



STATE OF MINNESOTA
OFFICE OF THE ATTORNEY GENERAL

Address Reply To:
OFFICE OF ATTORNEY GENERAL
MINNESOTA POLLUTION CONTROL AGENCY
1935 W. County Road B2
Roseville, Minnesota 55113
612/296-7342

May 2, 1979

Gary V. Welk, Manager
Regulatory Compliance & Services
Northern States Power Company
Minneapolis, Minnesota 55401

Thomas A. Ippolito, Chief
Operating Reactors Branch #3
Division of Operating Reactors
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Gentlemen:

This will confirm our telephone conversations of this morning in which it was agreed that representatives of NSP and the NRC Staff will meet with representatives of the Minnesota Pollution Control Agency at the offices of the MPCA, hopefully during the week of May 14, 1979, for the purpose of discussing the spent fuel storage racks at the Monticello nuclear generating facility. The MPCA deeply appreciates your willingness to participate in these discussions.

The final scheduling of the meeting is dependent on the NRC Staff's availability and will be arranged in the near future. If at all possible, we would prefer any day in the week of May 14 except May 17, because two key MPCA Staff members will be out of town on that day.

Unless you believe that the scope must be expanded, discussion will be strictly limited to the following six technical questions:

- (1) Given our knowledge of the rack design and fabrication methods, can it be concluded that open channels of communication presently exist along the entire 14-foot length of each and every corner?
- (2) Given our knowledge of the corrosion mechanisms and physical dimensions involved, is it possible that long-term corrosion may result in isolated blockage of corner channels so that localized swelling might reoccur during the thirty to forty-year projected life of the racks?

AN EQUAL OPPORTUNITY EMPLOYER

Enclosure (1)

7905080411

Adol
HS
1/0

Gary V. Welk, Manager
Thomas A. Ippolito, Chief
Page Two
May 2, 1979

- (3) If future isolated blockage of the corner vent channels is possible, are there technical or other reasons for failing to drill vent holes during fabrication at regular intervals along the entire 14-foot length of the channels?
- (4) Would an increase in the thickness of the inner stainless steel layer of the tubular wall make future swelling impossible, even if gas should become trapped in the future?
- (5) If an increase in the thickness of the inner stainless steel layer of the tubular wall would preclude all possibility of future swelling, regardless of the blockage of hydrogen gas in the future, are there technical or other reasons for failing to increase the thickness of that layer?
- (6) How could a jammed spent fuel assembly be safely removed in the event of renewed swelling, particularly if swelling is localized in the manner referred to in question (2), recognizing that the specific remedy employed at Haddam Neck was to drill vent holes which will already exist at Monticello?

The MPCA understands that there are specific answers to these technical questions which, for various reasons, were not fully explored in the Director's Decision dated April 24, 1979.

Because these discussions will be open to the public, it is important that members of the public fully understand the limited nature of the proposed meeting. As we have agreed, our discussions do not constitute a "hearing" in any sense of that term. No one will be testifying on behalf of any party and there will be no cross-examination. The meeting is not designed to be a search for fault but rather will provide a forum at which we all hope that the MPCA's narrow technical concerns about possible future rack swelling may be laid to rest.

I will be contacting you in the near future to request that you provide us with copies of a very limited number of the documents referred to in the Director's Decision or in our conver-

Gary V. Welk, Manager
Thomas A. Ippolito, Chief
Page Three
May 2, 1979

sations over the past few days. If you have any additional written materials on these six questions which could be provided at or before the meeting, that would be appreciated, but the MPCA is not asking you to prepare any further written materials for the meeting unless you believe that such materials might be helpful in addressing the questions.

As soon as the NRC Staff is able to suggest a meeting date, I will arrange a place at the MPCA. Thank you again for your cooperation in attempting to resolve the narrow technical concerns of my client.

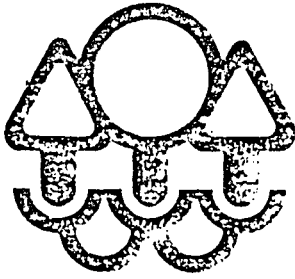
Very truly yours,

John-Mark Stensvaag
John-Mark Stensvaag
Special Assistant
Attorney General

JMS:rmn

cc: Russell Hatling
Thomas L. Donovan, Esq.
Grant J. Merritt, Esq.
Ken Peterson, Esq.
Joseph D. Bizzano, Esq.
Roland E. Olson
Gail Gendler
MPCA Board Members

MAY 14 1979



Minnesota Pollution Control Agency

May 11, 1979

Gary V. Welk, Manager
Regulatory Compliance & Services
Northern States Power Company
Minneapolis, Minnesota 55401

Thomas Kevern, Project Manager
Operating Reactors Branch #3
Division of Operating Reactors
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555

Gentlemen:

This will confirm our understanding that the meeting on the Monticello spent fuel storage racks will be held at the offices of the Minnesota Pollution Control Agency, Roseville, Minnesota, on Wednesday, May 16, 1979, at 9:00 a.m. The meeting will be held in the first floor Board room. Mr. Louis Breimhurst, Deputy Director of the MPCA, will chair the meeting for the purpose of coordinating discussion.

As you know, discussion is to center on six technical issues framed by the MPCA. In posing those questions, the MPCA has assumed, based on information previously provided by the Nuclear Regulatory Commission and Northern States Power Company, that the solution of drilling holes in the tops of the four existing racks has proven to be completely effective to eliminate swelling in the short term. In the April 24, 1979, Director's Decision at 4, for example, the NRC stated unequivocally:

At Monticello, the swelling was easily relieved by putting two holes in diagonal corners of the upper ends of the rack (venting). This allowed the trapped gas to escape and the water to fill the void annular spaces. The hydrostatic pressures were thus equalized and the swelling was relieved.

(Emphasis supplied).

Phone:
1935 West County Road B2, Roseville, Minnesota 55113
Regional Offices · Duluth · Brainerd · Detroit · Lakes · Marshall · Rochester
Equal Opportunity Employer

Enclosure (2)

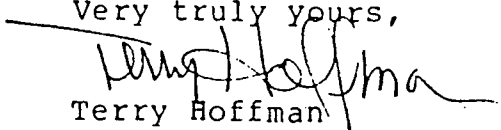
Gary V. Welk, Manager
Thomas Kevern, Project Manager
Page Two
May 11, 1979

Two days ago, the MPCA received an inspection report issued by R.F. Heishman of NRC Region III on April 10, 1979, which flatly contradicts previous representations by the NRC and NSP on this matter. That report indicates that NSP has known since last fall that the swelling was never successfully relieved in more than half of the affected cavities, and that swelling has subsequently reoccurred in two more of those originally swollen cavities.

To summarize the report, relevant portions of which are attached to this letter, six of the original eleven swollen tube locations would not accept the sizing gauge, despite the drilling of the holes and the "re-sizing of each tube by vacuum and mechanical means." Within sixty days, a seventh tube had swollen to the point where it would not accept the gauge. After ninety days, an eighth tube would also not accept the gauge. The report does not indicate whether the tubes have been rechecked in the past six months to ascertain whether swelling has also reoccurred in the three remaining tubes. Given the pattern of renewed swelling in tubes within the ninety-day period, such a possibility should certainly be fully explored.

In view of the previous assurances of the NRC and NSP that all swelling had been relieved, the MPCA is stunned by this new disclosure of such old information. We feel that this deeply disturbing information must be discussed at the forthcoming meeting, and will be eager to hear any explanation which you may have to offer.

Very truly yours,


Terry Hoffman
Executive Director

TH:js
Attachment

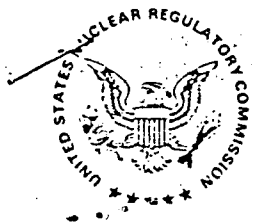
cc: Russell Hatling
Thomas L. Donovan, Esq.
Grant J. Merritt, Esq.
Ken Peterson, Esq.
Joseph D. Bizzano, Esq.
Roland E. Olson
Gail Gendler
MPCA Board Members

LIST OF ATTENDEES

NRC/NSP/MPCA MEETING

MAY 16, 1979

| <u>Name</u> | <u>Organization</u> |
|---------------------|---------------------|
| T. A. Ippolito | NRC |
| R. Bevan | NRC |
| T. Kevern | NRC |
| E. Lantz | NRC |
| F. Almeter | NRC |
| John-Mark Stensvaag | MPCA |
| L. Breimhurst | MPCA |
| J. Ferman | MPCA |
| G. Welk | NSP |
| L. Mayer | NSP |
| G. Neils | NSP |
| D. Vincent | NSP |
| E. Grimm | GE |
| W. Wheadon | GE |



UNITED STATES
CLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

RETURN TO REACTOR DOCKET
FILES

Mr. L. O. Mayer, Manager
Northern States Power Company
414 Nicollet Mall - 8th Floor
Minneapolis, Minnesota 55401

Gerald Charnoff, Esquire
Shaw, Pittman, Potts and
Trowbridge
1800 M Street, N. W.
Washington, D. C. 20036

Arthur Renquist, Esquire
Vice President - Law
Northern States Power Company
414 Nicollet Mall
Minneapolis, Minnesota 55401

Mr. L. R. Eliason
Plant Manager
Monticello Nuclear Generating Plant
Northern States Power Company
Monticello, Minnesota 55362

Russell J. Hatling, Chairman
Minnesota Environmental Control
Citizens Association (MECCA)
Energy Task Force
144 Melbourne Avenue, S. E.
Minneapolis, Minnesota 55414

Anthony Z. Roisman
Natural Resources Defense Council
917 15th Street, N. W.
Washington, D. C. 20005

The Environmental Conservation Library
Minneapolis Public Library
300 Nicollet Mall
Minneapolis, Minnesota 55401

Mr. Robert N. Lazo, Esquire
Chairman
Atomic Safety and Licensing Board
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dr. Richard F. Cole
Atomic Safety and Licensing Board
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dr. Walter H. Jordan
881 West Outer Drive
Oak Ridge, Tennessee 37830

Mr. Kenneth Dzigan
Environmental Planning Consultant
Office of City Planner
Grace Building
421 Wabasha Street
St. Paul, Minnesota 55102

Ms. Terry Hoffman
Executive Director
Minnesota Pollution Control Agency
1935 W. County Road B2
Roseville, Minnesota 55113

Mr. Steve Gadler
2120 Carter Avenue
St. Paul, Minnesota 55108

→ Docket File 50-263

NRC PDR
Local PDR
NRR Rdg
ORB#3 Rdg
H. Denton
E. Case
V. Stello
D. Eisenhut
B. Grimes
R. Vollmer
T. Ippolito
R. Reid
V. Noonan

G. Knighton
A. Schwencer
D. Ziemann
P. Check
G. Lainas
D. Davis
OELD
OI&E (3)
S. Sheppard
Project Manager
ACRS (16)
NRC Participants
TERA
J. Buchanan

JUNE 7 1979

DISTRIBUTION:

Docket
ORB#3 Rdg
NRR Rdg
Tippolito
TKevern
SSheppard

Docket No. 50-263

Mr. John-Mark Stensvaag, Esquire
Special Assistant Attorney General
Minnesota Pollution Control Agency
Office of Attorney General, State
of Minnesota
1935 W. County Road B2
Roseville, Minnesota 55113

Dear Mr. Stensvaag:

In my letter of May 22, 1979, I forwarded some of the material referenced in the Director's Decision of April 24, 1979 concerning Monticello's spent fuel storage. Enclosed are two additional reports; "Evaluation of Control Rod Materials" by L. Marti-Balaguer and W. R. Smalley, and "Corrosion of Materials in Spent Fuel Storage Pools" by J. R. Weeks. A third report, "Spent Fuel Storage Module, Corrosion Report No. 554" by L. Mollon was forwarded to you in November 1978 by Northern States Power Company. The material remaining to be forwarded are the four General Electric Company (GE) boron corrosion reports. I have been in contact with GE and am assured that non-proprietary versions of these reports will be available the week of June 4, 1979.

