, 6, and 10 weeks (Experiments 83 and 84) for visual examination. At the conclusion of the test the metal sample pieces appeared very shiny and silvery, suggestive of a cadmium-plated metal. Since the original solution had not been analyzed for cadmium initially, it was impossible to obtain any further information from this test, though the nitrate solution was clear as usual. Accordingly, 4 tests were run as follows (Experiments 99 thru 102): cadmium nitrate solution in the

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presence of zirconium and stainless steel, one each aerated and degassed tested at 500F and 600F for a period of 2 weeks. At the conclusion of the tests, a sample of the untested solution, and samples from Experiments 99 and 101, were quantitatively analyzed for cadmium with dithizone, with the following results:

Experiment	Time, wks	Temp, F	Cd/liter gm	% untested
Untested Solution	-	-	7.18	-
99	2	600	4.13	58
101	2	500	5.44	76

As is to be expected, the decomposition of cadmium nitrate is dependent upon temperature. By a careful study of the rare earth compounds, as discussed in the next section, it has been found that the nitrate ion is unstable and may cause the deposition of cadmium. For short-time (3 or 4 days) exposure to high temperatures the instability, while not desirable, may be tolerable.

The remaining data listed in Table IV were compiled with a view to measuring the extent of stability of the compounds listed. On two different occasions, a mixture of potassium iodide and cadmium iodide ($2K^+ + CdI_4^-$) was tested for a two-week period. In both instances the copper gasket sealing the autoclave was apparently attacked by the iodide ion, for, upon conclusion of the tests, only a small amount of moist, discolored deposit remained. The same situation resulted from the use of potassium cadmium cyanide. Here the solution was placed in a new, pickled stainless steel autoclave with a stainless steel gasket. Due, probably, to a faulty seal this solution had evaporated almost to dryness at the end of the two-week period yielding a white deposit, cellulose-like in appearance, which was insoluble in water. Both the iodide and cyanide complexes of cadmium are anionic, and it was hoped that this would give greater stability. Due to the attack of the copper gaskets and to the faulty seal with the stainless steel gasket the results are inconclusive. It would be desirable to repeat these tests using stainless steel instead of copper gaskets.

It has been reported³ that sodium cadmate, $Na_2 [Cd(OH)_4]$, and strontium cadmate, $Sr[Cd(OH)_4]$, have been prepared, but there seems to be a question whether they are true compounds or peptized hydroxide sols. If they are true compounds, they might offer definite possibilities, but if they are peptized sols there is a strong possibility that they would precipitate and deposit on fuel elements.

³F. Ephraim, "Inorganic Chemistry," (5th ed. (Rev.); New York: Interscience Publishers, Inc., 1948), p. 470.

D. Rare Earth Salts

Because of their high cross section, some of the rare earth elements have been of interest from the start of this investigation; thus, more tests have been made on rare earth compounds than any other group. The extremely high cost of the high-purity compounds combined with the low availability turned attention to a commercially available rare earth oxide mixture. Salts listed as "RE" in this report refer to an oxide mixture containing 26 % Gd_2O_3 , 58 % Sm_2O_3 and lesser amounts of Nd_2O_3 , Er_2O_3 and some of the other rare earth oxides. The samarium salts tested were prepared from 99 % Sm_2O_3 and the gadolinium salts from 95 % Gd_2O_3 . The methods used in preparing the rare earth compounds are described in Appendix B; the corrosion data are listed in Table V, Appendix C.

The rare earth oxide $(RE)_2O_3$ (Experiment 31-1) is extremely insoluble, which explains the white deposit in the autoclave. This deposit may explain the weight increase of the zirconium. The change in pH probably indicates some reaction with water during the test, but the low pH is surprising in view of the basic character of the rare earths. The oxide is probably the most stable of the rare earth compounds, but its low solubility limits its use in water solution.

Among the RE salts, the chlorides produced the greatest amount of corrosion of the stainless steel autoclave. The observed orange-red precipitate was identified as Fe_2O_3 . The formation of Fe_2O_3 in the presence of rare earth chlorides, as contrasted with the formation of Fe_3O_4 in the presence of other chlorides, has been mentioned in the discussion on cadmium.

The nitrates showed no precipitate or color change, and the appearance of the samples was quite good. In this respect, the nitrates were better than any of the other RE salts tested. However, the rather high weight loss for the samples and the appreciable drop in pH after test suggested that some change was occurring in the solution.

The RE sulfates did not particularly affect the zirconium, but iron oxide deposits indicate attack of the stainless steel autoclave. The acetates showed poor stability, but the bromide in Experiment 46-1 seemed to offer some degree of promise.

The gadolinium and samarium salts, as to be expected, proved to be quite similar and are discussed together. The chlorides showed the heavy orange precipitate identified previously as Fe_2O_3 ; this indicated appreciable attack on the stainless steel autoclave and the stainless steel sample. This precipitate occurred in both aerated and degassed solutions.

The bromides, particularly that of gadolinium, showed the orange Fe_2O_3 precipitate in the aerated solutions but not in the degassed solutions. The corrosion of the zirconium in the degassed solution was within acceptable limits, but the attack on the stainless steel was somewhat excessive, as shown

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both by the weight change and the presence of significant quantities of hydrogen in the autoclave. (Note: In Table IV hydrogen is stated to be present if on test a flame produced an explosion immediately after removing the cover from the autoclave.)

The nitrates produced low average weight changes in the zirconium and, in some cases, quite low weight changes in the stainless steel. In general, the appearance of both zirconium and stainless steel samples was very good. The solutions showed no visual evidence of instability, but the drop in pH indicated some chemical change. The mixture of gadolinium nitrate and boric acid showed no visual evidence of instability, but the high weight increases probably indicate some deposition. The zirconium, however, exhibited a good appearance. The mixture of samarium and cadmium nitrates, and the mixture of samarium and potassium nitrates, showed no improvement over the samarium nitrate.

