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UNITED STATES ATOMIC ENERGY COMMISSION

THE EFFECT OF RADIATION ON THE CORROSION OF METALS BY WATER.

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Chicago University
Metallurgical Lab.

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* * *

The Effect of Radiation on the Corrosion of Metals by Water

Problem No. 322 MLC 2213

A. O. Allen, M. G. Bowman, N. Goldowski,
R. G. Larson and L. Treiman *

July 6, 1944

* * *

* Experiments described herein were performed by the above authors and S. G. Davis, S. Gordon, G. Jenks, R. A. Day, F. Johnson, J. A. Ghormley and W. R. Burns.

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0. Abstract

Long-time tests have been made on the effect of various types of radiation on the corrosion of 2S aluminum in simulated W water. In no case was any acceleration of corrosion by the radiation observed; the effect of radiation, if any, appeared to be a protective one. Deuteron irradiation did accelerate the corrosion of mild steel at low flow rates in hot water of pH 6 to 7, but no appreciable effect was observed with copper, stainless steel, or tuballoy. The general theory of the effect of radiation on corrosion is discussed, with the conclusion that no acceleration of corrosion by radiation is to be expected in most cases of practical interest.

1. Introduction

This report covers all work done by Section C-II on the effect of radiation on the corrosion of metals by water. A considerable portion describes experiments on the corrosion of 2S aluminum by water of composition approximating the cooling water at Site W in the presence of deuteron, electron and neutron radiation. Some experiments with other metals are then described. Finally a general discussion on the theory of the effect of radiation on corrosion is given.

Our general conclusion is that in all cases of interest it is very unlikely that radiation will accelerate corrosion. Any effect is likely rather to be beneficial, because radiation tends to promote the formation and self-healing of the protective films on which corrosion resistance depends. Only in cases where no protective film is formed, so that corrosion is normally rapid, will radiation tend to have an accelerating effect.

2. Effect of deuteron irradiation on the corrosion of 2S aluminum

The experiments on deuteron irradiation were designed to simulate conditions in the W pile. Radiation will affect the pile cooling water chiefly through the formation of proton recoils arising from scattering of fast neutrons by the water. Such fast protons can be most conveniently simulated in the laboratory by the deuteron beam from a cyclotron. For our work, we desired the density of energy release in the water to be of the same order as that in the pile; this requires the use of unusually small deuteron beam currents from the cyclotron. For this reason, the experiments were done on the cyclotron at the University of Michigan, which uses a filament as source of current and is able to maintain its output very steadily at low beam currents.

The ultimate chemical result of such irradiation on water is the formation of hydrogen peroxide. It is believed that as an intermediate in this reaction, or accompanying it, there is considerable formation from the water of free radicals of short life, having such formulas as

H, OH and HO_2. The experiments were intended especially to discover whether such radicals, in concentrations that will be found at W, cause appreciable corrosion of aluminum.

A difficulty in designing the experiments arose from our ignorance of the mean lifetime, and therefore of the actual concentration, of the radicals. Water circulating past the cyclotron beam is irradiated over a path of only about 2 cm. If (as is probable) the mean radical lifetime is 10^{-3} sec or less, the steady-state radical concentration will be reached correspondingly quickly, and W conditions will be reached in the beam when the water has traveled a short distance into the irradiated zone, even if it is flowing with W linear velocity. However, it is possible that some unstable product may form of much longer lifetime, so that its concentration might continue to build up in the pile for the whole of the 2 sec required for passage of the water. This would argue in favor of very slow flow of the order of 1 cm/sec in the beam. But at such low flow rates the general corrosion characteristics are quite different than with the fast W flow. Consequently, it was decided to perform two long-time experiments: one fast-flow, in which the water was given a linear velocity of the W order, and one slow-flow, in which the water stayed in the beam a time of the order of the total time spent by the cooling water in traversing the W pile.

2.1 Fast-flow experiment

2.1.1 System

A circulating system was used, the water being pumped from a reservoir (a 5-liter 3-necked flask) through the irradiated sample cell and back again. Fig. 1 is a schematic diagram of the system. The water in the reservoir was maintained at 90°C, and the fall in temperature during its passage through the system was only one or two degrees. From the reservoir, the water passed through a Pyrex tube to a Nash all-glass centrifugal pump. Then it passed through a rotameter (for measuring flow) to a 2S aluminum tube and to the radiation cell, returning to the reservoir by another 2S aluminum tube. One-inch Pyrex piping was used for the glass tubing. All tubing connections were made by clamping gaskets of K-416 (fluorocarbon polymer) between the ends of the flanged tubing.

It is essential in corrosion experiments to avoid the presence in the water of ions of any metal more noble than the metal under test. Also, in radiation experiments it is essential that the water be kept scrupulously free of grease, wax or any other organic material, since organic substances otherwise inert are activated by radiation and behave as powerful reducing agents. In the present system the water came into contact only with 2S aluminum, Pyrex glass, K-416 gaskets, the stainless steel indicator in the rotameter, and the graphite sealing ring of the glass pump.

2.1.2 Water composition

An attempt was made to approximate ″ water composition, but no heavy metal ion and no silica was added for fear that such additions would introduce too many complicating effects. The solution used was made up by adding to doubly-distilled water enough Na_2SO_4, NaCl, and $NaHCO_3$ to give the following concentrations: $SO_4^{=}$, 70 ppm; Cl^-, 1 ppm; HCO_3^-, 35 ppm. Enough CO_2 was then added, as described below, to keep the pH at 6.5 (measured cold). These concentrations were suggested by C. P. Kidder for corrosion tests in a meeting on June 8, 1943, as reported by J. P. Howe in a supplement to MUC-JPH-51.

Maintenance of pH was accomplished by continuously bubbling through the reservoir a mixture of CO_2 and nitrogen, the proportions being adjusted so that the pH of the hot solution (as measured after cooling to room temperature in a closed flask) was 6.5. This bubbling also served to deoxygenate the solutions.

(A mercury manometer attached to the gas inlet line made contact for a relay controlling the pump. If the water level in the reservoir fell to a dangerously low level, which would occur in case the water line broke, the pump automatically shut off.)

The hydrogen peroxide concentration in the solution, which resulted from the radiation, was frequently checked. Within two hours of the start-up of radiation, it attained a steady-state value, which varied at different times between the limits of 1×10^{-5} and 3×10^{-5} *M*.

2.1.3 Cell and samples

The samples were square pieces of 2S Al sheet, 0.030 in. thick and 0.75 in. on a side. They were polished, first with carborundum, then with levigated alumina, and finally with magnesia powder until a smooth surface was obtained.

The samples were placed in the cell diagrammed in Fig. 2. The cell was machined from a bar of 2S Al; the shape was such as to allow a water depth of 0.020 in. between the samples and the foil window, and 0.025 in. on the other side of the samples. To hold the samples flat and to ensure correct spacing between the samples and the foil "window", a narrow strip of 0.020-in. 2S Al was placed on each side of the row of samples. A cover of 0.001-in. 2S Al foil was placed over the cell to serve as a "window" for the deuteron beam and as a gasket for the lid. The lid was a strip of 1/8-in. 2S Al; drilled in its center was an array of small closely spaced holes which served as a grid to allow the deuteron beam to enter the cell while providing support for the thin foil "window". To prevent leakage around the edges it was found necessary to place a second lid, made of 1/8-in. steel, over the Al lid. The lids were bolted tightly to the body of the cell with stainless-steel bolts.

The cell contained 15 samples; the center one was directly in the path of the beam, the seven exposed to the water before it reached the beam acted as controls, and the seven after the beam were to determine the effect of any material formed by the radiation and swept along with the water.

The flow rate was 0.8 gal/min, corresponding to a linear velocity of 13 ft/sec over the samples.

2.1.4 The deuteron beam

Unusual precautions had to be taken in reading the beam current because of its low value. The current was read on a galvanometer placed between the cell and ground; it was necessary to insulate the entire system carefully. This necessitated thoroughly evacuating the space between the cell and the window of the cyclotron, as any gas in this region became highly ionized and allowed current to leak away from the cell.

An experiment in which the lid of the cell alone was placed before the beam, and the current was read from a plate behind it, showed that only about 0.25 of the current incident on the grid passed through it, although the fraction of surface occupied by the holes was much greater. This means that the beam of deuterons was inclined at a slight angle to the direction of the holes, so that some of the radiation was absorbed in the walls. This angle was calculated to be such that the actual distance traversed by the particles in passing through the water was .021 in. (or .053 cm) rather than .020 in.

The distance between the window and the samples was chosen to be as nearly equal as possible to the range of the deuterons in water. From the observed range in air at room temperature of the deuterons from this cyclotron (60 ± 2 cm), subtracting the air equivalent of our 1-mil Al window (5 cm), and converting to range in water by use of the atomic stopping powers of H(0.19) and O(1.07) given by Bethe[1], we find the range in water at 90°C to be .057 cm. However, if we accept the work of Philipp[2], the range of α rays (and therefore presumably of deuterons) in liquid water is further reduced by an effect of the state of agreggation, amounting to 12% in the case of water. This would mean that the actual range of our deuterons would be only .051 cm. Dr. Bethe (private communication) states that the Philipp effect is probably spurious. Actually, the appearance of the samples indicates that the terminal portion of the beam was probably absorbed by the Al sample. The above calculations show that the distance traversed in the water (.053 cm) was at least very nearly the whole range, so that the fraction of the beam energy absorbed by the sample was small.

The current read on the galvanometer was maintained at 5.3×10^{-9} amp throughout the work. The current absorbed in the water was then 0.25 of this, or 1.3×10^{-9} amp. The energy of the deuterons entering the water was 8.6 Mev. Taking the irradiated volume as 0.025 cc, and assuming all the energy is released in the water, we find the average density of energy release in the water to be 2.7×10^{18} ev/cc-sec. This

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is of the same order as, but somewhat greater than, the density of energy release by proton recoils in the W cooling water, which according to Wigner (MUC-EPW-62) is 1.2×10^{18} ev/cc-sec.

2.1.5 Procedure

The cyclotron was nominally run continuously from 8 A.M. Monday morning until midnight Saturday (136 hr/week). Actually not all of this time was utilized, because of occasional troubles with the cyclotron or the corrosion system. During the run, the pH was frequently checked, as were the concentrations of H_2O_2 (iodometric titration), Cl^- and $SO_4^=$ (nephelometry). The chloride concentration was kept between 0.7 and 1.3 ppm, and the pH between 6.4 and 6.6.

Each Sunday, the cell was dismantled; the samples were removed, dried, weighed and examined; then they were returned to the same positions in the cell, and the apparatus was reassembled.

The experiment was continued for 7 weeks. The solution was circulated for a total of 685 hr, and received radiation for a total of 503 hr.