Sincerely,

Original Signed by
T. A. Ippolito

Thomas A. Ippolito, Chief
Operating Reactors Branch #3
Division of Operating Reactors

Enclosures:

"Evaluation of Control Rod Materials"
and "Corrosion of Materials in
Spent Fuel Storage Pools"

| | | | | | | |
|---------|-------------|-----------|--|--|--|--|
| OFFICE | ORB#3 | ORB#3 | | | | |
| SURNAME | TKevern:acr | Tippolito | | | | |
| DATE | 6/7/79 | 6/7/79 | | | | |

WPCA

CVTR PROJECT

CAROLINAS VIRGINIA NUCLEAR POWER ASSOCIATES, INC.

Research and Development Program

AT (30-1) - 2289

Terminal Report

EVALUATION OF CONTROL ROD MATERIALS

Sub-Task 6.03

by

L. Marti-Balaguer

and

W. R. Smalley

J. J. Lombardo

J. J. Lombardo, Manager

Core Process Development
and Fabrication Section

Westinghouse Electric Corporation

Atomic Power Department

TABLE OF CONTENTS

| | <u>Page No.</u> |
|---|-----------------|
| List of Figures | ii |
| List of Tables | iii |
| I. Abstract | 1 |
| II. Introduction | 2 |
| III. Conclusions | 5 |
| IV. Corrosion Test Program | 6 |
| A. Corrosion Tests in Static Water | 6 |
| B. Corrosion Tests in Helium-Water Vapor Atmosphere | 12 |
| V. Mechanical Tests | 12 |
| VI. Fabrication of Prototype Control Rod Absorber | 20 |
| VII. References | 27 |

LIST OF FIGURES

| <u>Figure No.</u> | | <u>Page No.</u> |
|-------------------|--|-----------------|
| 1 | Microstructural Composition of the Ternary and Quaternary Silver-Base Alloys After Exposure for 100 and 2000 Hours, Respectively in Demineralized Water at 190°F | 10 |
| 2 | Microstructure of Ag-In-Cd Corrosion Specimen After 3830 Hours in 190°F Water | 11 |
| 3 | Schematic Diagram of Apparatus Used for Corrosion Tests | 13 |
| 4. | Surface Appearance of Silver-Base Alloys and 1.5 w/o Boronated Stainless Steel After Exposure to Helium-Water Vapor Atmosphere at 530°F for 739 Hours . . | 15 |
| 5 | Microstructure of Ag-In-Cd-Sn Specimen After Exposure to Helium-Water Vapor Atmosphere at 530°F for 740 Hours | 16 |
| 6 | Typical Microstructure of 1.5 w/o B Stainless Steel | 22 |
| 7 | Construction Details of CVTR Control Rod | 23 |
| 8 | Control Rod Partially Withdrawn From a Test Chamber | 25 |
| 9 | Close-up View of Absorber Portion of Control Rod Showing 3-Layer Construction | 26 |

LIST OF TABLES

| <u>Table No.</u> | | <u>Page No.</u> |
|------------------|--|-----------------|
| 1 | Chemical Composition of Alloys Tested | 3 |
| 2 | Results of Corrosion Tests of Control Rod Materials in Static-Water | 8 |
| 3 | Results of Corrosion Tests of Control Rod Materials in Various Conditions | 9 |
| 4 | Results of Corrosion Tests in Helium-Water Vapor Atmosphere | 14 |
| 5 | Tensile Properties of Silver-Base Alloys at 250°F . . | 18 |
| 6 | Comparison of Creep Rates at 250°F | 18 |
| 7 | Comparison of Mechanical Properties of Ag-In-Cd Alloy in Annealed and Stress Relieved Condition | 19 |
| 8 | Mechanical Properties of Boronated Stainless Steel. . | 21 |

I. ABSTRACT

Mechanical and corrosion tests were performed on various control rod materials for CVTR application.

The corrosion tests were carried out in demineralized static-water at 190°F and in a helium-water vapor atmosphere at 530°F. The mechanical tests were carried out at room temperature and at 250°F.

The tests indicated that either boronated stainless steel or silver-indium-cadmium alloy would perform satisfactorily in the CVTR environment. Based primarily on the lower cost, boronated stainless steel was selected for the CVTR control rod. A prototype control rod was fabricated with boronated (1.5% B) stainless steel absorber material. The assembly was fabricated by riveting two absorber plates to AISI type 304 stainless steel center section.

II. INTRODUCTION

The CVTR control rod absorber material was selected from known and available material possibilities. A survey was made of available materials potentially useful for the CVTR control rod application. As a result, thereof, the following three general types of absorber materials were chosen to be evaluated for the CVTR:

- a. silver-base alloys
- b. boronated stainless steel
- c. boron carbide dispersion in an aluminum matrix ("Boral").

Materials, comprising all of the above absorber types, have been evaluated by various laboratories for specific environmental conditions, however, none were identical to CVTR's. Much of the data published by these laboratories was used in planning the CVTR evaluation program.

The specific absorber materials ultimately evaluated for the CVTR were as follows:

1. silver-base alloys:
 - a. Ag-In-Cd
 - b. Ag-In-Cd-Sn
2. boronated stainless steels with:
 - a. 1.0% natural boron
 - b. 1.5% natural boron
 - c. 2.0% natural boron
3. Boral (boron carbide dispersed in an aluminum matrix)

The chemical compositions of the materials are listed in Table I.

Silver-base alloys were considered as early as 1950¹ as possible control rod materials for pressurized water reactors. However, they were not used in actual reactors until a decade later because of their questionable corrosion resistance in high temperature water. Ag-In-Cd alloy was used in

TABLE I

CHEMICAL COMPOSITION OF ALLOYS TESTED

Elements (Weight Per Cent)

[illegible]

the Yankee and BR-3 reactors only after a suitable nickel plating technique was developed to protect the base alloy from high temperature water. Despite the questionable corrosion resistance in high temperature water, there were indications that the unplated alloy would perform satisfactorily in low temperature (200°F and below) water. On the basis of this evidence it was decided to evaluate unplated silver-indium-cadmium and silver-indium-cadmium-tin alloys for application in the CVTR.

Stainless steel with 1% Boron-10 was used in the Engineering Test Reactor at ARCO, Idaho and the Vallecitos Boiling Water Reactor (General Electric). In view of these applications, it was decided to evaluate boronated materials under CVTR conditions.

III. CONCLUSIONS

1. The highest corrosion rate exhibited by the boronated stainless steels was 0.7 mg/cm^2 per year.
2. The highest corrosion rate exhibited by the silver-base alloys was 1.00 mg/cm^2 per year.
3. The boron exhibited the highest corrosion rate of all the alloys tested. It ranged from 8.8 to 14.8 mg/cm^2 per year.
4. The silver-base alloys and boronated stainless steel exhibited corrosion rates of less than 0.5 mg/cm^2 per year in helium-water vapor atmosphere at 530°F .
5. Mechanical testing of the two silver-base alloys and $1.5\% \text{ B}^{\text{N}}$ stainless steel indicated that each material was adequate for the CVTR control rod design.
6. No serious difficulty was encountered in the fabrication of a prototype CVTR control rod absorber, and consequently, no problems are anticipated in the fabrication of the actual CVTR control rod absorbers.

Corrosion coupons, 2-1/8 inch x 3/4 inch x 1/8 inch, were used for evaluating the materials in two environments. One was static demineralized water at 190°F, at 7.0 ± 0.3 pH and atmospheric pressure. The other environment was a helium-water vapor atmosphere produced by passing helium through a tank of water at 180°F and conducting the vapor saturated helium to a specimen container in a furnace chamber which was kept at 530°F. The pressure inside the furnace chamber was kept slightly above atmospheric by inserting the end of a tube protruding from the specimen chamber below two inches of water.

A. Corrosion Tests in Static-Water

Test coupons of Boral, silver-base alloys, and boronated stainless steels were tested in the static-water environment described above. The Boral material was tested in the as-received condition only. The silver-base alloys were tested in two heat treated conditions, namely; stress-relieved at 750°F for two hours, and annealed at 1112°F for four hours. The boronated stainless steels were tested in the as-received condition and annealed at 1950°F for one hour.

Test specimens were suspended from a tree-like stainless steel fixture and immersed in the test environment. They were not in contact with each other, but not insulated from the fixture.

Corrosion data were obtained for exposures ranging from 100 hours to 3,830 hours. The corrosion behavior of the silver alloys and Boral was evaluated by weight change measurements and by metallographic examination. The boronated stainless steels were evaluated by weight change measurements only. No metallographic examination was performed because no internal damage was expected to occur in the material.

Tests on the Boral material and the 1.0% B stainless steel were discontinued after the first 2000 hours of testing. The Boral material showed a high corrosion rate in comparison to the other materials. Another objection to Boral was the fact that it was known to be

difficult to fabricate. The 1.0% B stainless steel was considered to have too low an absorption cross section for the intended control rod application, therefore, further testing was discontinued.

The corrosion data for materials exposed to static-water are presented in Tables 2 and 3. Boronated stainless steel showed a negligible corrosion rate; the highest weight gain being $0.7 \text{ mg/cm}^2/\text{year}$ which occurred at 100 hours exposure. However, at exposure periods beyond 200 hours the rate dropped below $0.1 \text{ mg/cm}^2/\text{year}$ which indicated that the initial oxidation was greatest and decreased with further exposure.

The silver-base alloys, unlike the boronated stainless steels, exhibited weight losses and showed slightly higher corrosion rates than the stainless steels. However, their rates were still very small; the highest value was $1 \text{ mg/cm}^2/\text{year}$. There was a general trend of lower corrosion rates for the silver alloy specimens annealed at 1112°F . The magnitude of the overall values were so small it was impossible to assign any significance to this.

The Boral exhibited the highest corrosion rate, 8.8 to $14.7 \text{ mg/cm}^2/\text{year}$, which was considerably higher than any of the other alloys. This, coupled with poor fabricability, disqualified Boral from further testing.

Published data^{1,2} indicated that Ag-In-Cd alloys were susceptible to internal oxidation in high temperature water (550°F). However, as shown in Figures 1 and 2, there was no evidence of internal oxidation as a result of testing. Internal oxidation is usually reflected as weight gain; these alloys showed weight losses.

The data indicated that neither the boronated stainless steels nor the silver-base alloys were significantly affected by the corrosion environment. It was concluded that from the corrosion standpoint either of the two materials was satisfactory for CVTR control rod absorbers.