The sulfates generally resulted in clear solutions and negligible attack on the zirconium, as judged by appearance and average weight change. The stainless steel showed slightly higher average weight changes and, in some cases, showed some evidence of attack or deposition. In other experiments, the stainless steel looked very good. The results with the mixture of lithium sulfate and gadolinium sulfate were not significantly different than those from the gadolinium sulfate alone. Although the sulfates under these conditions have shown some promise, it is doubtful whether they could be used in any high-temperature reactor because of their inverse temperature-solubility effect.⁴

The bromates and chlorates (Experiments 55-58) showed a high degree of instability and corrosivity.

Samarium iodide solutions showed evidence of possible instability by the change in color, the source of which could be identified by the spectrophotometer. The samarium m-nitro benzenesulfonate underwent decomposition.

Based upon corrosion and visual evidence of stability, the nitrate is the best among the various rare earth salts tested regardless of whether it is prepared from a rare earth mixture or from purified gadolinium or samarium. Among the three nitrates, the evidence seems to be slightly in favor of samarium, but this cannot be stated definitely since no stainless steel samples were exposed in the $\text{RE}(\text{NO}_3)_3$ solution. The rather consistent high weight losses in the solutions from the mixture compared to that from the purified Gd_2O_3 and Sm_2O_3 further supports this view. The data reported seems to be slightly in favor of samarium as compared to gadolinium, but this may be due to other factors such as degree of purity, etc.

⁴D. M. Yost, H. Russell, Jr., C. S. Garner, "The Rare Earth Elements and Their Compounds," (New York: John Wiley & Sons, Inc., 1947) p. 58.

Although there was no visual evidence of instability in the nitrate solutions, the drop in pH suggested some chemical change and this was the basis for the work described in the next section.

IV. SPECTROPHOTOMETRIC INVESTIGATION OF SOME RARE EARTH SOLUTIONS

Since the usual chemical analytical methods are unsatisfactory for use with rare-earth compounds, and since the spectrophotometer has a wide applicability for use with these materials, it was used in experiments described below.

The Beer-Bouguer law terms, with regard to absorption of light by solutions, may be expressed mathematically⁵ by

$$A_s = \log_{10} \frac{1}{T_s} = a_s b c \quad (1)$$

where

A_s = absorbance

T_s = transmittancy, the ratio of the transmittance of the solution to that of the solvent in equal thickness.

a_s = absorbancy index

b = length of the light path through the absorbing solution in centimeters.

c = concentration of the absorbing material in the solution in grams per liter.

The spectrophotometer, basically, combines (1) a light source capable of sending essentially monochromatic light of variable, known wave length through the sample; (2) a sample holder; and (3) a sensitive photometer for measuring the intensity of the light transmitted by the sample.

For any solution the value of T_s , or the term $\log_{10} \frac{1}{T_s}$, can be read directly from the spectrophotometer. Plotting T_s , A_s or a_s vs wave length gives an absorption spectrum curve for the solution. For the first two, a knowledge of concentration is unnecessary. The peaks in these curves show wave lengths where maximum absorption occur. The position of these peaks with respect to wave length is a characteristic property of the particular material under investigation. By making up a solution of the material of

⁵M. G. Mellon (Editor), "Analytical Absorption Spectroscopy," (New York: John Wiley & Sons, Inc. 1950), p. 307.

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known concentration and taking an absorbancy reading on it at a specific wave length (one which corresponds to a characteristic peak in the absorption spectrum curve), the value of the absorbancy index, a_s , can be calculated from Equation (1).

After this value has been determined for a particular material at a specific wave length, the amount of this material in a solution can be determined quantitatively by taking an absorbancy reading on the solution at the specific wave length, substituting numerical values for A_s , a_s and b in Equation (1) and solving for c .

After the initial series of salts were tested in the autoclave, 5 solutions of samarium were examined in a Beckmann DU spectrophotometer for absorbance at 402 millimicrons; the readings are given in Table I.

Table I

ABSORBANCY READINGS ON SAMARIUM SOLUTIONS

Solution	Pre-test	Post-Test	
		Air saturated	Degassed
$\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	0.042	0.028	0.019
$\text{SmBr}_3 \cdot (?)\text{H}_2\text{O}$	0.025	0.026	0.015
$\text{Sm}(\text{ClO}_4)_3$	0.033	0.017	0.029
$\text{Sm}(\text{BrO}_3)_3$	0.012	0.014	0.013
$\text{Sm}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	0.046	0.014	0.010

Because of its larger cross section, gadolinium for use as poison requires so much less material in solution than samarium that its concentration can not be determined spectrophotometrically with ease. Therefore, most of the exploratory work was done with samarium. Since the readings in Table I are all single point readings, their exact quantitative interpretation is impossible to make, for it was soon discovered that autoclave tests introduce so many impurities that the background readings change. For example, consider Figure 1. Though both the untested and the tested solutions give the same readings at 402 $m\mu$, those at 396 $m\mu$ are at variance. It is the difference between 396 $m\mu$ and 402 $m\mu$ which has quantitative significance.

On the basis of these findings it was decided to undertake a more thorough investigation of the absorption spectrum of samarium nitrate solution. Two solutions of samarium nitrate, one air saturated and one degassed, were corrosion tested at 600F for two weeks, followed by a careful determination of their absorbancies between the regions of 320 and 440 $m\mu$. The results are plotted in Figure 2. At first it was thought that the 3 peaks at

FIG. 1
ABSORPTION SPECTRA OF SAMARIUM NITRATE SOLUTIONS

RE-7-12072-A

FIG. 2
ABSORPTION SPECTRA OF SAMARIUM
NITRATE SOLUTIONS TESTED AT 600 F

RE-7-12072-A
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347, 358 and 372 $m\mu$ were caused by some intermediate complex of samarium which might not be stable over a long period of time. In order to evaluate the plausibility of this conjecture, the absorption curve of the untested samarium nitrate solution was determined and is plotted in Figure 3. The 3 very minor peaks between 340 and 380 $m\mu$ are sufficiently similar to those in Figure 2 to lend credulity to this conclusion. It was also noted from Figure 3 that the nitrate radical gave a clearly defined peak in the region of 300-302 $m\mu$. A further study of the data on the solutions in Table V, Appendix C, showed that the nitrate salt solutions, after testing for a period of two weeks, approached a pH of 3. Thus, it was reasoned that if the initial pH was adjusted to 3, perhaps greater stability would result. Figure 3 contains the absorption curve of the untested samarium nitrate solution adjusted to pH 3 by means of nitric acid addition. The absorption curve of the solution tested for two weeks is shown in Figure 4. It can readily be seen that not only is the samarium content decreased on testing, but so also is the nitrate ion concentration. Up to this time the instability of these salts was interpreted as the tendency of the metal ion to plate out, an assumption based on the behavior of the cadmium nitrate. While it is definitely known that solid alkali metal nitrates undergo the following reaction: $2MNO_3 \rightarrow 2MNO_2 + O_2$, it was not thought that neutral solutions of nitrates would suffer any change at a temperature of 600F.

