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THE EFFECTS OF WATER QUALITY ON PILE OPERATION
FINAL REPORT PRODUCTION TEST NO. 105-525-E

By

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HANFORD ATOMIC PRODUCTS OPERATION
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THE EFFECTS OF WATER QUALITY ON PILE OPERATION
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I INTRODUCTION

This production test⁽¹⁾ was carried out to determine the effects of the following water treatment variables on pile operation:

1. Lowering the pH of plant process water.
2. Reducing the amount of sodium dichromate added to the water.
3. Eliminating the filtration step in the water treatment process.

The pH studies were carried out to develop a water less corrosive to the aluminum components of the pile and which would not form boiler scale at as low a temperature as did pH 7.7 process water.

The value of lowering corrosion rates can be considered from two standpoints: the impact of the corrosion rate reduction on present operation and on future operation when water flow rates are increased and the piles are pressurized to permit higher outlet temperatures.

At present, one of the major pile operating problems is caused by the corrosion of the process tubes. A study of this problem has been completed recently.⁽²⁾ The study concludes that a major retubing operation will be required starting August, 1956. In the interim, it is estimated that 1,000 process tubes will require replacement. A reduction in tube corrosion rates would permit a reduction in tube replacement rates, save part of the retubing costs, and minimize the production loss required for retubing. Tube replacement techniques are now being perfected. Ultimate costs of money and time for the replacement of a tube are uncertain. Therefore, it is not possible to state a concrete figure for the

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- (1) Miller, N.R. "Production Test No. 105-525-E, The Effects of Water Quality on Pile Operation", HW-29406, 9-21-53.
 - (2) Goldsmith, S., and de Halas, D.R., "Process Tube Corrosion and Replacement Rates", HW-38708, 8-17-55.

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savings associated with a given rate reduction. Nevertheless, it can be said that a sizeable reduction in rates would effect major savings.

A project now is in progress to increase the coolant flow rate through some of the reactors. A study has been made to determine some of the aspects of increasing production at the older reactors after the flow increase by pressurizing the piles.⁽³⁾ For example, the study shows that a factor of eight reduction in rates would decrease minimum total unit costs by 10% and increase production, at minimum total unit costs, by 25%. Total unit costs include metal and separation costs as well as 100 Area costs. At different corrosion rates, minimum unit costs are obtained by controlling exposures times of the fuel, tube outlet temperatures and other operating variables.

Thus, the extreme importance of minimizing corrosion rates under present and future operating conditions is apparent.

The boiler scale problem is also of importance. With pH 7.7 water, boiler scale formation would occur if tube outlet temperatures were increased much above 120 C. If a factor of eight reduction in corrosion rates be obtained, optimum tube outlet water temperature is about 160 C. Thus, full utilization of a corrosion rate reduction depends on changing the water to permit operation at higher outlet water temperature without incurring boiler scale formation.

The studies on reducing the amount of dichromate added to the water were carried out to reduce chemical treatment costs. The cost of adding 2.0 ppm of dichromate to the water (in accordance with present specifications) after water flow rates are increased will be about \$800,000 annually, almost half of the total chemical treatment costs. Previous tests showed that the concentration of dichromate might be reduced to 0.2 ppm at pH 7.7 without ill effect; so further studies were made at

(3) Shields, R. J. and Goldsmith, S., "Some Economic And Technical Aspects of Increasing Production at D Reactor After Completion of Project CG-558", HW-37044, 7-12-55.

lower pH's.

Finally, studies were made on eliminating the filtration step in the treatment process. This study was undertaken because eliminating filtration might significantly reduce chemical treatment costs. Also, if an additional plutonium producing pile were to be built without provision for power recovery, elimination of the filtration plant would significantly reduce capital costs.

This document reviews the investigations made in the three fields prior to the initiation of this production test and reports data obtained from this test.

II SUMMARY

Studies have been made to determine the effects of reducing process water pH in the range 7.7 - 6.2; of reducing the dichromate concentration in process water from 2 ppm to 0.2 ppm; and of eliminating the filtration step of the water treatment process. These studies were carried out using the in-pile and out-of-pile facilities of the 105-D Flow Laboratory.