¹ P. 26

² P. 27-31

TABLE 2

RESULTS OF CORROSION TESTS OF CONTROL ROD MATERIALS IN STATIC-WATER

Test Conditions:

Medium
Temperature
Pressure

Demineralized Water, 7.0 ± 0.3 pH
 $190^{\circ}\text{F} \pm 10^{\circ}\text{F}$
Atmospheric

TEST RESULTS

| Material | 100 Hrs. Exposure | | 900 Hrs. Exposure | | 2000 Hrs. Exposure | |
|----------------------|-------------------|--|-------------------|--|--------------------|--|
| | Wt. Change Mgs | Corrosion Rate $\text{Mg}/\text{cm}^2/\text{yr.}$ | Wt. Change Mgs | Corrosion Rate $\text{Mg}/\text{cm}^2/\text{yr.}$ | Wt. Change Mgs | Corrosion Rate $\text{Mg}/\text{cm}^2/\text{yr.}$ |
| 80 Ag-15 In-5 Cd | 0.0* | - | -2.3 | 0.89 | -1.8 | 0.31 |
| Stress Relieved | -0.1 | 0.35 | -1.8 | 0.70 | -1.5 | 0.26 |
| at 750°F for 4 hrs. | 0.0 | - | -1.3 | 0.50 | -1.9 | 0.33 |
| | -0.1 | 0.35 | -0.7 | 0.27 | -1.8 | 0.31 |
| 80 Ag-15 In-4.5 | 0.0 | 0.35 | -1.6 | 0.61 | -1.2 | 0.21 |
| Cd-0.5 Sn Stress | +0.1 | 0.35 | -0.3 | 0.12 | -0.3 | 0.05 |
| Relieved at 750°F | +0.1 | 0.35 | +0.4 | 0.15 | -0.1 | 0.01 |
| for 4 hrs. | +0.1 | - | -0.1 | 0.04 | -1.4 | 0.20 |
| Boronated SS | +0.2 | 0.70 | +0.5 | 0.19 | 0.0 | - |
| 1.0% Nat. B | +0.1 | 0.35 | +0.3 | 0.12 | 0.0 | - |
| As-Received | +0.1 | 0.35 | +0.2 | 0.08 | +0.2 | 0.04 |
| | | | +0.3 | 0.12 | +0.1 | 0.02 |
| Boronated SS | +0.1 | 0.35 | +0.6 | 0.23 | +0.4 | 0.07 |
| 1.5% Nat. B | 0.0 | - | +0.7 | 0.27 | +0.1 | 0.02 |
| As-Received | +0.1 | 0.35 | +0.7 | 0.27 | +0.1 | 0.02 |
| | 0.0 | - | +0.6 | 0.24 | +0.2 | 0.04 |
| Boronated SS | 0.0 | - | +0.3 | 0.12 | -0.1 | 0.02 |
| 2.0 w/o Nat. B | 0.0 | - | +0.5 | 0.19 | -0.3 | 0.05 |
| As-Received | -0.1 | 0.35 | +0.4 | 0.15 | 0.0 | - |
| | 0.0 | - | +0.9 | 0.35 | +0.1 | 0.02 |
| Boral (Boron Carbide | +30.2 | 62.43 | +156.4 | 35.97 | +143.3 | 14.77 |
| in Aluminum Matrix) | +22.6 | 46.79 | + 73.7 | 16.94 | +114.8 | 8.81 |
| As-Received | | | | | +110.3 | 11.40 |
| | | | | | + 85.5 | 8.97 |

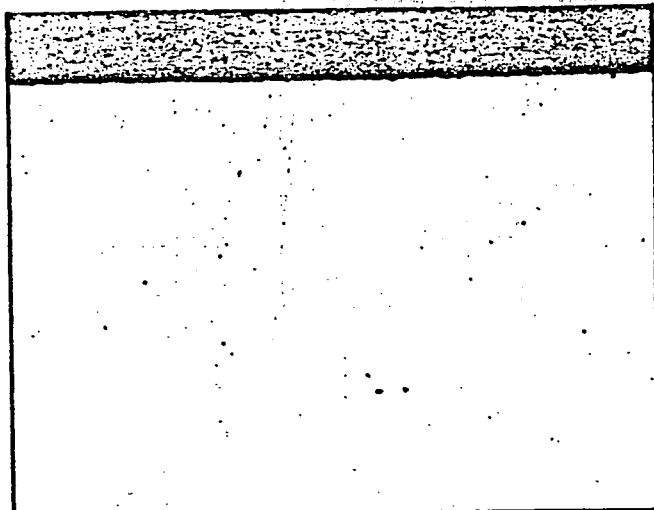
* New specimens were used for each exposure period.

RESULTS OF CORROSION TESTS OF CONTROL ROD MATERIALS IN VARIOUS CONDITIONS

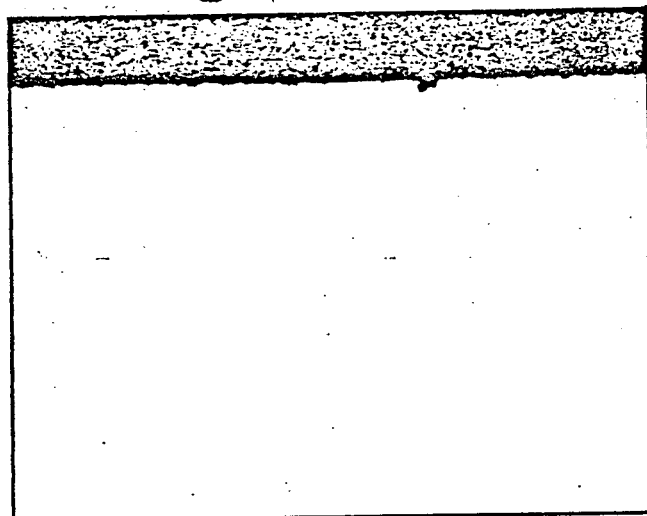
Test Conditions:

Exposure Temperature 190°F ± 10°F
 Environment Demineralized Water,
 pH 7.0 ± 0.3

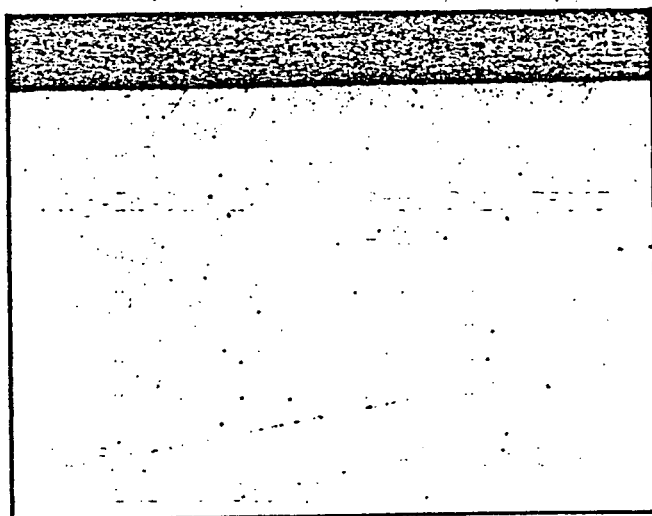
| MATERIAL | CONDITION | EXPOSURE TIME HOURS | WEIGHT CHANGE MILLIGRAMS | CORROSION RATE Mg/cm ² /year |
|------------------------------|---------------------------|------------------------|-----------------------------|--|
| Ag-In-Cd | Ann. 1112° -4 hrs. | 1812 | -2.1 | 0.41 |
| " | " | 1812 | -1.0 | 0.19 |
| " | " | 1812 | -1.6 | 0.32 |
| " | " | 1812 | -1.5 | 0.30 |
| " | " | 1812 | -0.8 | 0.15 |
| " | " | 1812 | -1.6 | 0.31 |
| Ag-In-Cd | Str. Rel. 750°F 4 hrs. | 2686 | -5.3 | 0.69 |
| " | " | 2686 | -7.7 | 1.00 |
| " | " | 2686 | -4.2 | 0.55 |
| " | " | 3830 | -8.2 | 0.75 |
| " | " | 3830 | -7.1 | 0.65 |
| " | " | 3830 | -6.4 | 0.58 |
| Ag-In-Cd-Sn | Ann. 1112°F -4 hrs. | 1812 | -0.8 | 0.16 |
| " | " | 1812 | -0.5 | 0.09 |
| " | " | 1812 | -0.1 | 0.19 |
| " | " | 1812 | -0.6 | 0.12 |
| " | " | 1812 | -0.2 | 0.04 |
| " | " | 1812 | -2.2 | 0.42 |
| Ag-In-Cd-Sn | Str. Rel. 750°F 4 hrs. | 2686 | -4.7 | 0.61 |
| " | " | 2686 | -4.3 | 0.59 |
| " | " | 3830 | -5.2 | 0.47 |
| " | " | 3830 | -5.9 | 0.53 |
| " | " | 3830 | -5.0 | 0.45 |
| " | " | 3830 | -6.1 | 0.55 |
| 1.5 w/o B Stainless Steel | As-Received | 3812 | +0.3 | 0.03 |
| " | " | 2660 | +0.6 | 0.08 |
| " | " | 2660 | +0.5 | 0.07 |
| " | Ann. 1950°F -1 hr. | 1912 | +0.4 | 0.07 |
| " | " | 2660 | 0.0 | 0.00 |
| " | " | 2660 | +0.6 | 0.08 |
| 2.0 w/o B Stainless Steel | As-Received | 3812 | +0.5 | 0.05 |
| " | " | 3812 | +0.6 | 0.06 |
| " | " | 3812 | +0.4 | 0.04 |
| " | Ann. 1950°F 1 hr. | 2686 | +0.5 | 0.06 |
| " | " | 2686 | 0.0 | 0.00 |
| " | " | 2686 | +0.3 | 0.04 |



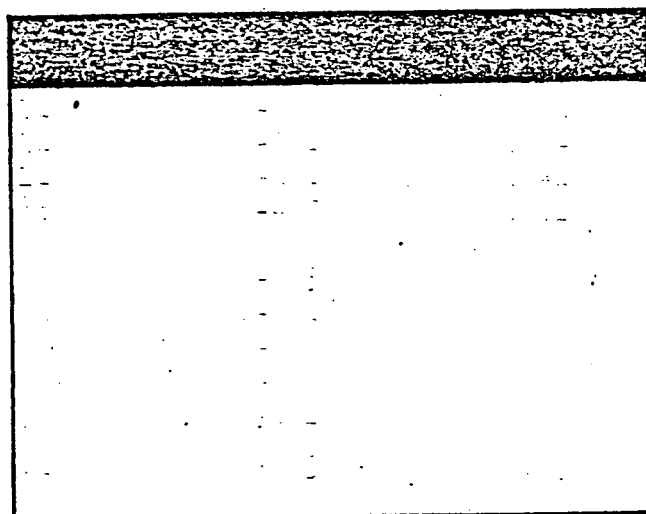
N-3426 250 x Mag
80 Ag-15 In - 5 Cd Alloy after
100 hours exposure