After it was realized that the nitrate ion might not be stable at 600F, it was decided to test approximately equimolar quantities of nitric acid and potassium nitrate in separate autoclaves. At the end of the customary two-week period, absorption curves of both tested and untested solutions were measured; the results are plotted in Figures 5 and 6. Because nitric acid solutions at the end of two weeks also showed 3 well-defined peaks between 340 and 380 $m\mu$, it is probable that, what was at first thought to be a unique enhancement of the 3 small peaks of samarium nitrate (Figure 2), is actually caused by some unstable or volatile decomposition product of nitrate ion after being subjected to heat. On the other hand, potassium nitrate solution showed a shift of the nitrate peak from 302 to 282 $m\mu$, with a single, large additional peak at 358 $m\mu$. Two possibilities as to the source of the peak at 358 $m\mu$ were investigated.

First, some standard iron wire was dissolved in about 20% nitric acid and the solution evaporated almost to dryness to eliminate excess acid. Water was added to dissolve the iron nitrate, and the solution was then diluted sufficiently to allow reading on the spectrophotometer. The absorption curve is shown in Figure 7. Since this curve bears no resemblance to that of the solution of potassium nitrate tested at 600F, the possibility of iron having been leached from the autoclave during testing was discarded.

Secondly, a solution of potassium nitrite was made up and its absorption curve determined. The curve shown in Figure 8 suggests that the decomposition product of potassium nitrate formed in autoclave testing is potassium nitrite, the end product when solid KNO_3 is thermally decomposed.

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FIG. 4
ABSORPTION SPECTRA OF SAMARIUM NITRATE
SOLUTIONS AFTER TWO-WEEK TEST AT 600 F

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FIG. 5
ABSORPTION SPECTRA OF NITRIC ACID
SOLUTIONS BEFORE AND AFTER TEST

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FIG. 6
ABSORPTION SPECTRA OF POTASSIUM NITRATE
SOLUTIONS BEFORE AND AFTER TEST

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FIG. 8
ABSORPTION SPECTRUM OF
POTASSIUM NITRITE SOLUTION

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From what has been written above, it must not be inferred that the cation present is without effect on the stability of the nitrate ion. Two solutions were prepared (Experiments 89-94, Table V, Appendix C), both containing equal quantities of samarium nitrate; to one was added a quantity of cadmium nitrate and to the other some potassium nitrate. The absorption curves (Figure 9 and 10) would seem to indicate that the nitrate and samarium ions are more stable in the mixture of potassium and samarium nitrates than with cadmium present; however, before any positive declarations could be made it would be necessary to find out if these results are reproducible. The lack of the expected intense nitrite peak from potassium nitrate makes these results even more interesting.

The decomposition procedure is apparently not unique for samarium nitrate. Figure 11 shows the result of testing a solution of samarium sulfate. The reading at $402\text{ m}\mu$, quantitative for samarium, is greatly reduced after testing.

Figures 12, 13 and 14 are included for the purpose of illustrating the type of anomalous absorption curves obtained from gadolinium nitrate solutions. Figure 12 compares an untested solution of gadolinium nitrate with the same solution after testing one month (a) with zirconium and air and (b) with stainless steel under degassed conditions. The peak at about $302\text{ m}\mu$ has decreased enormously. The curves presented in Figure 13 are more clearly defined. Upon completion of the two-week test period the solution which contained the zirconium test piece shows complete removal of the nitrate ion, while that which was in contact with stainless steel only apparently retained half of its nitrate concentration.

Because boric acid is stable under the conditions of testing at 600°F and gadolinium borate cannot be prepared due to the necessary pH limitation, tests were made to determine the effect of a mixture of boric acid and gadolinium nitrate on the respective stabilities of each other (Experiments 97 and 98, Table V, Appendix C). The absorption curve, Figure 14, shows the almost complete disappearance of the nitrate ion from solution, while a direct titration for boric acid indicated its complete stability within the limits of the method used. The presence of 2 very pronounced peaks between 260 and $280\text{ m}\mu$ may be due to gadolinium, but it may also be due to boric acid, and further testing would be necessary to answer this question.

As a check on the spectrophotometric readings, which indicated a decrease in the rare earth concentration during the test, it was decided to attempt recovery of the rare earth oxide by precipitation of the oxalate, followed by ignition. Twenty-five ml of each of four tested gadolinium nitrate solutions were made acid with 5 ml of 1:1 sulfuric acid, and 20 ml of hot saturated oxalic acid solution added to each. The precipitate was allowed to stand overnight, filtered on ashless filter paper, and ignited in a previously ignited porcelain crucible. A great deal of care was taken in the ignition of

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FIG. 9
ABSORPTION SPECTRA OF SAMARIUM NITRATE
SOLUTIONS IN THE PRESENCE OF CADMIUM NITRATE

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FIG. 10
ABSORPTION SPECTRA OF SAMARIUM NITRATE SOLUTIONS
IN THE PRESENCE OF POTASSIUM NITRATE

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FIG. II
ABSORPTION SPECTRA OF SAMARIUM
SULFATE SOLUTIONS

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FIG. 12
ABSORPTION SPECTRA OF GADOLINIUM
NITRATE SOLUTIONS

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RE-7-12074-A

RE-7-12084-A
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FIG. 14
ABSORPTION SPECTRA OF GADOLINIUM
NITRATE-BORIC ACID SOLUTIONS BEFORE
AND AFTER TESTING TWO WEEKS AT 600 F

