

NRC PUBLIC DOCUMENT ROOM

UNITED STATES OF AMERICA

NUCLEAR REGULATORY COMMISSION

BEFORE THE ATOMIC SAFETY AND LICENSING BOARD

In the Matter of Commonwealth) Docket Nos.
Edison Company (Zion Station,) 50-295
Units 1 and 2)) 50-304

TESTIMONY OF J. E. DRALEY



Contentions 2(e)(3): Corrosion
2(e)(4): Surveillance
Program

Contention 2(j) : Possible Boral
Corrosion and
Swelling

Contention 2(k) : Possible
Degeneration
of Boral Density

May 31, 1979

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Testimony relative to Commonwealth Edison Company proposed change to Operating License for Zion Nuclear Plant by J. E. Draley.

My testimony is in the form of general statements concerning corrosion and related reactions of the stainless steel/Boral storage rack tubes, followed by specific replies to the contentions of the State of Illinois, as identified as issues in this case by the NRC Licensing Board in the Board's "Order Following Prehearing Conference," January 19, 1979. A statement of my professional qualifications is attached, as are the references which appear in this testimony.

GENERAL STATEMENTS CONCERNING CORROSION

A. Boric Acid Solution

The solution used in the Zion spent fuel storage pool contains boric acid dissolved in high purity dionized water. The solution is purified by passing a stream (approx. 100 gallons per minute) through a mixed bed ion exchanger that does not remove boric acid substantially. This purification process has not been run at all times and the concentration of the boric acid has not been constant. The average concentration of boron has been a bit less than 2500 parts per million (ppm), ranging from 2000 to perhaps 2520 ppm and the typical pH has been 5.4, ranging from 4.7 to 5.6 in one period. The "normal" temperature of the pool water is 70°F, calculated

to increase to 111°F when a 1/3-core discharge of spent fuel is added (143°F if only one of the two cooling heat exchangers is operating).

Boric acid is typically a benign chemical in otherwise pure water from the point of view of corrosion, so long as the pH is not too low. A significant adverse effect on the aluminum corrosion can be predicted if the pH is below about 4, depending on the temperature, the presence of other solutes, and the rate of flow of solution past the metal surface.

B. Corrosion of Type 304 Stainless Steel

In pure water at storage pool temperatures, the uniform corrosion over the surface of austenitic stainless steels such as Type 304 is so slow as to challenge the ability of experimenters to measure it. In fact, I know of no accurate measurement of this corrosion rate. In my judgment the uniform penetration of 304 stainless steel is likely to be less than one ten thousandth of an inch in 40 years exposure to high purity water or to the 2500 ppm boric acid solution.

Under some circumstances, stainless steels, including Type 304, are susceptible to stress corrosion cracking. However, there is considerable experience with stainless steel racks and pool liners. No stress corrosion cracking of either has been found, even in weld-sensitized and residual stress regions,⁽¹⁾ and none is expected to occur in the Zion pool.

In sufficiently aggressive solutions such as those containing a high concentration of chloride ion, and especially in the presence of crevices, stainless steel has been known to suffer localized attack or pitting. This type of attack has not been observed in storage pool water and is not expected to occur for the lifetime of the Zion pool. (1)

C. Boral

This product is manufactured by Brooks and Perkins, Inc., and, for Zion, consists of about 48% by weight of boron carbide (B_4C) particles embedded in a matrix of commercially pure (1100) aluminum. The size of the B C particles is given as 60-200 mesh. This boron carbide-aluminium material is formed into a plate, clad with 1100 aluminum on both sides. The same aluminum alloy is inserted between the cladding plates at each end so that the resultant piece, after cutting for use in the racks, is covered on four of the six sides by 1100 aluminum; the side edges are left without cladding.

As in the case of stainless steel, the actual corrosion rates of aluminum alloys such as 1100 are so low after an initial period of exposure to pure water as to have challenged the skill of experimenters to determine it. In fact our own observations for tests running nearly three years have shown that after an initial period lasting for several days the amount of corrosion increases only very slowly with further exposure times for temperatures of 50°C (122°F) and 70°C (158°F) in pure water. At 70°C, after the

initial period, the amount of corrosion has been shown to vary with the logarithm of time for at least two years.⁽²⁾ The logarithmic intercepts and rate constants published in 1967 by Draley, Mori, and Loess⁽³⁾ indicate that for storage pool temperatures the amount of uniform corrosion of 1100 aluminum should not exceed one ten-thousandth of an inch in 40 years of exposure in high purity water. Tests in boric acid have not, to my knowledge, extended long enough to predict with precision the uniform corrosion rate to be expected. Short-term tests have shown that less corrosion occurs in the presence of a dilute boric acid solution than in water but it cannot confidently be stated that the corrosion after 40 years will be as low as or less than that for pure water. Consequently, I can only conservatively judge that the amount of corrosion in boric acid solution in the storage pool should be less than one thousandth of an inch in 40 years of exposure.

There has been enough testing of the bare edges of Boral in which the aluminum-boron carbide core material and the 1100 aluminum cladding is exposed to show that little or no accelerated corrosion occurs. For example, Weeks⁽⁴⁾ reports no measurable deleterious attack in 19-1/2 years exposure in the Brookhaven Medical Research Reactor.

In pure water or in boric acid concentrations not exceeding those in the storage pool no stress corrosion cracking or significant pitting is expected of Boral.

D. Boral-Stainless Steel Couples

When dissimilar metals are held in electrical contact, the corrosion of the metal that is electrochemically more active is sometimes accelerated and the corrosion of the metal that is electrochemically more noble is sometimes retarded. The increased corrosion of the more active metal is known as galvanic attack. In the present instance, 1100 aluminum and the layered Boral product are anodic to or more active than the stainless steel jacket. In deionized water, essentially free of chloride ion, galvanic attack of aluminum coupled to stainless steel is very slight as long as the water purity remains high. In the presence of boric acid solution, at concentrations corresponding to the storage pool water, one can expect some pitting of the edges of the Boral plates and perhaps the 1100 aluminum cladding when the electrical contact with the stainless steel jacket is good. The extent of pitting is not readily predictable because of lack of sufficient data in boric acid solution representative of that expected within the Zion tubes and uncertainties in the contact resistance between the two metals that form insulating oxide films in air prior to fabrication and in the presence of water or boric acid solution when exposed to that environment. In any event, the resultant galvanic pitting is likely to slow down to such a low rate as to lead to little further penetration. The explanation for this nearly self-limiting process is probably related to the

very limited conductivity of the solution through pores in the oxide that covers the growing pit. It is necessary for such ionic conductivity in the solution for the pit to continue to propagate. The formation of pits of limited depth and the expected existence of oxide on the surface make it unlikely that a significant amount of boron carbide will be lost from the edge of the Boral.

Although there are no known careful examinations of surfaces after galvanic corrosion in boric acid solution containing 2500 ppm boron, Brooks and Perkins has measured the electric current flowing between Type 304 stainless steel and Boral during such exposure, both in aerated and deoxygenated (bubbling nitrogen gas) condition at 65°C (149°F). In addition, a closed experiment has been run at 21°C (70°F), with no addition of gas (herein called stagnant). For the aerated and deoxygenated tests, the current varied irregularly with time, with an apparent trend downward after the first few weeks. The galvanic current deoxygenated was about one-fourth that in the aerated test. In the stagnant test, the current declined throughout, reaching negligible values after two or three months. Additional testing has also been done by Battelle Memorial Institute at a higher boric acid concentration, 32 g/l, containing about 5600 ppm boron. The pH was 3.8, the temperature 49°C (120°F). Galvanic currents between stainless steel and Boral or 1100 aluminum were higher than in the more dilute solution during the 54-day test.

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Periodic inspection of the 1100 aluminum specimen during the course of the test showed severe pitting that appeared visually to have grown little deeper but covered an increasing area. This galvanic corrosion was clearly more severe than that which occurred in the more dilute boric acid solution.

REPLIES TO CONTENTIONS

Contention (2)(e) The amendment request and supporting documentation do not adequately discuss monitoring procedures. In the light of the proposed modification and long time storage of nuclear spent fuel the Applicant should clarify the following:

- (3) Method for detecting the loss of neutron absorber material and/or swelling of stainless steel tubes in storage racks.
- (4) Details of a corrosion test program to monitor performance of materials used in the construction of the racks.

Reply

Consideration of the corrosion behavior of the Boral leads to the judgment that significant amounts of boron will not be lost from the Boral composite by corrosion. Similarly it is anticipated that no serious swelling of the vented steel tubes will occur in the storage racks, since the only known mechanisms that might produce substantial swelling involve the entrapment of gas inside the tubes or the production of

solid corrosion product with a volume greater than that of the metal from which it was produced. The former should not occur because the tubes will be vented and swelling by the latter mechanism should not reach serious proportions, as will be shown in the reply to Contention (2)(j)(3).

To assure that unexpected damage is not occurring, the surveillance program that will be put into effect when the new racks are installed⁽⁵⁾ will provide an opportunity for inspection of specimens that are expected to behave in the same way as the actual tubes. Small vented specimens, very similar in character to the actual tubes, will be stored in the pool. These will be removed periodically, opened, and examined carefully for corrosion damage. In addition, two full-size storage tubes will be exposed in the pool near stored fuel so as to reproduce the radiation condition as well as exposure to the solution. These tubes will be examined periodically for visual signs of swelling and will be opened and examined for loss of boron if examination of the small specimens indicates ¹⁰Boron content in those specimens below 0.02 gm/cm².

It is believed that with this program, indications of corrosion damage involving the possible loss of neutron absorber or swelling or other damage to the tubes will be detected in time to take any necessary remedial action for the storage tubes in the pool. It is believed that the corrosion reactions will be sufficiently slow that any

damage that occurs will not endanger the safe and effective operation of the storage pool.

Contention (2)(h) The amendment request and supporting documentation have not analyzed the long term (including storage during the operating lifetime of the reactor) electrolytic corrosion effects of using dissimilar alloys for the pool liners, pipes, storage racks and storage rack bases, such as the galvanic corrosion between unanodized aluminum as is used in Brooks and Perkins storage racks, and the stainless steel pool liner.

Reply

As has been indicated above in sections C and D it is not expected that there will be a significant electrolytic corrosion effect between boron carbide and 1100 aluminum, although it is likely that there will be a galvanic corrosion effect between the Boral and the stainless steel tube. Whatever the magnitude of this effect, and it is not expected to pose a problem with respect to the integrity of the Boral, there will be no residual effect of the galvanic interaction outside of the stainless steel tubes, so that the materials inside the tubes will have no interaction with fuel or with the tank liner.

Contention (2)(j) The amendment request and supporting documentation do not give sufficient data to fully assess the durability and performance of the Boral-stainless steel tubes which form the spent fuel storage racks:

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- (1) There is inadequate analysis of the corrosion rate of the tubes.

Reply

In Section B above I have provided information concerning the anticipated corrosion behavior of Type 304 stainless steel, the material of which the tubes are comprised. It is expected that the corrosion will be negligible as indicated in that section.

- (2) There is no calculation of the effect of water chemistry on the Boral within the stainless steel.

Reply

This is discussed in Section C above. It is judged that the water chemistry will be favorable for the corrosion of Boral and that the total uniform corrosion of this material will not be in excess of 1/1,000 in. for the forty year lifetime of the racks. There could be a greater amount of local attack on the edges of the Boral and possibly at some locations on the 1100 aluminum cladding on the Boral where it faces the stainless steel. In neither of these two locations is the attack expected to be great enough to lead to serious loss of the neutron absorbing boron, or to cause swelling to an extent that would interfere with free movement of the stored fuel.

- (3) There is no mention of the possible swelling of Boral within the stainless steel tubes, a condition which could affect, among other things, removal of fuel assemblies from the racks.

Reply

I am aware of two processes that could lead to swelling of the Boral within the stainless steel tubes. In the first, if the quality of the Boral is poor so that there is porosity, there could be a path for permeability of the core material by water. It would then be possible for reaction of this water with the aluminum at some internal place to produce hydrogen gas in quantities sufficient to expand the Boral, as by the formation of an internal blister. The location of such a blister might be some distance beyond that of the water that produced the gas, the hydrogen diffusing ahead of the water. This type of swelling should be self-limiting, since expansion of the blister should deform the piece enough to allow release of the hydrogen pressure. In the second mechanism some local corrosion or pitting might be induced by galvanic interaction between the aluminum of the Boral and the stainless steel tubes (where the plates are pressed together). The solid corrosion product has a greater volume than that of the corroded metal, and local swelling could result.