N-3700 250 x Mag
80 Ag-15 In - 5 Cd Alloy After
2000 hours exposure

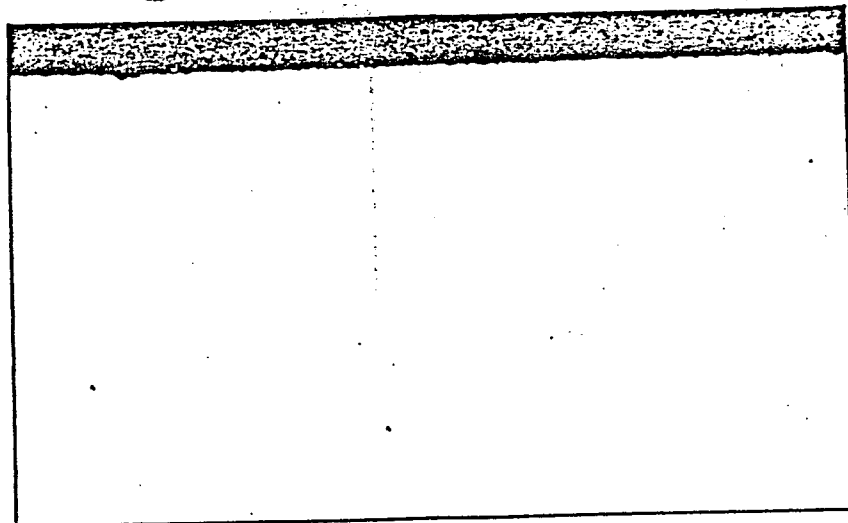


N-3427 250 x Mag
80 Ag - 15 In - 4.5 Cd - 0.5 Sn Alloy
After 100 hours exposure



N-3699 250 x Mag
80 Ag - 15 In - 4.5 Cd - 0.5 Sn
Alloy after 2000 hours exposure

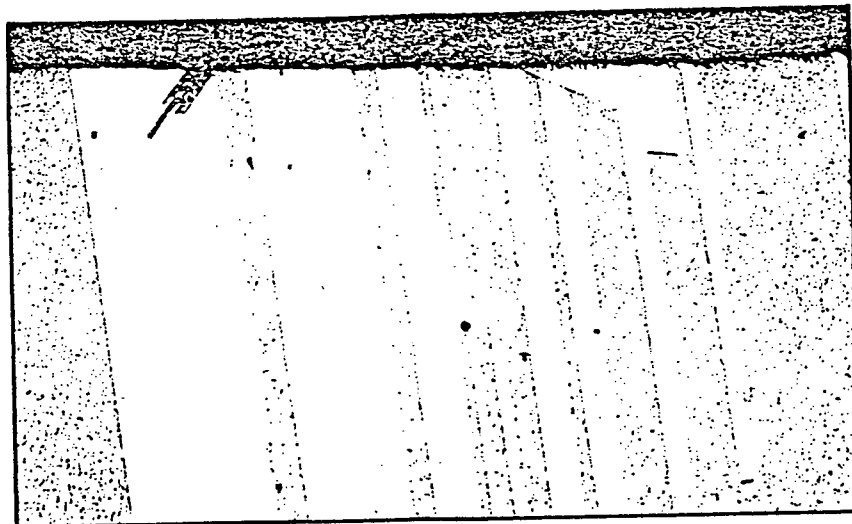
Figure 1 - Microstructural comparison of the ternary and quaternary silver base alloys after exposure for 100 and 2000 hours to demineralized static water at 190°F. As indicated by the structure, no internal oxidation developed.



N-4524

A

Mag. 250 x



N-4524

B

Mag. 250 x

Figure 2 - Microstructure of Ag-In-Cd Corrosion specimens after 3830 hours in 190°F Water

A - Unetched

B - Etched with Sulfuric Acid Water-Chromic Acid Solution

B. Corrosion Tests in Helium-Water Vapor Atmosphere

The apparatus used to produce the helium-water vapor atmosphere is shown in Figure 3. The atmosphere was intended to simulate conditions above the moderator in the header cavity during plant operation.

Six coupon type specimens of each of the two silver-base alloys and of the 1.5% B stainless steel were exposed to the helium-water vapor atmosphere at 530°F for 739 hours. The silver-base coupons were annealed at 1112°F for four hours and the boronated stainless steels were annealed at 1950°F for one hour. The corrosion behavior was evaluated by weight change measurements and, in the case of the silver alloys, by metallographic examination.

Corrosion data are presented in Table 4. Representative specimens are shown in Figure 4 after exposure to the helium-water vapor atmosphere. Metallographic examination of the silver alloys revealed no internal oxidation. Figure 5 shows the etched and unetched microstructure in which there was no evidence of internal oxidation or attack. The weight change was insignificant for both silver alloys and the boronated stainless steel. Unlike the behavior in static-water, the silver alloy specimens gained weight in this environment.

The surface appearance was good for both materials. There was some tarnish reflecting the exposure temperature, but there was no evidence of surface deterioration. It was concluded that either material would perform satisfactorily for CVTR control and rod absorbers.

V. MECHANICAL TESTS

As part of the program to develop and select a suitable alloy for the CVTR control rod absorber plates, mechanical tests were performed on the more promising candidate materials which included:

- a. Ag-In-Cd Ternary Alloy
- b. Ag-In-Cd + 0.5% Sn
- c. Boronated Stainless Steel
(Type 304 with 1.5% natural B)

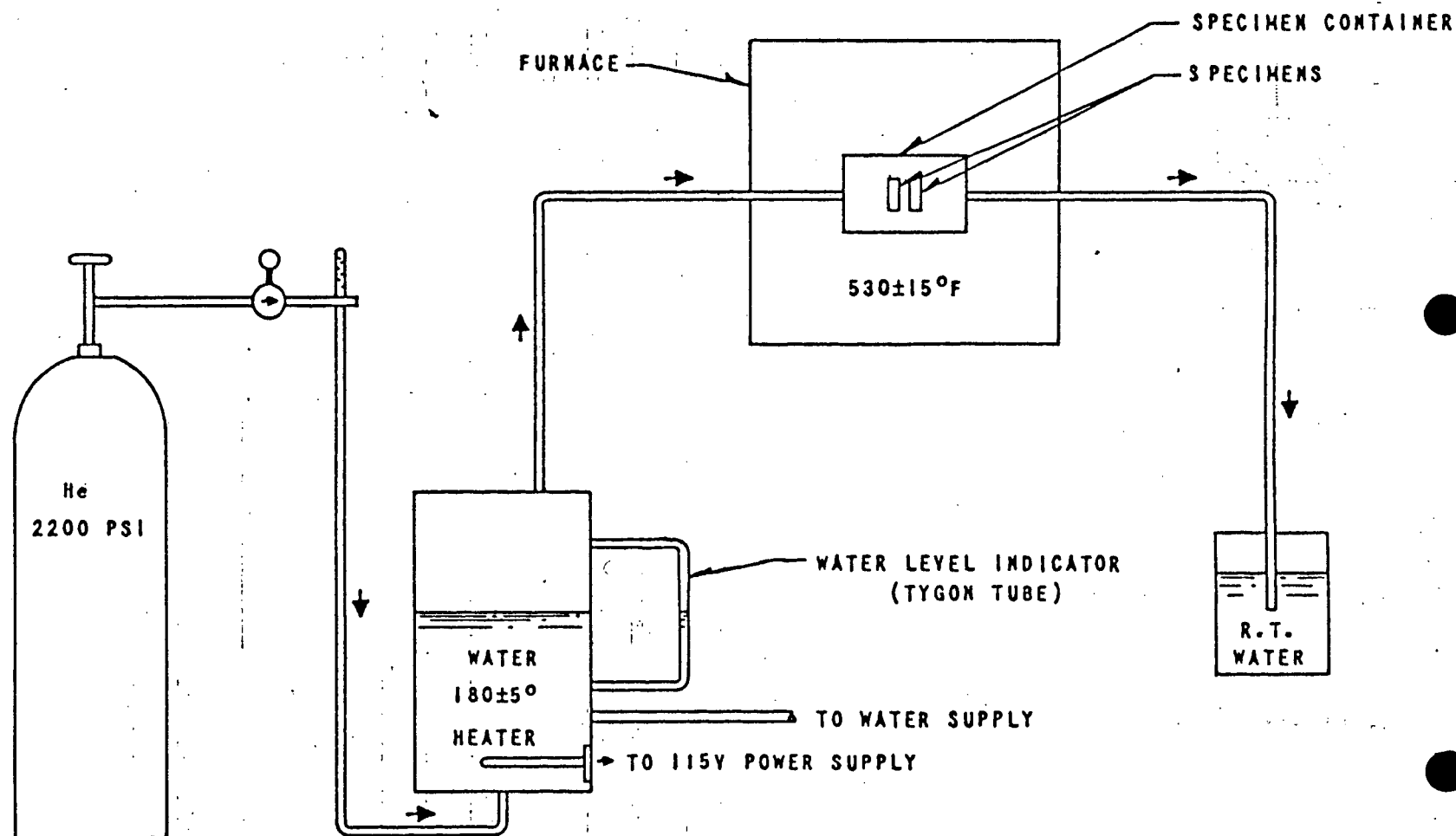


Figure 3 -

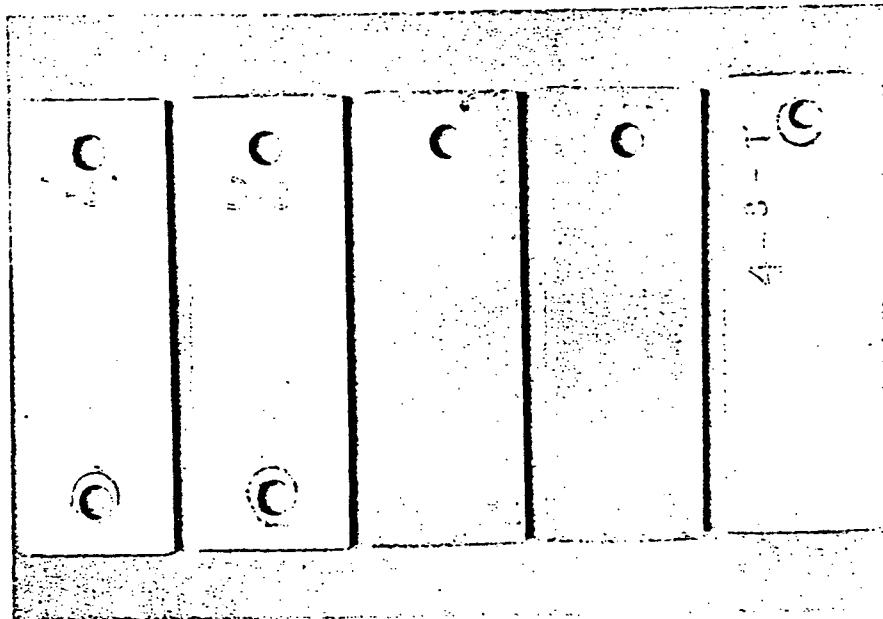
SCHEMATIC DIAGRAM OF APPARATUS
USED FOR CORROSION TEST