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these precipitates to guard against too rapid a combustion. The theoretical amount of oxide to be recovered from these gadolinium solutions is about 0.02 gm/25 ml. The results are listed below:

<u>Experiment No.</u>	<u>Mass recovered, Grams/25 ml.</u>
49-1	0.0035
49-2	0.0005
52-1	0.0009
52-2	0.0005

These results showed about a 6- to 40-fold decrease of gadolinium during the test, with the greater decrease occurring with the longer test period as would be expected. In the same manner, 2 tested samarium nitrate solutions were treated for oxide recovery. By calculation, 0.05 gm of samarium oxide should be recoverable. The yields obtained were:

<u>Experiment No.</u>	<u>Grams recovered</u>
68-1	0.002
68-2	0.010

Here there were decreases of 25- to 6-fold, but the greater decrease did not occur with the longer test period.

An examination of the resistivity data on these experiments (Table V, Appendix C) shows a fairly good correlation between the conductivity (reciprocal of resistivity) of these solutions and the rare earth content as determined by oxalate precipitation, except for Experiment 68-2. No explanation for the anomalous results on this experiment can be given, but there is a possibility that the presence of impurities, or the condition of the autoclave surface, may have been contributing factors.

It is evident that while the corrosion-stability tests indicated that the gadolinium and samarium nitrate solutions might be satisfactory from the standpoint of corrosion and visual evidence of stability, the spectrophotometric and oxalate precipitation techniques showed a decrease in the poison concentration, such as would occur if the poison precipitated or plated out.

V. SUMMARY AND RECOMMENDATIONS

Lithium is not particularly attractive because the neutron cross section, even of the Li^6 isotope, is quite low. Of the lithium compounds tested, the borates, and possibly the sulfate, show the greatest promise from the standpoint of stability and corrosion behavior. The sulfate, however,

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has an inverse temperature coefficient of solubility, which might cause trouble by deposition on fuel plates or heat exchangers. Further work should be done on the nitrate to determine whether more stable preparation can be produced by the addition of nitric acid and/or nitrates and nitrites. Since no analytical data have been obtained for lithium before and after test, it would be desirable to repeat some of the experiments using this technique. It would also be desirable to use stainless steel as well as zirconium samples.

The results on boric acid and related compounds indicate that boric acid shows the greatest stability combined with the least corrosion of all materials tested. Quantitative corrosion studies in dynamic loops should be made at various temperatures and with various oxygen concentrations, as well as with hydrogen, on materials of interest.

Cadmium is very attractive from a nuclear standpoint because it has, in effect, a positive temperature coefficient for neutron absorption in certain temperature ranges. The only cadmium salts that show promise are the sulfate and the bromide, and the results here are incomplete, inconclusive, and should be extended. The sulfate has an inverse temperature coefficient of solubility, which makes its use in reactor cores questionable. Other possibilities that warrant investigation are the complex ions $\text{Cd}(\text{CN})_4^{--}$, CdI_4^{--} , the cadmates, and cadmium nitrate in the presence of nitric acid with and without added nitrates or nitrites.

The work on the rare earth salts, although rather extensive, has not produced any material that can be definitely recommended for use in high-temperature water reactors. The nitrates show the greatest promise from the standpoint of corrosion and visual evidence of stability. Spectrophotometric measurements, however, showed a change in the nitrate ion, apparently to nitrite, and a decrease in the rare earth content which was confirmed by analyses based on oxalate precipitation. Further investigation should be made with a view to increasing the stability of the nitrate, possibly by addition of nitric acid with or without added nitrates and/or nitrites.

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The observation that the nitrate disappeared almost completely in the presence of zirconium, whereas the stainless steel was less effective, have possible significance with regard to the mechanism, in view of the well-known tendency of zirconium to pick up nitrogen from the air during fabrication.

Since samarium is slightly more than twice as basic as gadolinium it should be slightly more stable⁶ and might offer a better chance of success. Samarium has another advantage in that it shows a slight effective temperature coefficient of neutron absorption cross section in some temperature regions.

VI. CONCLUSIONS

From the data which appear in this report, it may be concluded that the best choice of a poison for use in a high-temperature water reactor is boric acid. The apparently complete stability of this compound in 600F water, combined with its low corrosive action, makes it unique among all others tested.

⁶F. Ephraim, "Inorganic Chemistry" (5th Edition; New York: Interscience Publishers, Inc., 1948) p. 441.

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APPENDIX A

ANALYTICAL PROCEDURES

Boric Acid and Tetraborate Analyses

By direct titration with 0.1 N sodium hydroxide to a phenolphthalein end-point the concentration of boric acid in solution may be determined. This method of analysis requires the addition of glycerine or some other polyhydroxy organic compound, such as mannitol, to the titration solution to enhance the ionization of the boric acid. Since the first ionization constant has been determined to be 6.4×10^{-10} moles/liter, the titration is the same as that for a monobasic acid, and the equivalents of acid in solution may be calculated on this basis.

In the case of a tetraborate, a mineral acid is added to adjust the pH of the solution to 2.5-3.0, thus converting all of the alkali metal to the mineral salt and all of the tetraborate to boric acid. Titration is then carried out as described for boric acid, making certain that the original and tested solutions have both been adjusted to the same pH with very small quantities of acid.

Cadmium Analyses

The colorimetric method used for determining cadmium is the standard one employing dithizone. One ml of the cadmium solution is diluted to one liter, and 5 ml of this solution are taken for analysis. An approximately equal portion of 10% sodium hydroxide is added, after first mixing the diluted cadmium sample with 2-3 ml 20% sodium potassium tartrate to complex any interfering ions. The solution is then extracted with at least four 5 ml portions of dithizone dissolved in carbon tetrachloride and the extracts led into another separatory funnel. After a final extraction with carbon tetrachloride, the combined extracts are washed with a dilute solution of sodium hydroxide to remove the last traces of any concentrated sodium hydroxide that may have been carried along. The red complex dissolved in carbon tetrachloride is run into a 50 ml volumetric flask and made up to volume with the solvent. Measurement of the absorbance is then made by use of a Beckmann DU spectrophotometer at 520 m μ .