The results of the pH studies gave indication that corrosion rates could be markedly reduced. It appears that slug jacket corrosion rates may be reduced by a factor of 15-20 by lowering the pH from 7.7 to 6.2; a pH reduction from 7.7 to 7.0 would reduce rates by a factor of four. Data obtained at a temperature of 120 C show that tube corrosion rates may be reduced about a factor of two by lowering pH from 7.7 to 7.0 and a factor of four by lowering the pH further to 6.2.

Boiler scale formation had previously been found to occur with pH 7.7 water at about 135 C and with pH 7.3 water at 145 C. At pH 7.0, scale formation did not occur at temperatures of 150 C or lower; at pH 6.5 formation did not occur at 170 C or lower.

Thus, it appears that the significant savings discussed above can be obtained by decreasing process water pH.

Carbon steel corrosion rates in water containing 2 ppm of dichromate did not change materially between pH 7.7 and 6.6 at 90 C. The tests were run at 90 C because the present carbon steel effluent system is not adaptable to pressurization. Thus even if pile bulk water temperatures are increased to over 100 C, quenching to less than 100 C will probably be required unless the effluent line is redesigned.

Film formation rates increase as the pH is lowered. There is a good possibility, though, that low pH water produced on a plant scale can be controlled to prevent excessive filming. The filming probably will not be too serious at pH 7.0 in any case. Plant tests will be required to investigate this effect at pH's lower than 7.0.

Preliminary radiochemical studies indicate that the addition of additional sulfur to the water in the form of sulfuric acid will not produce significantly higher P^{32} concentrations in the water. P^{32} is produced from sulfur by a (n,p) reaction.

Data on lowering the dichromate concentration in pH 7.3 and 7.0 water from 2 ppm to 0.2 ppm were promising from the standpoint of aluminum corrosion effects. No localized attacks occurred on the aluminum at these dichromate concentrations and over-all rates were not significantly changed. Some data did indicate, however, that water containing 0.2 ppm of dichromate at pH 7.3 would cause a serious pitting of the carbon steel portions of the system at 90C.

Results showed that the use of unfiltered water was feasible from the standpoint of aluminum corrosion. No detectable erosive attack occurred with the unfiltered water even at turbidity concentrations as high as 100 ppm. At a given pH, over-all rates of aluminum corrosion may be increased by a factor of two when unfiltered rather than filtered water is employed. Of importance is the fact that film formation did not occur in tubes cooled with unfiltered water. All the unfiltered water tests were conducted with 5 ppm of dichromate added to the water.

Radiochemical analyses did show, though, that the use of unfiltered water increases the radioactivity of the effluent water. The concentration of P^{32} with unfiltered water was increased by roughly a factor of five. Because of this effect the elimination of the filtration step in the process is not immediately feasible.

III HISTORICAL BACKGROUND

The purpose of this section is to show briefly how the testing reported here is a continuation of a testing program which has been carried on for several years by several investigators. A more complete description of previous testing is included in Appendix I.

Early water quality studies were carried out by the Clinton Laboratory⁽⁴⁾ and by the CMX Project at Hanford.⁽⁵⁾ These tests showed that over-all aluminum corrosion rates would be minimized by maintaining the pH of the process water in the range 6.0 to 7.0. Nevertheless the original specification required that the pH be maintained in the range 7.5 - 7.8. This was done because it was decided to add dichromate to the water to inhibit localized corrosion attacks. With dichromate in the water, data showed that film formation might be severe at a pH lower than 7.5.

Later testing showed that pitting and erosion corrosion did occur with dichromate-free process water^(6, 7) and these attacks became more severe at lower pH's.^(8, 9) Further tests, however, showed that film

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- (4) Draley, J. E., "The Corrosion of Aluminum in Dilute Solutions: Laboratory Studies," CT-3027, 6-19-45.
 - (5) Kidder, C. P., "CMX Final Report," HW-7-4444, 4-31-46.
 - (6) Wilson, C. D., "Flow Laboratory Investigations of 'F-Type' Pitting of Slugs and Tubes," HW-28027, 6-1-53.
 - (7) Lutton, J. M., "Sodium Dichromate as a Process Water Additive: An Evaluation," HW-27158, 3-19-53.
 - (8) Atwood, J. M., "Process Water pH Effects," HW-24007, 5-15-52.
 - (9) Miller, N. R., "Interim Report No. 1, Production Test 105-509-E, The Effects of Low pH Alum Treated Water on Pile Operation," HW-30574, 6-1-53.

formation was not serious if the pH of process water with dichromate were lowered below 7.5⁽¹⁰⁾ This discovery made it practical to evaluate the corrosivity of process water containing dichromate in the pH range 6.2 - 7.3. This evaluation was done by this test.