2.2 Slow-flow experiment

For this run, the circulating water system was replaced by a once-through gravity-feed system, diagrammed in Fig. 3. The temperature of the reservoir was maintained at 90°C and the pH at 6.5, as before. During the first week of operation, the water was allowed to cool down during its passage through the cell, and its temperature fell to as low as 40°C. For the remainder of the run, the cell was warmed by radiant heaters, and was maintained at 90°C, as measured by a thermocouple inserted into a hole drilled in the body of the cell.

The arrangement of cell, samples and beam was the same as in the fast-flow run, except that a slightly greater beam current was used, so that the current entering the water was 1.7×10^{-9} amp, instead of 1.3×10^{-9}. The density of energy release in the water was therefore 3.6×10^{18} ev/cc-sec, instead of 2.7×10^{18}.

The flow rate was 10 ml/min corresponding to a linear velocity of 1.42 cm/sec over the irradiated surface. Passage of the water through the beam therfore required about 1.3 sec, as compared with 0.0047 sec in the fast-flow experiment. The amount of energy received from the deuterons by the average particle of water was 350 times as great in the slow-flow experiment as in the fast-flow run.

Weekly weighing and examination of the samples was carried out as in the previous run. This experiment lasted 4 weeks, and a total of 365 hr of irradiation was obtained.

2.3 Results

In both experiments, the weight changes of the samples were insignificant. During the entire fast-flow run the samples lost from 0 to 0.3 mg.; in the slow-flow run, the samples gained from 0 to 0.3 mg. Variation in weight changes as between the different samples was quite random with respect to position in the cell; the irradiated sample showed no difference in weight change from the others.

There was no significant pitting in any sample. A general roughening of the surface occurred in all samples, which the microscope revealed to consist of the formation of numerous minute round depressions, of insignificant depth. These appeared shortly after the start of the run, but did not appear to become any deeper as the run continued. The number of these spots was apparently about the same on the irradiated samples as on the others. These spots may have been caused by local corrosion occurring around particles of polishing powder which had become imbedded in the surface of the samples.

Although there was no more real corrosion in the irradiated samples than in the others, their naked-eye surface appearance was strikingly different. In both runs, the irradiated sample showed a pattern of whitish spots, corresponding to the points where the beam, after passing through the grid, impinged on the sample. Extending from these spots in the direction of flow of the water were streaks which carried over onto samples following the irradiated sample in the cell. In the fast-flow run, these streaks faded out after covering about 1 cm of the next sample; but in the slow-flow run, they extended the entire length of the cell, covering all seven of the after-beam samples (5.25 in.). The streaks were much less well-marked than the spots. While the spots appeared as a striking white color, the streaks involved only a slight alteration of the nature of the surface and could be seen only when the samples were held at certain angles to the light.

A photograph of the samples is shown in Fig. 4. The two samples at the top are the irradiated sample and the next following it in the fast-flow run, the former being on the left in the picture. The light and dark patches appearing in the picture are caused by differing reflections of light from areas which had been polished in different directions. These patches appear more conspicuous in the picture than on the original samples. The pattern of spots on the irradiated sample can however be seen in the picture. The eight samples at the bottom of the picture are from the slow-flow run; the spots on the exposed sample (next to the right) and the streaks extending over all seven of the following samples (extending towards the left) are more clearly marked here. The sample at the right-hand end is the control sample which was on the upstream side of the irradiated sample; the absence of streaks on this sample is in contrast to the others.

The spots where the beam struck were clearly visible under the microscope as sharply defined areas of increased roughness. They were neither appreciably raised above nor depressed below the surrounding surface. This roughness was of a much finer texture than the general roughness (due to discrete round depressions) referred to above, and was superimposed on it. The streaks, on the other hand, were very difficult to find under the microscope, being much more clearly seen with the naked eye. It is clear that the spots were of a different nature from the streaks, but that both were merely alterations in the surface coating of the metal, insignificant from the corrosion standpoint.

The foils which formed the upper surface of the cell, and which were changed each week, showed no markings in the fast-flow run, but gave a pattern of spots and streaks in the slow-flow run similar to that found on the samples. A photograph of one of the foils from the slow-flow run is shown in Fig. 5.

2.4 Discussion

The sharply-defined whitish spots on the irradiated sample, corresponding to the pattern of the deuteron beam, are to be ascribed to the tail-end of the beam being absorbed in the surface, with consequent local heating and perhaps structural changes in the surface layer.

The streaks extending from them are obviously caused by some agent produced in the water by the radiation. In the slow-flow run, this agent must have lasted for the length of time necessary for the water to flow over seven samples (about 9 sec). It must therefore have been the stable radiation product, namely hydrogen peroxide. The flow in this experiment was certainly streamline; so that the presence of the grid caused the formation of alternate zones of zero and of finite peroxide concentration, which were maintained down the length of the cell. It is not surprizing that the surface oxide formed in the presence of H_2O_2 should have a somewhat different nature from that formed in its absence--a difference which is reflected in the appearance of streaks on the samples and foil.

The streaks seen in the fast-flow experiment cannot, however, be caused by hydrogen peroxide. From the known yield of hydrogen peroxide by deuteron radiation (CC-733) and the flow rate in this experiment, it is calculated that the H_2O_2 concentration in the irradiated zones will be increased by no more than $6\text{x}10^{-8}$ *M* during a single passage through the beam. As the H_2O_2 concentration in the circulating water fed to the beam was over 10^{-5} *M*, it is clear that the quantity formed by passing through the beam cannot have caused the appearance of streaks. Some other agent formed by the radiation and having a lifetime of at least 0.006 sec must be responsible. It is possible that the agent is actually the short-lived free radicals formed by the radiation. It is also possible that the absorption of radiation by the aluminum surface causes occasional disengagement of minute aluminum hydroxide particles or of gas bubbles which cause the streaks to appear by a process of the erosive type.

The main conclusion of the experiment, not to be lost sight of in considering the above-discussed minor phenomena, is that heavy-particle radiation of W intensity has no dangerous effect on the corrosion of 2S aluminum. This conclusion is of major importance for operation of the pile.

3. Effect of electron irradiation on the corrosion of 2S aluminum

3.1 Purpose

To supplement the deuteron beam experiments described above a similar study was performed with electron irradiation. There were two reasons for this study. (1) The effect on water is quite different for β and γ radiation on the one hand and for heavy particle radiation on the other. Since the pile will contain γ as well as neutron radiation it seemed desirable to perform experiments with light particles. (2) The experiments afforded an opportunity to run at a much higher radiation intensity (corresponding to a higher radical concentration) than obtained in the cyclotron work, thus giving an accelerated or exaggerated test of the effect of free radicals. Although the mechanism of the action of heavy particles and electrons on water is different, it is believed that the free radicals present are of the same type, so that insofar as the effect of the radicals is concerned the electron experiments can probably give direct information applicable to heavy particle fields.

3.2 Apparatus

Since the range of the electrons of a given energy is much greater than that of heavy particles, the thin windows used for the cyclotron work were not required here. The entire circulating system was therefore made of Pyrex glass tubing.

The Van de Graaff generator at Chicago was used as a source of electron radiation. The electron beam produced by such a generator diverges as the distance from the generator increases. It was therefore possible by going a proper distance from the window to run three systems simultaneously, all of which received the same amount of radiation. Figure 7 shows the position of the three sample tubes with respect to the generator snout. Throughout this study three different systems were operated simultaneously.

The samples were small cylinders of 2S aluminum, 3/16" in diameter and 3/4" long, cut from a solid rod. They were polished with 400 mesh carborundum, cleaned with distilled water and dried by an acetone rinse. The samples were supported in a boat of pyrex glass shown in diagrammatic section in Figure 6. The boat was made by grinding down on the side of a piece of Pyrex tubing until about 2/3 of the tube had been ground away, and then sealing on pieces of Pyrex of an appropriate shape to hold the samples. A notch was filed in the end of each sample to fit the glass holder. The boat with samples was inserted into a Pyrex tube, 9 mm ID, which had been thinned over a length of about 1" in the center to provide a window for entrance of the electrons. A tungsten lead was sealed in near the end of the tube for measuring the current received by the tube from the electron bombardment. The dimensions of the boat were such that the samples were centered in the outer tube and were surrounded by a space, 2 mm wide, where the water flowed.

The three circulating systems were exactly similar in design to the system used for the fast-flow run with the cyclotron. The arrangement of pump, rotameter, reservoir, and the provision for bubbling gas were exactly the same. As the electron beam from this instrument is vertical, the sample tubes were placed in a horizontal position. The various sections of glass tubing comprising the systems were joined with ball joints which were clamped so that water-tight seals were obtained without the use of any lubricant. Of the three pumps used one was an all-glass Nash pump identical with the one used for the cyclotron work; the other two were Eastern Engineering "Midget" stainless steel pumps, which were well pickled before use. One of the Midget pumps was fitted with a special high-speed motor to increase its pumping rate.

The use of three systems allowed study of waters of different composition. The first water, W1, was intended to simulate demineralized W water. It contained 5 ppm bicarbonate and 0.1 of chloride, pH 6.5. The second composition, W2, was the same as that used for the cyclotron work, namely 70 ppm of sulfate, 35 ppm of bicarbonate, 1 ppm of chloride, and pH 6.5. Both these compositions had been suggested by C. P. Kidder (MUC-JPH-51). The third system was used for determining the effect of higher concentration of chloride in water otherwise of the W2 composition; first 100 ppm of chloride was used, later 5 ppm. A difference from the cyclotron system was that instead of controlling the pH by bubbling through the reservoir a mixture of CO_2 and nitrogen, a mixture of CO_2 and air was used. This allowed formation by the radiation of some H_2O_2 which does not form with electron radiation in the absence of dissolved oxygen. Also it is believed that the concentration of free radicals is considerably greater in water containing oxygen than in deaerated water, because of the formation in the presence of oxygen of some OH radicals in excess of the quantity of H atoms or H_2 molecules which can react with them; these extra OH radicals must eventually recombine with one another to form H_2O_2, but this process is slow so that the radicals must build up to a high concentration (CC-1321, p.9). The temperature was maintained at 90°C throughout the experiments. The concentration of H_2O_2 in the water built up to steady-state values of the order of $3x10^{-5}$ $\underline{M}$.

The flow rates were as follows: W1 (glass pump), 1.7 gal/min (12 ft/sec linear velocity over samples); W2 (midget pump with high-speed motor), 1.5 gal/min (10 ft/sec over samples); third system (high chloride), 1.07 gal/min (7 ft/sec over samples).

Each tube received a total of 10 ± 3 μa of electrons at 1.0 Mev. Taking the irradiated volume as 0.6 cc, and assuming that one-half the energy of the electrons is absorbed in the water (the other half being absorbed in the glass), we find that the density of energy release in the water was 5.2×10^{19} ev/cc-sec. This is ~43 times the total expected energy release in the W pile cooling water.

At intervals of a few days the systems were demounted, the boats withdrawn and the samples wiped with Kleenex, dried, weighed and inspected. Because of rather frequent breakdowns of the Van de Graaff generator, the time during which the radiation was actually received was only about 1/3 of the total time during which the water was circulated.