Gadolinium and Samarium

Since gadolinium and samarium both belong to the rare earth group of metals and have similar chemical and physical properties they are treated together in the following discussion.

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Salts of the rare earth metals possess the property of having characteristic absorption bands due to the cation itself.⁷ However, the influence of the anion is apparent when one inspects an absorption spectrum of two different salts of the same element, as the height of the characteristic peak varies slightly. Moeller and Brantley⁸ have shown that the absorption spectra of several rare earth elements may be used to estimate quantitatively the amount of the substance present in a given solution. There are 2 possible sources of error. Several ions mutually interfere with each other; others must be corrected for background readings. The maximum sensitivity of these bands is not great, and while the concentration of samarium necessary to poison the reactor is adequate for direct spectrophotometric determination, the small amount of gadolinium salt is determined with difficulty and much indecision. A typical absorption curve of a mixture of rare earth oxides converted to the acetate is shown in Figures 15 and 16. The gadolinium bands are weak and narrow and are, therefore, shown on a more sensitive scale in Figure 15. The prominent peaks are marked with the element responsible for the peak.

A secondary analytical procedure involves the precipitation of the rare earth oxalate in acid medium, ignition of the oxalate to convert it to the oxide, and weighing the residual oxide. The exact acid strength and length of time necessary to produce complete precipitation is subject to speculation, but fairly precise results can be obtained by pouring nitric or hydrochloric acid, equal to 5% of the volume of solution, into a hot solution of 10 gm of oxalic acid, and allowing the precipitate to stand for several hours.⁹ Solubilities of decahydrated oxalates in water are about 1×10^{-6} mole per liter.

⁷D. M. Yost, H. Russell, C. S. Garner, "The Rare Earth Elements and Their Compounds," (New York: John Wiley & Sons, Inc., 1947), pp. 22-23.

- ⁸T. Moeller and J. C. Brantley, "The Rare Earths - Spectrophotometric Estimation of Certain Rare Earth Elements," *Analytical Chemistry*, 22, 433-441, (1950).

⁹W. W. Scott, "Standard Methods of Chemical Analysis," (New York: D. Van Nostrand Co., Inc., 1939) I, p. 248.

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FIG. 15
ABSORPTION SPECTRUM OF RARE EARTH
ACETATE SOLUTION CALCULATED ON THE
BASIS OF 100% GADOLINIUM ACETATE

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FIG. 16
ABSORPTION SPECTRUM OF RARE EARTH
ACETATE SOLUTION CALCULATED ON
BASIS OF 100% GADOLINIUM ACETATE

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APPENDIX B

PREPARATION OF RARE EARTH COMPOUNDS

By the addition of 1,4-dioxan it was found possible to precipitate the chloride and bromide salts of the rare earth metals from their 95% alcohol solutions. Thus, in addition to aiding the preparation of these salts, the use of 1,4-dioxan enabled recrystallization and consequent purification. The sulfate salts are easily recrystallized from water by the addition of 95% alcohol to the smallest volume of water necessary to dissolve the amount of salt used.

Nitrate salts were difficult to precipitate and recrystallize. With any variety and combination of the common organic solvents, such as petroleum ether, butyl alcohol, dioxan, carbon tetrachloride, etc., the nitrate could not be precipitated from solution. It was found that the best procedure for the nitrate was to evaporate off the excess water and acid used in its preparation by means of an aspirator, keeping the mixture at room temperature or below to prevent hydrolysis. When no more acid could be detected by its odor, the syrupy mass was poured into a beaker, and immediately started to crystallize. Any attempt to dry the salt further, even at 60C, partially affected a different crystal form, so that concentrations could not be determined by direct weighing.

The bromate salts were made by adding an equivalent weight of barium bromate to a solution of the rare earth sulfate. After filtering off the barium sulfate formed, the remaining solution was evaporated to dryness without heat, and the crystals of the rare earth bromate weighed to make up the desired solution. For the perchlorate, just enough perchloric acid is added to a slurry of the rare earth oxide to completely dissolve it. This solution upon evaporation to dryness yielded the perchlorate salt, which was very hygroscopic.

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APPENDIX CTABULATED RESULTS OF CORROSION-STABILITY TESTSTable NomenclatureSalt Solution and Concentration

The concentration of the various salts used was based on the thermal neutron cross section of the poison element. In the case of lithium, the cross section for Li^6 was used as a basis for calculation. The amount of each poison used was arbitrarily selected as the amount per 100 ml calculated to produce a macroscopic cross section of 0.1 cm^{-1} .

Experiment Number

Hyphenated numbers indicate repeated tests on same sample, using fresh solution in each instance.

Corrosion

Corrosion results are expressed in terms of sample weight changes in milligrams per square centimeter per month.

Gas

Air refers to the use of an air-saturated solution at room temperature. Deg. refers to partially degassed solutions.

pH

Before and after test pH values as measured with a glass electrode.

Resistivity

Before and after test values as measured with a conductivity meter.

Time and Temperature are self-explanatory.

Remarks

Unless otherwise noted, remarks pertain to appearance of samples tested.