Other tests were carried out to determine if the original concentration of dichromate, 2 ppm, were required or if a lower concentration would suffice. These other tests showed that 0.2 ppm of dichromate would be adequate at pH 7.7⁽¹¹⁾ This present test studied the effects of lower dichromate concentrations at pH 7.3 and pH 7.0.

Out-of-Pile tests were carried on to determine if dichromate would inhibit erosion-corrosion if unfiltered water were used. The turbidity concentration in unfiltered water is considerably higher than in process water thus increasing the likelihood of a serious erosion attack. These tests showed that inhibited unfiltered water did not cause erosion-corrosion.⁽¹²⁾ This test further studied the effects of using unfiltered water as a pile coolant.

IV DESCRIPTION OF TESTS

The tests were carried out using the facilities of the 105-D Flow Laboratory. These facilities have already been described in detail elsewhere^(9, 13) and these descriptions will not be repeated here. In general, the laboratory provided facilities for pumping water to five tubes in the 105-D Pile and to mock-up tubes in the out-of-pile laboratory. Provisions were available to add a variety of chemicals to the water. Water pumped to the mock-up tubes was pre-heated in carbon steel heat

(10) Miller, N. R., HW-30574.

(11) de Halas, D. R., and Miller, N. R., "Slug and Tube Corrosion With Reduced Dichromate Concentrations," HW-30952, 4-9-54.

(12) Etherdige, E. L., "Preliminary Test Results of Unfiltered Water as a Pile Coolant," HW-32664, 8-4-55.

(13) Atwood, J. M., HW-24007.

(9) Miller, N. R., HW-30574.

exchangers.

Corrosion data on the slugs charged into the in-pile tubes were obtained by weighing the slugs before irradiation and cleaning, inspecting, and re-weighing the slugs after irradiation. This work was done by the Fuel Examination Unit, Fuel Technology Sub-Section. The average slug surface temperature experienced by the slugs was calculated from operating data and flux distributions in the method outlined by Woods.⁽¹⁴⁾

Information on the dummy slugs exposed in the out-of-pile tests was obtained from weight loss, film weight, and visual inspection data.

To obtain information on the in-pile tubes, the tubes were removed, slit longitudinally and visually inspected. Also, sections of the tubes were obtained and the wall thickness measured to gain information on tube penetration rates. This work was done by members of the Pile Coolant Studies Unit, Pile Materials Sub-Section. Out-of-pile data on tube corrosion were obtained by passing heated water through short weighed sections of process tubing.

Data on steel corrosion rates were obtained by passing the treated water through small stainless steel heat exchangers, to test chambers which were open to the atmosphere. The test coupons, which had been mechanically descaled, were totally immersed in the water in the tests chambers. Each test coupon was prevented from touching the carbon steel test chamber, other coupons, or other metallic surfaces by the use of glass hanger rods and plastic spacers. After exposure, the samples were cleaned, weighed and inspected. (Details on the cleaning methods used for the various specimens are outlined in Appendix II.)

Continuous sampling of each type of treated water was carried out and routine analyses for certain constituents made. Also, radiochemical analyses of the in-pile tube effluent water were made periodically.

(14) Woods, W. C. A., "Summary of In-Pile Corrosion Data at Hanford," HW-28011, 5-25-53.

V CORROSION

One of the main fields of investigation in these tests was to determine the effects of the treatment variables on the corrosion of in-pile aluminum components of the cooling system. Many of the tests were intended specifically to develop a water less corrosive to the slug jackets and process tubes. Also, there was interest in the corrosion of the out-of-pile carbon steel portion of the plant. This interest was somewhat negative. It was not anticipated that savings could be effected by reducing steel corrosion rates. Rather, it was feared that treatment changes desirable from the standpoint of aluminum corrosion might adversely effect the carbon steel parts of the system.

In the discussion of corrosion, the topic is split into three main parts: corrosion of slug jackets, corrosion of process tubes, and corrosion of carbon steel. While the discussions of slugs and tubes corrosion are separate, it should be noted that the data on slugs apply to some extent to the tubes and vice versa.