RESULTS OF CORROSION TESTS IN HELIUM-WATER VAPOR ATMOSPHERE

Test Conditions:

| | |
|---------------|--|
| Medium | Helium Saturated with Water Vapor at 180°F |
| Temperature | 530°F ± 15° |
| Pressure | Atmospheric |
| Exposure Time | 739 Hours |

| <u>MATERIAL</u> | <u>WT. CHANGE Mgs.</u> | <u>CORROSION RATE</u> <u>Mg/cm²/year</u> |
|---------------------|------------------------|--|
| 80 Ag-15 In-5 Cd | +0.3 | 0.14 |
| Annealed at 1112°F | +0.6 | 0.29 |
| for 4 hours | +0.2 | 0.10 |
| | +0.2 | 0.10 |
| | +0.2 | 0.10 |
| | +0.0 | 0.00 |
| 80 Ag-15 In-4.5 Cd | +0.0 | 0.00 |
| -.5 Sn Annealed at | +0.2 | 0.10 |
| 1112°F for 4 hours | +0.1 | 0.05 |
| | +0.3 | 0.14 |
| | +0.2 | 0.10 |
| | +0.1 | 0.05 |
| 1.5 w/o B Boronated | +0.7 | 0.34 |
| Stainless Steel | +0.5 | 0.24 |
| | +0.6 | 0.29 |
| | +0.8 | 0.39 |
| | +0.6 | 0.29 |
| | +0.6 | 0.29 |



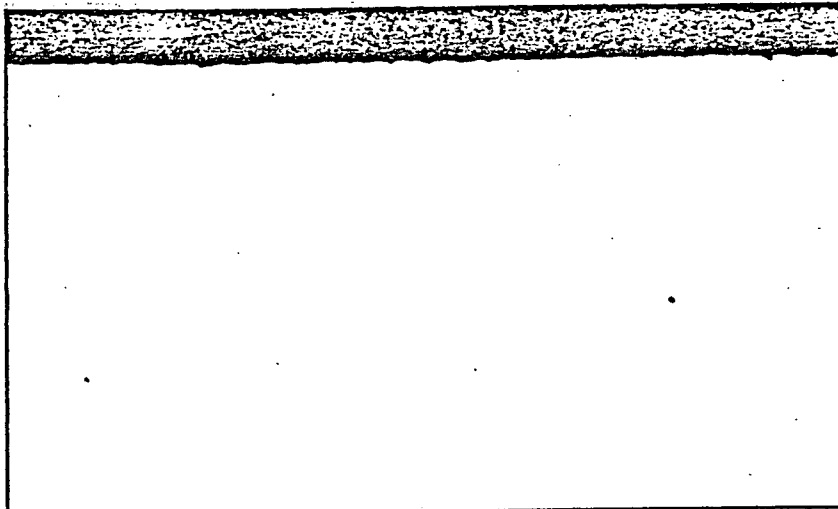
N-1096

1 x Mag.

From left to right: First 2 specimens 80Ag-15In-5% Cd
 Next 2 specimens 1.5 w/o Boronated Stainless Steel
 Last specimen 80Ag-15In-4.5 Cd -0.5% Sn

Figure 4

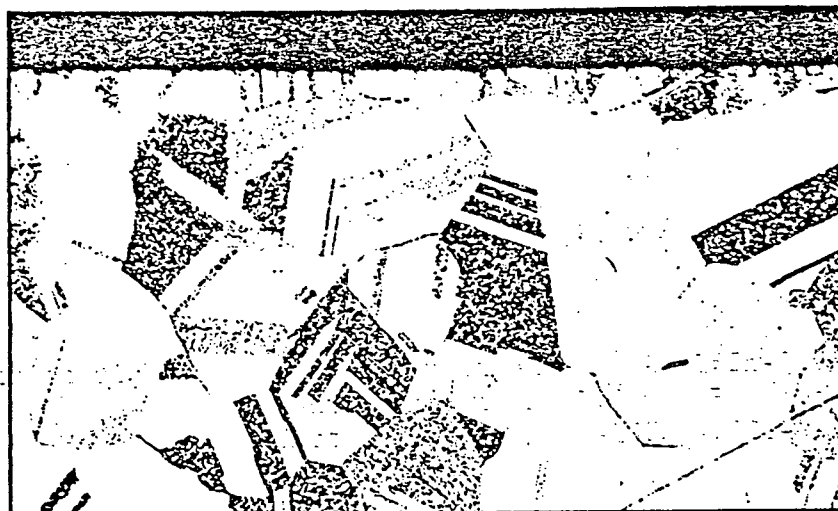
Surface Appearance of Silver-Base Alloys and 1.5 w/o Boronated Stainless Steel After Exposure to a Helium-Water Vapor Atmosphere at 530 $^{\circ}\text{F}$ for 739 Hours



N-4372

A

Mag 250 x



N-4372

B

Mag 250 x

A - Unetched

B - Etched with Sulfuric Acid-Water-Chromic Acid Solution

Figure 5 - Microstructure of Ag-In-Cd-Sn Specimen After Exposure to Helium-Water Vapor Atmosphere at 530°F for 740 hours.

The prime purposes of the testing program were to determine tensile and creep properties of Ag-In-Cd and Ag-In-Cd-Sn alloys at 250°F and to obtain mechanical properties for boronated stainless steel at CVTR operating temperatures with emphasis on ductility and toughness.

Tensile and creep testing of the silver alloys were conducted on conventional specimens machined from extruded round bar stock. Tensile results are shown in Table 5 and creep properties for the two materials are presented in Table 6. Initial testing was performed on material which was annealed at 1112°F for four hours. Generally, the data indicated that the Ag-In-Cd-Sn alloy possessed higher tensile and creep strengths at 250°F than the ternary alloy. Some of the apparent superiority may be accounted for by the difference in hardness (Brinell 45 versus 37), which in turn could be the result of different extrusion conditions and/or response to the 1112°F 4 hours annealing treatment. On the other hand, Bettis Atomic Power Laboratory experience had previously shown that 0.5% Sn additions slightly increased the strength of Ag-In-Cd alloys.

Because of the low yield strengths and extreme softness of the silver-base alloys, consideration was given to a stress relief heat treatment instead of the high temperature anneal. Such a measure was expected to provide increased yield strengths, finer grain size, and improve fabrication characteristics. Therefore, the overall program was modified to include tensile and creep tests at 250°F for the Ag-In-Cd alloy, stress relieved at 750°F for one hour. Table 7 summarizes the test results and indicated, as anticipated, the stress relieved Ag-In-Cd alloy had considerably higher yield strength than the annealed material, although ductility was essentially unchanged. Creep properties were changed to the extent that plastic strain on loading and total elongation were significantly reduced. On the other hand, creep rates were slightly higher for the stress relieved material. With respect to overall mechanical properties for potential CVTR applications, it appeared that the 750°F for one hour stress relief was the preferable heat treatment. Although the strength properties of both Ag-In-Cd alloys were relatively low, the nature of the CVTR control rod design would permit the use of either of these alloys.

TABLE 5

TENSILE PROPERTIES OF SILVER-BASE ALLOYS AT 250°F

| | <u>Ag-In-Cd</u> | <u>Ag-In-Cd-Sn</u> |
|--------------------------|-----------------|--------------------|
| 0.2% Yield Strength, psi | 6,230 | 9,800 |
| Ultimate Strength, psi | 37,700 | 44,500 |
| % Elong. in 1.4" | 65 | 58 |
| % Reduction of Area | 62 | 60 |
| Brinell Hardness (500Kg) | 37 | 45 |

TABLE 6

COMPARISON OF CREEP RATES AT 250°F, PER CENT PER HOUR, Ag-In-Cd VERSUS Ag-In-Cd-Sn

| <u>Stress (psi)</u> | <u>Ag-In-Cd</u> | <u>Ag-In-Cd-Sn</u> |
|---------------------|-----------------|--------------------|
| 5,000 | 0.0009 | 0.0002 |
| 20,000 | 0.0018 | 0.0021 |
| 30,000 | 0.0138 | 0.0126 |
| 35,000 | 0.1087 | 0.0142 |

COMPARISON OF MECHANICAL PROPERTIES OF Ag-In-Cd ALLOY
IN THE ANNEALED AND STRESS RELIEVED CONDITIONS

| | Annealed 1112°F 4 Hrs. | Stress Relieved 750°F 1 Hr. |
|-------------------------------------|---------------------------|--------------------------------|
| A. <u>Tensile Properties, 250°F</u> | | |
| 0.2% Yield Str., psi | 6,230 | 12,600 |
| Ultimate Strength, psi | 37,700 | 41,600 |
| % Elong. in 1.4" | 65 | 65 |
| % Reduction of Area | 62 | 70 |
| Brinell Hardness (500 Kg) | 37 | 53 |
| B. <u>Creep Properties, 250°F</u> | | |
| At 20,000 psi: | | |
| Plastic Strain on Loading % | 14.4 | 3.8 |
| Total Elongation, % | 15.1 | 4.8 |
| Creep Rate, % per Hour | 0.0018 | 0.0025 |
| At 30,000 psi: | | |
| Plastic Strain on Loading % | 27.6 | 13.0 |
| Total Elongation % | 32.2 | 16.3 |
| Creep Rate, % per Hour | 0.0112 | 0.0174 |

The tensile and impact data on boronated stainless steel bar stock are shown in Table 8. The room temperature properties were consistent with those obtained in previous investigations. Compared with boron-free AISI Type 304, strength levels were slightly higher, with ductility and toughness considerably lower. It was noted also that ductility as well as strength were lower at 250°F than at room temperature. The microstructure of the material tested, shown in Figure 6, is considered typical of boronated stainless steel of this composition. Note the numerous particles of boron-rich second phase aligned in the direction of rolling.

Mechanical properties were also determined on samples machined from excess stock from the prototype control rod absorber section and are included in Table 8. Generally, the longitudinal properties were comparable to those of the bar stock. Transverse specimens showed lower toughness and ductility as expected, and also lower ultimate strength. Despite the relatively low toughness and ductility, the overall properties of boronated Type 304 stainless steel was considered adequate for the CVTR control rod design.

VI. FABRICATION OF A PROTOTYPE CONTROL ROD ABSORBER

While the materials evaluation program was in progress, various designs were being considered for the control rod. The design finally selected was one involving a sandwich-type construction as shown in Figure 7.

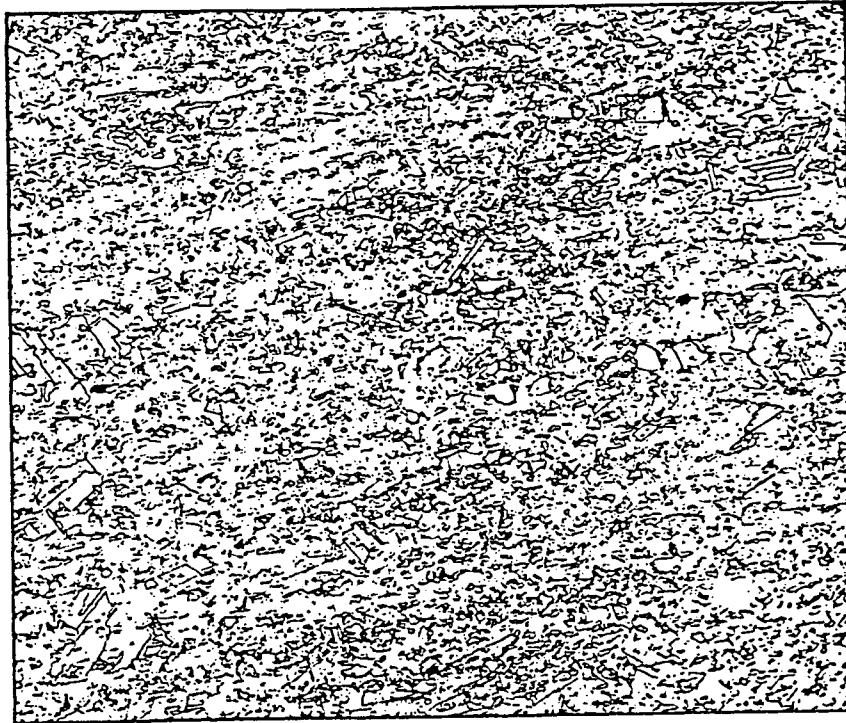
As illustrated, the control rod consisted of two absorber plates riveted to a support plate, made of AISI Type 304 stainless steel. The absorber material was 1.5 percent boronated stainless steel, but any of the alloys under consideration at the time the design was selected could have been used in the construction which was one of the criteria in choosing the design.