3.3 Results

3.3.1 W1 (0.1 ppm of chloride)

This system was run for a total of 590 hr of circulation and 197 hr of radiation. Very little change was observed in the appearance or the weight of the samples during this time. During the first 60 hr of circulation the samples gained from .01 to .08 mg; then a slow decrease in weight set in until at the end the samples weighed .07 to .43 mg less than at the start of the run. Although these changes are small it is noteworthy that the irradiated sample (#6) and the next following in the water stream (#7) gained more weight at first and subsequently lost less than any others, so that their weight loss at the end was the least. The final weight losses for all the samples are given in Table 1 below. Samples #6 and #7 also appeared somewhat lighter in color than the others, suggesting a slightly heavier or at any rate somewhat different type of oxide film. There was no significant pitting observed on any of the samples, but a very slight roughness could be seen under the microscope. It is clear that the radiation had no accelerating effect on the corrosion; its effect, if any, must be regarded as a protective one.

Table 1. Weight losses of samples during W1 run.

Sample No.	1	2	3	4	5	6*	7	8	9	10
Weight loss (mg.)	.35	.23	.27	.36	.29	.07	.15	.41	.43	.42

* Irradiated sample

3.3.2 W2 (1 ppm of chloride)

This system received 559 hr of circulation and 182 hr of radiation. The samples in general became lighter in color than with the lower chloride concentration, and the oxide film appeared to be heavier. Again the radiation showed no corrosive effect. An accident which occurred during the run led to some interesting observations. The tube holding the sample boat became warped so that it was impossible to withdraw the boat in order to take the periodic observation The tube was straightened by heating in the middle with a bushy flame and the boat was withdrawn. This heating dried and split the oxide film on samples #5 and #6, yielding a checked appearance under the microscope. Sample #6 was located directly under the electron beam and #5 also probably received considerable irradiation, as this experiment was performed in the tube farthest from the generator snout so that the beam where it struck the tube was quite wide. During the following 100 hr of circulation, including 33 hr of radiation, the samples #5 and #6 gained respectively .15 and .14 mg in weight. Later, samples #2, 3 and 9, located entirely outside the electron beam, were heated similarly and a similar microscopically checked surface was obtained. In ~100 hr circulation after this heating #2 lost .51 mg, #9 lost .40 mg, #3 gained .03 mg. The other specimens, which were not heated, showed nearly constant weight during this time, registering gains or losses of a few hundredths of a mg. The gain in weight of the irradiated specimens may indicate a healing effect of radiation. This would imply acceleration by the radiation of formation of the protective film in the cracks, or possibly modification of the nature of the film to a more protective one. This result is not to be regarded as certain, especially since the heating was not performed in an accurately reproducible manner. Increased formation of the protective film is however consistent with the observations on the W1 experiment. It is at any rate certain that the electron radiation did not accelerate corrosion.

3.3.3 Third system

This system was initially run with water of W2 composition in which, however, the chloride concentration was increased to 100 ppm. Here the corrosion was very severe with the formation of many large pits and oxide protrusions. The swelling of the samples from oxide formation broke the supporting boat and the run was discontinued after 60 hr of circulation (13 hr of radiation). The irradiated sample appeared the same as the others.

The system was then run with a water of W2 composition containing 5 ppm chloride. During the first 100 hr of circulation the samples lost .2 - .3 mg and remained nearly constant thereafter. A total of 394 hr of circulation including 101 hr of radiation was obtained. The surfaces appeared under the microscope to have been roughened more than at lower chloride concentrations but no pitting of the samples was noticed. The irradiated sample appeared no different from the others in any respect.

3.4 General conclusion

Electron irradiation of intensity far in excess of the radiation level in the W cooling water did not accelerate corrosion of 2S aluminum. On the contrary, there is some evidence that corrosive tendencies may be reduced by radiation through enhancing the formation of the protective oxide film.

4. Effect of neutron irradiation on the corrosion of 2S aluminum

4.1 Purpose

Although available neutron intensities are much lower than W levels, it appeared desirable to obtain direct observations as to the effect of neutrons on Al corrosion. A special effect which it was feared might occur at W concerns the possible build-up of H_2O_2 (because of the neutron radiation present) to a relatively high concentration in the static film of water which will be trapped between adjacent slug-ends. Such peroxide build-up would cause the formation of a concentration cell which might induce corrosion at the place where the static film joins the flowing water--that is, the region of the weld, which is also especially dangerous from the corrosion standpoint for other reasons. This effect can be studied best in the laboratory with actual neutron radiation, the only heavy-particle radiation which can readily penetrate into the inaccessible region between the slugs.

4.2 Apparatus

The 60-in. cyclotron at the University of California was used with a beryllium target as the neutron source. The deuteron energy of this intrument is 16 Mev, and the maximum energy of the neutrons emitted from the target should be 20 Mev. We assume that the average neutron energy is 16 Mev.

Two separate corrosion studies were made concurrently. One was a comparison of the static corrosion of 2S aluminum by synthetic W water under neutron bombardment with the corrosion under similar conditions without the neutron irradiation. In this determination samples of the aluminum were placed in a sealed glass tube with the W water, and maintained at a temperature of ~90°C.

The other study was a comparison of the corrosion of the aluminum welds, which will be used to cap the aluminum cans covering the metal slugs for the W pile, by pure distilled water, with and without neutron bombardment. Two welds were butted together, and the water (maintained at ~80°C.) was circulated past the aluminum welds by a thermal-siphon arrangement. The purpose of this experiment was to determine whether the static region between the two welds might cause the formation of a concentration cell, under the effects of radiation, and lead to an accelerated corrosion rate.

The apparatus shown in Figure 8 was designed to permit heating of the static W water corrosion test, and heating and circulating the distilled water in the thermal siphon apparatus, from a single source of steam. The steam from the steam generator first passed into tube (B) which contained the sealed tube of W water and aluminum samples. It then passed into the heating jacket (C) where it heated the distilled water and caused it to circulate through the tube (A) which contained the aluminum welds. The condenser (D) condensed the steam and the water then returned to the steam generator.

The apparatus was placed in front of the target, as shown in Figure 8. The centers of the two tubes (A) and (B) were about two inches from the face of the target. A previous monitoring of this area with aluminum foil indicates an average neutron flux of $\sim 2\times10^{10}$ neutrons per cm^2-sec for a deuteron current of 200 μa.

The control run, made with duplicate apparatus, was started and terminated at the same time as the radiation run. A total of 642 hr of heating was obtained. The bombardment was intermittent, and the total time of irradiation was 351 hr.

The average current during the irradiation was 173 μa, so that the average neutron flux may be taken as 1.7×10^{10} n/cm^2-sec. Taking the average neutron energy as 16 Mev, the cross-section for scattering by protons as 0.5×10^{-24} (3), and the fraction of the neutron energy transferred on scattering as 0.5, we find the density of energy release in the water to be 4.4×10^{15} ev/cc-sec, or only 0.004 of the value for W.

4.3 Results

4.3.1 Static corrosion in simulated W water

The water used contained 35 ppm of bicarbonate, 1 ppm of chloride, 70 ppm of sulfate, and sufficient CO_2 to bring the pH to a value of 6.4 at 22°C. At the end of the run the pH of the solution under irradiation had increased to 6.57 at 22°, while that of the control solution increased still more, to 6.81.

The samples were strips of 2S aluminum weighing close to 0.23 g, with total areas varying from 2.6 to 3.1 cm^2. They were prepared by cleaning with dilute NaOH solution, washing with distilled water and drying. Before and after the test, the samples were weighed with a precision of ± .01 mg. The observed weight changes are given in Table 2.

Table 2. Weight changes in static corrosion of 2S Al.

Control Samples		Irradiated Samples	
Sample No.	Wt. change (mg.)	Sample No.	Wt. change (mg.)
1	-.15	8	-.11
2	-.14	10	+.14
3	-.10	11	+.11
4	-.07	12	+.05
5	-.11	13	-.06
6	-.06	14	+.32

A visual inspection of the samples indicated that the samples that were not exposed to radiation had suffered a slightly greater corrosion. The white coating appeared thicker. The weight changes are sufficiently small to have no significance when taken alone, but the general trend of the weight changes does corroborate the conclusion that the blank corrosion was more severe. The fact that the pH of the blank solution had increased more than that of the irradiated solution also supports this conclusion. There was also a very slight amount of almost transparent precipitate floating in the tube from the blank corrosion. This was so small in quantity that identification was not made, but it was assumed to be aluminum hydroxide.

The hydrogen peroxide concentration of the solutions was not determined until nearly twenty-four hours had elapsed after the termination of the irradiation. The temperature was maintained at 80°C for part of this time. When the solutions were titrated, that which had been irradiated contained about 8×10^{-5} N hydrogen peroxide. The blank solution contained a comparable amount. Little significance can be attached to the hydrogen peroxide concentrations at the time of titration, since undoubtedly there had been considerable decompostion.

It is not known whether the apparently greater protection of the irradiated specimens is to be ascribed to a higher concentration of peroxide or to a specific effect of the radiation. At any rate, it is clear that neutron radiation of the intensity here used does not accelerate corrosion of 2S aluminum.

4.3.2 Corrosion of butted slug-jacket welds

The corrosion of the aluminum welds in the circulating systems was determined by visual inspection only. There was no detectable difference in the appearance of the surfaces of the samples, either at the welds themselves, or on the surface next to the supposedly static part of the system between the two welds.

There was no evidence of pitting in any of the samples. In general the corrosion of the samples that had not been exposed to neutron radiation appeared to be more severe. The white powdery coating appeared to be thicker, and more easily dislodged from the surface.

The fact that there was no evidence of "concentration-cell" corrosion in this experiment does not eliminate the possibility that this might be a problem in the W pile, where both the neutron flux and the rate of flow of the water will be greater, and thus contribute more readily to the formation of concentration cells at the junctions of the slugs.

5. Effect of deuteron irradiation on the corrosion of other metals

5.1 Purpose

Experiments described in this section were undertaken because of a request to determine the effect of radiation on the corrosion of metals which might be used as pipes to carry cooling water in the base shield at W. The cyclotron at the University of Michigan was used as a radiation source. No attempt was made to simulate the radiation intensities in the shield, as it was believed that 1 μa-hr of deuteron irradiation would yield more energy to the water than the neutron radiation in 100 days of operation. The purpose of the test was therefore merely to determine in a qualitative manner whether radiation had any effect on the rate of corrosion. The metals studied were copper, stainless steel, and mild steel (SAE 10-20). Uranium was also studied.

5.2 Apparatus

The cells used to hold the samples had to be constructed so that the water came into contact only with glass, mica, and the metal of the samples. The geometry of the cells was dictated more by experimental convenience than by any other considerations. A diagram of the cell is given in Figure 9. The samples were circular discs of metal which were placed in a glass tube perpendicularly to its axis and were spaced 5 mm apart by glass rings. Water entered through a small glass tube passing through the samples along the axis of the cell, and flowed out through small holes drilled in each sample around its periphery. For the entrance of the deuterons, the front of the cell was fitted with a sheet of mica, pressed against the carefully ground end of the glass cell by a brass ring, which was screwed into a collar cemented to the outside of the cell. The distance between the mica window and the front sample of a cell was fixed at .020 inches by inserting a thin spacer ring of the same material as the sample.