With respect to the first process, due to accidentally porous Boral, there has been no experience of this kind of swelling at pool temperatures of commercial grade good quality Boral either in the old formulation (see reference to the material in the Brookhaven Research Reactor above in Section C) or in the new formulation, for which

there is less extensive experience. It did occur in some tests run by Exxon Nuclear Company⁽⁶⁾, using specimens of material, not used commercially, containing quantities of fine boron carbide, of the order of minus 300 to 350 mesh. It was at locations of such fine material that Exxon found the blisters to form. During mechanical testing of this type of material (not in contact with water or aqueous solution), Brooks and Perkins found areas of imperfect bonding between the core and cladding. Specifications for the boron carbide powder (size range) were then set at -60 + 200 mesh, and no areas of poor bonding were discovered. This is the product that is used commercially. Because of universally good experience with the commercial product and the non-applicability of the Exxon results to such a product, no swelling of this type is expected in the Zion pool.

Concerning the second swelling mechanism, the extent of galvanic corrosion may be limited by solution depletion, depletion of available oxygen in the stagnant area, or poor electrical contact, as indicated above in Section D. If it is not so limited, it is conceivable that the entire thickness of the Boral might be converted to the aluminum corrosion product, a hydrated oxide, expected predominantly to consist of a crystalline form known as bayerite. Using the density of bayerite (2.42), it can be calculated that the corrosion product will occupy a volume some 3.2 times that of the aluminum from which it is formed. For a total Boral thickness of

0.073 inch, the maximum swelling would then be 0.234 inch, an amount that would not interfere with the movement of fuel within storage tubes.

Another possible swelling mechanism for unvented tubes, not involving the swelling of Boral, is the accumulation of entrapped gas between the Boral and the stainless steel tube. Assuming a leak near the bottom, access of solution to the aluminum and the production of some hydrogen as a corrosion product will be allowed. If the resultant gas (perhaps a mixture of the hydrogen and the air originally entrapped during the manufacture of the tube) nearly fills the free space between the Boral and the stainless steel tube, its pressure near the top will be in excess of that outside the tube by an amount that would bulge the stainless steel sheet. This is the mechanism believed to explain the swelling of some tubes in the spent fuel storage pool at the Monticello Plant last year. It should not occur at Zion due to the use of vented tubes.

Contention (2)(k) The amendment request and supporting documentation do not consider possible degeneration of the Boral density due either to generic defects or to mechanical failure which would diminish the effectiveness of Boral as neutron absorber, thus leading to criticality in the spent fuel pool.

Reply

Generic effects in the form of porosity have been discussed

in the preceeding reply. If there are mechanical defects, in which the Boral would fragment or break, the stainless steel tubing would keep it largely in position. However, the fragmentation is considered highly unlikely in view of the good record of Boral products and in view of the excellent record for integrity of the Boral cladding alloy, 1100 aluminum. The risk of developing criticality in the pool on the basis cited is deemed negligible.

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REFERENCES

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2. J. E. Draley, Shiro Mori, and R. E. Loess, The Corrosion of 1100 Aluminum in Oxygen-saturated Water at 70°C, J. Electrochemical Society, 110, pp. 622-627 (1963).
3. J. E. Draley, Shiro Mori, and R. E. Loess, The Corrosion of 1100 Aluminum in Water from 50°-90°C, J. Electrochemical Society, 114, pp. 353-354 (1967).
4. BNL-NUREG-25582, J. R. Weeks, Corrosion Considerations in the Use of Boral in Spent Fuel Storage Pool Racks, January 1979 (Brookhaven National Laboratory report).
5. Commonwealth Edison Co., "Neutron Absorber Sampling Plan - In Pool," May 25, 1979.
6. XN-NS-TP-009; Fuel Storage Racks Corrosion Program, Boral-Stainless Steel, November 9, 1978 (Exxon Nuclear Company non-proprietary version).

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PROFESSIONAL RESUME FOR JOSEPH E. DRALEY

Education

Attended the Catholic University of America, 1935-9, awarded Bachelor of Applied Chemistry degree, 1939.

Attended Catholic University, 1939-42 and 1945-46, awarded Ph.D. degree in Chemistry, 1947.

Professional Career

Metallurgical Laboratory, University of Chicago, 1942-1945.

Group Leader in Technical Division, then in Metallurgy Division, in charge of laboratory investigations in corrosion related to design and development of nuclear reactors. Aqueous corrosion of aluminum, uranium, thorium and their alloys; hydriding of uranium and thorium; formation and deposition of hydrous oxide films.

Kellex Corp., New York City, 1945-46.

Project engineer. Established plan for examination and evaluation of corrosion in gaseous diffusion plant; assisted in making company plans for the future.

Kellex Corp., Applied Physics Lab., Silver Spring, Maryland, 1946-47.

Project Engineer. Assisted in ram-jet development; research on heat transfer in supersonic airflow.

Oak Ridge National Laboratory, Oak Ridge, Tenn., 1947-48.

Metallurgy Division Section Chief in charge of corrosion research activities. Studied aqueous corrosion of beryllium and aluminum.

Argonne National Laboratory, Argonne, Ill., Associate Chemist, 1948; promoted to Senior Chemist, 1955.

Group Leader in Metallurgy Division, in charge of basic corrosion research, 1948-1968 (for applied research also during a part of this period). Corrosion of a number of metals and alloys in water, steam, and oxygen; application of materials to nuclear reactors. Coordinator for the Laboratory's program in sodium technology (Liquid Metal Fast Breeder Reactor Program), 1967-1969. Assistant Manager of the sodium technology program (Chemical Engineering Division), 1970-1971. Member Environmental Statement Project, preparing National Environmental Policy Act impact statements for nuclear power plants, 1971-1974. Ass't. Laboratory Director for Program Planning 1974-1978. Manager, OTEC Biofouling, Corrosion and Materials Project, Materials Science Division, 1978-present. Member, Argonne Senate Committee on Scientific programs, 1968-1972, Chairman 1970-1971. Member, Argonne's CTR (Controlled Thermonuclear Research) Study Group, 1970-1973, Chairman 1972-1973.

Awards:

W. R. Whitney Award (National Association of Corrosion Engineers), 1961, for outstanding contributions to the science of corrosion.

Merit Award of the Chicago Technical Societies Council, 1970, for outstanding technical and social achievements.

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PROFESSIONAL RESUME FOR
JOSEPH E. DRALEY (Contd)

Technical Societies:

Member of

American Chemical Society
Electrochemical Society
American Nuclear Society (1969-1978)
Amer. Inst. Min. Met. Pet. Engrs., The Metallurgical Society
Amer. Assn. for the Advancement of Science
Sigma Xi

Chairman, Corrosion Division, Electrochemical Society, 1956-7
Editor, Corrosion Division, Electrochemical Society Journal, 1957-8
Member, Corrosion Resistant Metals Comm., TMS AIME, 1959- , Chairman, 1967-9
Member, Corrosion Research Council, 1963-5
Chairman, Symposium on Corrosion by Liquid Metals, The Met. Soc., 1969

Other Professional Activities:

Originator of periodic AEC Contractor Corrosion Symposia, 1951
Member, Shippingport Fuel Panel, 1953-6
Contributor to International Conferences on the Peaceful Uses of Atomic Energy,
Geneva, 1955, 1958, 1964; participated in first and third
Chairman, Gordon Research Conference on Corrosion, 1958
Member, Fluid Fuel Reactors Task Force, 1959
Organizer, International Symposium on Aqueous Corrosion of Reactor Materials,
Brussels, 1959
Chief U. S. Delegate to International Atomic Energy Agency meeting on
Corrosion of Reactor Materials, Salzburg, 1962
Exchange visitor to Russian Corrosion Chemistry Institutes, 1962
Advisor to Advances in Corrosion Science and Technology since 1965
Consultant to the Atomic Energy Commission on Minimization of River Pollution
by Radioactive Effluents, 1966-8
Member, ANL Study Group on Environmental Pollution, 1967
Participant, U. S. - U. K. Libby-Crocroft Exchanges on Corrosion, Harwell, 1967
and Columbus, Ohio, 1968
Chairman, International Conference on Sodium Technology, Argonne, 1968
Invited lecturer at the Workshop on Biofouling at Thermal Power Plants, June 16-17,
1975, Johns Hopkins University
Invited lecturer at the American Chemical Society, the Electrochemical Society,
and the National Association of Corrosion Engineers series of lectures
on Chemistry in Corrosion, Chicago, IL, March 30, 1976

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TECHNICAL PUBLICATIONS OF JOSEPH E. DRALEY

and of Those under His Supervision

(Publications are listed in the order: journal articles--contributions to books and symposia--Manhattan Project and A.E.C. reports)

I. Dissertation for the Ph.D. degree:

Joseph E. Draley, Complex of Cupric Ion with Acetate and Glycinate Ions in Aqueous Solution, the Catholic University of America, 1946.

II. Publications in the Area of the Corrosion of Aluminum and its Alloys by Water:

J. E. Draley and W. E. Ruther: Aqueous Corrosion of Aluminum: Part 1 - Behavior of 1100 Alloy; Corrosion, 12, 441-448t, Sept. 1956.

J. E. Draley and W. E. Ruther: Aqueous Corrosion of Aluminum: Part 2 - Methods of Protection Above 200°C; Corrosion, 12, 480t-490t, October 1956.

J. E. Draley and W. E. Ruther: Corrosion of Aluminum in Reactor Service; Trans. Am. Nuc. Soc., 4, 197-8, Nov. 1961.

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J. E. Draley, Shiro Mori, R. E. Loess: The Corrosion of 1100 Al in Oxygen-Saturated Water at 70°C; J. Electrochem. Soc., 110, 622-627, June 1963.

S. Mori, R. E. Loess and J. E. Draley: An Eddy Current Gauge for Measuring Al Corrosion; Corrosion, 19, 269t-271t, Aug. 1963.

J. E. Draley, W. E. Ruther, and S. Greenberg: Corrosion Experience with Al Powder Products; J. of Powder Met., 1, 28-41, April 1965.

S. Mori and J. E. Draley: Oxide Dissolution and Its Effect on the Corrosion of 1100 Aluminum in Water at 70°C; J. Electrochem. Soc., 114, 352-353, April 1967.

J. E. Draley, S. Mori and R. E. Loess: The Corrosion of 1100 Aluminum in Water from 50 to 95°C; J. Electrochem. Soc., 114, 353-354, April 1967.

R. A. Legault and J. E. Draley: An Electrochemical Study of Aluminum Corrosion in Boiling High Purity Water; Corrosion, 23, 365-370, December 1967.

J. E. Draley and W. E. Ruther: Corrosion of Aluminum and Its Alloys at Elevated Temperatures; Proc. Met. Info. Meeting, Oak Ridge April 11-13, 1955; TID-6502, pp. 669-680 (1960).

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- J. E. Draley and W. E. Ruther: Aqueous Corrosion of Aluminum Alloys at Elevated Temperatures; Progress in Nuclear Energy, Series IV, pp. 333-351, 1956 (Pergamon Press).
- J. E. Draley: Contrib. to Conf. Corr. Aluminum in Water at High Temp., Chalk River, Dec. 18-19, 1956, Minutes by M. D. Ferrier, CRMet-700, June 1957.
- J. E. Draley, C. R. Breden, W. E. Ruther and N. R. Grant: High Temperature Aqueous Corrosion of Aluminum Alloys; Second United Nations International Conference on the Peaceful Uses of Atomic Energy, September 1958, Vol. 5, p. 113.
- Also in Progress in Nuclear Energy Series, IV, Vol. 2, 1960, Pergamon Press pp. 284-300.
- J. E. Draley: Problems of Fuel Element Corrosion in Water; First International Symposium on Nuclear Fuel Elements, Jan. 1959, pp. 314-328 (Reinhold Publ. Co.).
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- J. E. Draley and W. E. Ruther: The Corrosion of Aluminum Alloys in High Temperature Water; LAEA Conf. Corrosion of Reactor Materials, Salzburg, June 1962, Vol. I, pp. 477-498.
- W. E. Ruther and J. E. Draley: Aluminum Alloy Corrosion; Research Reactor Fuel Element Conf., Gatlinburg, Sept. 17-19, 1962; TID-7642, pp. 601-611.
- J. E. Draley and W. E. Ruther: Aluminum Alloys; Contribution to "Behavior of Cladding Materials in Water and Steam Environments", Edited by Sherman Greenberg; Reactor Technology, Selected Reviews - 1964, pp. 215-223 (USAEC).
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- CT-3057 J. E. Draley and G. C. English: Corrosion Research--The Sealing of Cracks in Aluminum Surfaces; October 19, 1944.