Based primarily on lower cost, boronated stainless steel was selected for the CVTR control rod. The lowest bid for fabricating one assembly with a silver-base alloy absorber was \$4,717.00 while the actual cost of fabricating one prototype with boronated stainless steel absorber was \$2,882.00. It was assumed that for quantity purchases, the unit costs would remain in about the same proportion.

TABLE 8

MECHANICAL PROPERTIES OF BORONATED STAINLESS STEEL

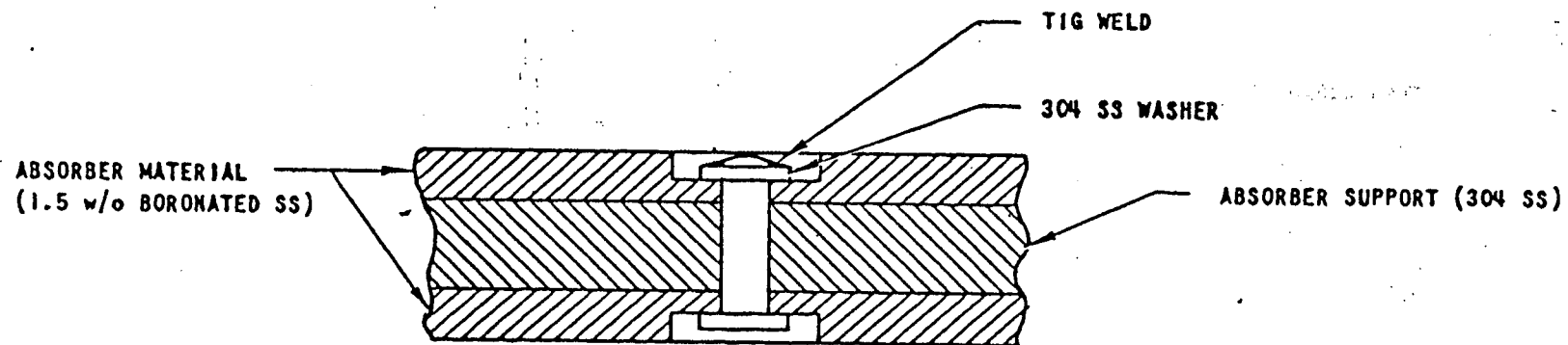
| <u>Material</u> | <u>Test Temp °F</u> | <u>0.2% Yield Str. (psi)</u> | <u>Ultimate Str. (psi)</u> | <u>Elong. (%)</u> | <u>Red. Area (%)</u> | <u>Impact Energy (Ft-Lbs)</u> |
|-------------------------------------|-------------------------|----------------------------------|--------------------------------|-----------------------|--------------------------|-----------------------------------|
| Bar Stock | Room T. | 48,600 | 93,500 | 21 | 23 | 16 |
| Absorber Plate(Long'l) | " | 44,100 | 92,400 | 17 | 20 | 10 |
| Absorber Plate (Trans- verse) | " | 51,100 | 77,100 | 9 | 8 | 4 |
| Bar Stock | 250 | 42,100 | 82,000 | 14 | 14 | 13 |
| Absorber Plate(Long'l) | 250 | 51,000 | 76,300 | 14 | 18 | 10 |
| Absorber Plate | 250 | 49,400 | 69,600 | 9 | 9 | 4 |



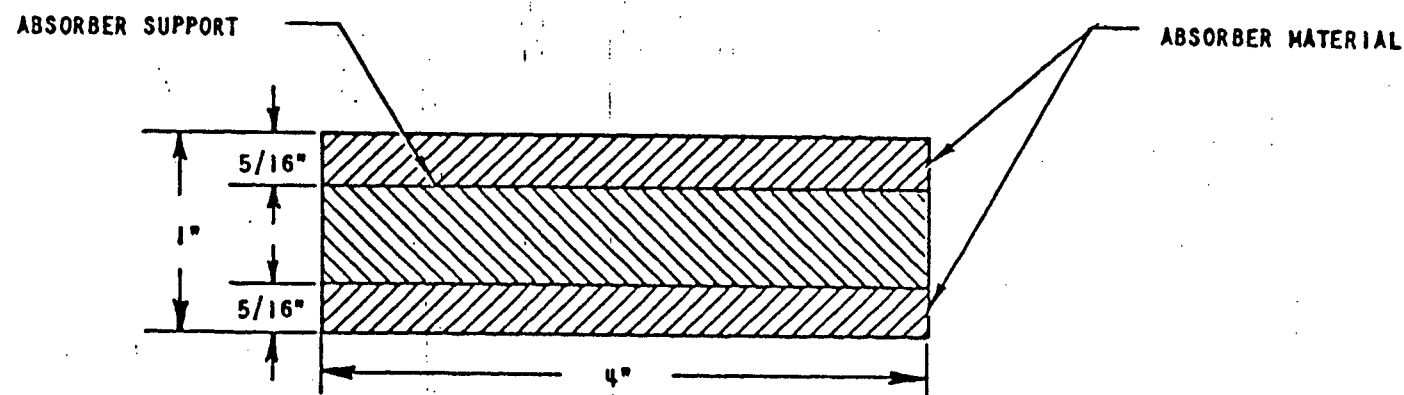
Met. #4381

100 x

Figure 6 - Typical Microstructure of 1.5 w/o Boronated Stainless Steel



METHOD OF ASSEMBLING ABSORBER PLATES AND THEIR SUPPORT



CROSS-SECTIONAL VIEW OF ABSORBER PLATES AND SUPPORT
APPROXIMATE LENGTH OF ABSORBER PORTION OF CONTROL ROD IS 115"

Figure 7 -

CONSTRUCTION DETAILS OF
CVTR CONTROL ROD

The prototype rod was fabricated by an outside supplier. The only difficulty encountered in the fabrication of the assembly was in keeping the absorber plates from bowing after the machining operation. This difficulty could be eliminated by machining the absorber plates in shorter lengths (about 24 inches) instead of full length (about 117 inches).

Based on the experience obtained from fabricating the prototype, no problems are anticipated in the fabrication of control rods for the CVTR plant.

The prototype assembly was transferred to the mechanical design group for performance tests. Figure 8 shows the control rod partially withdrawn from a test chamber. A close-up view showing the sandwich construction is shown in Figure 9.