The circulating system for the water was similar to that used for the aluminum run described in Section 2, and the composition of the synthetic W water used was also the same. A stainless steel "Midget" pump was used to circulate the water; the remainder of the system was all of glass. To free the water entering the cell from hydrogen peroxide, a decomposition catalyst consisting of a mixture of MnO_2 and sand was placed in the line immediately before the cells. The water entering the cells was thus essentially free of peroxide, but did contain dissolved oxygen equivalent to the peroxide content in the water of the reservoir.

The water entering the cell passed over the face of the front sample and parallel to it, but the flow over the other samples was turbulent and its general direction was perpendicular to the sample faces. The rear samples were thus not adequate controls for the front irradiated sample because of the different flow conditions. In most of the work three separate cells were accordingly used in series, one being placed in the line before the irradiated cell, the other after the irradiated cell.

5.3 Results

5.3.1 Stainless steel (18-8)

With this metal the weight changes found, in the course of a few hours at 70°C, were negligible and there were no changes in the appearance of the specimens. The irradiated sample appeared no different from the others in any respect. The data are given in detail in CC-1036.

5.3.2 Copper

Only one cell was used in the study of this metal. The water temperature was kept at 70°C and the flow rate was varied. Runs were made for as long as 18 hr with irradiations up to 12.2 μa-hr. Weight changes were quite small and the irradiated sample showed no significant differences from the others in its weight loss. The corrosion product was a mixture of green and black materials. That the irradiation did have some small effect on the corrosion was demonstrated by the formation of an adherent dark ring around the hole on the face of the irradiated sample, which was not seen on the others. This effect was too small to be reflected in the weight changes, and was regarded as having no practical significance. Details are given in CC-983.

5.3.3 Uranium

A single run was performed of 14 hours duration, with 3.3 μa-hr of irradiation. The temperature was 70°C and the flow rate about 400ml/min. Three cells were used in series. The cells were periodically dismantled for inspection and weighing of the specimens. The system was then reassembled and the run continued. Detailed data on the weight losses are given in CC-1036. The weight losses found were very erratic, ranging from 2.6-17.1 mg for different specimens over the entire time of the run. No correlation was apparent with respect to position of the samples in the cells; the weight loss of the irradiated specimen occupied an intermediate position (6.4 mg). As with copper, the irradiated specimen developed, after some hours, a different color from the others.

The corrosion of uranium is known to be a complicated matter. The present results suggest that the metal used was not of uniform character. About all that can be said regarding the results is that, under the conditions used, deuteron radiation at a level of 0.5 μa does not appreciably accelerate the corrosion of this metal.

5.3.4 Mild steel (SAE 10-20)

Data. Since a significant acceleration of corrosion by the radiation was observed with this metal, it was studied at much greater length than any of the others. A large number of runs was made under different conditions of flow rate, temperature, and pH, the last being varied by changing the composition of the N_2-CO_2 mixture which was passed through the reservoir. In three of the runs the distance between the window and the irradiated sample was increased from .020 in. to .040 in. The radiation level was kept at .5 μa. At the end of each hour of irradiation the cells were dismantled and the samples were wiped with Kleenex, dried and weighed; the system was then reassembled and the run continued. A formidable collection of weight loss data was thus obtained, which is given in full in Table 2.1 of CC-1036. For the purposes of this report it is sufficient to present only the data for the weight losses in the front sample of each cell, and to give only the total weight losses for the entire run, the losses measured at the end of each hour of radiation being added together. These data are presented in Table 3.

Many cases were found in which the irradiated sample corroded more than the others. A study of Table 3 leads to the following conclusions:

1) The irradiation increases the corrosion rate whenever the flow rate is 350 ml/min or less, the pH is over 6, the temperature is 50°C or more, and the distance from the window is .020 in. The radiation effect is not significant at 700 ml/min (runs 6, 13, 14, 16), at pH 5 (run 12), at 30°C (run 17), and when the spacing is increased to .040 in. (runs 20, 22).

2) The corrosion in the cell placed after the irradiated cell tends in general to be greater than in the cell placed before the radiation beam. The only difference between these cells resides in the fact that hydrogen peroxide was present after the beam, while only dissolved oxygen was present before the beam. It may then be concluded that hydrogen peroxide accelerates corrosion more than an equivalent quantity of oxygen.

3) The corrosion rate in general decreases as the pH is increased. This is, of course, a well-known fact.

4) The effect of increasing the temperature is to increase the rate of corrosion (runs 17, 11, 19). At the low flow rates used in these three runs, the temperature has more effect on the irradiated sample than on the others.

Table 3. Radiation corrosion of mild steel.

Expt. No.	6	7	10	11	12	13	14	15	16	17	18[a]	19	20[a]	21	22[a]
Temp.	70	70	70	50	70	70	70	70	70	30	70	70	70	70	70
Av. flow rate ml/min	650	300	350	100	250	700	700	100	700	200	700	100	100	100	100
pH	6.4	6.6	7.1	6.5	5.2	6.4	6.4	6.5	7.0	6.7	6.7	6.5	6.6	6.5	6.6
Total time, hr.	4.0	2.8	7.0	5.8	4.6	6.0	5.3	6.1	4.4	5.9	6.2	5.5	6.0	6.5	4.5
Total beam energy, a-hr.	1.5	0.7	2.0	2.0	1.5	2.0	2.0	2.0	1.5	2.0	1.5	2.0	2.0	2.0	1.5
H_2O_2, $\underline{M} \times 10^5$	2	3	3	5	2	2	4	5	2	8	2	4	7	3	5
Wt. losses, mg., for															
Beam sample	6.3	4.6	10.3	6.4	15.6	9.8	8.3	17.6	4.5	1.1	7.6	12.3	5.0	12.5	3.8
Before-beam sample	4.5	2.3	3.6	1.5	15.2	8.5	5.7	3.1	3.4	0.5	4.1	3.0	2.3	5.0	2.6
After-beam sample	---	---	---	---	---	8.1	7.9	4.2	4.7	1.8	7.3	3.1	3.7	4.9	3.5

(a) Spacing between window and specimen increased to 40 mils.

5) The effect of increasing the flow rate, while holding other variables constant (compare runs 15, 19 and 21 with runs 13 and 14), is to increase markedly the corrosion rate of the control samples, while decreasing somewhat the corrosion rate of the irradiated sample.

In the low-temperature run (#17) the corrosion product was reddish-brown, presumably $Fe(OH)_3$. In all the higher temperature runs the chief corrosion product was a black ferromagnetic material, presumably Fe_3O_4, while a relatively small quantity of the reddish material was also produced.

Discussion. These experiments should be considered in the light of the corrosion experiments of Roetheli and his collaborators[4], in which mild steel cylinders were rotated at various velocities in aerated water at room temperature. They found that at low rotation speeds the corrosion product was the black Fe_3O_4; as the speed was increased a point was reached at which the black product changed to reddish $Fe(OH)_3$, this change being marked by an abrupt decrease in the corrosion rate. The black material was found to form whenever dissolved oxygen acts upon $Fe(OH)_2$. The reddish material was gelatinous and adherent, and was much more protective to the metal than the black oxide. Their explanation of the observations is that when the layer of water near the metal surface is relatively quiescent, the corrosion of iron renders the surface region alkaline so that $Fe(OH)_2$ can be deposited. This hydroxide is then oxidized by dissolved oxygen to the black oxide, which falls away from the metal and offers little protection. The rate of corrosion under these conditions is determined by the rate of diffusion of oxygen into the surface layer. At higher velocities of rotation of the specimens, the dissolved oxygen was able to diffuse in more rapidly and the OH^- ion was also carried away from the surface region more rapidly. Then the pH never became high enough to precipitate $Fe(OH)_2$, so that Fe^{++} ions were oxidized directly to $Fe(OH)_3$ (which can precipitate at a much lower pH than $Fe(OH)_2$); the $Fe(OH)_3$ is a thick gelatinous precipitate which clings to the metal and stifles corrosion.

The present work was apparently concerned entirely with the range in which the black Fe_3O_4 was the principal product, except for the run at the lower temperature (30°). The effect of temperature on the corrosion mechanism is not clear, since many processes are involved, each having its own characteristic temperature coefficient. It will be noted that the H_2O_2 concentration in the reservoir (and consequently the O_2 concentration in the water reaching the samples) is greater at the low temperature, because less thermal decomposition occurs in the reservoir. The higher concentration of oxygen will favor the precipitation of the higher-valent, more protective oxide.

Probably the chief effect of radiation is to render the solution in the irradiated zone more oxidizing. This effect would be caused by the formation of both hydrogen peroxide and oxidizing free radicals in the radiation beam. The effect should thus be similar to that of increasing the concentration of oxygen in the work of Roetheli. In the language of the electrochemical theory, the cathodic polarization is decreased. As long as the conditions of flow rate, etc., are in the range where the black oxide is the chief product, the corrosion rate will increase with an increasing supply of the oxidizing agent, and the irradiated sample will corrode more rapidly than the controls. With radiation, the supply of oxidizing agent to the metal does not have to depend upon diffusion. Hence, increasing the rate of flow of water actually decreases the rate of corrosion of the irradiated sample by decreasing the concentration of oxidizing agent produced in the beam, while the corrosion rate of the controls is increased as the diffusion of oxygen to the metal is speeded up. At sufficiently high flow rates, the rate of formation of oxidizing agents by the radiation becomes small compared to the rate of diffusion of oxygen to the metal, so that the corrosion rate is the same for the irradiated sample as for the control. At a pH of 5, the hydrogen ion concentration is so high that the depolarizing effect of oxidizing agent on the cathodic reaction is no longer of major importance, and the effect of radiation on the corrosion rate disappears. When the distance from the window to the sample is increased so that the sample is out of the radiation field, the oxidizing products of radiation no longer reach the surface of the metal in any important amount (as the flow in this region is probably largely streamline), and the radiation then has no effect on the corrosion rate.

Whether the chief effective oxidizing agent here is H_2O_2 or free radicals such as OH and HO_2 cannot be told from the data. The irradiated sample is exposed to a maximum concentration of H_2O_2, since at the end of the deuteron range (where the beam meets the sample) the ionization is greatest, and the H_2O_2 concentration will therefore also be highest. The radiation corrosion may therefore be entirely a hydrogen peroxide effect. It is probable, however, that the radicals have some effect also.

An entirely different effect may also come into play. The deuterons at the end of their range probably actually strike the solid surface; this should cause local heating of the oxide layer, causing it to break up, the corrosion rate being thereby increased. At high flow rates the inequalities of temperature will be less, and the oxide on the control samples also will be rapidly broken up by the flow of the water, so that the radiation heating effect becomes unimportant. How great this effect may be compared to the oxidizing effect cannot be determined. It seems probable, however, that the oxidizing effect is the more important.