TECHNICAL PUBLICATIONS OF JOSEPH E. DRALEY (Contd)

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- ANL-4958 J. E. Draley, W. E. Ruther and Nancy Williams: Aqueous
Corrosion of Aluminum-Lithium Alloys; December 29, 1952.
(Classified)
- ANL-5001 J. E. Draley and W. E. Ruther: Aqueous Corrosion of 2S
Aluminum at Elevated Temperatures; Feb. 1, 1953.
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Above 200°C; July 15, 1955.
- ANL-5658 J. E. Draley and W. E. Ruther: Experiments in Corrosion
Mechanism: Aluminum at High Temperatures; April 1957.
- ANL-5889 Shiro Mori, J. E. Draley and R. B. Bernstein: Deuterium-
(Adden.) Hydrogen Exchange in Boehmite Corrosion Product Formed
On Pure Aluminum in Boiling Water; April 1961.
- ANL-5927 J. E. Draley and W. E. Ruther: Corrosion Resistance and
Mechanical Properties of Aluminum Powder Products; March 1959.
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Aluminum in Boiling H₂O and D₂O; July 1959.
- ANL-6053 W. E. Ruther and J. E. Draley: Corrosion of Aluminum-Uranium
Alloys in High-Temperature Water; Nov. 1959.
- ANL-6207 J. E. Draley, W. E. Ruther and S. Greenberg: Corrosion of
Aluminum and Its Alloys in Superheated Steam; April 1961.
- ANL-6236 S. Mori, J. E. Draley and R. E. Loess: Crevice-Galvanic
Corrosion of Aluminum; June 1966.
- ANL-6785 J. E. Draley, W. E. Ruther and S. Greenberg: Corrosion
Experience with Aluminum Powder Products; Nov. 1963.
- ANL-7227 J. E. Draley and W. E. Ruther: Corrosion of Aluminum Alloys
by Flowing High Temperature Water; January 1967.

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- F. E. DeBoer: Discussion of Impedance Characteristics of Isolated Aluminum
Oxide Films, by D. F. MacLennan; Letter to Editor, Corrosion,
15, 643t, Dec. 1959.
- R. K. Hart and W. E. Ruther: The Morphology of Surface Reaction Products
on Aluminum; J. Nuc. Mat., 4, 272-280, Aug. 1961.
- R. K. Hart and J. K. Maurin: Morphology and Structure of Oxides Grown on
Aluminum in Superheated Steam; Corrosion, 21, 222-234,
July 1965.

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- CT-3095 John Mann: Improvements in Internally-Heated Slug Test; June 30, 1945.
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Professional Qualifications of

Joseph E. Draley

At Argonne National Laboratory I manage the OTEC (Ocean Thermal Energy Conversion) Biofouling, Corrosion, and Materials Project, carrying out a national program for the Department of Energy. In the present instance, testifying before the NRC Licensing Board, I speak on my own behalf and do not represent Argonne National Laboratory. At the Metallurgical Laboratory of the University of Chicago (3 years), Oak Ridge National Laboratory (1-1/2 years), and Argonne National Laboratory (20 years) I studied the corrosion and oxidation of metals, serving as group leader or Section Chief before going into management. A considerable amount of the corrosion work done has been of direct interest for nuclear power plants. I have also studied the environmental impact of nuclear power plants in connection with construction permit or operating license applications. A professional resume is attached, giving these and other details.

Over 150 technical publications have been authored by me or people working in groups I headed. Of these, I was author or coauthor of nearly 100 publications. The preponderant majority of all these publications were on the topic of corrosion or oxidation; many dealt with the aqueous corrosion of aluminum and a smaller number with the aqueous corrosion of stainless steel and zirconium alloys. In a number of instances, publications dealt with nuclear systems. A list of technical publications is attached.

I have been active in corrosion affairs in the Electrochemical Society and the Metallurgical Society of the AIME, serving as Corrosion Division Chairman and corrosion editor of the official journal for the former, and chairman of the Corrosion Resistant Metals Committee of the latter. I helped to originate American Corrosion symposia related to nuclear energy and an international meeting (Brussels, 1959) on the same topic. I participated in the Geneva Conferences on the Peaceful Uses of Atomic Energy.

I hold a bachelor's degree in chemical engineering (1939) and a PhD degree in chemistry (1947).

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INFORMAL REPORT

CORROSION OF MATERIALS
IN
SPENT FUEL STORAGE POOLS

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JULY 1977

DEPARTMENT OF APPLIED SCIENCE - BROOKHAVEN NATIONAL LABORATORY
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July 1977

POOR ORIGINAL

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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.

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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.

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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 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⁾

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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.

POOR ORIGINAL

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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.

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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.

POOR ORIGINAL

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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

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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 ⁻ , F ⁻ < 0.15 ppm
BRUNSWICK (BWR)	304 SS E308 17-4 PH - H1150, H1025	Liner, racks Electrodes Bolts	125°F (max 150°F) cond < μmho/cm pH 6.0 - 7.5 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- alize
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 I (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 Watts 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

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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

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CORROSION CONSIDERATIONS
IN THE
USE OF BORAL IN SPENT FUEL STORAGE POOL RACKS

J.R. WEEKS

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JANUARY 1979
DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY
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308 093

CORROSION CONSIDERATIONS
IN THE
USE OF BORAL IN SPENT FUEL STORAGE POOL RACKS

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December 1978

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INTRODUCTION

Boral is a cermet of Boron Carbide " B_4C " in aluminum clad in aluminum. It is manufactured in rolled sheets using techniques similar to those used in the production of uranium aluminum fuel elements. The core of the standard Boral contains 35% boron carbide by weight. Cladding material is typical 1100 aluminum. Where it is exposed to water in service, the edges of the Boral are recommended by the manufacturer to be clad with aluminum by welding.

In Spent Fuel Pool (SFP) racks, the Boral is usually not a structural member but is inserted in cavities between the spent fuel storage positions in the racks. In these locations it is sealed by welding to prevent access of water. Inherently, however, the corrosion of the Boral, both the boron carbide-aluminum cermet and the aluminum cladding, should be minimal in a spent fuel storage pool. The cavities into which the Boral is sealed are typically fabricated of aluminum alloys, i.e. type 6061, or stainless steel. In either case, these are the structural members of the SFP racks.

In an SFP, water chemistry tends to be strictly controlled because the SFP water mixes with the reactor coolant during refueling procedures. In SFP's at BWR sites, water chemistry is typical of that of a BWR i.e. high resistivity neutral water. In SFP's at PWR sites water chemistry typically contains 2 to 3,000 parts per million ppm boron as boric acid, which is there primarily to prevent dilution of the reactor primary coolant during refueling and is not relied on for criticality considerations. The water chemistries and anticipated

corrosion of SFP materials were reviewed in an earlier report. BNL-NUREG 23021, July, 1977.

CORROSION OF BORAL

Corrosion problems have developed in SFP's where water has inadvertently leaked into the cavities containing the Boral. In a BWR pool, swelling of the racks has been observed when water leaked into the cavities through a flaw in the seal weld at the bottom of the cavity.

The swelling observed arises from the rapid initial corrosion of Al by water. Draley and Ruther (ANL-5001, Feb. 1, 1953) have shown that aqueous corrosion of 1100 Al can be described in terms of a steady state slope and an intercept, as sketched in Fig. 1. This intercept was measured by them to be 21 ± 5 mg/dm² "metal corroded" over a range of temperatures (100 - 175°C) and pH (5 - 8.5). This "intercept" corrosion occurs within the first 5 days of immersion in water by a reaction of the type



Thus 21 mg Al can produce $\frac{21 \times 3}{27 \times 2}$, or slightly more than

1 millimole H₂ per dm² of surface. The Brooks & Perkins Report #577 says there are 3.4×10^2 dm² Boral per tube in SPF racks such as those at Monticello or Brown's Ferry, so one could produce approximately $3.4 \times 10^2 \times 22.4 =$ approximately 7500cc H₂/tube, at STP. This is more than enough to produce the necessary 6 psi to bulge the cladding in a void volume of 130cc.

There is no reason to believe, however, that any B₄C will be lost from the Boral by corrosion in the SFP water. In the Brookhaven

Medical Research Reactor, Boral has been exposed to the reactor coolant since January, 1959. Figure 2 shows a schematic of this reactor. The 1/4 inch Boral sheets are in the form of 2 half-cylinders. The upper edge of these sheets is unclad. The vertical edges appear by examination in situ with a periscope to be clad. In July of this year, samples were removed in the form of small punchings, three from each of the half-cylinders as shown on the attached sketch, figure 3. Each of these six specimens was cut in half, and one-half mounted for metallography. The resultant microstructures are shown in figures 4-9. Clearly there appears to be no systematic loss of the boron carbide. The other half of each of these specimens was analyzed by neutron attenuation at the University of Michigan under contract with Brooks and Perkins, the primary supplier. The neutron attenuation results are shown in figure 10. All the results are within 20%, which with the small size of the specimens is probably within analytical error. One specimen, #5, was analyzed wet chemically by Brooks and Perkins to contain 41.3% B₄C in the core, which is in the upper range of boron concentrations for material produced in the 1950's. It, therefore, seems reasonable to conclude that no boron was lost from the core of this Boral by exposure to the BMRR coolant over the 19 1/2 year period. In the location of the BMRR where it is used, there is little measureable neutron flux. Water chemistry in this reactor is outlined in Table 1.

PITTING OF ALUMINUM IN CONTACT WITH STAINLESS STEEL

When aluminum is contacted with stainless steel in impure water, a potential exists for a galvanic attack of aluminum at the point of contact. In a SFP environment, this attack is especially likely in a PWR pool containing boric acid at a pH around 4.5. Further, aluminum

borates can be produced which appear as a white fluffy dispersion in the water at a pH greater than about 4.5. Maintaining the pH below 4.2 causes the white fluffy material to disappear. Corrosion currents at a stainless steel to aluminum galvanic couple in boric acid were measured to average 2 mils per year although the presence of oxygen or hydrogen peroxide increased this value substantially.

A number of references exist showing that pitting corrosion can occur in slightly acid waters at aluminum to stainless steel junctions. English and Griess (ORNL-TM-1030, 1966) report pitting depths up to 45 mils in 12,500 hours (1 1/2 years) in pH 5 nitric acid solutions at 100°C. Lennox et al. (Materials Performance, Vol. 13, #2, page 31, 1974) measured pitting where type 5086 aluminum is coupled to type 304 stainless steel of the order of 30 mils in a year and one-half in Gatun Lake, Panama, and up to 40 mils in two years in the Potomac River at Washington. The general corrosion of this alloy was negligible in both environments.

In the HFBR SFP, water chemistry is similar to that in a BWR SFP except that conductivity may be slightly higher, and the pH slightly lower. Typical data are given in Table 2. Specimens of aluminum and stainless steel in contact with one another have been exposed in the HFBR pool for a period of six months at which time they were examined and then reinserted for continued testing. There appears to be a general discoloration of the aluminum where it contacted the stainless steel and a small amount of pitting around the edges as shown in figure 11. It is highly unlikely, however, that pitting of this magnitude would result in significant loss of the boron should the Boral containing cavities be flooded over an extended period of time.

Venting the upper end of the Boral chambers would probably alleviate any concerns over swelling due to hydrogen generation. It might produce pitting corrosion and some of the white aluminum borate deposits. I would recommend that a surveillance program including aluminum to stainless steel couples be installed in SFP's in which the Boral cavities are vented. Any swelling due to hydrogen production should occur within a week or so of the time the water enters the annulus containing the Boral. However, should a leak develop in one of the seal welds at some future date after the racks are installed, the swelling could occur at that time. For this reason, venting or the capability for future venting, is probably desirable. In general, I think the localized pitting corrosion that might result from venting the Boral cavities in SFP racks would be less of a safety concern than the swelling that might occur should they not be vented. In all SFP's the rack design should prevent contact between Al and the zircaloy fuel cladding, as this galvanic couple (especially in boric acid pools) can lead to hydriding of the zircaloy during storage, as described by A. B. Johnson in BNWL 2256, September, 1977.

CONCLUSIONS AND RECOMMENDATIONS

1. The swelling that has occurred in the Monticello SFP racks and might be anticipated to occur in other similar SFP racks results from initial corrosion of aluminum and not from corrosion of the boron carbide cermet.
2. Venting of these cavities in a BWR pool should not produce significant loss of the boron and should, therefore, be accepted by NRC provided the venting occurs at the upper edge so that any hydrogen pressure from corrosion of the aluminum cladding will not build up to cause swelling of the racks.

3. Venting of the Boral cavities in a PWR rack might produce more pitting corrosion of the Boral. Again, however, it should not lead to major loss of the boron carbide.
4. Anodizing the Boral in these cavities would tend to reduce the hydrogen production in the cavities should SFP water leak in to them. Anodizing would probably not, however, prevent pitting of the aluminum.
5. In any fuel pool in which the Boral cavities are flooded intentionally or inadvertently, surveillance specimens should be present to determine on a periodic basis, i.e. once every few years, what is happening to the Boral in these cavities.
6. In any SFP, galvanic coupling between Al in the racks and the zircaloy fuel cladding should be avoided, to prevent hydriding of the cladding during long term storage.

