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Exploration of Aluminum Passivity  
by Aqueous Additives 25-400°C;  
Potential Application to ORNL  
Advanced Neutron Source (ANS)

William L. Marshall

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CHEMISTRY DIVISION

EXPLORATION OF ALUMINUM PASSIVITY BY AQUEOUS ADDITIVES 25-400°C;  
POTENTIAL APPLICATION TO ORNL ADVANCED NEUTRON SOURCE (ANS)

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## TABLE OF CONTENTS

TITLE AND ABSTRACT.....	v
INTRODUCTION.....	1
EXPERIMENTAL PROCEDURES.....	2
RESULTS.....	4
Experiments at 25-400°C.....	4
Experiments at 25-90°C.....	5
Experiments at 180°C.....	6
CONCLUSIONS.....	6
REFERENCES.....	8
TABLE 1, Analysis of Aluminum Used.....	10
TABLE 2, Experiments at 25-400°C.....	11
TABLE 3, Experiments at 25-90°C.....	17
TABLE 4, Experiments at 180°C.....	20



EXPLORATION OF ALUMINUM PASSIVITY BY AQUEOUS ADDITIVES 25-400°C;  
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ABSTRACT

In anticipation of an ORNL Advanced Neutron Source (ANS) and possible limitations on neutron flux because of aluminum oxide buildup on heat exchanger surfaces, an exploration was made of aqueous additives for inhibiting corrosion. This study has confirmed previous, extensive studies during 1955-1965 showing that aluminum corrosion is a function of acidity, temperature, nature and concentration of electrolyte additive, and other variables. The exploration confirms that phosphate ion (of the electrolyte ions explored) appears to be a good corrosion inhibitor for aluminum in acidic media, depending upon acidity and concentration at a given temperature. Nitrate ion at 25-200°C in acidic media does not inhibit as well, but at temperatures of 200-400°C seems to be relatively good. As the temperature rises, the pH (25°C) must be lowered for best inhibition. Surprisingly, an alkaline, one molar ammonium bicarbonate solution appears to provide good corrosion resistance at temperatures up to 180°C, appearing to be the best corrosion-protection additive (to 180°C) of those explored.



## INTRODUCTION

If aluminum is to be used in high-capacity heat-transfer systems, a serious problem is the formation of corrosion product on its heat-transfer surface. This problem arises because of the very low thermal conductivity of aluminum oxide compared to that of aluminum and its alloys. Thus the ability of coolant to remove heat is seriously impaired if formation of aluminum oxide becomes large. If aluminum is continually oxidized (thus not passivated) and the oxide dissipated, this also becomes a serious problem for very thin aluminum-sheet cladding. ORNL is designing an Advanced Neutron Source (ANS), a second generation reactor to provide increased capabilities over those presently offered by the High Flux Isotope Reactor (HFIR). The ANS is planned to provide approximately seven times higher neutron flux than the HFIR, thus requiring much greater heat removal. The general design will be similar to that of the HFIR, wherein the outlet coolant-water temperature will be near 88°C.

The present study explores the ability of electrolyte additives in water solution to inhibit or prevent corrosion of aluminum metal at temperatures up to 400°C. It is recognized that extensive work of this nature has been performed previously. Several excellent studies and evaluations at temperatures up to 350°C within ORNL, other government installations, and elsewhere have been made (1-8), with one conclusion (4) that phosphate ion, of those studied, was perhaps the best corrosion inhibitor for aluminum and particular aluminum-alloys. We have tested the earlier conclusions and searched for other additives that might serve as well or better. A new solution additive explored in this

study ( $\text{NH}_4\text{HCO}_3$ ) appears to show merit, and is suggested for further laboratory study or for possible testing in the ORNL ANS Corrosion Test Loop recently constructed and in operation. The findings and conclusions are given below.

#### EXPERIMENTAL PROCEDURES

Reynolds Aluminum Co. heavy duty aluminum foil No. 665 was used (Table 1). The foil thickness was 0.10 mm, one side was shiny-bright and the other side dull-bright. Samples for testing were washed with acetone and alcohol, and then dried at 25°C. For the initial experiments at temperatures up to 400°C, thin sections of foil were cut in pieces approximately 0.6 mm wide and 5 mm long. A piece was inserted into a fused-silica capillary tube (1.0 mm I. D., 3.0 mm O. D.) containing a particular water solution (Table 2). The contents were sealed within the tube, and the tube (with an attached handle) inserted into a semi-micro apparatus capable of producing temperatures from 25° to 500°C as described earlier (9). Vigorous mixing is accomplished by an on-off vibrator attached to the handle end, while the sample contents are observed visually through a short-range telescope. The tube with contents can be removed quickly and cooled rapidly to 25°C for immediate examination under a low-power microscope; it can then be reinserted. This procedure was done frequently during an experiment.