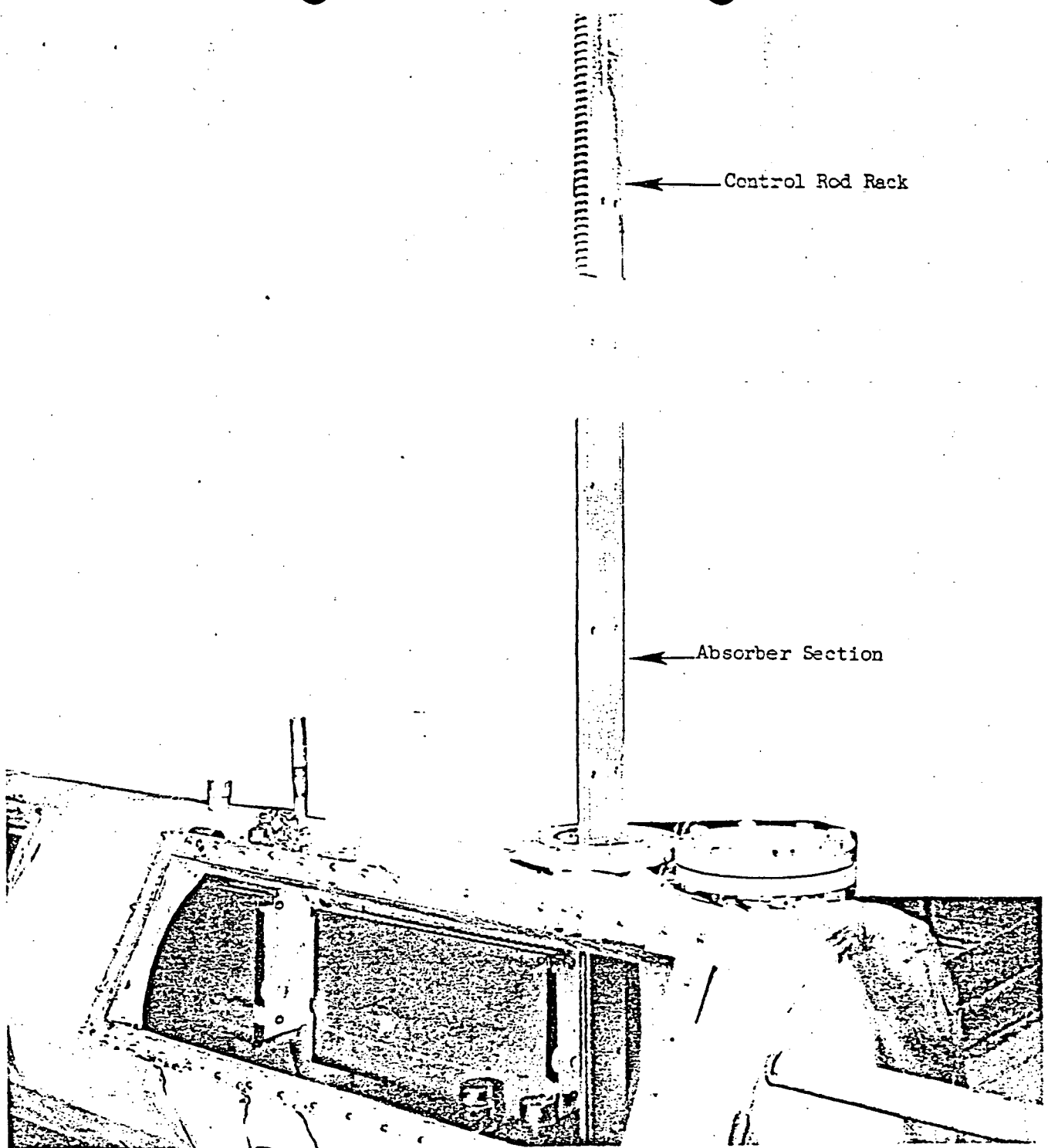


Figure 3 Prototype Control Rod Partially Withdrawn from Test Chamber

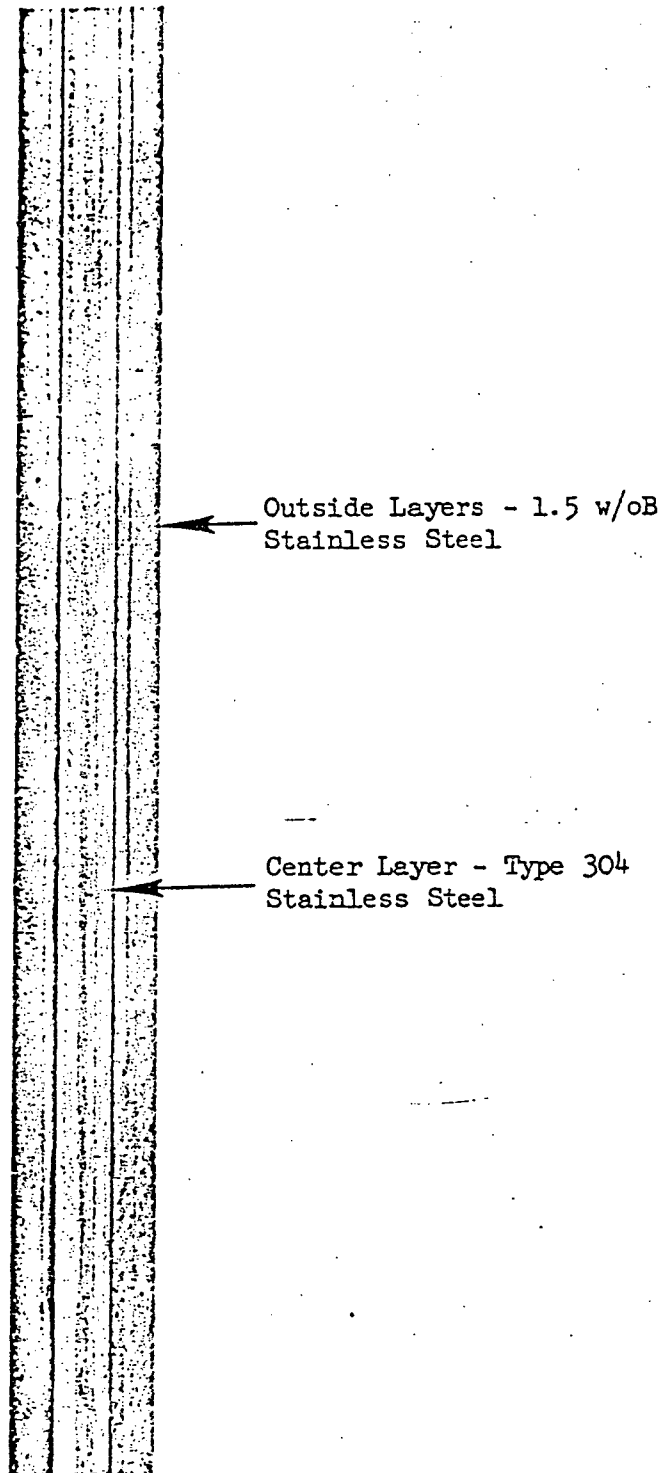


Figure 9 Close-up View of Absorber Portion of
Control Rod Showing 3-Layer Construction.

VII. REFERENCES

1. Development and Properties of Silver-Base Alloys as Control Rod Materials for Pressurized Water Reactors, AEC Research and Development Report WAPD-214, Cohen, I., December 1959.
2. Corrosion of Silver-Indium-Cadmium In Borated High Temperature Water, Report YAEC-147, Whyte, D. D. and A. Krieg, June 1960.

mpeA

CORROSION OF MATERIALS
IN
SPENT FUEL STORAGE POOLS

J.R. Weeks

July 1977

Corrosion Group
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973

TABLE OF CONTENTS

| | |
|---|------------|
| LIST OF TABLES----- | ii |
| INTRODUCTION----- | 1 |
| I MATERIALS----- | 2 |
| II WATER CHEMISTRY----- | 3 |
| 1. BWR Fuel Pool Chemistry----- | 3 |
| 2. PWR Fuel Pool Chemistry----- | 3 |
| 3. Biocides----- | 4 |
| III CORROSION OF MATERIALS IN FUEL STORAGE POOLS----- | 5 |
| 1. Stainless Steels----- | 5 |
| 2. Aluminum Alloys----- | 5 |
| 3. Zircaloy Cladding----- | 6 |
| 4. Other Materials----- | 6 |
| 5. Stress Corrosion----- | 6 |
| 6. Galvanic Corrosion----- | 7 |
| IV SURVEILLANCE----- | 9 |
| V SUMMARY AND CONCLUSIONS----- | 10 |
| ACKNOWLEDGEMENTS----- | 11 |
| REFERENCES----- | 12 |
| TABLE----- | 13, 14, 15 |

LIST OF TABLES

TABLE 1 MATERIALS AND WATER CHEMISTRIES IN LWR FUEL

STORAGE POOLS-----13 & 14

INTRODUCTION

The current delays in establishing a national fuel reprocessing center have required many of the LWR licensees to expand their fuel storage capabilities either by modification of existing pools or addition of new fuel storage pools. This report reviews the potential corrosion problems that might develop during the long-term (10 plus years) storage of nuclear fuels in these storage pools. A detailed review of the integrity of the fuel in storage pools is being prepared by Johnson for ERDA,⁽¹⁾ which has served as a basis for much of this report. Zircaloy-clad fuels with burnups up to 33,000 MWd/MTU have been successfully stored in fuel storage pools for periods up to 13 years in U.S. pools and 14 years (at lower burnups) in Canadian pools.

I MATERIALS

Three types of materials are generally in contact with the fuel storage pool water: the pool liner which is commonly stainless steel, the storage racks which are commonly stainless steel or aluminum, and the materials present in the fuel element bundles which commonly include stainless steel, Inconel 718, 17-4 PH, and Zircaloy 2 or Zircaloy 4 cladding. Table 1 lists the materials and water chemistry used in the fuel storage pools at a number of LWR nuclear stations, as available to the writer as of July 15, 1977.

Experience with storing these materials for long periods of time in reactor canals has been reviewed by A.B. Johnson, Jr.⁽¹⁾ Maximum residence in U.S. Pools of spent zircaloy-clad fuel is 13 years. None of these materials should suffer significant corrosion in this environment in periods well in excess of 10 years, as has been borne out by experience.

II WATER CHEMISTRY

Because during the fuel unloading procedure the water in the fuel storage pool and the reactor primary coolant mix, an attempt is made to maintain water purity in the fuel storage pool to approximately the same limits that are set for the primary reactor coolant.

1. BWR Fuel Pool Chemistry

In a BWR this means that high purity demineralized water is typically maintained with a filter-demineralizer to a total heavy ion content of < 0.1 ppm, a pH range of 6.0 to 7.5, and a conductivity of < 1 $\mu\text{mho/cm}$. The water is sampled daily to measure conductivity, and weekly for other impurities, including chlorides. The demineralizers primarily remove silicates from the water, and are typically checked for their capacity to remove this species once weekly. The primary source of the silicates may be dust from the air; the pools are normally uncovered. On the average, fresh resin beds are installed monthly, primarily because of increased pressure drops from silicate absorption.⁽²⁾ The primary contribution to the conductivity is dissolved CO_2 ; when the conductivity exceeds 1 $\mu\text{mho/cm}$ the demineralizers are changed.⁽²⁾ During a visit in June, 1977, the water in the Vermont Yankee fuel pool appeared extremely clear, with a distinct blue tinge to it, apparently as a result of scattering of the longer light waves by the water and the use of mercury vapor lighting.

2. PWR Fuel Pool Chemistry

In a PWR, the fuel pool frequently contains several thousand ppm boric acid, which is added to other otherwise highly pure water. No neutralization with LiOH is used in the fuel storage pools; a typical $\text{pH}^{(3)}$ value is 4.5. A portion of the fuel pool

coolant is continuously passed through a demineralizer resin and impurities, such as halides or sodium ions, maintained below 0.15 ppm. Periodically the demineralizer resins are checked for their ability to remove halides and sodium ions; resins have been developed by Rohm and Haas that are specific for removing halides in the presence of boric acid. The manufacturer's claims in this matter have been confirmed experimentally by one of the reactor vendors.⁽⁴⁾

3. Biocides:

Biocides are not commonly used in fuel storage pools at nuclear power plants. Maintaining the water of the high purity needed for safe storage of fuel appears to inhibit biological growth, and the use of stainless steel liners in the storage pool also tends to control biological growth. The radiation levels from the spent fuel stored in the pool also tend to sterilize the water, although radiation resistant bacteria are known. Finally, the continuous demineralization of a portion of the pool water serves to filter out any biological growth. No biological fouling has been observed in 3 1/2 years operation of the Prairie Island spent fuel pool,⁽³⁾ in 3 1/2 years operation of the Vermont Yankee, > 5 years operation of the Maine Yankee, and > 10 years operation of the Yankee-Rowe fuel storage pools,⁽²⁾ and no biocides have been added.

The use of biocides can lead to the presence of chloride ions in the pool which are potentially harmful to the corrosion resistance of the materials stored in the pool, and would be unacceptable during the mixing with the reactor primary coolant that occurs during refueling. They have been used in the ICPT fuel pool at Idaho Falls, which is a painted concrete pool.⁽¹⁾

III CORROSION OF MATERIALS IN FUEL STORAGE POOLS

The corrosion rates of zirconium, stainless steels and Inconel in water of the quality maintained in the fuel storage pools should be negligible during periods upwards of twenty years. General corrosion rate measurements for these materials in water of this quality and temperature are not generally available, and any estimates of corrosion rates must be extrapolated from measurements at much higher temperatures. The primary difference between the water chemistry in the fuel pools and that in the reactor (other than the temperature) is that the pools are exposed to the air and are presumed to contain dissolved oxygen up to the saturation point. Since all the materials used are passivated by oxide films, the presence of oxygen in the water should not affect their corrosion rates.

1. Stainless Steels

Since the stainless steels are used for the primary piping at substantially higher temperatures and in the presence of oxygen in BWR's where stainless steels are deemed satisfactory for periods up to 40 years, corrosion in the fuel pool should be much less than in the reactor, because of the lower temperature.

2. Aluminum Alloys

The anticipated corrosion of the aluminum alloys, 1100 or 6061, is negligible in water of this quality at temperatures up to the boiling point of water: at 125°C (257°F) a corrosion rate of 1.5×10^{-4} mils/day⁽⁵⁾ has been measured for alloy 6061 aluminum, in water of pH 7, which corresponds to a total corrosion of 1.1 mils in twenty years. Since the oxidation rate will continue to decrease slightly over this period, this estimate should be conservative. At lower temperatures, the rate will be even

lower. There is little difference in the corrosion rates of these two alloys at temperatures below 150°C. The anodization of the aluminum components, which is occasionally used, should protect them even further from corrosion.

3. Zircaloy Cladding

The rate of corrosion of zircaloy in fuel storage pool waters is very low. Berry⁽⁶⁾ gives a corrosion rate in 500° water of 2×10^{-2} mils/year, and shows it to be continually decreasing up to times in excess of 10 or 15 years. At the lower temperatures that prevail in fuel storage pools, the corrosion rates should be even lower. Morgan⁽⁷⁾ describes the corrosion rate of zircaloy in pool water as being sufficiently low to provide an adequate containment barrier for at least 100 years.