ACKNOWLEDGEMENTS

The assistance of the BNL Reactor Division staff, R.W. Powell, Head, in obtaining the Boral punchings from the BMRR spent fuel shielding is deeply appreciated. The metallography was performed by K. Sutter of BNL. The neutron attenuation and wet chemistry results were obtained through the courtesy of Mr. R. C. Karzmar of Brooks and Perkins, Inc. More detailed analyses of these specimens are underway at G.E., by A. Jacobs, and at Brooks and Perkins, and will be the subject of a future report.

TABLE I

BMRR WATER CHEMISTRY

Temperature	Inlet	Outlet	T.S.
Reactor ON	100°F	115°F	136°F
Reactor OFF	75-80	75-80	-

(Reactor ON less than 10% of time)

Conductivity	Normal	Regenerate Demineralize	Alarm	T.S.
($\mu\text{mho/cm}$ @25°C)	<2	2	5	10

Alarmed only once in 20 years, during HX leak. T.S. never exceeded.

TABLE II

HFBR SFP CHEMISTRY

Resistivity meg-ohm-cm	Temp. °C	ppb Cl ⁻	pH
.24 - .6	30-35	4-20	5.9-7.0

(low pH coincides with low resistivity)

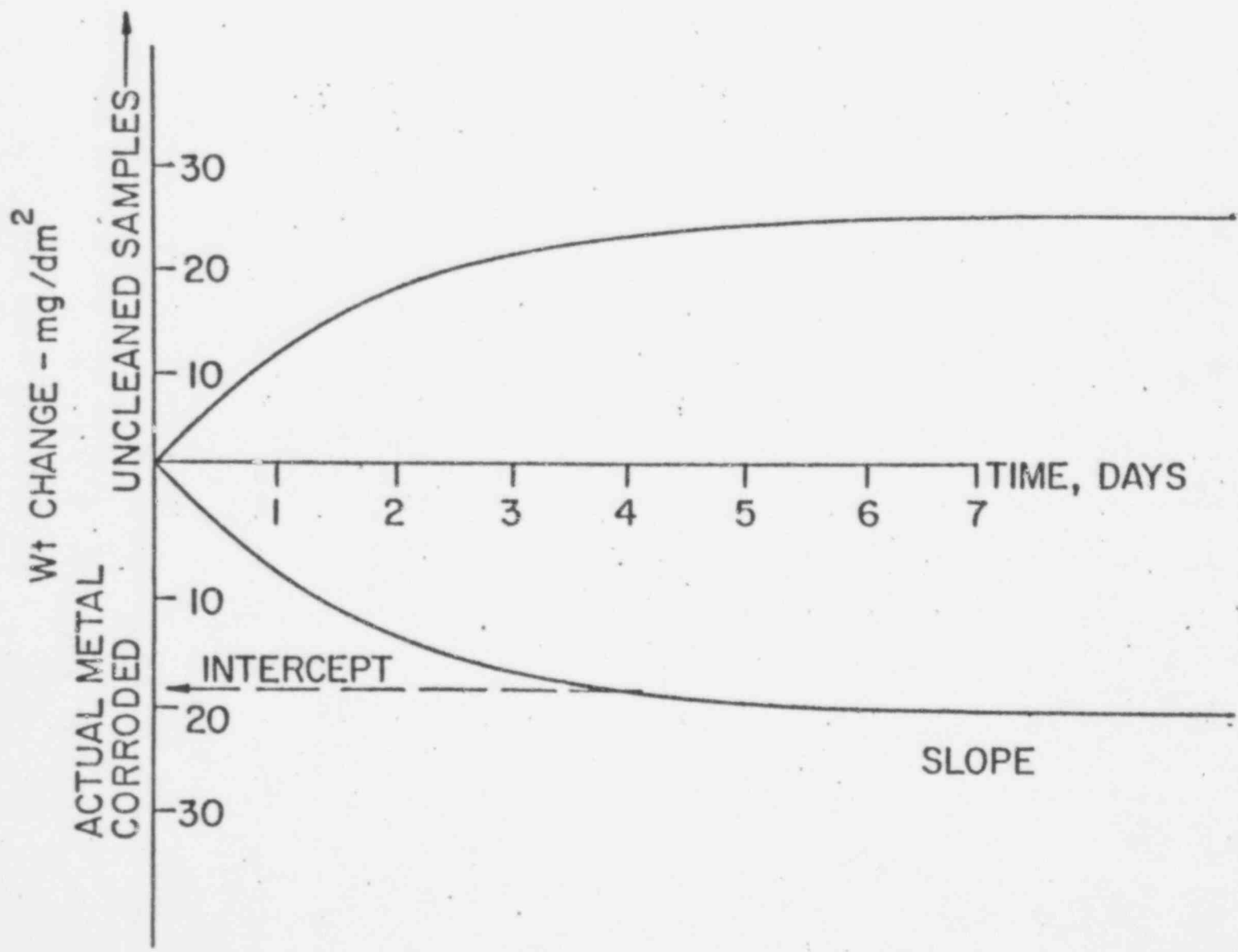


FIG. 1 Typical Corrosion Pattern for 1100 Al in Water
(From ANL-5001)

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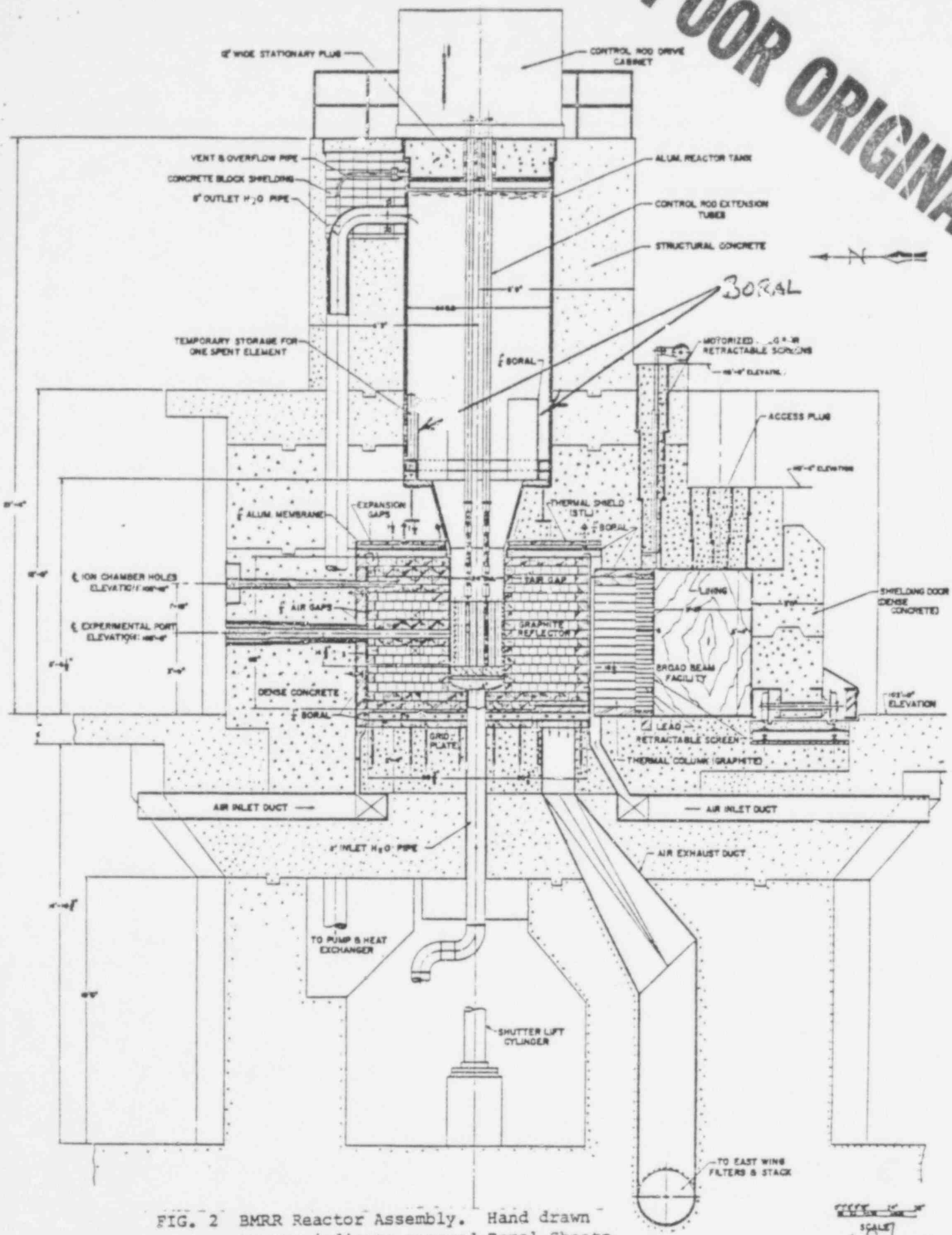


FIG. 2 BMRR Reactor Assembly. Hand drawn arrows indicate exposed Boral Sheets. From BNL-600.

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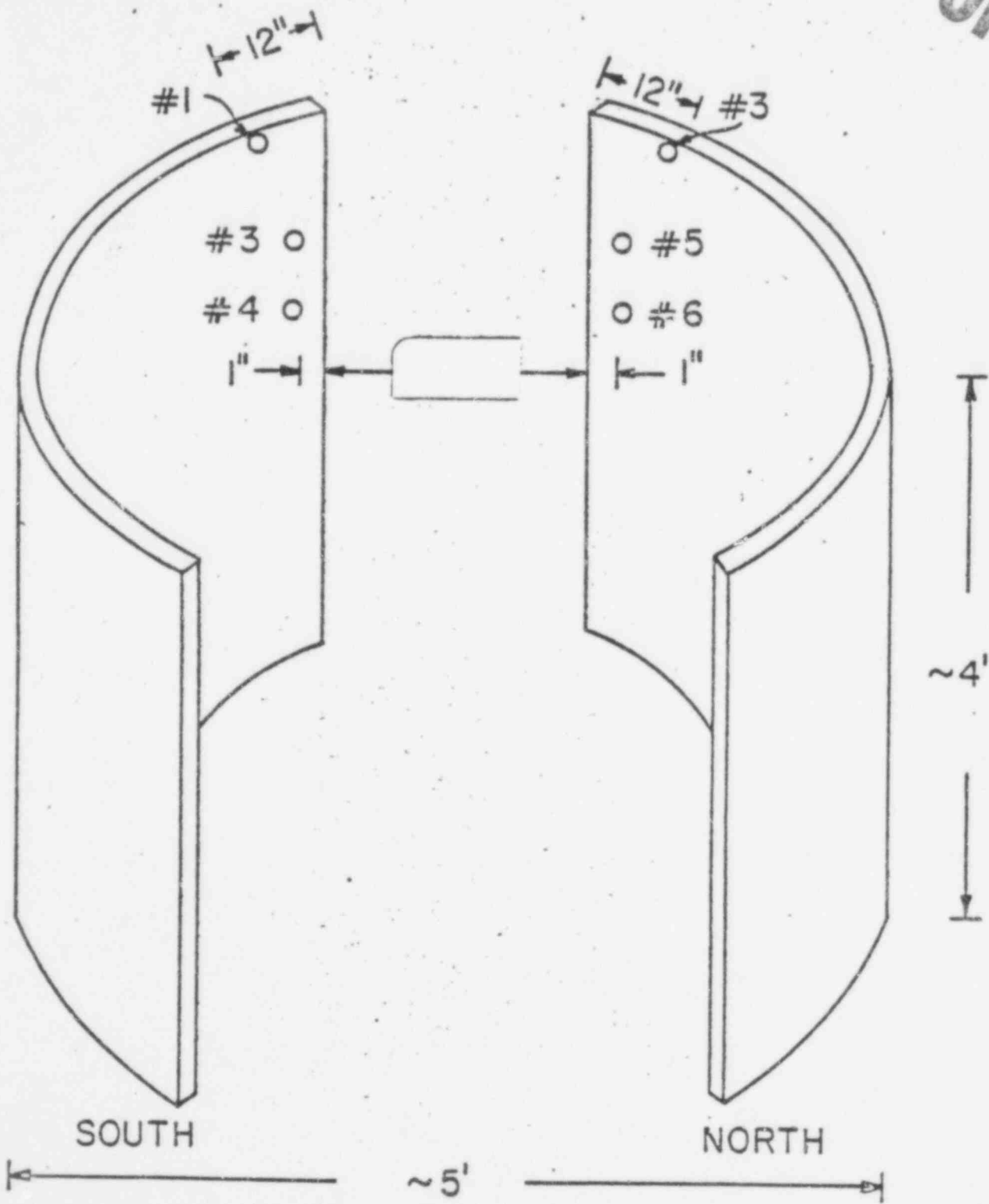
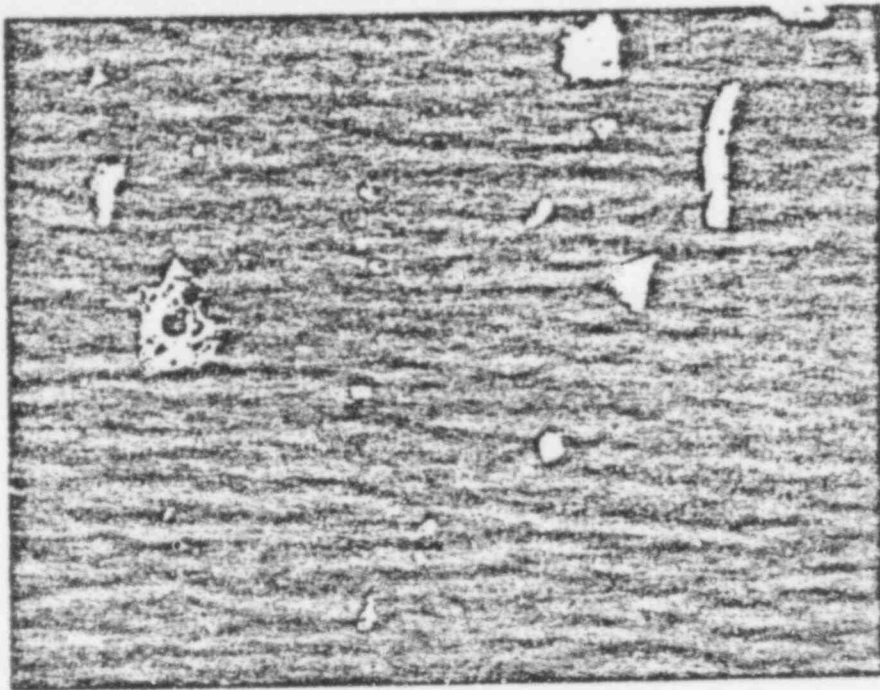