Only visual examination, with comparison to the original foil, was used for differentiation of the results. In these explorations, the approach taken allowed fast, qualitative conclusions and provided quick detections of gross differences in behavior. Aside from observed rapid

dissolutions or extensive solid formations, the major visual distinctions were (a) no apparent difference from the shiny-bright appearance of the original aluminum foil (with the fine-machine-marks of the specimen appearing to be untouched), (b) the conversion of the shiny-bright surface to a grey or dull-grey appearance, (c) appearance of spots, either white or dark, (d) appearance of whitish "scum" on the aluminum surface, and (e) pitting and/or hole formation. The conclusion was made that an untouched appearance indicated essentially no attack (although this conclusion still might be erroneous) and that a change in color indicated buildup of an aluminum oxide film. The question whether buildup would continue with time remained unanswered, but a dull-grey surface appeared to remain stable for times at least up to eight hours at the high temperatures (300-400°C), the extent of some of the runs, in contrast to those specimens that quickly formed an aluminum oxide, gelatinous solid.

Aluminum samples for the observations made at 25-90°C (Table 3) and at 180°C (Table 4) were cut to approximately 3 mm x 15 mm and sealed in Pyrex tubes (4 mm I. D., 6 mm O. D., 60 mm length) containing a designated aqueous solution. A set of filled tubes was inserted vertically into a protective metal vessel that was placed in a furnace thermostat. The tubes were kept at the particular temperatures for varying lengths of time (Tables 3 and 4). The vessels were easily removed and the aluminum-metal surfaces quickly examined under a low-power microscope as done for the specimens held and vibrated at the higher temperatures.

## RESULTS

Experiments at 25-400°C. Table 2 gives results for experiments at temperatures up to 400°C. Here we observe that aluminum specimens held at high temperatures in contact with particular solution additives (example:  $\text{HNO}_3$ ) and concentrations appeared to remain unchanged after subsequent exposure up to 110 days at 25°C, although aluminum held only at 25°C with the same solution additives showed corrosion (Table 3). Small blisters appear on several of the aluminum specimens in some of the solutions, in particular in the presence of the  $\text{NH}_4\text{HCO}_3$  or  $\text{NH}_4\text{NO}_3$  additives at temperatures greater than 200°C. Of much surprise is the rapid attack by  $\text{NaNO}_3$  solution to form aluminum oxide gel. The reaction proceeds quickly until the surface is covered by the gel, and then it stops. When  $\text{HNO}_3$  is present also, the  $\text{NaNO}_3$  does not react, and so this reaction would appear to be a function of an initial amount of oxide formed (when  $\text{HNO}_3$  is absent) that raises the alkalinity and allows formation of a sodium aluminate gel. Lithium nitrate additive produces similar behavior.

Some of these runs appear to show that (a) passivation by a short time exposure at the high temperatures can be effective for maintaining subsequent passivity at 25°, (b) with some additives, metal blisters form (originating from gas formation beneath the metal surface) at temperatures roughly above 200°C, and (c) particular additives, not passivating at 25°C, do passivate at the high temperatures. These observations confirm many of those already seen in the previous studies (1-5), but they also add information on effects of electrolytes not previously explored ( $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ , and  $\text{NaNO}_2$ ) and  $\text{SiO}_2$  gel.