The oxygen concentration in the pool water should not adversely affect corrosion of zircaloys. Zirconium and its alloys are protected from aqueous corrosion by a strongly passivating oxide film. The oxygen in the water should serve to promote and maintain this passivation. Further, Uhlig⁽⁸⁾ has stated that this passivity is maintained both in strong acids and in strong alkalis.

4. Other Materials

The fuel bundle and storage rack materials may also include type 17-4 PH stainless steel and Inconel 718. Neither of these alloys should undergo measurable general corrosion in fuel storage pool waters.

5. Stress Corrosion

Stress corrosion of stainless steels and zircaloys in fuel storage pools is highly unlikely to occur provided the water

chemistry is maintained within the specified limits. Stress corrosion of sensitized stainless steels that are highly stressed has been observed in oxygenated water acidified to pH 5 nitric acid at temperatures up to 140°F.⁽⁹⁾ This is, however, a slow process which took 6 years to develop and occurred only in one highly stressed, highly sensitized area. While it is impossible to rule out completely that stress corrosion of the stainless steel or Inconel components will occur in the fuel storage pool, any such occurrence would be highly localized and rare, and not lead to serious problems with the storage racks or fuel bundle components. No significant difficulties have been observed in fuel bundles examined from a number of reactors. Stress corrosion of 17-4 PH is unlikely to occur if the material has received an 1100°F heat treatment. This heat treatment is commonly specified for this material when it will be exposed to reactor coolants. Components of 17-4 PH given this heat treatment have been in service in the Brookhaven High Flux Beam Reactor (HFBR), which contains high purity D₂O acidified with nitric acid to a pH of 5 and containing greater than 8 parts per million of oxygen, for periods in excess of 12 years without any evidence of stress corrosion or pitting.⁽¹⁰⁾ This water chemistry and temperature (145°F max.) are similar to that prevalent in PWR fuel storage pools.

6. Galvanic Corrosion

Galvanic couples between stainless steels, Inconel and zircaloy do not appear to give rise to any localized corrosion in fuel pool environments, since all of these materials are protected by highly passivating oxide films, and are, therefore, at similar potentials in pure water. Aluminum alloys, which are also protected by passivating films, nevertheless can be pitted in an acid environment such as that present in PWR fuel storage pools, when coupled to stainless steel. The anodization of aluminum fuel storage racks

should minimize this occurrence. In BWR storage pools, the high electrical resistivity of the water should also serve to prevent galvanic attack.

At the Oyster Creek Nuclear Power Station, aluminum racks were originally placed directly in contact with the stainless steel pool liner. Some of these racks have been removed and examined after approximately 7 years of service in typical BWR pool water.⁽¹¹⁾ No observable pitting of the aluminum was found at the point where it contacted the stainless steel.⁽¹¹⁾ At least one nuclear utility (Vermont Yankee) has also elected to provide additional protection against this potential problem by placing stainless steel feet on the racks, which, in turn, are electrically insulated from the aluminum with ABS plastic inserts. These have been determined to be sufficiently far from the radiation source to prevent their decomposition by high energy gamma flux.⁽²⁾ These organic inserts are, in my opinion, additional insurance that galvanic corrosion will not occur.

IV SURVEILLANCE

A spent UnReprocessed Fuel (SURF) program is under development by the ERDA Division of Waste Management, Production and Reprocessing, to be initiated in FY 1978.⁽¹²⁾ Under this program, the characteristics and condition of spent fuel in storage will be evaluated on a continuing basis. Although the details of the examination to be performed in this program have not yet been worked out, the national scope of this program, including periodic examination of a few selected fuel bundles from both PWR and BWR storage pools, will provide additional assurance to the NRC of the continued integrity of fuels in storage throughout the country.

V SUMMARY

Significant corrosion of nuclear fuel components is highly unlikely to occur during storage in fuel storage pools at the reactor sites in periods of upwards of 20 years, provided that the water quality in the fuel storage pools is maintained within specifications, and that chloride levels in the pool water are kept to minimum levels (< 1 ppm). Stress corrosion of stainless steel components or Zircaloy cladding cannot be entirely ruled out because of the lack of understanding of the stress states and the degree of sensitization of stainless steel. Should such a problem develop on the Zircaloy cladding it would be readily detected by routine monitoring of the fuel pool water for radioactivity. Should it develop on the stainless steel or Inconel components of the fuel bundles, it would be highly localized and unlikely to lead to significant overall deterioration. Periodic surveillance of the materials in storage at a number of nuclear utilities is being planned under the auspices of the U.S. Energy Research and Development Administration.

ACKNOWLEDGEMENTS

The assistance of Dr. A.B. Johnson, Jr., of Battelle Pacific Northwest Laboratory, in providing draft copies of his review (Reference 1) and in several useful discussions is gratefully acknowledged. Representatives of the Northern States Power Company, Yankee Atomic Electric Company, Duquesne Power and Light Company, Jersey Central Power and Light Company, and the Portland General Electric Company were very helpful in preparing this review. This work was performed under the auspices of the United States Nuclear Regulatory Commission

REFERENCES

1. A.B. Johnson, Jr., "Behavior of Spent Nuclear Fuel in Water Pool Storage", BNWL-2256, Draft, May, 1977, also private communications, May, June and July, 1977.
2. John R. Hoffman, Yankee Atomic Electric Company, Private communications, June 6 and 7, and July 14, 1977.
3. Peter Jones, Northern States Power Company, Private communications June 1 and July 15, 1977.
4. C. McCracken, Combustion Engineering, Private communication, June 3, 1977.
5. J.E. Draley and W.E. Ruther, Report No. ANL-5001, February, 1953.
6. W.E. Berry, "Corrosion in Nuclear Applications", John Wiley & Sons, N.Y., 1971, pages 107-116
7. W.W. Morgan, "The Management of Spent CANDU Fuel", Nuclear Technology 24, 1974, pages 409-417.
8. H.H. Uhlig, "Corrosion and Corrosion Control", John Wiley & Sons, N.Y., Second Edition, 1971, pages 367-371.
9. R.W. Powell, J.G.Y. Chow, W.J. Brynda, M.H. Brooks, J.R. Weeks "Experience With Stress Corrosion Cracking and Materials Compatibility at the High Flux Beam Reactor", CONF-730801, 166-180, 1973.
10. R.W. Powell & J.G.Y. Chow, Brookhaven National Laboratory, Private communications.
11. T.J. Madden, Jersey Central Power & Light Company, Private communication, May 19, 1977.
12. C.R. Cooley, U.S.E.R.D.A., Private communication, July 14, 1977

TABLE I

MATERIALS AND WATER CHEMISTRIES IN LWR FUEL STORAGE POOLS

| PLANT | MATERIAL | USE | ENVIRONMENT |
|--------------------------------|--|-------------------------------------|---|
| ARKANSAS (PWR) | 304 SS A-276-71 or A-167-74 308 or 308L 304L ASTM-A-167 | Rack Electrode Liner | 1800 ppm boron as boric acid 120°F |
| BEAVER VALLEY (PWR) | SS, 17-4 PH | Racks, bolts | 2000 ppm boron as boric acid, Cl^- , $\text{F}^- < 0.15$ ppm |
| BRUNSWICK (BWR) | 304 SS E308 17-4 PH - H1150, H1025 | Liner, racks Electrodes Bolts | 125°F (max 150°F) cond < $\mu\text{mho/cm}$ pH 6.0 - 7.5 $\text{Cl}^- < 0.2$ ppm |
| DRESDEN 1, 2 and 3 (BWR) | Stainless steel Al-6061-T6 ASTM-B-209 | Liner Racks | Demineralized water cuno filters and deep bed deminer- alizers |
| FT. CALHOUN | 304 SS ASTM-A-276-71 or A-167-74 308 or 308L | Racks Weld | 120°F 2000 ppm boron as boric acid |
| GINNA, R.E. (PWR) | 304 SS | Racks | Boric acid |
| LACROSSE (BWR) | Borated SS and 304 SS | Racks | Demineralized water |
| MILLSTONE POINT 1 (BWR) | 304 SS | Liner, racks | Demineralized water Filter and deminer- alizer |
| MILLSTONE POINT 2 (PWR) | 304 SS | Liner, racks | Demineralized water + 2000 ppm boron as boric acid |

TABLE I
(continued)

| PLANT | MATERIAL | USE | ENVIRONMENT |
|------------------------------------|--|---|---|
| NINE MILE POINT 1 (BWR) | 304 SS | Rack | Demineralized water of BWR primary cool- ant quality 125°F |
| OYSTER CREEK (BWR) | Entire rack 304 SS ASTM-A-240 ASTM-A-193 ASTM-A-194 308 SS, ASME SFA 5.9 | Plate, bar sheet Rivets, bolts Nuts Weld material | Demineralized water Undissolved solids < 0.5 ppm |
| PALISADES (PWR) | 304 SS | Racks | 122°F - 157°F 2000 ppm boron as boric acid |
| PILGRIM (BWR) | Same rack design as Vermont Yankee | | |
| POINT BEACH 1 and 2 (PWR) | 304 SS | Racks | 2000 ppm boron as boric acid 130°F |
| PRAIRIE ISLAND 1 and 2 (PWR) | 304 SS Zircaloy, IN-718 | Racks, liner Fuel bundles | Demineralized water (Cl ⁻ , F ⁻ < 0.15 ppm + 2000 ppm boron as boric acid pH 4.5, 120°F |
| QUAD CITIES 1 and 2 (BWR) | Same rack design as Dresden | | |
| TROJAN (PWR) | 304 SS Inconel 17-4 PH - H1100 | Racks, liner Grid Mat'l. Bolts and Module threaded feet | 2000 ppm boron as boric acid 140°F Cl ⁻ , F ⁻ , 0.15 ppm maximum each |

TABLE I
(continued)

| PLANT | MATERIAL | USE | ENVIRONMENT |
|----------------------------------|---|---|---|
| TURKEY POINT 3 and 4 (PWR) | Entire rack 304 SS Free standing rack ASTM-A-240 ASTM-A-276 AWS-E-308-15 AWS-E-308-16 | Sheet, plate Bar Weld wire Weld wire | Demineralized water with 1950 ppm boron as boric acid |
| VERMONT YANKEE (BWR) | 356-T51 ASTM-B-26 Alum. 6061-0 or 5052-H32 Alum. 6061-T651 Alum. 2024-T4 Alum. All aluminum alloys, anodized 304 SS ABS plastic insulators between feet & alum. cans | Grid castings Cans Plates Bolts, Pins Liner, feet | pH 6 - 7.5 (Cu, Ni, Fe, Hg, etc.) < 0.1 ppm 125°F Radionuclide < 10 ⁻⁴ |
| YANKEE ROWE | 6061-T6 Alum. Stainless Steel | Rack Liner | 130°F, some boron, chlorides < 0.5 ppm |
| ZION (PWR) | 304 SS | Rack | Borated water 105°F |

DISTRIBUTION LIST

L.C. Shao (5)

R.J. Stuart

W.S. Hazelton

F.M. Almeter

H. Levin (5)

W.Y. Kato

D.H. Gurinsky

Corrosion Group Files (10)