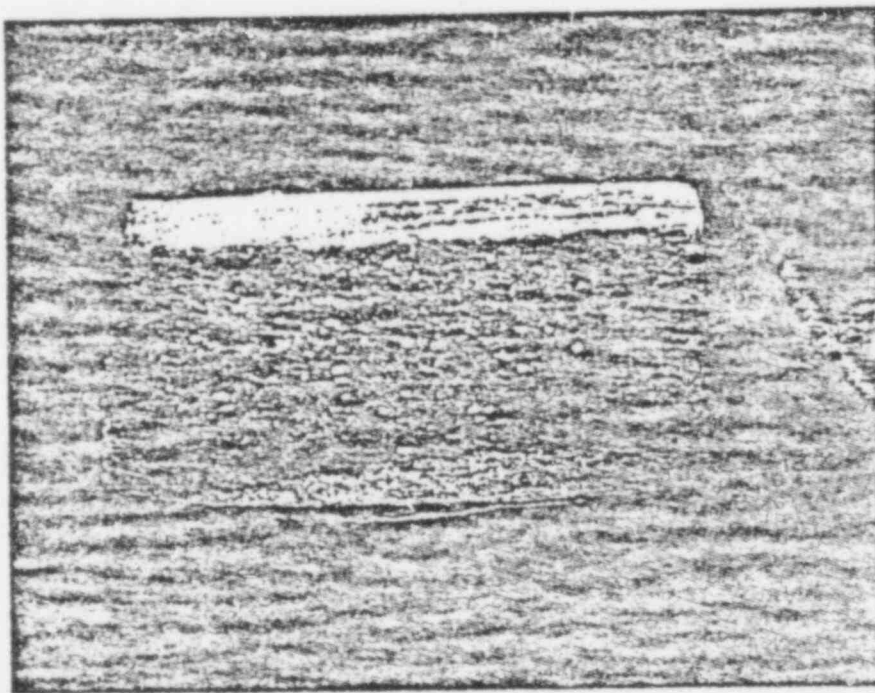
FIG. 3 Schematic of 1/4" Boral Sheets in BMRR, Indicating Location of Punchings

308 108



X100

Sample #1

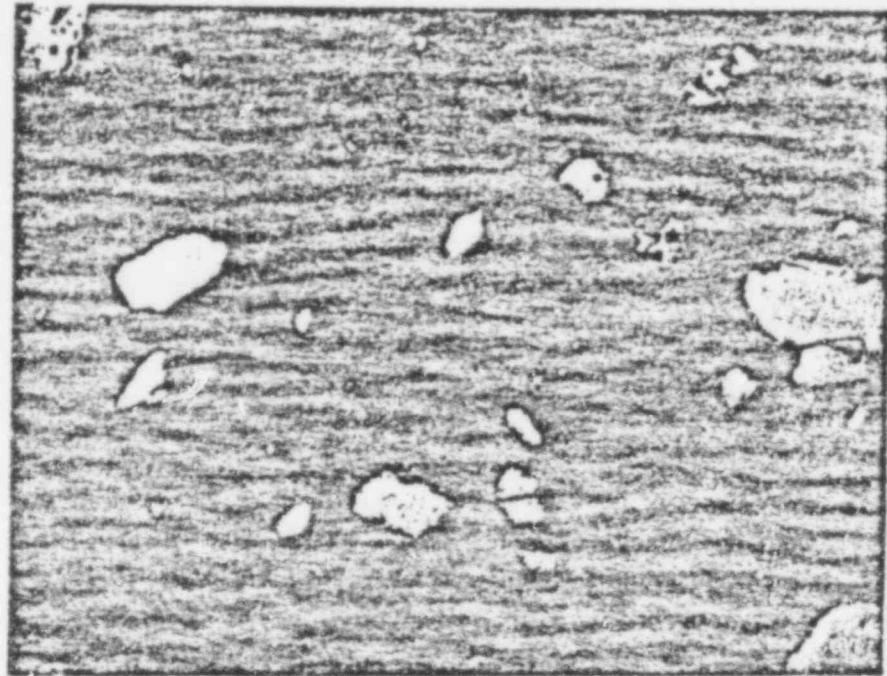


X7

↑
Exposed end

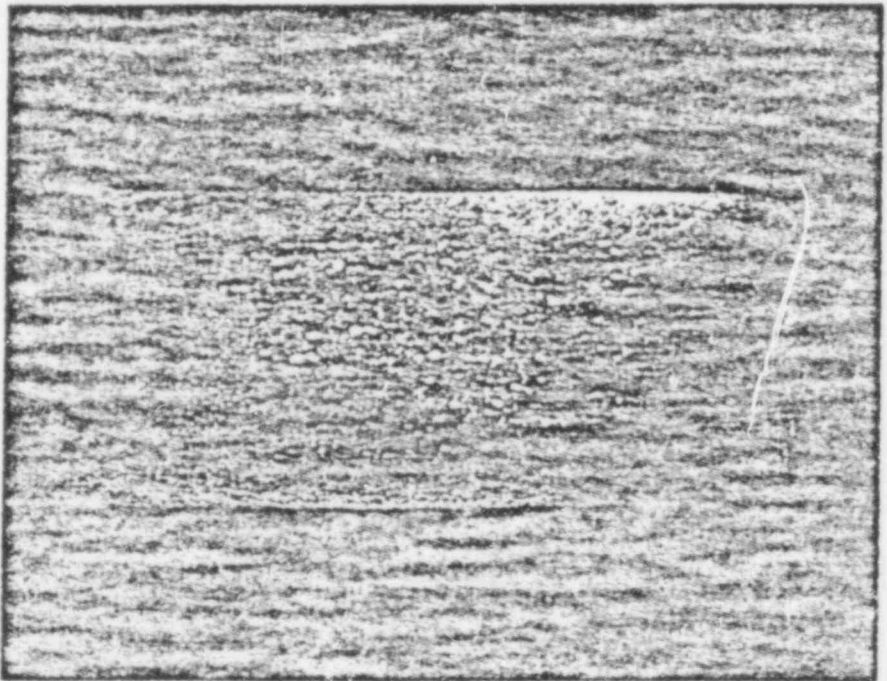
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FIG. 4



X100

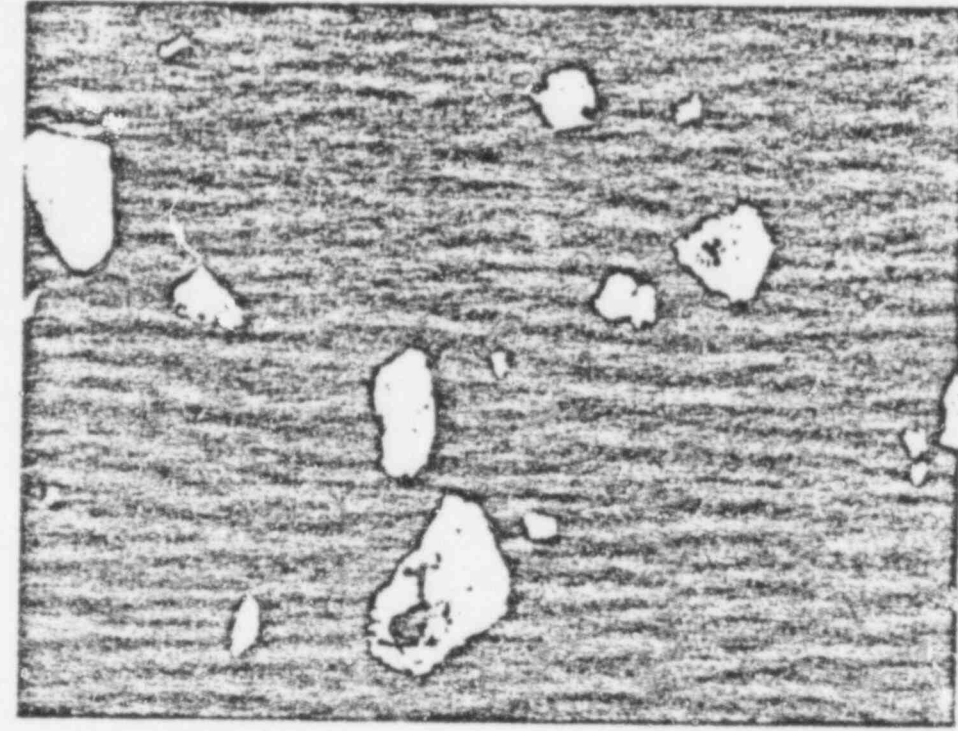
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X7

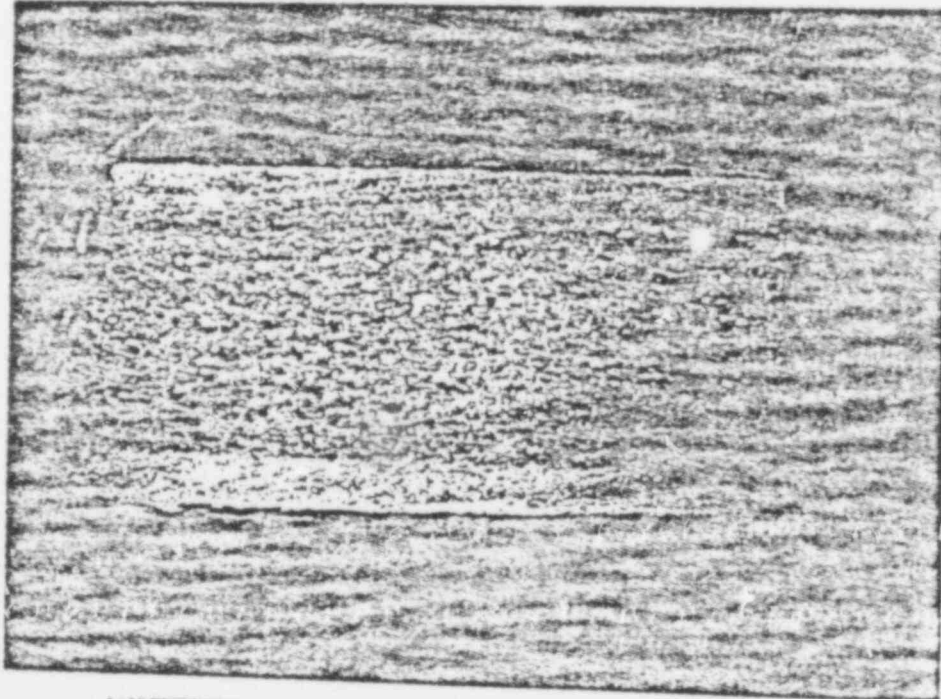
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FIG. 5