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CORROSION - STABILITY TESTS ON LITHIUM SALTS AT 600F

Salt Solution	Exp No	Salt Conc gm/100 ml	Weight Change, mg/cm ² /mo		Gas	pH		Resistivity, ohm-cm		Time, hr.	Remarks
			Zr	SS		Before	After	Before	After		
LiCl	1-1	0.794	+0.018	--	Air	9.3	7.0	10000	100	365	--
	3-1		-0.195	--	Deg	9.4	6.6	10000	75	354	--
	9-1		+0.121	--	Air	6.6	6.3	90	95	331	Slight white film over dark tarnish.
	9-2		-0.892	--	Air	6.5	7.8	65	--	740	Slight white film.
	9-3		-0.335	--	Air	7.0	6.3	64	69	716	Black residue in solution.
	10-1		+3.92	--	Deg	6.6	6.6	90	60	331	White film over dark tarnish.
	10-2		-0.781	--	Deg.	6.5	7.4	65	--	690	White film.
LiNO ₃	2-1	1.291	+0.018	--	Air	7.1	7.0	10000	90	365	After test solution yellow.
	4-1		+0.088	--	Deg	7.1	5.2	10000	90	354	After test solution yellow.
	11-1		+0.302	--	Air	5.9	5.5	75	80	331	Slight white film over dark tarnish.
	11-2		+0.139	--	Air	6.4	6.1	67	69	690	Slight white film.
	11-3		0.00	--	Air	6.6	4.2	67	70	716	Yellow solution.
	11-4		0.00	--	Air	6.1	5.9	68	75	715	Yellow solution.
	12-1		+0.243	--	Deg.	5.9	10.7	75	40	331	Slight white film over dark tarnish.
	12-2		+0.203	--	Deg.	6.4	6.2	67	72	690	Slight white film.
	12-3		0.00	--	Deg.	6.6	5.1	67	72	716	Yellow solution.
	12-4		0.00	--	Deg.	6.1	5.5	68	68	715	Yellow solution.
Li ₂ SO ₄ · H ₂ O	5-1	1.198	+0.27	--	Deg.	8.9	6.9	500	12	306	--
	6-1		+0.242	--	Air	8.9	7.1	500	10	306	--
	13-1		+0.370	--	Air	6.0	--	80	--	331	Dark film.
	13-2		+0.114	--	Air	8.0	7.2	73	91	738	Slight white film.
	13-3		0.00	--	Air	8.8	6.3	69	76	744	Dark adherent film.
	13-4		0.00	--	Air	8.8	4.5	81	80	713	Dark adherent film.
	14-1		+0.123	--	Deg.	6.0	--	80	--	331	Dark film, trace of white film.
	14-2		+0.276	--	Deg.	8.0	6.8	73	91	738	Slight white film.
	14-3		0.000	--	Deg.	8.8	7.3	69	71	744	Dark adherent film.
	14-4		0.000	--	Deg.	8.8	5.4	81	71	713	Dark adherent film.
LiBO ₂	17-1	0.932	+0.370	--	Air	11.0	10.6	170	210	332	Slight dark film.
	17-2		-0.056	--	Air	10.9	10.1	166	580	716	Slight white film.
	17-3	0.930	0.000	--	Air	10.6	9.7	150	280	744	Slight black deposit.
	17-4		0.000	--	Air	10.8	9.9	155	425	713	Adherent film.
	18-1	0.932	0.000	--	Deg.	11.0	10.5	170	230	332	Slight dark iridescent film.
	18-2		-0.085	--	Deg.	10.9	10.2	166	400	716	Slight white film.
	18-3		0.000	--	Deg.	10.6	--	150	--	764	No solution left.
	18-4		0.000	--	Deg.	10.8	10.2	155	300	693	--
	81-1 (10 wk test)	0.930	(2 wk) +0.860 (4 wk) -0.130 (4 wk) +0.080	-0.24 -0.02 +0.25	Air	11.1	10.2	205	410	336 672 672	Orange crystals on Zr after 10 wks. (New solution for last mo.)
	82-1 (10 wk test)		(2 wk) 0.00 (4 wk) +0.090 (4 wk) 0.410	0.00 0.00 +0.23	Deg.	11.0	9.9	190	1200	336 672 672	Orange crystals on Zr after 10 wks. (Same solution throughout.)
Li ₂ B ₄ O ₇ · 5H ₂ O	7-1	2.429	+0.021	--	Air	8.9	8.0	200	257	361	--
	8-1		+0.043	--	Deg.	6.8	8.5	200	150	361	--
	15-1		+0.246	--	Air	8.7	--	150	--	331	Dark film.
	15-2		+0.221	--	Air	8.9	7.9	119	340	738	Slight white film.
	15-3	2.430	0.000	--	Air	8.5	8.2	120	158	744	White coating on Zr.
	15-4		0.000	--	Air	8.5	7.7	137	300	713	White coating.
	16-1	2.429	+0.432	--	Deg.	8.7	--	150	--	331	Dark film, trace of white film.
	16-2		+0.332	--	Deg.	8.9	7.9	119	390	738	White film.
	16-3	2.430	0.000	--	Deg.	8.5	8.3	120	140	744	White coating.
	16-4		0.000	--	Deg.	8.5	7.9	137	220	713	White coating.
LiOH	91-1	0.076*	+4.870	--	Air	12.5	12.5	55	14	353	Orange crystals.
	92-1		+7.880	--	Deg.	12.5	12.5	55	14	353	Orange crystals.

*Calculated from pH.