6. General discussion

6.1 Introduction

Ionizing radiations may be expected to affect corrosion in two general ways, the direct and the indirect. The indirect effects will result from permanent changes produced in the corroding water by the radiation, such as the formation of hydrogen peroxide and changes in the concentration of various dissolved materials at the metal surfaces. Such changes can be calculated from experimental data on the efficiency of the various reactions in solution, and from the geometry of the radiation intensities and the flow rates in the system considered. The corrosion rates can then be determined by experimental tests (or a priori consideration) of the effects of the resulting solution. Simple examples of such considerations are given by the effects of the formation of hydrogen peroxide and of the reduction of sodium dichromate in W water on the corrosion of the aluminum pile tubes. A more complicated example is given by the possible formation of peroxide concentration cells at the ends of the slugs in the W pile, as discussed in Section 4. The direct effects of radiation on corrosion, on the other hand, are concerned with the influence of the radiation itself, or of short-lived free radicals formed by the radiation, on the rates of the various processes which occur at the metal surfaces. The experimental work described in the preceding sections of this report was aimed at the study of such effects. The discussion of this section is concerned entirely with these direct effects, which must always be regarded as superimposed upon the indirect effects mentioned above.

We have been able to find only one reference in the literature to the effect of ionizing radiation on corrosion rates. Pestrecov[5] found that the rate of solution of copper in aqueous potassium cyanide was initially increased 30% by irradiation with X rays (intensity not stated), but that with long irradiation the metal appeared to become passive. However, there is considerable mention in the literature of the effect of ultraviolet light on the corrosion rates and the electrochemical potentials of various metals. This matter will now be considered.

6.2 The effect of light on corrosion

Bowden[6] and Price[7], working together, discovered that the overvoltage in the electrolysis of water at various kinds of metal cathodes and anodes was decreased on illumination with ultraviolet light. According to their reports, which are described as preliminary, the entire light of a small mercury lamp was found to increase the current density at constant voltage by as much as 5 μa/cm^2. It was claimed that on anodes of Pt and Pd and on cathodes of Pb, Co, Bi, Sb, Hg, Al, and graphite, the threshold wave length for production of the effect was always the same--namely, 3970 Å--and that the observed rise in current increased rapidly as the wave length was decreased below this threshold. The promised final report on this work has never been published. If the data given are assumed to be correct, the independence of the threshold wave length from the nature of the metal shows that in all cases the light was being absorbed by the same molecular species, presumably a layer characteristic of an interface in an electric field but not of its metallic component. The light provides a part or all of the activation energy required for the transformation of the interfacial molecules.

It is therefore to be expected that ultraviolet light should tend to depolarize both anodic and cathodic areas in electrolytic corrosion processes.

A careful study of the effect of light on the electrode potentials of various metals was made by Bannister and Rigby[8]. Two identical electrodes were immersed in 3% KCl solutions in fused silica tubes, the solutions differing only in their oxygen concentration. The potential difference between the electrodes was determined and the effect of illuminating one of the electrodes with ultraviolet light from a mercury lamp was ascertained. Results were as follows.

1. Zinc. When both solutions were completely deaerated there was no potential difference between the electrodes and illumination did not produce any change. When a little oxygen was added to one solution the oxygenated electrode became more cathodic ("noble") to the extent of 0.13 v. Illuminating the oxygenated electrode increased this figure to 0.18 v--that is, the illumination produced an additional ennoblement of 0.05 v. On standing with no further addition of oxygen, the potential difference dropped, presumably because of the consumption of oxygen by corrosion; during this time the presence of light still produced an increase in potential. When the potential difference had dropped to zero the whole cycle could be repeated. The greater the oxygen concentration at any time (as shown by the differential aeration potential) the greater the effect of light on the potential. At the end of the experiment it was observed that corrosion of the illuminated electrode had occurred chiefly on the side away from the light.

2. Aluminum. The effects observed with this metal were the same as those obtained with zinc, although more care had to be taken with the deaeration in order to obtain reproducible results. The magnitude of the illumination effect was greater here, the light causing increases of potential as great as 0.15 v.

3. Lead. Similar effects were also observed with this metal. In contrast to the others, however, the illumination was found to accelerate markedly the return of the potential difference to zero when aeration was stopped, the necessary time being reduced from ~24 hours to ~0.5 hours. This implies that light accelerates the oxidation of lead, which forms less stable oxide films that those of zinc or aluminum.

4. Antimony, tin, cobalt and platinum showed little or no response to aeration and none to illumination.

5. Copper. Like zinc and aluminum, copper showed no response to light in deaerated solution. When oxygen was added very slowly the aerated electrode became cathodic and light slightly increased this effect, as with zinc and aluminum. With prolonged illumination, however, the light response died out. This fatigue of the light response of copper in an electrolytic solution had previously been observed by Case[9], who

ascribed the effect to a change in the nature of the oxide film from the cuprous to the cupric state. On more rapid bubbling of oxygen the aerated electrode became anodic, a previously observed effect which is caused by the removal by turbulence of the copper cations from the region of the interface[10].

6. Iron (mild steel). In the complete absence of oxygen, illumination caused the potential to become slightly anodic. When oxygen was added the aerated electrode became highly cathodic, and illumination rendered it still more cathodic, as with zinc. On standing, the oxygen was used up, and on the second day the cycle was repeated. On the third day, however, when considerable corrosion product had accumulated, the illumination caused the potential to become more anodic both before and after aeration, and this effect was again found on the fourth day.

Using a filter which transmitted only between 3400 and 4200 Å, effects on the potential of zinc were obtained which were of the same order as those given in the full arc. This would indicate that the effect is confined to the near ultraviolet portion of the spectrum, which surprisingly (cf. Bowden) appears to be more effective than the farther ultraviolet. That the effect was not caused simply by temperature changes was demonstrated by warming one electrode, which produced a potential difference in the opposite direction from that produced by illuminating the electrode.

We may assume that light stimulates both cathodic and anodic processes, the direction of the potential change obtained depending on which reaction is controlling under the particular conditions used. Aluminum, zinc and lead stand high in the electrochemical series and owe their stability to the presence of hydrated oxide films. When a high concentration of chloride ion is present, as in these experiments, the film tends to be less protective. Such conditions are the most favorable for showing differential aeration effects. The oxygen acts as a depolarizer for the cathodic reaction, rendering the potential of the metal more noble, and at the same time tending to repair the pores, which are regarded as being continually produced in the film by the penetrating effects of the chloride ion. This depolarizing process is the controlling one in fixing the potential of the metal, and is stimulated by the action of the light. Such a state of affairs will exist only when the film is not fully protective--i.e., can be penetrated by halide or other ions present. When the film is completely protective (Sb, Sn, Co in neutral solution) or the metal itself is unreactive (Pt), aeration and light have no effect on the potential.

In air-free solution, on the other hand, illumination rendered mild steel anodic with no effect on zinc or aluminum. On the last two metals the anodic reaction is inhibited by the presence of the oxide film; with steel the cathodic reaction is limited by the low concentration of electron acceptors (H^+, O_2), while the anodic reaction is not limited by any adherent film, but only by the normal interface polarization.

Light, by decreasing this polarization, therefore makes the steel more anodic. When oxygen is added the cathodic reaction is greatly stimulated andthe metal becomes much more cathodic. The illumination at first increases the cathodic character of the electrode, as with Zn, by decreasing the overall activation energy of the total process required for the reduction of the oxygen. When corrosion has proceeded for some time, however, rust accumulates on the surface and various complicating effects must come into play. For one thing, the access of oxygen to the metal is now limited by its diffusion through the rust so that the concentration of the electron acceptors again becomes more important than the activation energy of the reaction. Also the reaction of metal with a higher-valent oxide may become a controlling process, and stimulation of this reaction by light would tend to make the electrode anodic.

In the printed discussion on the J. Inst. Metals paper, a good summing up of the mechanism was given by Vernon. When the conditions are such that a given amount of light energy will have a greater effect on the cathodic reaction than on the anodic, the potential will become more cathodic; and when the energy absorbed will give the greater effect on the anodic reaction the potential will become more anodic.

The above experiments allow us to predict the effect of light on certain types of corrosion processes. With zinc, aluminum and similar metals in halide solution, which tend to give corrosion of the pitting type, light should have a protective effect, by stabilizing the protective film. (If the illuminated zone is small the corrosion in the dark areas may be enhanced by the setting up of differential illumination currents.) The expectation that light should protect appears to be confirmed by the observation of Bannister and Rigby that the illuminated side of their zinc specimen was less corroded than the dark side. With iron, where at least after the initial stages the metal becomes more anodic under illumination, one can expect the corrosion rate to be increased. This is borne out by the observations of Friend[11] and Wood[12], both of whom found that ordinary daylight increased the rate of corrosion of iron in water by about 20%. With copper, which also posseses oxides of lower and higher valence, one might expect under certain conditions acceleration of corrosion by light, similar to the effects on iron. Bengough and Hudson[13] state that copper tarnishes more rapidly in distilled water in the light than in the dark, and Vernon[14] found that in the pickling of brass in acid "anodic and cathodic areas make their appearance coinciding with areas of maximum and minimum illumination." With lead, the oxidation of the metal should be accelerated by light, and Liverseege and Knapp[15] find that ordinary daylight increases the amount of lead dissolved by ordinary water. We should expect, however, that corrosion of the pitting type on lead should be inhibited by light, as with aluminum or zinc.

In general, if a metal is corroding rapidly, one may assume that neither the anodic nor the cathodic action is being inhibited by film or concentration effects, and light should accelerate the corrosion.

Also, in any system, if we are considering only the initial stage of corrosion where oxide is being formed, the effect of light will be accelerating. But if corrosion is being inhibited by film formation, or by lack of oxygen, light should not accelerate it. In the case of the incompletely protective films on aluminum in acid or halide solutions, light should actually inhibit corrosion by accelerating the repair of the pores which form in the film.

6.3 Comparison of light and ionizing radiation

Ultraviolet light acts only at the metal-water interface, while ionizing radiations act throughout the entire body of the water. The effects of the two kinds of radiation on corrosion should, however, be qualitatively very similar; the effect of the absorption of energy in both cases is to reduce the activation energy for both cathodic and anodic processes at the interface. The ionizing radiation will dissociate the water to oxidizing and reducing fragments, some of which will travel to the interface and then may receive an electron from, or give an electron to, the metal; the result will be the same as if the molecules located at the interface had originally been activated by ultraviolet light.