Experiments at 25-90°C. Table 3 shows exploratory experiments made at temperatures from 25 to 90°C over times varying from one hour to five days at the higher temperatures (75-90°C). Electrolyte additives explored for their effects were HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, HCl, NH<sub>4</sub>HCO<sub>3</sub>, NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, and NH<sub>4</sub>OH. Although several of the observations are well known and are included only for completeness (i. e., rapid dissolution of aluminum in 1 M HCl), some may be surprising. For example, a 0.1 M Al(NO<sub>3</sub>)<sub>3</sub> solution rapidly dissolves the aluminum even at 25°C (hydrolysis of Al(NO<sub>3</sub>)<sub>3</sub> produces HNO<sub>3</sub>). With the possible exception of 0.0033 M HNO<sub>3</sub> (pH = 2.5), all other concentrations of HNO<sub>3</sub> studied, both higher and lower, corroded the aluminum. A 0.01 M H<sub>3</sub>PO<sub>4</sub> appeared to passivate the aluminum surface; yet 0.0001 M, 0.1 M and 1.0 M H<sub>3</sub>PO<sub>4</sub> gave a bronze-like color, a dull surface, and complete dissolution, respectively. NH<sub>4</sub>NO<sub>3</sub> additive for the several concentrations studied (0.01-4 M) corroded the aluminum, as did a moderately concentrated NH<sub>4</sub>OH solution. A 1.0 M NH<sub>4</sub>HCO<sub>3</sub> appeared to be the best for protecting the surface of the aluminum specimen.

The conclusions from this first series of runs were that a low concentration (not greater than 0.01 M) H<sub>3</sub>PO<sub>4</sub> solution and a moderately concentrated (1 M) NH<sub>4</sub>HCO<sub>3</sub> solution were the only ones that offered some protection when the temperature could also be in the range of 25°C sometime during the lifetime of the system. In the earlier series of runs (Table 2), however, there is evidence that initially maintaining the system at a higher temperature (e.g., 150-200°C) might offer later passivation protection at 25°C.

Experiments at 180°C. Results for exposures at 180°C are given in Table 4. These runs were made after the experiments reported in Tables 2 and 3, and they represent those additives that would appear to be best studied in detail. From these experiments at 180°C, we might choose which additive and conditions to suggest for further study in the ANS Corrosion Test Loop. Table 4 shows that the best additive of those explored appeared to be a 1.0 M  $\text{NH}_4\text{HCO}_3$  solution, an alkaline solution with a pH of 9.2. The acidic solutions, 0.001 M  $\text{H}_3\text{PO}_4$  and 0.0033 M  $\text{HNO}_3$ , might be good also, but as Table 4 indicates they did not appear to equal that of the  $\text{NH}_4\text{HCO}_3$  solution.

#### CONCLUSIONS

Of the additives explored, a 1 M  $\text{NH}_4\text{HCO}_3$  solution appears to be the best for keeping aluminum closely to its original condition at temperatures up to 180°C for times up to 5.5 days (the extent of the present exploratory runs) and certainly longer. A 0.001 M  $\text{H}_3\text{PO}_4$  and 0.0033 M  $\text{HNO}_3$  are also believed to be likely candidates for maintaining passivity of aluminum at 25-180°C and even to higher temperatures. But still, with 0.001 M  $\text{H}_3\text{PO}_4$  some corrosion of aluminum was observed visually (after a 180°C experiment, with no observable effect) after 38 days at 25°C (Table 4). Yet aluminum in contact with the 1 M  $\text{NH}_4\text{HCO}_3$  solution with similar treatment (38 days, 25°C, after 5.5 days at 180°C) showed no change from the original appearance. Although the bulk (outlet) temperature of ANS coolant water will be near 88°C, these explorations were designed for searching out a coolant additive that would allow aluminum passivity at higher temperatures. At the coolant-metal interface, one expects to observe higher metal temperatures,

perhaps 150-200°C, with a consequent temperature discontinuity between metal and coolant. Any discovery of passivity at the higher temperatures possibly might be expected to favor also greater passivity at 88°C. However, these and previous observations of greater passivity at higher temperatures for particular additives (for example, some depending upon acidity) might void this supposition.

There are other considerations, however, and these include (a) neutron-radiation compatibility, (b) coolant flow of about 30 meters/second expected for the ANS, and (c) temperature gradients within the aluminum cladding. Nitric acid does not seem to be as good an inhibitor as  $H_3PO_4$ . However,  $HNO_3$  possesses one property more favorable than  $H_3PO_4$  in that nitrate ion predominantly forms very soluble salts, in contrast to analogous phosphate salts of low solubility that upon precipitation could cause difficulties for acidity control. This was pointed out by Griess, et al. (3, page 42). In addition to unwanted (reactor produced) radioactivities from phosphorous (3), the low solubility of phosphate salts was thus one reason  $HNO_3$  additive was chosen over  $H_3PO_4$  for use in the HFIR to provide a pH of about 5.