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CORROSION - STABILITY TESTS ON CADMIUM SALTS

Salt Solution	Exp. No.	Salt Conc., gm/100 ml	Weight Change, mg/cm ² /mo		Gas	pH		Resistivity, ohm-cm		Time, hr.	Temp, F	Remarks
			Zr	SS		Before	After	Before	After			
CdCl ₂ · 2½ H ₂ O	27-1	1.5	+0.13	--	Deg.	5.5	6.7	130	--	332	600	Black residue. Very little solution left.
	27-2		0.00	--	Deg.	5.4	--	128	--	331	600	No solution left.
	27-3		0.00	--	Deg.	5.6	--	135	--	712	600	No solution left.
Cd(Ac) ₂ · 3H ₂ O	28-1	1.9	+0.99	--	Deg.	7.1	5.0	220	5900	332	600	Solution clear. Inflammable gas present.
	28-2		+0.70	--	Deg.	7.1	4.5	220	4900	331	600	Inflammable gas. Some ppt.
	28-3		+4.07	--	Deg.	7.1	--	220	--	712	600	No solution left.
CdSO ₄ · 8/3H ₂ O	29-1	1.7	+0.43	--	Deg.	6.3	4.1	170	260	332	600	Clear solution. Small amount of yellow precipitate. Fe and S identified.
	29-2		0.00	--	Deg.	6.2	3.6	165	169	331	600	Autoclave has green coating. Fe and S in ppt.
	29-3		0.00	--	Deg.	6.24	--	162	--	712	600	No solution left.
Cd(NO ₃) ₂ · 4H ₂ O	30-1	2.06	+0.12	--	Deg.	6.4	4.0	89	86	334	600	Solution clear. No coating on sample.
	30-2		0.00	--	Deg.	6.0	4.5	87	90	331	600	Solution clear.
	30-3		0.00	--	Deg.	6.1	4.0	88	480	712	600	Metal looks good.
	83-1	(10 wk test)	(2 wk) +0.33 -0.36	}	Air	6.6	3.2	100	110	336	600	SS piece shiny and silvery; Cd plated.
	(4 wk)		-0.18 -0.06							672		
	(4 wk)		+0.23 +0.25							672		
	84-1	(10 wk test)	(2 wk) -0.14 -0.79	}	Deg.	5.2	3.5	98	125	336	--	SS piece shiny and silvery; Cd plated.
	(4 wk)		0.00 +0.13							672		
	(4 wk)		+0.25 0.00							672		
	99-1		+1.21	+0.13	Air	5.7	3.7	100	190	349	600	Solution clear. Test piece plated.
	100-1		+4.14	+0.21	Deg.	5.7	3.7	100	108	349	600	Solution clear. Test piece plated.
	101-1		+1.05	+0.13	Air	5.7	2.8	100	103	349	500	Solution clear. Test piece plated.
	102-1		+0.83	+0.21	Deg.	5.7	3.7	100	109	349	500	Solution clear. Test piece plated.
Cd ₃ (BW ₁₂ O ₄₀) ₂ · xH ₂ O	121-1	10.00	--	--	Air	--	--	--	--	307	600	No solution left.
CdI ₂ + 2KI	122-1	2.60	--	--	Air	--	--	--	--	307	600	No solution left.
		2.36	--	--	Air	--	--	--	--	307	600	No solution left.
Cd(H ₂ PO ₄) ₂ (1.3 gm Cd(OH) ₂ + H ₃ PO ₄ to keep in solution)	123-1		--	--	Air	--	--	--	--	307	600	Excessive corrosion and discoloration.
K ₂ Cd(CN) ₄ + KOH (1 gm Cd(OH) ₂ + KCN to dissolve)	125-1		--	--	Air	--	--	--	--	307	600	No solution left.
CdBr ₂ · 4H ₂ O	126-1	3.1	--	--	Air	--	--	--	--	330	600	7.2 gm Cd/1 before; 8.7 gm Cd/1 after.
CdCl ₂ · 2½ H ₂ O	127-1	2.0	--	--	Air	--	--	--	--	330	600	8.3 gm Cd/1 before; 5.7 gm Cd/1 after.
Cd(NO ₃) ₂ · 4H ₂ O + 4KCN	128-1	2.0	--	--	Air	--	--	--	--	330	600	No solution left.
CdI ₂ + KI	129-1	2.6	--	--	Air	--	--	--	--	330	600	No solution left.
		2.4	--	--	Air	--	--	--	--	330	600	No solution left.
CdSeO ₄ (1.3 gm Cd(OH) ₂ + H ₂ SeO ₄ to dissolve)	130-1		--	--	Air	--	--	--	--	330	600	2.0 gm Cd/1 before; 0.08 gm Cd/1 after.
CdSO ₄ (1.3 gm Cd(OH) ₂ + H ₂ SO ₄ to dissolve)	131-1		--	--	Air	--	--	--	--	330	600	7.4 gm Cd/1 before; 7.2 gm Cd/1 after.
			--	--	Air	--	--	--	--	330	600	7.4 gm Cd/1 before; 7.2 gm Cd/1 after.
Cd ₃ (BW ₁₂ O ₄₀) ₅ · xH ₂ O	133.1	10.0	--	--	Air	--	--	--	--	330	600	6.7 gm Cd/1 before; 0.07 gm Cd/1 after.

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Table V (Cont'd.)