X100

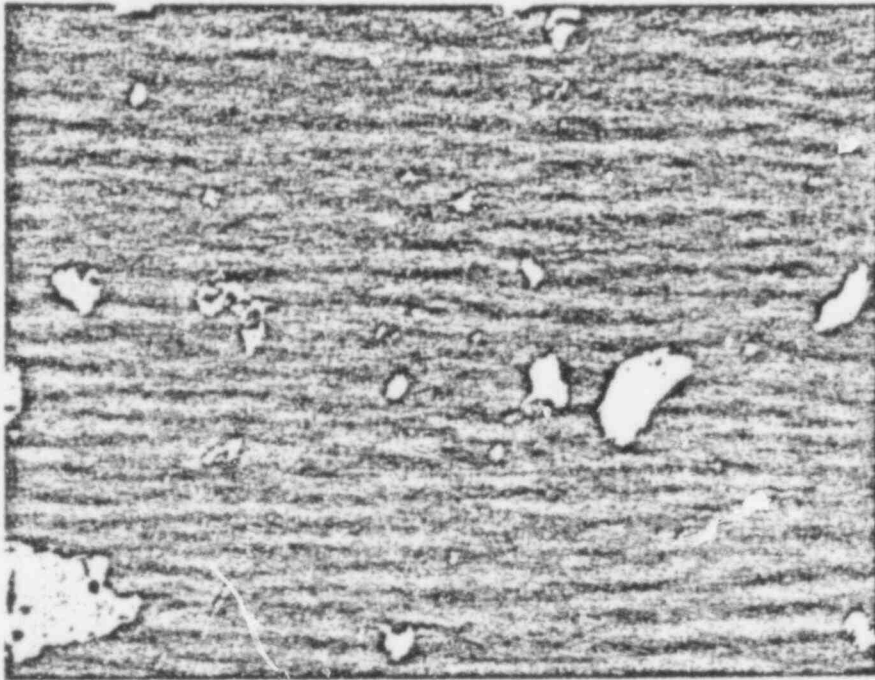
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X7

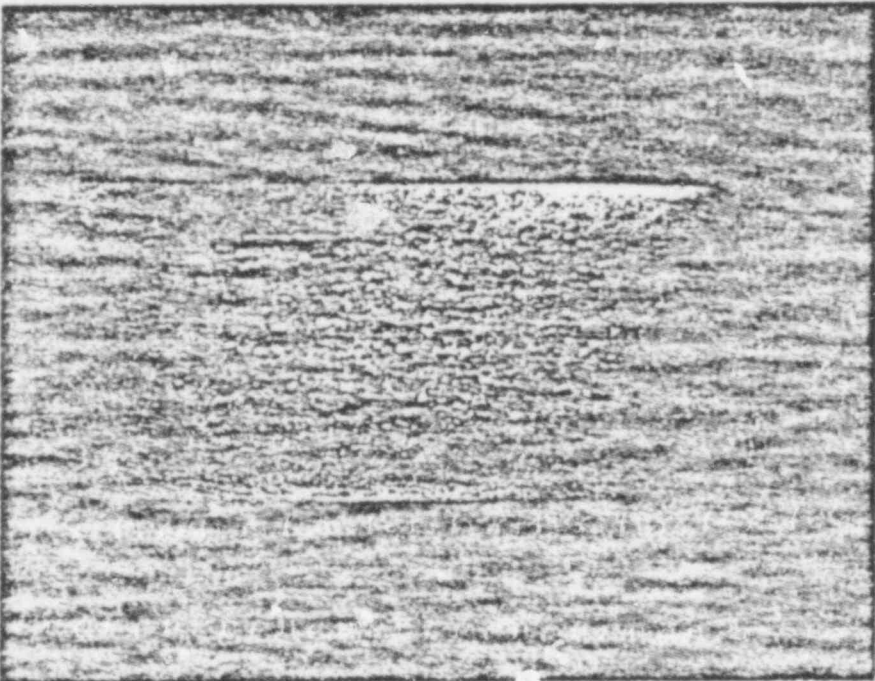
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FIG. 6



X100

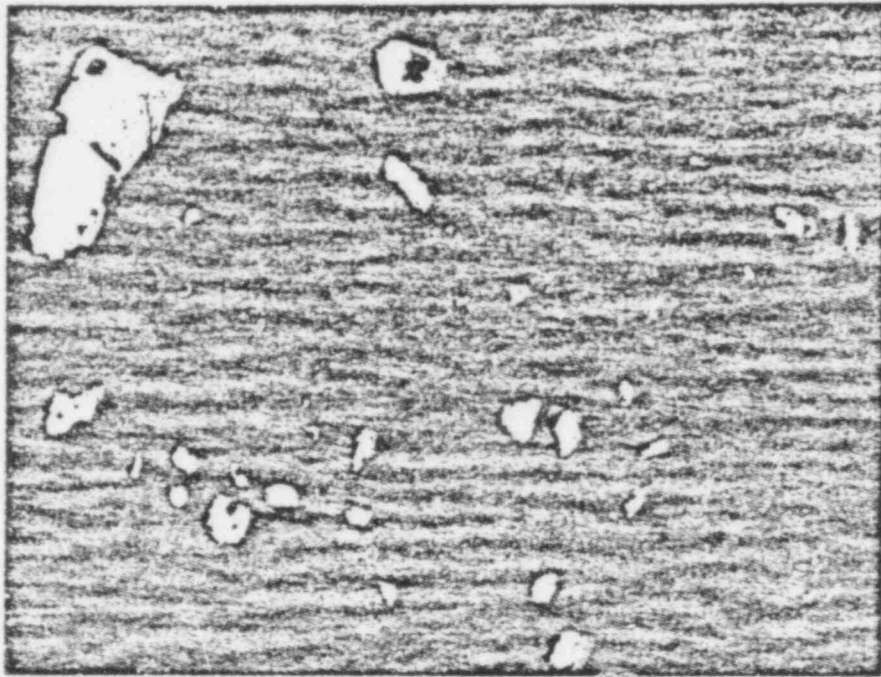
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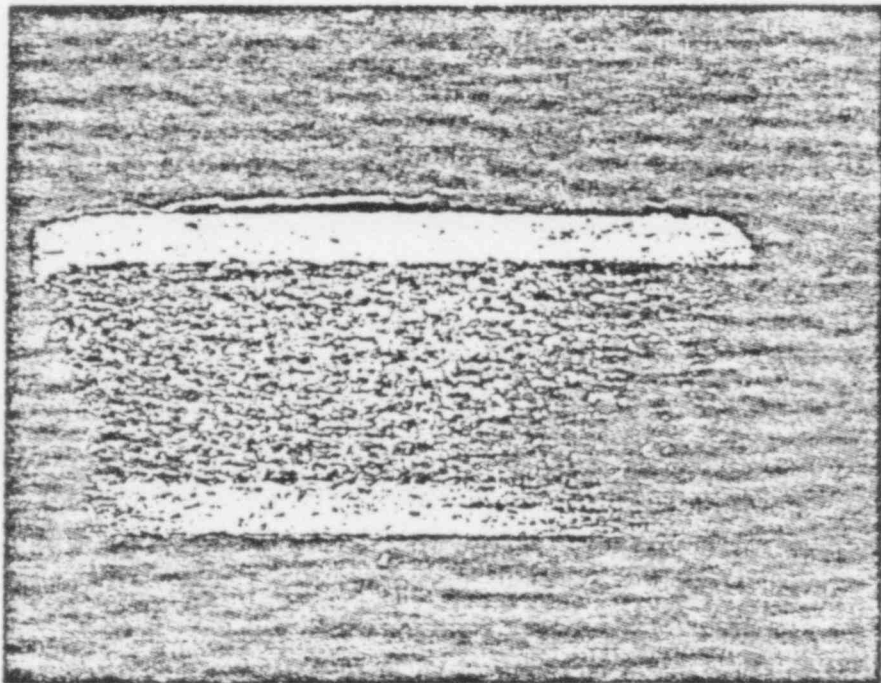
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FIG. 7



X100

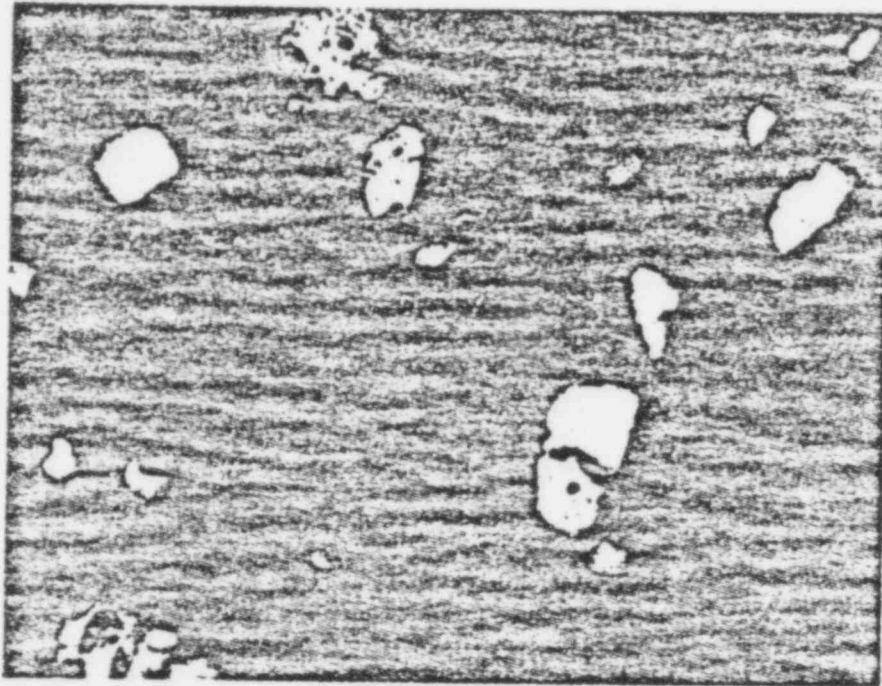
Sample #5



X7

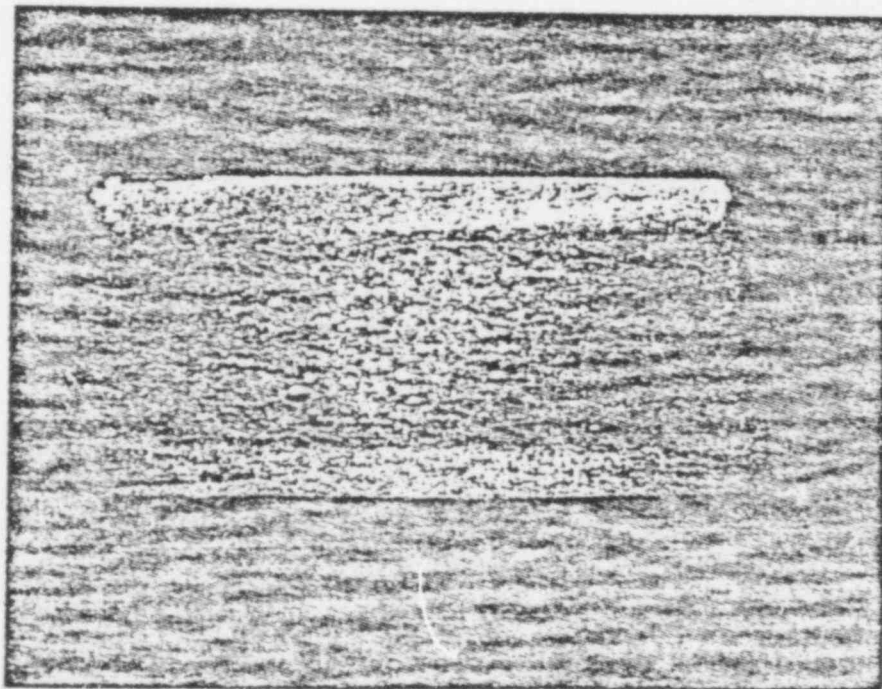
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FIG. 8