From these explorations, we could tentatively suggest corrosion-testing in the ANS Corrosion Test Loop with  $NH_4HCO_3$  solutions of 1.0 M under the expected conditions of ANS operation (other than neutron flux). However, such a large concentration of added electrolyte might void its practical feasibility for ANS operation. For example, there would be problems maintaining water purity (other substances) by ion-exchange resins. Water with a pH in the range of 5 (adjusted with  $HNO_3$ ) will certainly be tested extensively. The above explorations on aluminum

indicate that at higher temperatures perhaps higher acidities (lower pH) might be beneficial for aluminum passivation; nevertheless, high acidity suggests special caution.

It is well known that conclusions from corrosion studies may be ambiguous especially from explorations of this type. Nevertheless, the apparently favorable results with  $\text{NH}_4\text{HCO}_3$  solutions do indicate that they might be considered further for other coolant systems if not for the ANS.

These explorations do not offer quantitative evaluations (other than rudimentary) for some of the observed behaviors. If studies are continued, considerable time must be invested to find new, more reliable methods for evaluations on more fundamental bases.

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TABLE 1. Analysis of Reynolds Aluminum Co. Heavy-Duty Aluminum Foil  
No. 665 Used in all Experiments.<sup>a</sup>

<u>Element</u>	<u>Percent</u>
Aluminum	98.6 minimum
Iron	0.55-.75
Silicon	0.45-.65
Copper	0.05 maximum
Manganese	0.03 maximum
Magnesium	0.02 maximum
Zinc	0.03 maximum
Titanium	0.06 maximum
Lead	0.009 maximum
Lithium	0.003 maximum
Cadmium	0.009 maximum
Arsenic	0.009 maximum
All Others	0.15 maximum

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<sup>a</sup> From James Martin, The Reynolds Aluminum Co. Technology  
Center, Richmond, Virginia, (804)743-6623, June 6, 1987.

Table 2. Effect of Aqueous Solution Additives on Corrosion-Passivation Behavior of Aluminum Foil<sup>†</sup>, 25-400°C (6 table pages).

Experiment No.	Temp. (°C)	Aqueous Solution	Approximate Time (Hours, Non-Cumulative)	Observations on Aluminum Specimen
32-4-46	300-350°C	H <sub>2</sub> O	8	Initially a few gas bubbles, then none; grey metal finish; blisters on both sides indicating corrosion.
	25°C		1700	NFC*
33-4-93	230°-350°C	3 Wt. % H <sub>2</sub> O <sub>2</sub>	1.5	Dull surface, indicating corrosion.
	25°C		1700	NFC*
33-4-30	220-400°C	10 <sup>-5</sup> M HNO <sub>3</sub>	0.35	Dull-grey surface.
	25°C		1700	NFC*
33-4-31	260-400°C	10 <sup>-4</sup> M HNO <sub>3</sub>	0.35	Initially much gas bubbling; dull-grey surface in less than 0.05 hour.
	25°C		1700	NFC*
33-4-32	260-400°C	10 <sup>-3</sup> M HNO <sub>3</sub>	0.25	Dull-grey surface.
	25°C		1700	NFC*
33-4-34	343-400°C	0.0018 M HNO <sub>3</sub>	0.25	Some initial gas bubbling, then none; dull-grey surface on about 90% of metal.
	25°C		1700	NFC*
33-4-47	260-400°C	0.0033 M HNO <sub>3</sub>	8	Sample unchanged; shiny-bright surface.
	25°C		1700	NFC*
33-4-44	400°C	0.01 M HNO <sub>3</sub>	2	No apparent reaction.
	71-350°C	0.01 M HNO <sub>3</sub>	6	No apparent reaction.

Table 2 (Continued), page 2 of 6.