Salt Solution	Exp. No.	Salt Conc, gm/100 ml	Weight Change, mg/cm ² /mo		Gas	pH		Resistivity, ohm-cm		Time, hr.	Remarks
			Zr	SS		Before	After	Before	After		
Gd(NO ₃) ₃ · 6H ₂ O H ₃ BO ₃	97-1	{ 0.12 0.72	+1.66	+0.63	Air	4.8	7.0	1150	4080	349	NO ₃ completely destroyed. H ₃ BO ₃ by titration remains essentially unchanged. Zr-dark lustrous film-very slight trace of white.
	98-1	0.12 0.72	+2.11	+0.59	Deg.	4.8	6.3	1150	8400	349	Same comments as 97. Zr-dark lustrous film-very slight trace of white.
Gd ₂ (SO ₄) ₃ · 8H ₂ O	53-1	0.10	0.00	+0.67	Air	5.7	5.4	2700	4300	330	Small amount Fe ₂ O ₃
	53-2		+0.481	-0.175	Air	6.0	5.8	2700	8900	667	Zr-dark film, trace of white. SS-shiny film, part dull, trace of white. Clear solution.
	54-1		-0.36	+0.31	Deg.	5.7	5.3	2700	4800	330	Small purple deposit, Cr ₂ O ₃ .
	54-2		0.00	+0.330	Deg.	6.0	5.7	2700	7200	667	Clear solution. Zr-dark film, trace of white. SS-dark dull film, trace of white.
Li ₂ SO ₄ · Gd ₂ (SO ₄) ₃ · 2H ₂ O	59-1	0.11	-0.55	0.00	Air	6.6	4.3	168	205	330	Small ppt, Fe ₂ O ₃
	59-2		+0.145	+0.131	Air	6.3	5.4	168	825	691	Zr-dark shiny film, very slight trace of white. SS-dark dull film, trace of white.
	60-1		0.00	+0.63	Deg.	6.6	5.3	168	185	330	Heavier ppt, than aerated.
	60-2		0.00	-0.131	Deg.	6.3	5.2	168	590	691	--
Gd(BrO ₃) ₃ · xH ₂ O	55-1	0.15	0.00	+1.3	Air	5.6	4.9	1500	1650	330	Very heavy orange colored ppt, suspended throughout solution. Identified as Fe ₂ O ₃ .
	56-1		+0.424	+0.864	Deg.	5.6	4.9	1500	2475	330	Very heavy orange colored ppt, suspended throughout solution. Identified as Fe ₂ O ₃ .
Gd(ClO ₃) ₃ · xH ₂ O	57-1	0.16	+1.03	-1.334	Air	6.2	4.4	1275	1300	330	Very heavy rust-colored ppt. Fe ⁺⁺⁺ , Cl ⁻ , Gd ⁺⁺⁺ identified.
Gd(ClO ₃) ₃ · xH ₂ O	58-1	0.16	0.00	-1.38	Deg.	6.2	3.7	1275	1400	330	Very heavy rust-colored ppt. Fe ⁺⁺⁺ , Cl ⁻ , Gd ⁺⁺⁺ identified.
SmCl ₃ · 6H ₂ O	36-1	0.44	+0.30	--	Air	5.8	4.4	283	690	304	Heavy ppt, Fe ₂ O ₃ .
	77-1	0.43	-0.28	-0.92	Air	6.0	4.4	300	660	356	Heavy orange ppt, Fe ₂ O ₃ .
	78-1		0.00	-1.21	Deg.	6.0	4.3	300	1500	356	Heavy orange ppt, Fe ₂ O ₃ .
SmBr ₃ · 6H ₂ O	75-1	0.60	0.00	-0.97	Air	6.0	4.2	475	525	353	H ₂ present.
	76-1		-0.25	+1.56	Deg.	6.0	4.4	475	4850	353	--
	76-2		0.00	+0.816	Deg.	5.97	--	475	--	--	No solution left.
SmI ₃ (0.36 gm Sm ₂ O ₃ + HI to dissolve)	132-1		--	--	Air	--	--	--	--	--	Yellow solution after testing. Unable to analyze by spectrophotometer.
Sm(NO ₃) ₃ · 6H ₂ O	35-1	0.503	+0.342	--	Air	6.25	3.43	320	240	304	--
	67-1	0.53	0.000	0.00	Air	5.6	3.4	330	700	329	Clear solution. Zr-dark lustrous film. SS-shiny reddish-brown tarnish film.
	67-2		0.000	-0.13	Air	4.7	2.3	330	315	691	--
	68-1		0.00	-0.32	Deg.	5.6	3.2	330	950	329	Clear solution.
	68-2		0.00	0.00	Deg.	4.7	2.4	330	305	691	Zr-dark adherent film. Very slight trace of white. SS-shiny tarnish film.
Sm(NO ₃) ₃ · 6H ₂ O HNO ₃ (pH = 3)	87-1	0.53	0.00	-0.29	Air	3.0	2.4	170	280	355	Clear solution. Zr-dark adherent film trace of white. SS-dark adherent film, slightly shiny.
	88-1		0.00	-0.29	Deg.	3.0	2.4	170	280	355	Clear solution. Zr-dark adherent film. SS-reddish-brown adherent tarnish film.
Sm(NO ₃) ₃ · 6H ₂ O	*103-1		+0.60	+0.13	Air	4.6	2.5	265	268	349	--
	*104-1		+0.23	+0.17	Deg.	4.6	2.3	265	235	349	--

*Tested at 500F

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Table V (Cont'd.)

Salt Solution	Exp. No.	Salt Conc., gm/100 ml	Weight Change, mg/cm ² /mo		Gas	pH		Resistivity, ohm-cm		Time, hr.	Remarks
			Zr	SS		Before	After	Before	After		
Cd ⁺⁺ + Sm ⁺⁺⁺ nitrates	89-1	--	-0.20	-0.42	Air	4.6	2.2	250	220	353	Zr-dark lustrous film. Very slight trace of white. SS-shiny reddish-brown film.
Cd ⁺⁺ + Sm ⁺⁺⁺ nitrates	90-1	--	+0.46	--	Deg.	4.6	2.8	250	685	353	Dark adherent film. Very slight trace of white.
K ⁺ + Sm ⁺⁺⁺ nitrates	93-1	--	+0.198	--	Air	4.50	2.45	250	300	353	Dark lustrous film, very slight trace of white.
K ⁺ + Sm ⁺⁺⁺ nitrates	94-1	--	0.000	--	Deg.	4.50	2.32	250	300	353	Dark lustrous film, very slight trace of white.
Sm ₂ (SO ₄) ₃ · 8H ₂ O	73-1	0.43	0.000	-0.39	Air	5.7	5.2	775	3400	353	--
	73-2		+0.694	+0.731	Air	4.7	4.2	775	2900	691	Zr-dark film, slight white deposit. SS-dark film, slight white deposit.
	74-1		0.000	+0.34	Deg.	5.7	5.3	775	3950	353	--
	74-2		+0.694	+0.064	Deg.	4.7	4.9	775	2050	691	Zr-dark film trace of white. SS-dark film, trace of white.
Sm(ClO ₄) ₃ · xH ₂ O	69-1	0.54	0.000	-2.90	Air	6.0	3.8	390	775	353	H ₂ present. Heavy rust colored ppt. Zr and SS pitted and discolored, mostly black.
Sm(ClO ₄) ₃ · xH ₂ O	70-1	0.54	0.000	-5.04	Deg.	6.0	4.0	390	575	353	H ₂ present. Heavy rust colored ppt. Zr and SS pitted and discolored, mostly black.
Sm(BrO ₃) ₃	71-1	0.64	0.000	0.59	Air	3.5	4.6	963	3150	353	Very heavy rust colored ppt. Samples look fairly good. H ₂ present.
	72-1		0.000	-0.63	Deg.	3.5	4.3	963	1250	353	Very heavy rust colored ppt. Samples look fairly good. H ₂ present.
Sm m-NO ₂ -Benzenesulfonate (Sm ₂ O ₃ 0.36 gm + m-NO ₂ · C ₆ H ₄ · SO ₃ H to dissolve).			--	--	Air	--	--	--	--	--	Decomposed. Black tarry ppt.

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