Therefore, all the qualitative discussion given above as to the effect of ultraviolet light on corrosion should hold for ionizing radiations also. Stable metals like stainless steel or tin, which owe their passivity to an adherent oxide film, should not be affected by radiation. This conclusion was verified for stainless steel (Section 5.3.1). When the oxide film is less stable, as with aluminum in chloride solution, the corrosion rate would be decreased by the presence of radiation, as was indicated by the experiments of Sections 3 and 4. On the other hand, when protective oxide films do not play an important role the corrosion rate should be increased by radiation. The experiments of Section 5.3.4 on mild steel demonstrate this, as well as the publication of Pestrecov[5] on the increase of the corrosion rate of copper in cyanide solution by X rays. The passivation which Pestrecov found on prolonged exposure could not easily be predicted and could be properly explained only by a detailed study of the copper-cyanide reaction.

The passive nature of stainless steels may not be caused entirely by a protective film, as the nature of the energy levels of the electrons in these alloys may be different from those of the pure components[16]. However, the experiments of Forrest, Roetheli and Brown[4a] show that an oxide film does form on stainless steel; and the effect of halide ions in producing corrosion indicates that this film plays an important role. As it appears probable that the action of fluoride ion in promoting the corrosion of stainless steel is similar to its action on aluminum, we would predict that the presence of radiation should actually decrease the corrosion rate of stainless steel in fluoride solution. This consideration has a bearing on the choice of medium to be used for a homogeneous pile.

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6.4 General conclusion

The above qualitative conclusions are very encouraging. In any particular case where corrosion resistance is important, the metal chosen will nearly always be protected by oxide films. In these cases the effect of radiation, if any, will probably be to protect the metal. Usually, radiation will accelerate corrosion only when the corrosion is in any case so rapid that the system would not be considered for practical use.

These considerations are qualitative only. The quantitative effect on corrosion by radiation of any given type and intensity can only be determined by experiment. Such experiments are bound to be difficult and expensive, as they involve the exposure of corrosion specimens to expensive radiation sources for a long period. It is hoped that the above discussion (taken in conjunction with the confirming results of our experiments) is sufficiently convincing to eliminate the idea that radiation must inevitably have an adverse effect on corrosion, and to obviate the necessity of performing many expensive radiation-corrosion tests in the future.

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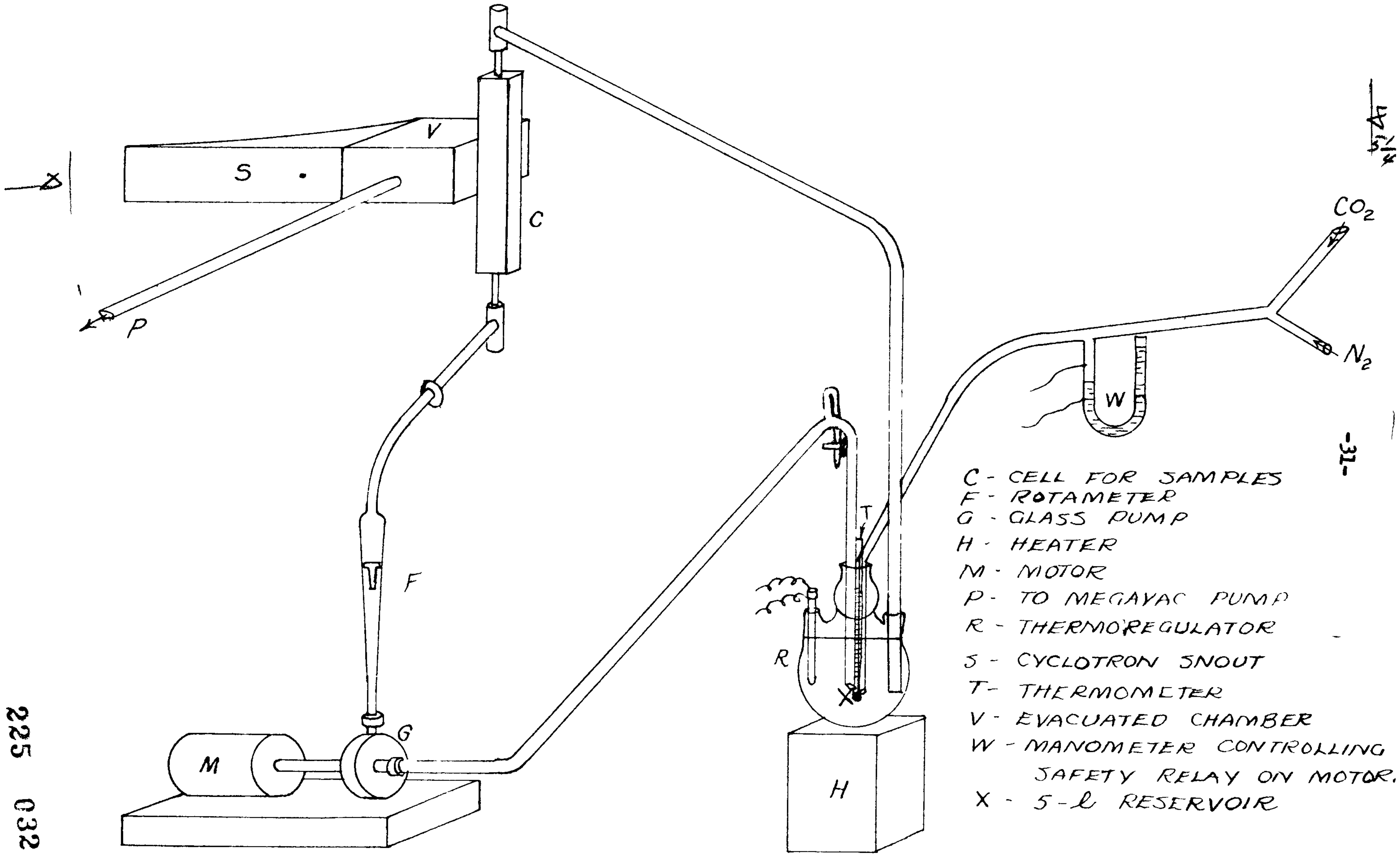
FIGURE 1

CIRCULATING SYSTEM FOR FAST-FLOW CORROSION STUDY OF ALUMINUM IN DEUTERON BEAM.



C - CELL FOR SAMPLES
F - ROTAMETER
G - GLASS PUMP
H - HEATER
M - MOTOR
P - TO MEGAVAC PUMP
R - THERMOREGULATOR
S - CYCLOTRON SNOUT
T - THERMOMETER
V - EVACUATED CHAMBER
W - MANOMETER CONTROLLING SAFETY RELAY ON MOTOR.
X - 5-ℓ RESERVOIR

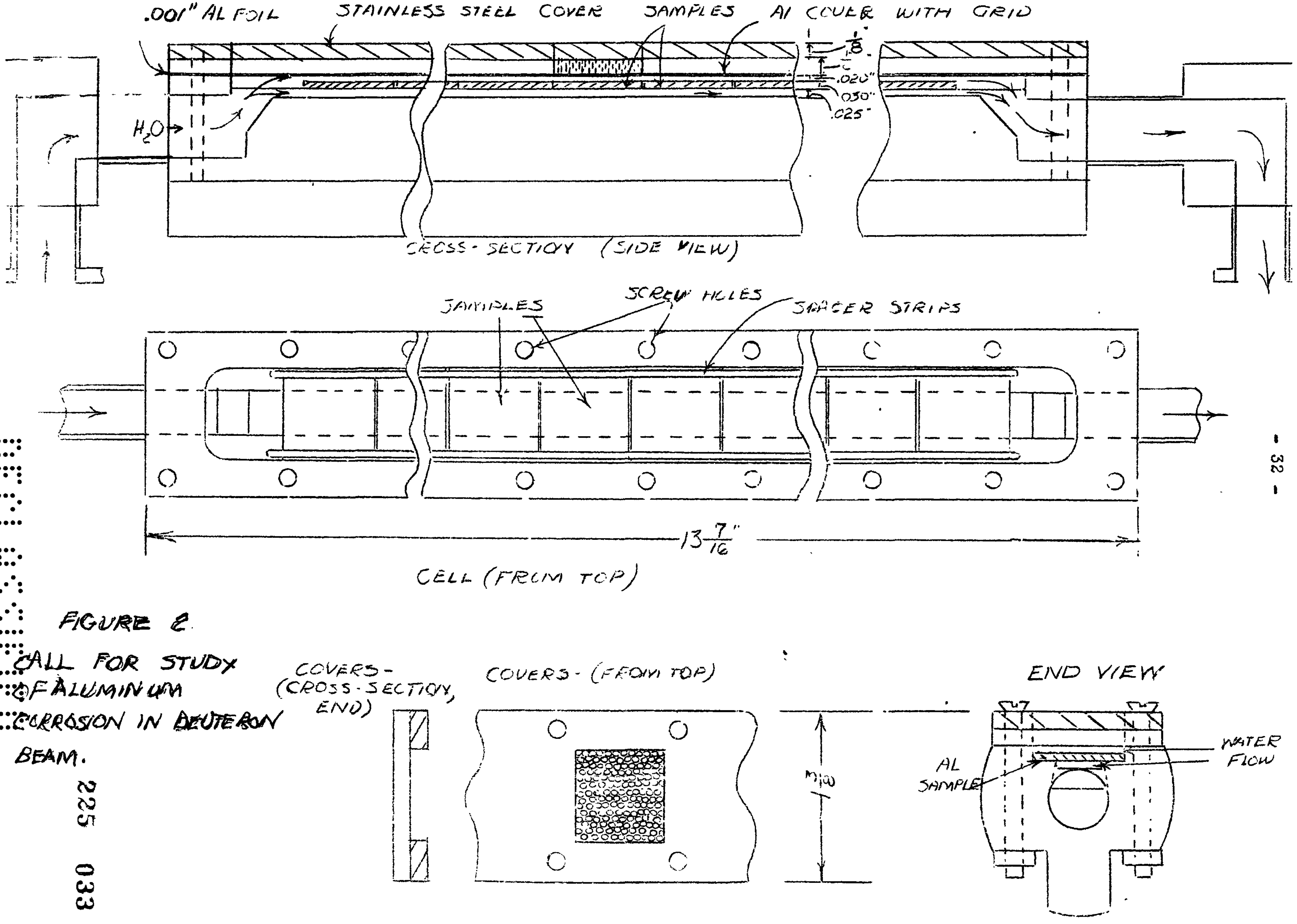
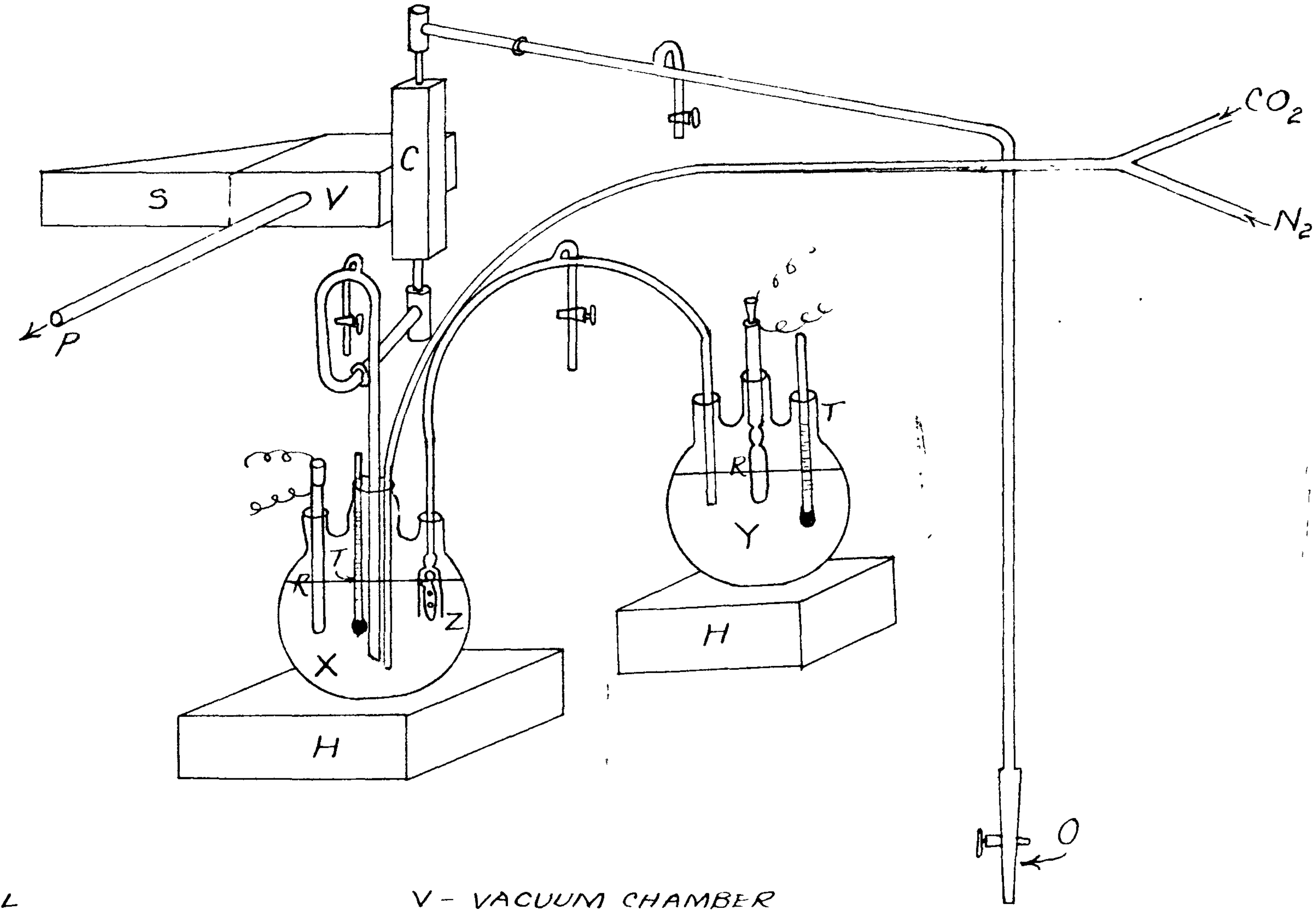