In addition to dividing the subject of corrosion into the three major phases, the discussions on slug corrosion and tube corrosion were further divided into discussions of data obtained from out-of-pile and in-pile testing.

A. Slug Jacket Corrosion - Out-of-Pile Test

Previous work has shown that corrosion data on slugs obtained from out-of-pile tests cannot be directly extrapolated to in-pile slug corrosion rates. Experience has shown, though, that corrosion data on slugs from out-of-pile tests do generally show trends which hold for in-pile conditions.

Tests with 2S aluminum jacketed dummy slugs were conducted at 120 C at pH's of 7.7, 7.3, 7.0, 6.6, and 6.2. Weight loss versus time curves for each of the pH's are shown in Figures 7 and 8, Appendix III. Over-all corrosion rates, as determined by the slope of the weight loss

versus exposure time curves, are shown in Figure 1 as a function of pH. The data indicate that quite important reductions in corrosion rates can be obtained by decreasing the pH. Over-all corrosion rates were reduced from a high of 0.60 mils/month at pH 7.7 to approximately zero at pH 6.2. In a short term test, slugs exposed to pH 6.2 water for five days at 120 C lost about 20 milligrams per slug. There was no further measurable weight loss during the next 15 days.

Of interest is the fact that at pH 7.3, the slugs exposed to water containing 0.2 ppm dichromate had corrosion rates essentially the same as slugs exposed to water containing 2 ppm dichromate.

Each of the dummy slugs used in the testing was inspected after exposure to get information on localized attack as a function of pH. Detailed descriptions of the slugs are included in Appendix III. In brief, however, at 120 C the frequency and severity of localized corrosion was proportional to the over-all corrosion rate. At pH 7.3 there was no detectable differences in the localized attack on slugs exposed to water containing 0.2 and 2.0 ppm of dichromate. The above is important because if pitting became severe it would be impractical to lower the pH to reduce over-all corrosion rates or to reduce the dichromate concentration to save on treatment costs.

In addition to the tests at 120 C, other corrosion tests were made at 150 C. These tests were made with pH 6.2, 6.6 and 7.0 waters. It was not possible to test pH 7.7 or pH 7.3 water at this temperature because at these pH's carbonate scaling begins at temperatures less than 150 C. This scaling effect will be discussed more fully later.

Over-all weight loss versus exposure time curves are shown in Figure 9, Appendix III. Over-all corrosion rates as determined from the curves shown tabulated below:

FIGURE 1
CORROSION OF 2 - S ALUMINUM SLUG JACKETS AT
120C FROM OUT-OF-PILE TESTING

TABLE 1
Over-all 2S Aluminum Slug Jacket Corrosion Rates At 150 C

<u>pH</u>	<u>Over-all Corrosion Rate Mils/Month</u>
7.0	0.42
6.6	0.70
6.2	0.30

Comparing these rates with those obtained at 120 C shows again the major importance of pH on aluminum corrosion rates. At 120 C, the rate obtained with pH 7.7 water was 0.60 mils/month. By decreasing the pH to 7.0 or 6.2, lower rates were obtained at 30 C higher temperature.

An interesting feature shown by the above data is that the corrosion rates at pH 7.0 were actually lower than with pH 6.6 water. This relationship was not anticipated. Previous experience had indicated that minimum corrosion rates at lower temperatures, 65 C-120 C, occurred at pH 6.6 or lower. Also, other investigations have established that the pH of minimum corrosion decreases with increases in temperature. Thus, it was expected that corrosion rates at pH 7.0 might be several times higher than rates at pH 6.6. Also, results from this test indicate that pH 7.0 was not the pH of minimum corrosion for, if this were so, the rates obtained at pH 6.2 would be expected to be higher than at pH 6.6. Actually, the corrosion rates were lower at pH 6.2 than at pH 6.6 or pH 7.0.

An explanation for the above can be advanced from the following observations made from the tests:

1. The rates obtained with pH 6.6 and 6.2 water did not change with time during the period of the tests.
2. The corrosion product on the slugs exposed to pH 6.6 and 6.2 water was soluble in oxalic acid and was presumably an amorphous aluminum oxide.
3. The rates obtained with pH 7.0 water initially were quite high, about 5.4 mils/month, then decreased after about

10 days to 0.42 mils /month.