X100

Sample #6



X7

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FIG. 9

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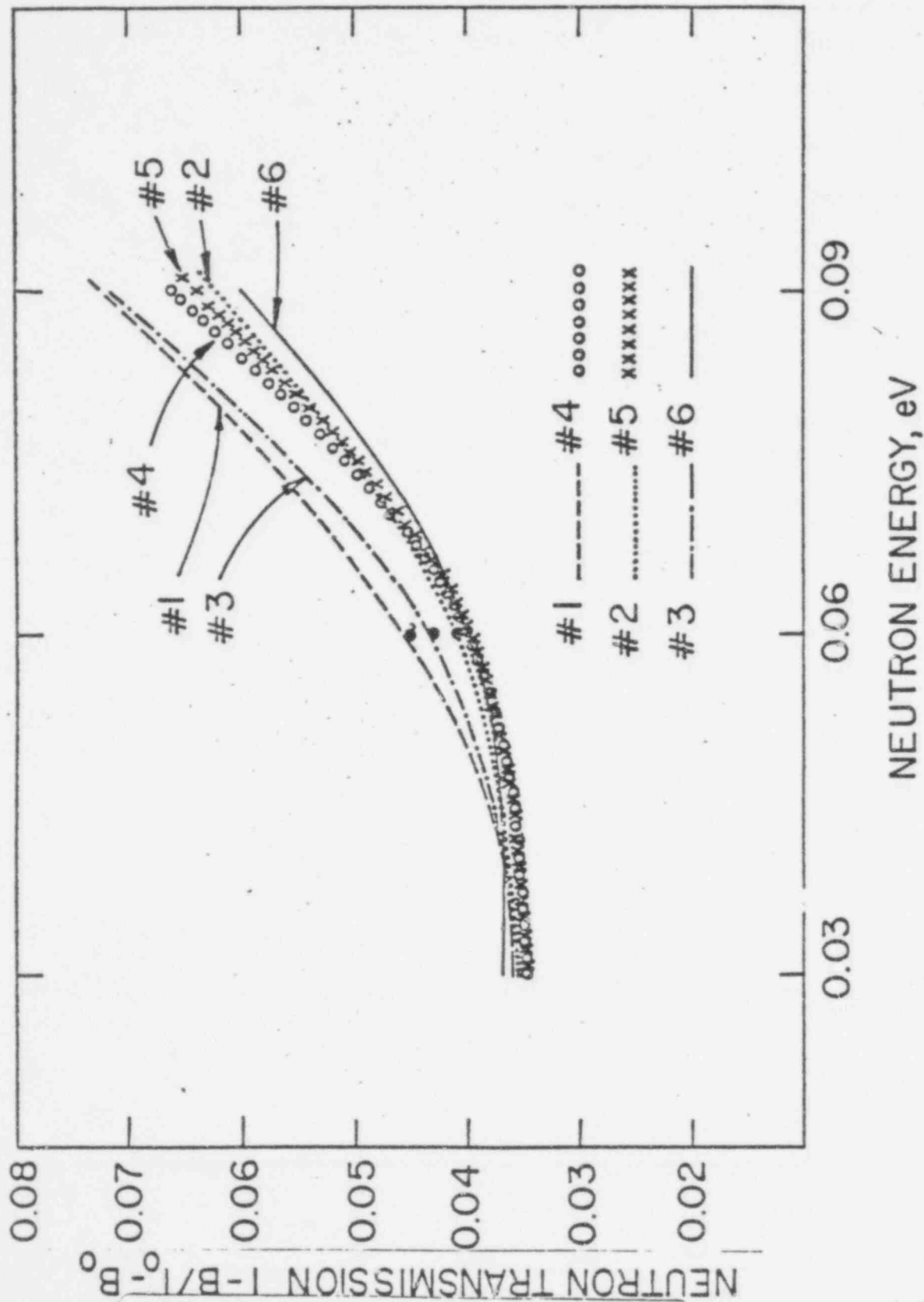


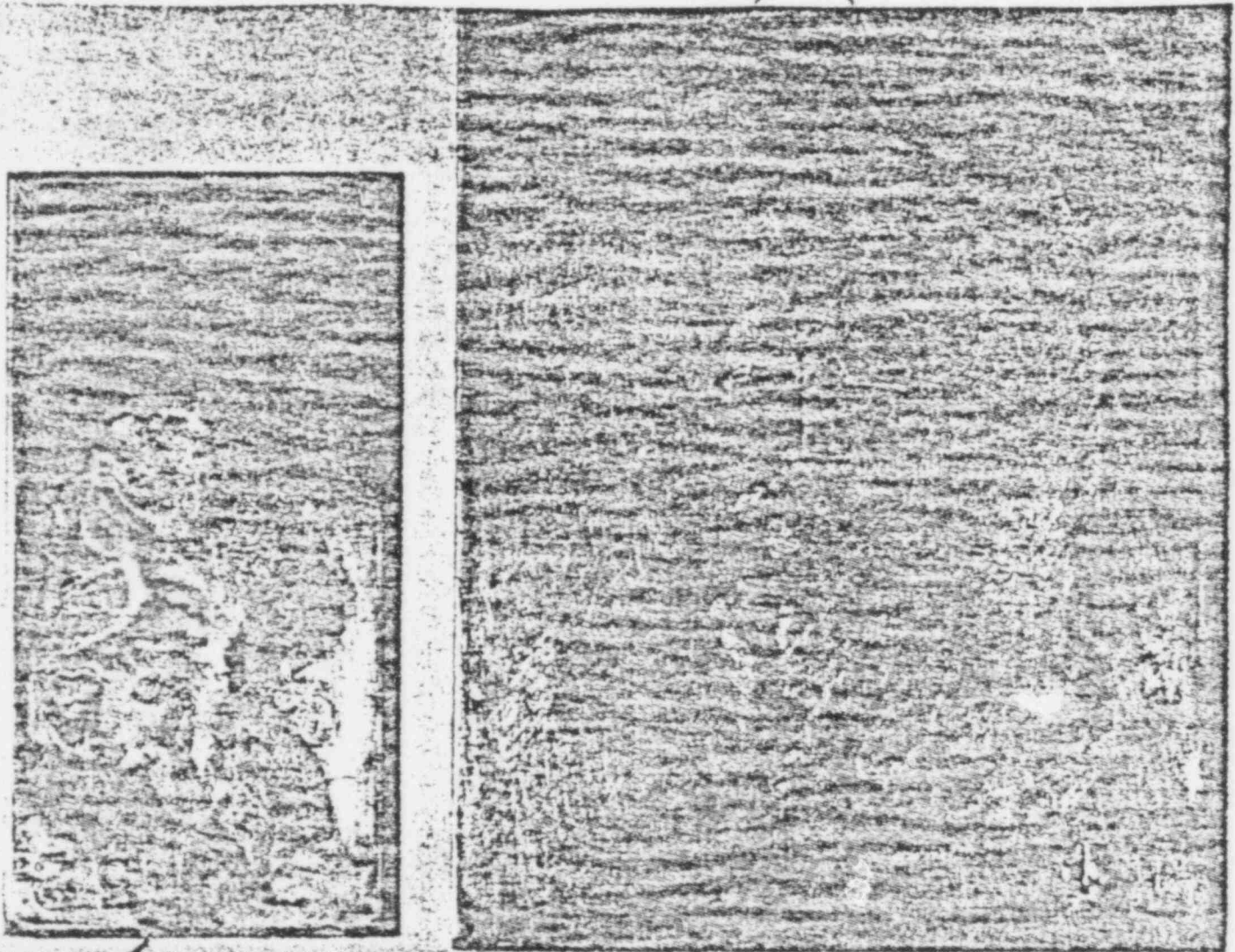
FIG. 10 Neutron Attenuation Results on Samples 1-6 (Performed at U. of Michigan, Courtesy of Brooks & Perkins)

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PITS



PIT

FIG. 11 Aluminum Surfaces in Contact with Stainless Steel
after 6 1/2 months Exposure in the HFBR SPP 2.5x

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NEUTRON ABSORBER SAMPLING PLAN - IN POOL

A sampling plan to verify the integrity of the neutron absorber material employed in the high density fuel racks in the long-term environment is described.

The test conditions represent the vented conditions of the spent fuel tubes. The samples will be located adjacent to the fuel racks and suspended from the spent fuel pool wall. Eighteen (18) test samples are to be fabricated in accordance with Figure 1 and installed in the pool when the racks are installed.

The procedure for fabrication and testing of samples shall be as follows:

1. Samples shall be cut to size and dried in an oven for five hours at 170°F, followed by a cycle at 600°F for three hours.
2. Samples shall be weighed immediately following removal from the oven and weight in milligrams recorded for each sample.
3. Samples shall be fabricated in accordance with Figure 1 and installed in pool.
4. Two samples shall be removed per schedule shown in Table 1.
5. Carefully cut samples apart at the weld without damaging the neutron absorber, wash with a soft brush in a mild abrasive and detergent solution, immerse in nitric acid to remove surface products, followed by a rinse of clean water and alcohol. Dry in a 175°F oven for five hours, followed by a cycle at 600°F for three hours.
6. Weigh the samples and evaluate the weight change in the neutron absorber material in milligrams per square centimeter per year.
7. Visually examine the clad surface for pitting. Take micrographs of the edge surface and any other suspect areas.
8. If pitting is present, the depth of the four major pits are to be recorded and the average pit penetration in mils of an inch per year determined.

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9. Prepare report of sample test results and observations.
10. Should any adverse conditions be detected, the samples may be subject to a B^{10} loading analysis.
11. Additionally, two full length vented fuel storage tubes will be suspended in the pool. They will be observed periodically for signs of swelling, and they will be opened and examined should the small specimens indicate any loss of absorber material below $.02\text{gm/cm}^2$, Boron 10 .
12. Retain samples.

FUEL STORAGE RACKS CORROSION PROGRAM,

BORAL - STAINLESS STEEL

(NON-PROPRIETARY VERSION)

MARCH 1979

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ABSTRACT

Exxon Nuclear Company, Inc. has conducted a Boral*-Stainless Steel Corrosion Program during the past 18 months to establish additional performance information for use of Boral plates in spent fuel storage applications. The program consisted of a detailed review of related literature, an evaluation of test programs conducted by others, and additional corrosion tests performed at Exxon Nuclear facilities.

The objective of the Exxon Nuclear test program was to obtain corrosion data for Boral-304 stainless steel test specimens in simulated PWR fuel pool environments so that reliable predictions could be made of what physical changes would occur in a defective, i.e., unsealed spent fuel storage cell after a 40-year exposure.

The Exxon Nuclear tests indicate that storage cells, containing a leak simulating hole, will sustain aluminum corrosion at a rate which can be expected to consume _____ of the aluminum in the Boral core after a 40-year exposure.

Should Boral plates be exposed to a typical PWR pool environment, the material is subjected to pitting, edge attack, and internal gas pressurization; but no effect on criticality safety is expected over the lifetime of storage cells due to dislodgement of B₄C particles.

* The Boral test samples discussed in this report are a neutron absorbing, shielding material manufactured by the Brooks and Perkins Company. The Boral specimens are a composite material consisting of boron carbide evenly dispersed within a matrix of aluminum and clad with aluminum.

1.0 INTRODUCTION

Prior to designing racks utilizing stainless steel clad Boral plates in PWR pool environments, Exxon Nuclear initiated, (during 1976 and early 1977), a review of applicable material corrosion literature and conducted analyses of test results performed by others.

Exxon Nuclear's review of the related literature*, and performance of Boral in similar environments, indicated that there should be no adverse effect on nuclear safety analyses of storage racks in a PWR pool environment. To provide further assurance of satisfactory material performance, Exxon Nuclear initiated a test program in February, 1977 to evaluate Boral clad in stainless steel 304 specimens in environments simulating utilization in Exxon Nuclear PWR storage rack applications.

* List of appropriate material contained in Reference section of this report.

2.0 TEST PROGRAM DESCRIPTION

2.1 SPECIMEN DESCRIPTION

Exxon Nuclear's test program placed emphasis on investigation of Boral utilized in conditions typical of expected storage cells and PWR pool water environments. Consequently, storage cell component sections were fabricated which resembled the larger, full-size storage cells. Specifically, these reduced-size storage cell specimens consisted of inner and outer stainless steel 304 shrouds into which four (4) Boral plates were inserted. The complete assembly was sealed welded, resulting in 6" high x 6" wide test specimens. Each completed cell specimen was made to simulate a leaking condition by drilling 1/16-inch holes as described in Appendix A.

In order to separately observe and measure various corrosion and material properties during the test, additional test specimens were utilized. These additional specimens consisted of 2" x 2" coupons made as follows:

- 1) Open-edge Boral/stainless steel composite;
- 2) Sealed-edge Boral/stainless steel composites with a leak simulating hole; and,
- 3) Unencapsulated Boral coupons.

2.2 ENVIRONMENT DESCRIPTION

Insulated nine (9) gallon polyethylene tanks, with fitted covers, were used for the plain Boral and open-edged Boral-stainless specimens. Thirty (30) gallon tanks of the same construction were used for the closed-edge tests. Each tank was fitted with a stainless immersion heater and stirring mixer, which were affixed through openings in the tank covers.

A stainless steel screen was used to hold the specimens off the bottom of the tanks and permit circulation of the environment on all sides. In order to isolate the plain Boral specimens from the stainless steel screen, a pedestal was fashioned from phenolic plastic. The open-edged composite samples, a 2" x 2" Boral piece sandwiched between two 2" x 2" stainless steel pieces, were held together with four (4) Met-clip springs, one along each edge. These were placed on the stainless screens so that the clips held the specimens in a horizontal position over the screen.

The initial environment in each tank was deionized water with a pH of 5.85 and a conductivity of 0.75 μ mho/cm. Boric acid (H_3BO_3) and lithium hydroxide ($LiOH \cdot H_2O$) additions were made to produce the following:

Environment A) Deionized water plus 13.3 g/l Boric Acid
(resulting in 2300 ppm Boron at 150°F).