FIGURE 2

CELL FOR STUDY OF ALUMINUM CORROSION IN DEUTERON BEAM.

FIGURE 3.

GRAVITY FEED SYSTEM FOR SLOW FLOW CORROSION STUDY OF ALUMINUM IN A DEUTERON BEAM.



C - CELL
H - HEATER
P - MEGAVAC PUMP
R - REGULATOR
S - CYCLOTRON SNOUT
T - THERMOMETER

V - VACUUM CHAMBER
X - 5 LITER RESERVOIR
Y - 5 LITER RESERVOIR
Z - FLOAT VALVE TO KEEP WATER LEVEL CONSTANT
O - OUTLET

[redacted]

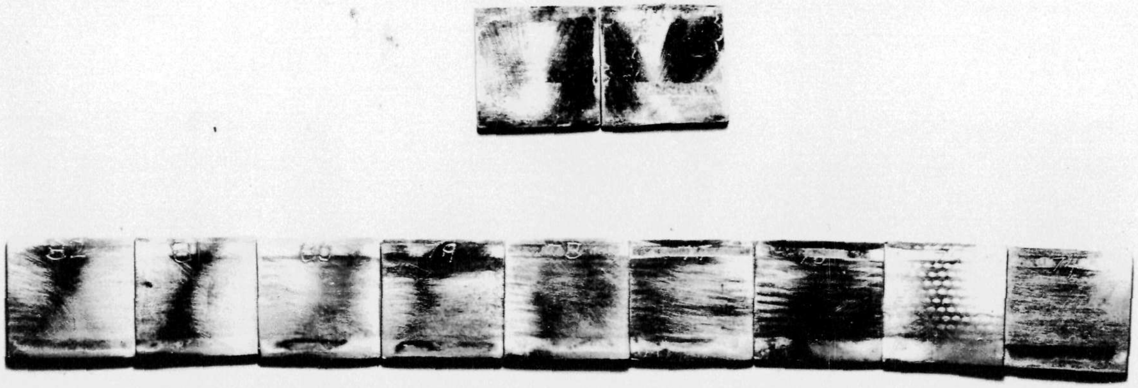


Fig. 4. Samples of 2S aluminum subjected to water corrosion in presence of deuteron radiation. Top: Fast-flow run; irradiated sample at left. Bottom: Slow-flow run; irradiated sample next to right-hand end.

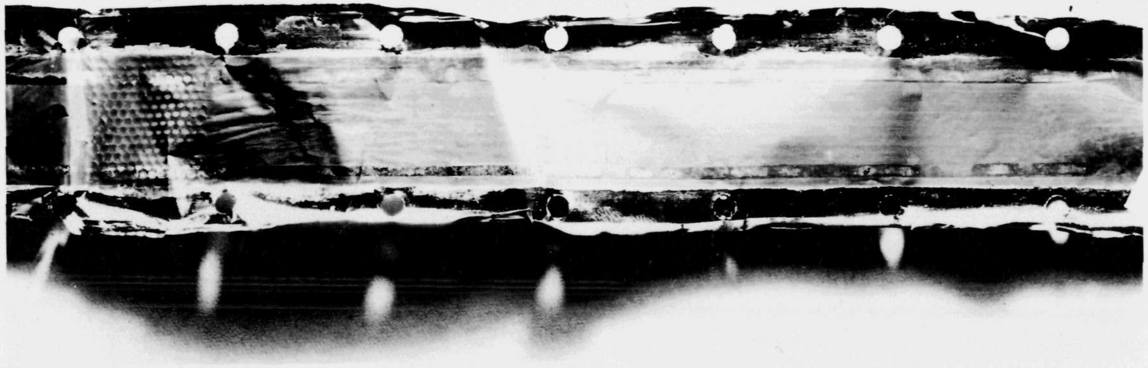


Fig. 5. "Window" of 2S aluminum foil from slow-flow deuteron-beam corrosion experiment.

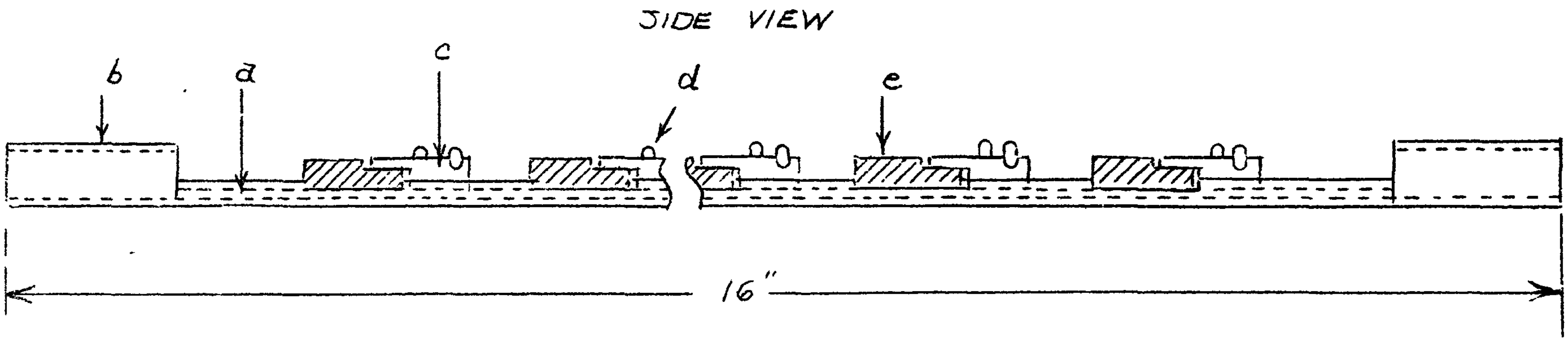


Figure 6. Boat for supporting samples for corrosion study of aluminum in electron beam.

a) 7 mm O.D. pyrex tubing concentric in 9 mm O.D. pyrex tubing. Tubes were ground on flat plate until about 2/3 was ground away, leaving shallow boat for holding cylindrical samples.
b) 9 mm O.D. pyrex tubing to act as end guides for boat.
c) 5 mm pyrex rod cut to shape by glass cutting saw and fused at base of spacer to the 7 mm ground tubing.
d) Glass nibs on spacer to support boat against upper part of circulation tube.
e) 3/16" rod of sample cut to shape in order to make close fit with sample holder.