Experiment No.	Temp. (°C)	Aqueous Solution	Approximate Time (Hours, Non-Cumulative)	Observations on Aluminum Specimen
32-133-17	330-400°C	0.01 M HNO <sub>3</sub>	2	No detectable change; like original aluminum; shiny-bright surface. NFC*
	25°C		2700	
32-133-12	173-350°C	0.01 M HNO <sub>3</sub>	0.1	Perfectly shiny-bright; Smooth holes have developed (corrosion).
	25°C		1200	
32-133-13	167-350°C	0.10 M HNO <sub>3</sub>	0.3	Slow gas bubbling at 167°C; bubbling stops at 200°C; some bubbling at an edge of metal at 250°C; gelatinous buildup at 305°C; patchy corrosion but still shiny parts; gel converts to compacted form at 328-350°C; no bubbling at 300-350°C; but bubbles below 300°C; appears to be passivating at 300-350°C.
	25°C		1440	
32-133-14	325-350°C	0.10 M HNO <sub>3</sub>	1.0	Initial bubbling, then stops quickly. Some gelatinous (Al <sub>2</sub> O <sub>3</sub> ) buildup ?; metal is shiny-bright, but it appears to have dissolved somewhat because machine lines appear to be not so sharp (?). Many holes are observed (corrosion).
	25°C		1440	
32-133-16	145-305°C	0.10 M HNO <sub>3</sub>	1.2	Much bubbling in cycling sample from 275 to 305°C; metal 50% dissolved to form alumina gel; still some smooth shiny-bright portions. NFC*
	25°C		1440	

Table 2 (Continued), page 3 of 6.

Experiment No.	Temp. (°C)	Aqueous Solution	Approximate Time (Hours, Non-Cumulative)	Observations on Aluminum Specimen
32-133-15	325-350°C	1.0 M HNO <sub>3</sub>	0.2	Vigorous bubbling as Temp. rises; stops when solution-vapor turns yellow-brown (N <sub>2</sub> O <sub>4</sub> ); but now most of foil has dissolved; abundant Al <sub>2</sub> O <sub>3</sub> white gel has formed; About 20% of metal remaining after run.
32-133-6	170°C	1.0 M HNO <sub>3</sub>	0.5	Fast reaction
32-133-5	230°C	1.0 M HNO <sub>3</sub>	0.5	Fast reaction
33-4-48	25-350°C	0.010 M HCl	3	90% converted to Al <sub>2</sub> O <sub>3</sub> gel (remainder appears to be like original aluminum).
32-133-19	350-400°C	0.005 M HCl + 0.005 M HNO <sub>3</sub>	0.5	Slight bubbling then stops; bubbling starts vigorously at 2 spots; gel buildup; other parts dull-shiny.
	25°C		1440	A hole has formed. (corrosion).
32-133-20	357°C	0.05 M HCl + 0.05 M HNO <sub>3</sub>	0.05	Vigorous bubbling at several spots; much gel buildup.
	25°C		1440	Extensively corroded; many holes.
33-4-24	347-350°C	0.10 M H <sub>2</sub> SO <sub>4</sub>	1.5	Extensive reaction; gel buildup.
33-4-92	360°-400°C	0.0001 M H <sub>3</sub> PO <sub>4</sub>	0.25	Immediate few bubbles, then stop; light bronze; corrosion evidenced by blister formation.
33-4-38	220-400°C	0.01 M H <sub>3</sub> PO <sub>4</sub>	2.4	No apparent reaction.
	25°C		240	Bronze-bright surface.

Table 2 (Continued), page 4 of 6.

Experiment No.	Temp. (°C)	Aqueous Solution	Approximate Time (Hours, Non-Cumulative)	Observations on Aluminum Specimen
33-4-27	360-400°C	0.10 M H <sub>3</sub> PO <sub>4</sub>	0.2	No apparent reaction; shiny-bright as original aluminum foil.
	25°C		720	Metal has bronze-dull surface; no holes.
33-4-28	360-400°C	1.0 M H <sub>3</sub> PO <sub>4</sub>	0.2	No apparent reaction; microscopic examination: much apparent reaction but no aluminum oxide gel; perhaps gel dissolved?
	25°C		720	Much gel; no holes.
33-4-80	70-374°C	0.10 M NH <sub>4</sub> HCO <sub>3</sub>	1	White gel formation and some dark and white spots. corrosion.
33-4-85	200-310°C	1.0 M NH <sub>4</sub> HCO <sub>3</sub>	2	Blisters on shiny-bright surface; internal corrosion.
33-4-86	200°C	1.0 M NH <sub>4</sub> HCO <sub>3</sub>	0.6	Still shiny-bright; no apparent corrosion.
	250°C		0.2	Dull appearance develops; apparent corrosion.
33-4-74	330-400°C	0.01 M NH <sub>4</sub> NO <sub>3</sub>	4.5	Small blisters throughout shiny-bright surface, indicating corrosion.
33-4-67b	200-400°C	0.10 M NH <sub>4</sub> NO <sub>3</sub>	1.5	Appears unchanged.
	75°C		16	NFC*
33-4-70	240-400°C	1.0 M NH <sub>4</sub> NO <sub>3</sub>	2	Gas bubbling; then stops. aluminum shiny-bright; no gel formation.
	90°C		16	Shiny-bright surface covered by corrosion holes.