- Environment B) Deionized water, 13.3 g/l Boric Acid,
0.0121 g/l lithium hydroxide
- Environment C) Deionized water plus 0.0121 g/l lithium
hydroxide

The specimens, were immersed in each environment on July 1, 1977. The initial temperature and pH of each environment were measured as follows:

<u>Environment</u>	<u>pH</u>	<u>Temperature, °F</u>
1	5.20	146.4
2	5.53	147.2
3	9.15	153.4

The temperature and pH were measured daily. The temperature showed some fluctuations and variacs were installed in order to gain better temperature control. The pH in the borated solutions, 1 and 2, remained constant but in the alkaline tank, C, it dropped into the 7 range within days. In order to keep the solution pH in the alkaline range, additional additions of lithium hydroxide were made.

2.3 INITIAL MEASUREMENTS

Appendix A of this report contains descriptions of all Boral and stainless steel specimens utilized for the test program. The initial measurements and conditioning programs are also provided in Appendix A.

3.0 SUMMARY

No corrosion, pitting, nor stress-corrosion cracking was observed on any of the stainless steel coupons, or storage cell specimens used in this study. The austenitic stainless steel can be expected to withstand exposure to borated fuel pool environments for the projected forty-year life of spent fuel racks. Similarly, without a leak path through the stainless steel liners, the interior Boral plates would not be subject to degradation as a result of aqueous corrosion. In the situation of a leak path through the stainless liners which permits the interior space to fill with the pool environments, the results of the 2 month, 6 month, and 12 month exposure studies, show that Boral is subject to general corrosion, pitting and edge attack, and clad deformation due to internal gas pressurization. To various degrees, the severity of each of these corrosion effects depends on the particular environment chemistry and the specific geometry of the exposed materials. Based on comparisons between the four (4) specimen types and the three (3) environments used in this study, the following summary can be drawn concerning the corrosion resistance of Boral and its suitability for use when exposed in stainless lined storage cells to borated environments.

The general corrosion rate, as determined by weight gain measurements,

When all the storage cell specimen data are examined on a semi-log plot, the amount of aluminum consumed in conversion to oxide after a 40-year exposure, is: percent for the low pH and percent for the higher pH environments.

The weight gains were lowest for the storage cell specimens in each of the three (3) environments, followed in general by the plain, open-edged, and edge-sealed specimens. The weight gains, measured for the plain and open-edged specimens, were nearly identical to each other in the three (3) environments. This similarly indicates that galvanic coupling between the stainless steel in the open-edged specimens does not accelerate general corrosion in the Boral. In all three (3) environments, the edge-sealed specimens showed the greatest weight gain.

Similar considerations apply to edge attack of the Boral. However, the depth of edge attack did not increase significantly between the

6 and 12 month exposure. The deepest edge penetration, 0.028", was measured on the open-edged specimen in the low pH environment. No measurable edge attack was observed in the vicinity of the leak simulating hole in the Boral plates of the storage cell specimens.

Gas generation, due to corrosion of the aluminum in Boral, has been observed in the edge-sealed specimens and the storage cell specimens. This gas has been observed to bubble from the upper hole in each of the storage cells. In several of the specimens removed after 12 months, bulges were observed between the aluminum cladding and the B_4C aluminum core.

The occasional unbonded layers of the Boral matrix occurred randomly and were observed in concentrated areas of very small B_4C particles (i.e., ≥ 150 mesh). It has been determined that the Boral specimens provided by Brooks and Perkins for the ENC corrosion test program contained a much higher concentration of small B_4C particles than utilized for production Boral plates. Accordingly, it is possible that the small bulges observed on the sealed specimens may not occur in finished plates where improved B_4C and aluminum bonding result with larger B_4C particles.

The occasional lack of bonding between B_4C and aluminum particles also allows a small amount of water to enter the inner portions of the bulged specimens. Normally, water does not penetrate into well-bonded Boral plates and no internal corrosion can occur.

The small bulges have not been reported or observed in prior related corrosion test programs. They appear to be a self-limiting phenomenon,

where the gaseous corrosion product both causes the bulge and displaces the water causing the corrosion. An inspection of both the aluminum cladding and inner Boral matrix demonstrates that no clad pitting or deterioration of the inner face of cladding and Boral material occurred near the bulged areas. Consequently should random small bulges occur, any dislodgement of B_4C particles will be of no significance on neutron shielding or attenuation properties.

4.0 RESULTS

On June 30, 1978, after a nominal 12-month exposure, the remaining three (3) plain Boral and three open-edged Boral-stainless composite specimens, were removed from the three (3) heated tanks. On August 10, 1978, the edge-sealed, and storage cell specimens, were removed from their environments. These twelve (12) samples were subjected to visual, metallographic, weight gain, and pit depth measurement analyses.

This section of the report places emphasis on the detailed results obtained from the storage cell specimens. Appendix B presents additional test results for other specimens and contains most referenced tables and figures for information presented in this section. Table 4.1 provides specimen identification numbers and exact lengths of exposure for each of the twelve (12) specimens evaluated during the final period.

4.1 Internal Environment Of Edge-Sealed And Storage Cell Specimens

The pH of the solution, within the edge-sealed and storage cell specimens, was measured using indicator paper for the former, and a Beckmann pH meter for the latter. Approximately 2.5 grams of solution was contained in the edge-sealed specimens and 39 grams in the cell specimens.

In Table 4.2 is a summary of the interior pH of the edge-sealed and cell specimens for the 2-, 6-, and 12-month exposures.

For the high pH lithium environment, the interior pH consistently shows a decrease in pH toward a neutral value for all exposure times. A similar trend toward a more neutral pH is exhibited for the acidic environments for exposures up to 6-months. After 12-months, the interior pH is the same as the bulk solution or, slightly more acidic.

4.2 Visual Appearance

The storage cell specimens were disassembled and cut open to separate the Boral plates from the stainless liners. A visual examination of each Boral piece was conducted using a low power stereo-microscope. The following observations were noted:

Storage Cell Specimen #3 (S.C.S.-3)

Surfaces were generally metallic in coloration. Extra corrosion products, and some pitting, were seen on the faces and along the edges where the leak simulating holes were drilled through the stainless liners.

Storage Cell Specimen #6 (S.C.S.-6)

Specimens are darker than SCS-3. Pitting is much less. Rust existed along edges where holes were drilled. Bulges were observed in the dimple area of plate S.C.S.-6(1), on both the outside and inside.

Storage Cell Specimen #9 (S.C.S.-9)

Specimens were white in coloration with rust colored deposits along the edges where holes were drilled. B_4C stringers were evident, but no pitting. Plate S.C.S.-9(4) had a 1-1/4" pure aluminum strip on one short edge.

4.3 Weight Gain

After the visual analysis, the appropriate Boral plate specimens were weighed, oven-dried, and reweighed in order to determine the amount of absorbed moisture in the core and the change in weight due to exterior and interior corrosion. The specimens were dried in stages in an air-circulating oven for two (2) hours at 150, 200, 250°F, and for 24 hours at 300°F. The original weight, the weight prior to oven-drying, and the dried weight for each specimen, is listed in Table 4.3.

A summary of the moisture absorbed weight percentages, for the 2-month, 6-month, and 12-month exposures, is given in Table 4.4. The overall average for all specimens, environments, and exposures, was This corresponds to a minimum average porosity level in the Boral core of approximately The absorbed moisture decreased between 2-months and 6-months and increased between 6-months and one year. This may be the result of an initial decrease in porosity as corrosion products were generated in the core followed by a porosity increase as additional corrosion enlarged the pores. The greatest moisture absorption occurred in the open-edged specimens in the A environment. This specimen also showed the greatest number of pits and would, therefore, contain the greatest amount of material capable

of absorbing moisture. The least moisture, on the average, was in the storage cell Boral plates, which may be due to their larger size and lower edge to volume ratio.

In Table 4.5, the corrosion weight gain percentages are summarized for all the specimens tested in the program. The values, in brackets, have been corrected to account for the fact that certain of the 6" x 4" Boral plates in the cell specimens contain a strip of solid aluminum along one edge. Since this strip did not contain the normal porous core structure, it could contribute weight gain only by external surface corrosion. To make valid comparisons, using these specimens, their weight was reduced by a factor corresponding to the reduced core volume. Under the assumption that the weight gain percentages are an indication of the extent of uniform corrosion in these specimens, the results presented in Table 4.5 show that the corrosion rates have decreased with increased exposure time. The results are plotted for each specimen type as a function of environment in Figures 4.4 through 4.6.

The weight gains are largest for the edge-sealed specimens in each environment. Similarly, they are the smallest for the storage cell specimens. In between, with very similar results, are the plain and open-edged specimens. The similar weight gains, experienced by these two (2) specimen types, show that the general corrosion is not accelerated due to coupling with stainless steel.

When the weight gain values for the storage cell specimens are considered on a semi-logarithmic scale, the relationship appears to be amenable to extrapolation, as shown in Figures 4.7 through 4.9. From these figures, the extrapolated weight gain percentage and the calculated percent of aluminum consumed after 40 years exposure, are:

4.4 Pitting

To evaluate the extent of pitting in the 12-month exposure specimens, the corrosion products were cleaned from the surfaces of a portion of one of the four (4) plates from each cell specimen. A summary of the pitting frequency and pit depth, for the 6-month and 12-month exposures, is given in Table 4.6. The pit diameter for the 12-month specimens is also given in the table.

Table 4.6 shows that the pitting characteristics after 12-months were very similar to those after 6-months. Those specimens and environment combinations which did not pit or showed little pitting tendency after 6-months, showed no or few pits after 12-months, however, those with significant pits after 6-months had a large number of pits after 12-months. Increased pitting was observed in the plain specimens in the A environment and in the edge-sealed specimens in the A and B environments. The other specimens showed nearly the same number of pits after 12-months as after 6-months.

The pit depth, however, increased with the extended 12-month exposure. In some cases where pits had not penetrated the aluminum clad in 6-months, they had done so after 12 months.

4.5 Metallography

Sections of Boral from each specimen were mounted and metallographically polished in order to observe the thickness of surface oxidation films, the depth of edge attack, the undercutting around drilled holes, and the nature of surface bulges. Sections were made along an edge for the plain and open-edged specimens, and through the drilled hole in the Boral for the edge-sealed and storage cell specimens. In addition, sections through bulges in the specimens were made to characterize these structures. The specimens were back-filled with epoxy under vacuum conditions to impregnate surface porosity, then rough polished on silicon carbide papers and final polished on diamond using automatic vibratory equipment.

4.5.1 Surface Corrosion Films

The surface corrosion films on several of the specimens were thick enough to measure using a filar eye piece at a magnification of The film thickness, as measured for these specimens, is listed in Table 4.7. The thickness for the C environment specimens was thickest, being a maximum of for the plain specimen. Where the bulge in this specimen caused the surface layer to break apart, the corrosion films were much thicker. Appendix B contains photographs showing the surface film in one area away from a bulge and, for comparison, on a bulge.

4.5.2 Edge Attack

Table 4.7 also shows the depth of corrosive attack at the Boral coupon edges in the plain and open-edged specimens. The attack was greatest in the A environment and was somewhat greater in the open-edged specimen than in the plain specimen. Only one specimen of the six (6) edge-sealed and storage cell types showed accelerated corrosion around the partially drilled leak simulating hole. This was the edge-sealed specimen in the C environment. The similarity in edge attack between the plain and open-edged specimens again indicates a lack of corrosion acceleration due to galvanic coupling of the Boral to stainless steel.

4.5.3 Bulges

Several bulges were observed on the 12-month exposure specimens. Similar bulges were not observed on specimens exposed for 2- or 6-months. Table 4.8 lists the number of bulges observed on each specimen. Photographs demonstrating bulged areas are shown on Figures 4.2 and 4.3.

The bulges are separations between the aluminum clad and the B₄C-aluminum matrix. They appear to result from gas pressure caused by internal corrosion. The corrosion of aluminum would generate hydrogen gas following the reaction



Such gas generation has been observed in the edge-sealed and storage cell specimens. To generate a bulge would require sealing of the edges with corrosion products to enable the internal gas pressure to increase sufficiently to expand the ten mil aluminum cladding. The edge-sealed specimens each had four (4) bulges. These specimens also showed the largest corrosion weight gains which could result in the sealing of edges in these specimens.

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UNITED STATES OF AMERICA

NUCLEAR REGULATORY COMMISSION

BEFORE THE ATOMIC SAFETY AND LICENSING BOARD

In the Matter of Commonwealth) Docket Nos.
Edison Company (Zion Station,) 50-295
Units 1 and 2) 50-304

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I hereby certify that copies of "Testimony of J. E. Draley" dated May 31, 1979, have been served upon the following by deposit in the United States mail, first class, postage prepaid, this 31st day of May, 1979:

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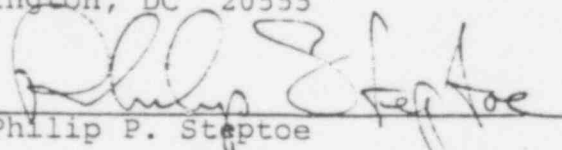
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