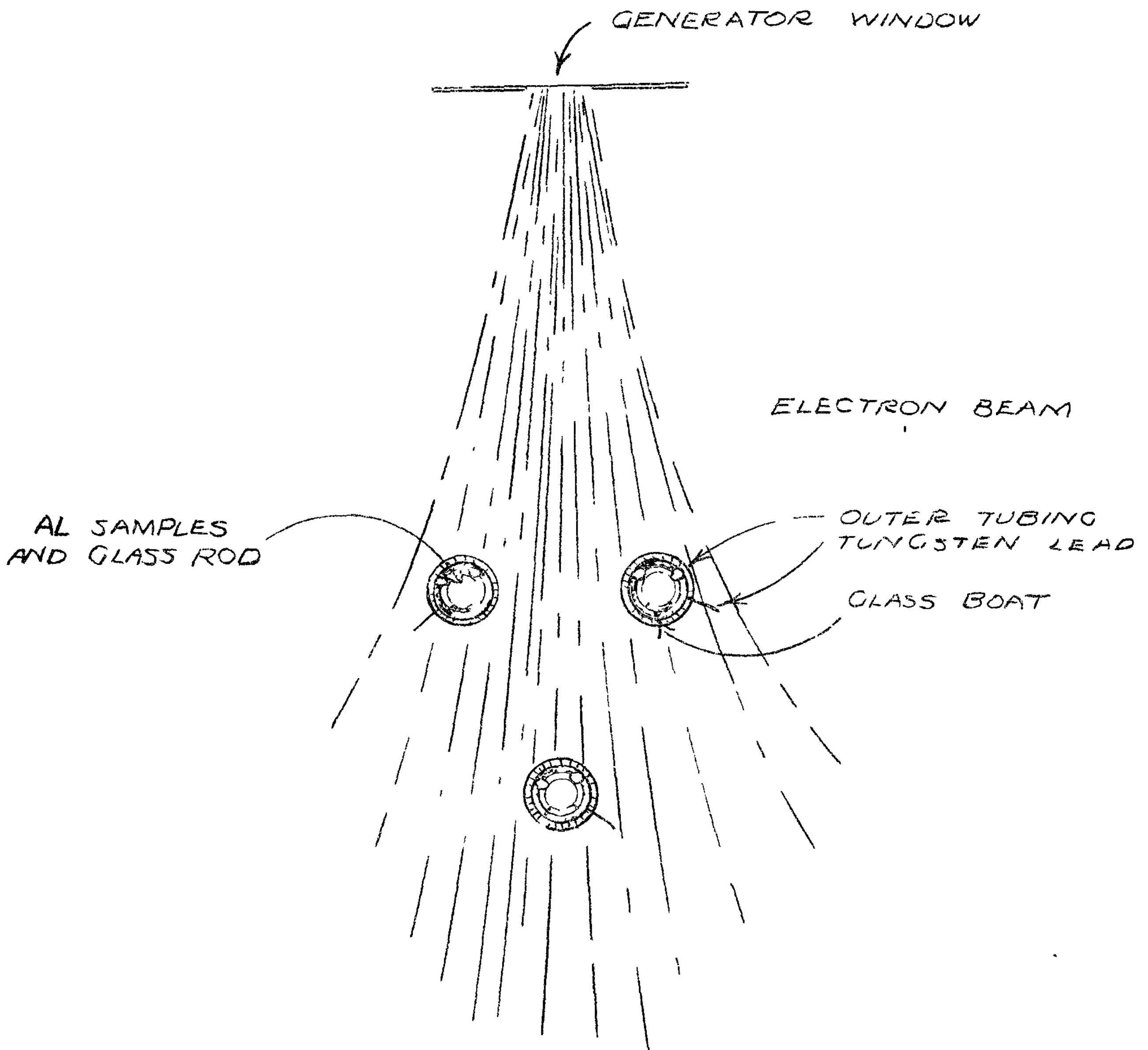
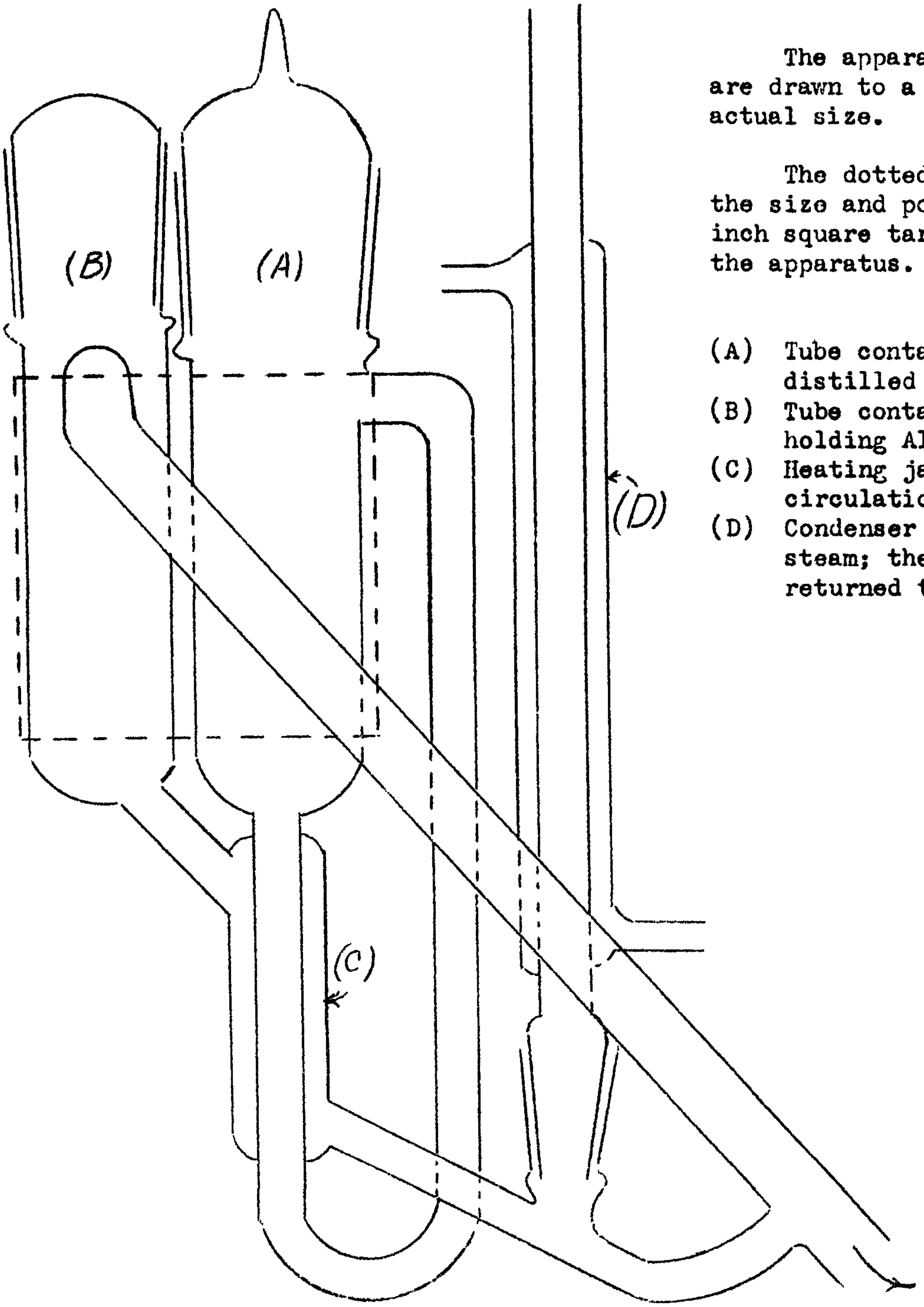


FIGURE 7. - END VIEW OF TUBES CONTAINING SAMPLES IN ELECTRON BEAM OF VAN de GRAAFF GENERATOR (ACTUAL SIZE)

Figure 8. Apparatus for study of aluminum corrosion in neutron beam.

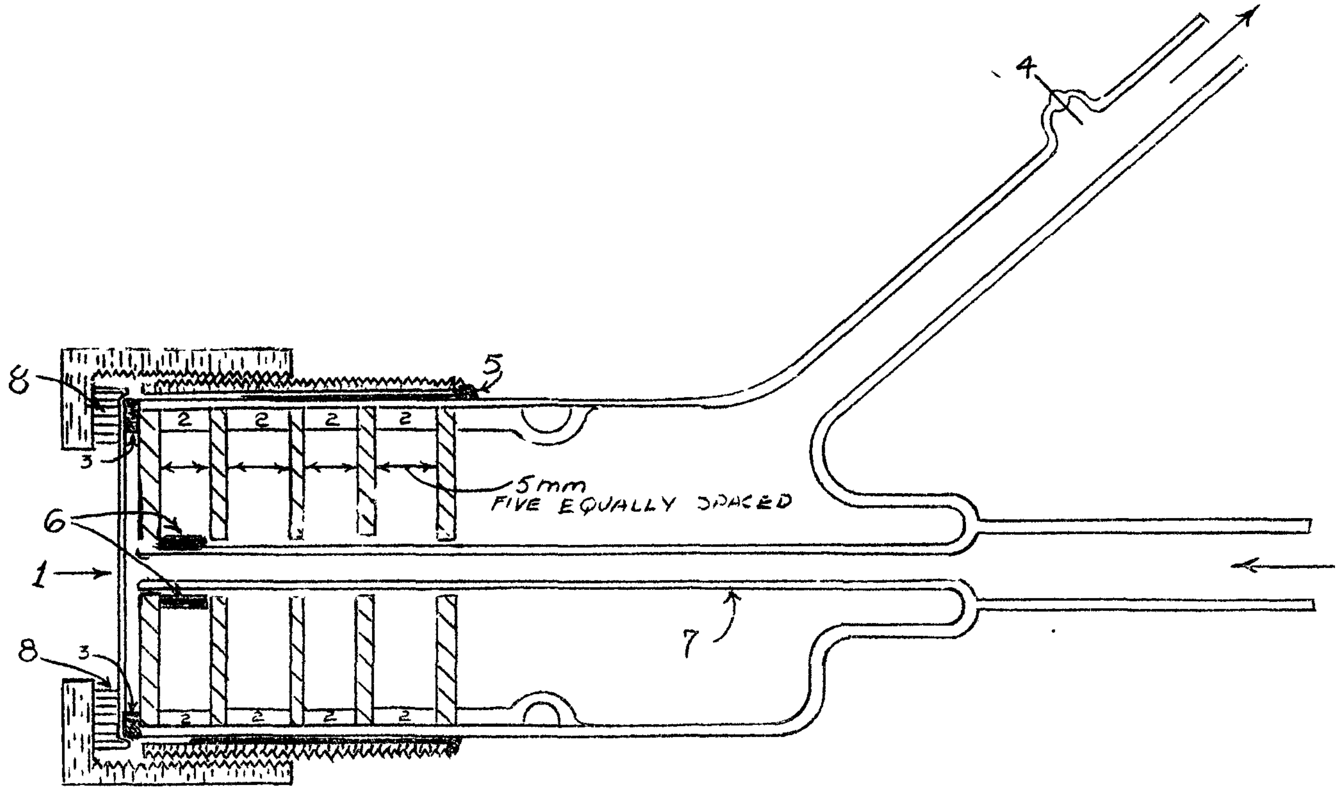


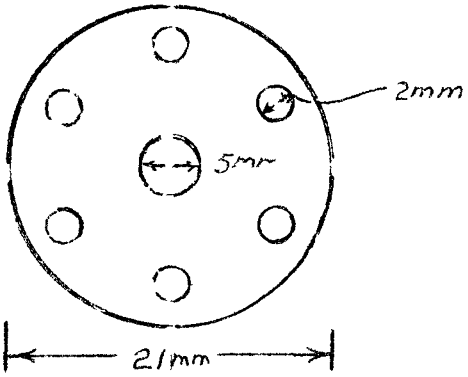
The apparatus and target face are drawn to a scale of one-half actual size.

The dotted square represents the size and position of the four inch square target with respect to the apparatus.

(A)	Tube containing Al welds and distilled water
(B)	Tube containing sealed tube - holding Al samples in W water
(C)	Heating jacket to produce circulation of water in tube A
(D)	Condenser for condensing the steam; the water formed is returned to the steam generator

Figure 9. Cell for corrosion study of iron and other metals in deuteron beam.





Front elevation of
metal sample.

▨ Metal samples

▦ Brass ring and cap
(Threaded)

1. Mica window
2. Glass spacers
3. Metal spacer
4. Tungsten lead
5. Cement
6. Glass sleeve
7. Water inlet tube
(4 mm O.D.)
8. Rubber gasket