Table 2 (Continued), page 5 of 6.

Experiment No.	Temp. (°C)	Aqueous Solution	Approximate Time (Hours, Non-Cumulative)	Observations on Aluminum Specimen
33-4-71	333-400°C	4.0 M $\text{NH}_4\text{NO}_3$	2	Initial bubbling then stops. yellow colored liquid-vapor indicating $\text{N}_2\text{O}_4$ gas; No apparent corrosion.
	90°C		16	Shiny-bright surface covered with corrosion holes.
33-4-43	347-400°C	0.10 M $\text{Na}_2\text{SO}_4$	0.35	No detectable corrosion; still shiny-bright.
	170-371°C		4	Metal is converted to $\text{Al}_2\text{O}_3$ gel, 95%. 5% remaining is shiny-bright.
33-4-72	115-274°C	1.0 M $\text{LiNO}_3$	0.75	Rapid gas bubbling; 50 % dissolved ( $\text{LiAlO}_3$ , $\text{Al}(\text{OH})_3$ gels?)
33-4-25	350°C	0.10 M $\text{NaNO}_3$	0.05	Extensive reaction; foil splits; gel buildup.
32-133-21	356°C	1.0 M $\text{NaNO}_3$	0.2	Rapid reaction; reaction stops; on examination: extensive gel formation on surface until free metal can no longer be reached, so reaction stops.
33-4-37	260-400°C	0.010 M $\text{HNO}_3$ + 0.10 M $\text{NaNO}_3$	4	No detectable change; metal remains shiny-bright. NFC*
	25°C		720	
32-133-8	280°C	1.0 M $\text{NaCl}$	1.5	Initially a few gas bubbles form, then stop; dull-grey surface.
	25°C		1440	Large hole covered with apparent $\text{Al}_2\text{O}_3$ gel.
33-4-22	213-390°C	1.0 M $\text{NaCl}$	0.5	Dull-grey surface but some apparent $\text{Al}_2\text{O}_3$ gel.
	25°C		1440	Hole has developed (corrosion).

Table 2 (Continued), page 6 of 6.

Experiment No.	Temp. (°C)	Aqueous Solution	Approximate Time (Hours, Non-Cumulative)	Observations on Aluminum Specimen
33-4-23	280-400°C	5.0 molal NaCl	0.9	Initial bubbling then stops; no apparent change; under microscope, still shiny.
	25°C		1400	Two holes have developed.
33-4-73	275-400°C	1.0 M Mg(NO <sub>3</sub> ) <sub>2</sub>	0.3	Slow reaction. Metal becomes greatly dulled, both sides.
33-4-51	25-222°C	0.010 M NaOH	0.5	Many (expected) bubbles of hydrogen. Rapid reaction.
32-133-10	130-350°C	Silica Gel + H <sub>2</sub> O	1	Shiny-bright surface; machine marks (initially visually unchanged); no observed corrosion.
	25°C		1440	Corrosion holes.
33-4-45 (Orig. 32-133-10)	245-340°C	Silica gel + H <sub>2</sub> O	2	Holes originally developed after first run (and time at 25°C) have enlarged.
32-133-11	170°C	Silica Gel + 1 M HNO <sub>3</sub>	0.1	Rapid reaction to form H <sub>2</sub> and Al <sub>2</sub> O <sub>3</sub> gel.

+ Aluminum analysis in Table 1.

\* NFC = No further (observed) change from previous observation.

TABLE 3. Effect of Aqueous Solution Additives on Corrosion-Passivation Behavior of Aluminum<sup>†</sup> at 25-90°C (3 table pages).

Experiment No.	Temp. (°C)	Aqueous Solution	Approx. Time (Hours, Non-cumulative)	Observations of Aluminum Specimen
33-4-69	75°-90°C	H <sub>2</sub> O	24	Dark and whitish spots; surface dull grey. NFC*
	25°C		96 1600	
33-4-66	25°C	0.0001 M HNO <sub>3</sub>	24	Visually perfect. Whitish-grey and dark spots. NFC*
	75°-90°C		24	
	75°-90°C		96	
33-4-65	25°C	0.00033 M HNO <sub>3</sub>	24	Visually perfect. Apparent corrosion; dark spots. NFC*
	75°-90°C		24	
	75°-90°C		96	
33-4-64	25°C	0.001 M HNO <sub>3</sub>	24	Cloudy ring. Corrosion; dark spots; Al <sub>2</sub> O <sub>3</sub> gel. NFC*
	75°-90°C		24	
	75°-90°C		96	
33-4-63	25°C	0.0033 M HNO <sub>3</sub>	24	Visually perfect; no corrosion. NFC* NFC* Some dark spots.
	75°-90°C		24	
	75°-90°C		96	
	25°C		1608	
33-4-62	25°C	0.01 M HNO <sub>3</sub>	24	Slightly dull surface. Small holes; corrosion. Additional holes.
	75°-90°C		24	
	75°-90°C		96	
33-4-61	25°C	0.033 M HNO <sub>3</sub>	24	Corrosion. Extensive corrosion; holes. NFC*
	75°-90°C		24	
	75°-90°C		96	
33-4-35	25°C	0.10 M HNO <sub>3</sub>	17	Dull surface. Mostly dissolved.
	25°C		720	
33-4-60	25°C	0.10 M HNO <sub>3</sub>	24	Dull appearance. 70% dissolved; rest shiny-bright as original. Mostly dissolved.
	75°-90°C		24	
	75°-90°C		96	

Table 3 (Continued), page 2 of 3.

Experiment No.	Temp. (°C)	Aqueous Solution	Approx. Time (Hours, Non-cumulative)	Observations of Aluminum Specimen
33-4-36	25°C	1 M HNO <sub>3</sub>	72	Aluminum dissolved.
33-4-89	80°C	0.0001 M H <sub>3</sub> PO <sub>4</sub>	14	Bronze-like color.
33-4-88	80°C 25°C	0.01 M H <sub>3</sub> PO <sub>4</sub>	14 1600	Appears untouched. Dull bronze; corrosion.
33-4-90	80°C 25°C	0.10 M H <sub>3</sub> PO <sub>4</sub>	14 1600	Dull bronze. NFC*
33-4-91	80°C	1.0 M H <sub>3</sub> PO <sub>4</sub>	14	Aluminum dissolves.
32-133-9	100°C	0.10 M HCl	12	Reaction occurs.
32-133-2	25°C	1 M HCl	2	Dissolves rapidly
33-4-87	80°C	0.0001 M NH <sub>4</sub> HCO <sub>3</sub>	96	Corrosion; dark spots.
33-4-78	80°C	0.01 M NH <sub>4</sub> HCO <sub>3</sub>	24 120	Dull finish; bronze color. NFC*
33-4-77b	80°C  25°C	0.10 M NH <sub>4</sub> HCO <sub>3</sub>	24  120 1600	Dull finish; some bronze color. NFC* NFC*
33-4-77a	80°C  25°C	1 M NH <sub>4</sub> HCO <sub>3</sub>	24  1820	Shiny-bright, just like original; apparently no corrosion; acidity: pH 9.2. NFC*
33-4-82	80°C	0.001 M NH <sub>4</sub> NO <sub>3</sub>	22	Corrosion; bronze finish on parts of aluminum.
33-4-81	80°C	0.01 M NH <sub>4</sub> NO <sub>3</sub>	2  22	Most shiny-bright; some dark areas. Bronze-like appearance in some areas; corrosion.

Table 3 (Continued), page 3 of 3 pages.

Experiment Number	Temp. (°C)	Aqueous Solution	Approx. Time (Hours, Non-cumulative)	Observations on Aluminum Specimen
33-4-67	75°-90°C	0.10 M $\text{NH}_4\text{NO}_3$	24	some dark spots.
33-4-84	80°C	0.01 M $\text{NH}_4\text{HCO}_3$ + 0.01 M $\text{NH}_4\text{NO}_3$	14	Corrosion.
33-4-75	80°C	1.0 M $\text{NaNO}_2$	1	Corrosion.
33-4-83	80°C	1 M $\text{Mg}(\text{NO}_3)_2$	24	Corrosion; hole through aluminum.
33-4-68	25°C	0.10 $\text{Al}(\text{NO}_3)_3$	24	Aluminum dissolved.
33-4-76	80°C	Mod. Conc. $\text{NH}_4\text{OH}$	24	Corrosion; dull appearance.

+ Aluminum analysis in Table 1.

\* NFC = No further (observed) change from previous observation.

Table 4. Effect of Aqueous Solution Additives on Corrosion-Passivation Behavior of Aluminum Foil at 180°C (2 table pages).

Experiment No.	Solution Additive	Observations of aluminum specimens (time in hours, and temperature)
33-55-18	H <sub>2</sub> O	(60,180°C) Dull surface of original shiny-bright.
33-55-1	10 <sup>-5</sup> M H <sub>3</sub> PO <sub>4</sub>	(60, 180°C) Bronze color; some dark spots; shiny side dull.
33-55-2	10 <sup>-4</sup> M H <sub>3</sub> PO <sub>4</sub>	(60,180°C) Bronze color.
33-55-3	10 <sup>-3</sup> M H <sub>3</sub> PO <sub>4</sub>	(60,180°C) Perfect appearance; no change from original. (900,25°C) White, adhering thin solid; many dark spots.
33-55-4	10 <sup>-2</sup> M H <sub>3</sub> PO <sub>4</sub>	(60,180°C) Almost perfect; some whitish rings.
33-55-5	0.10 M H <sub>3</sub> PO <sub>4</sub>	(60,180°C) Dull appearance; dark spots.
33-55-6	1.0 M H <sub>3</sub> PO <sub>4</sub>	(60,180°C) Aluminum dissolved;
33-55-7	10 <sup>-5</sup> M HNO <sub>3</sub>	(60,180°C) Some whitish solid on shiny side.
33-55-8	10 <sup>-4</sup> M HNO <sub>3</sub>	(60,180°C) Dull, whitish solid on surface.
33-55-9	10 <sup>-3</sup> M HNO <sub>3</sub>	(60,180°C) Dull, whitish solid, indicating attack.
33-55-10	0.0033 M HNO <sub>3</sub>	(60,180°C) Much better than 33-55-8 and 33-55-9 specimens, but still some whitish solid.
33-55-11	0.01 M HNO <sub>3</sub>	(60,180°C) Much corrosion; One large hole.
33-55-12	0.10 M HNO <sub>3</sub>	(60,180°C) Aluminum nearly dissolved; covered with holes and white oxide.

Table 4 (Continued), page 2 of 2.

Experiment No.	Solution Additive	Observations of Aluminum Specimens (Time in hours, and temperature)
33-55-13	0.01 M $\text{NH}_4\text{HCO}_3$	(60,180°C) Bronze color; gelatinous particles on tube walls; dull, indicating corrosion.
33-55-14	0.10 M $\text{NH}_4\text{HCO}_3$	(60) Still shiny-bright, but some whitish substance on dull side.
33-55-15	1.0 M $\text{NH}_4\text{HCO}_3$	(130,180°C) Perfect; no change from original. (900,25°C) Perfect; no change from original.
33-55-16	0.01 M HCl	(60,180°C) Milky-white suspension; most of aluminum dissolved; still some shiny-bright fragments left.
33-55-17	0.01 M $\text{H}_2\text{SO}_4$	(60,180°C) Milky-white suspension; bronze colored Al; <u>no</u> pitting; lots of white solid.
33-55-19	0.001 M $\text{H}_3\text{PO}_4$ +0.001 M NaCl	(36,180°C) Much pitting; 5 small holes surrounded by gelatinous solid; most of metal looks perfect: shiny-bright.
33-55-20	0.001 M $\text{H}_3\text{PO}_4$ +0.01 M NaCl	(36,180°C) One large hole and one small hole, corroded through; rest of metal looks perfect.
33-55-21	1.0 M $\text{NH}_4\text{HCO}_3$ +0.001 M NaCl	(36,180°C) Metal looks perfect, but bronze tinge.
33-55-22	1.0 M $\text{NH}_4\text{HCO}_3$ +0.01 M NaCl	(20,180°C) Metal looks perfect, but bronze tinge.
33-55-23	0.001 M NaCl	(36,180°C) Dull; corrosion.
33-55-24	0.01 M NaCl	(36,180°C) Dull; corrosion.
33-55-25	0.001 $\text{KH}_2\text{PO}_4$	(20,180°C) Perfect; like original. (900,25°C) Whitish solid; many spots.



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