4. The corrosion product on the slugs exposed to pH 7.0 water for ten days or less was similar to the corrosion product on the slugs exposed to pH 6.6 and pH 6.2 water. After ten days the corrosion product found on slugs exposed to pH 7.0 water was changed. The product after 10 days formed a thick, adherent crystalline layer which was not soluble in oxalic acid and which x-ray analysis showed to be alpha aluminum oxide monohydrate. ⁽¹⁵⁾

Apparently the crystalline oxide is much more effective in controlling corrosion than the amorphous oxide. Also, it appears that whether or not the crystalline oxide forms depends both on the pH and the temperature of the water. Formation of the crystalline oxide appears to be favored at higher temperatures and higher pH's. At pH 7.0, crystalline oxide appeared at 150 C but not at 120 C. At 150 C, formation of the crystalline oxide occurred at pH 7.0 and not at pH 6.6 or 6.2; also in tests with aluminum process tubing, the crystalline oxide occurred at temperatures lower than 150 C at pH's higher than 7.0.

Plots of the film removed from the slugs exposed to pH 7.0 water at 150 C with oxalic acid and the total film removed are shown in Figure 10.

The above conclusions were based on a hypothesis advanced by Groot and Peekema. ⁽¹⁶⁾ In another test, they noted a transformation of the corrosion product from an amorphous state to a crystalline form. They found that a reduction in corrosion rates occurred when the crystalline film formed and concluded that the crystalline film was responsible for the rate reduction.

(15) Lewis, M. Private Communication.

(16) "Pile Technology Section Monthly Report, "HW-36928 G, 6-10-55.

If the above explanation is correct, the initial rate determined with pH 7.0 water at 150 C should be consistent with the rate determined at pH 6.6 and 6.2, for all three rates were determined for aluminum without the crystalline oxide film.

Plotted in Figure 2 are the rates obtained at 150 C. Both the initial and final rate obtained with pH 7.0 water are shown. It should be emphasized that the lower rate at pH 7.0 is the steady state final rate, the rate of practical importance. It can be seen that a line drawn to the high initial rate obtained at pH 7.0 is similar to pH vs corrosion rate curves obtained at lower temperatures.

So far as is known, the heavy crystalline corrosion product film has never been noted on slugs exposed in-pile. It is difficult to predict what role this film would play under in-pile conditions. In addition to being a corrosion barrier, it would also be a barrier to heat transfer. If a slug operating at high power level were covered with the film, the metal temperature would be markedly increased - possibly leading to an intergranular attack. At least the high metal temperature would tend to increase corrosion rates. Whether the tendency of the film to reduce corrosion rates would predominate over the tendency to increase rates by increasing the temperature is not known.

Whatever the role of the adherent film was in slowing over-all corrosion attacks, it was effective in protecting the slug from localized attack. The pH 6.6 and 6.2 slugs experienced localized attacks at rib marks and other places where the surface was mechanically damaged. The surfaces of the slugs exposed to the pH 7.0 water were characteristically smooth and undamaged. The slugs exposed to the pH 6.6 and 6.2 water at 150 C were less damaged by localized attacks than were slugs exposed to pH 7.7 water at 120 C for similar periods of time.

FIGURE 2

CORROSION OF 2-S ALUMINUM SLUG
JACKETS AT 150C FROM OUT-OF-
PILE TESTING

B. Slug Jacket Corrosion - In-Pile Tests

1. Over-all Corrosion Rates

A total of 16 charges of slugs were exposed in the five special tubes in 100-D Pile supplied with water from the 105-D Flow Laboratory. Also, three additional charges of slugs were exposed in regular pile tubes to provide control corrosion data. The operating conditions of those charges are summarized below:

TABLE II
OPERATING CONDITIONS OF IN-PILE TUBES USED TO
OBTAIN IN-PILE CORROSION DATA

<u>Charge Number</u>	<u>Type of Water</u>	<u>pH</u>	<u>Dichro- mate concen- tration ppm</u>	<u>Av^g Tube Outlet Temp., C</u>	<u>Av^g Tube Power KW</u>	<u>Av^g Tube Flow Rate GPM</u>	<u>Time of Exposure Days</u>
2170-D-1	Unfiltered	7.5	5	78	540	29	36
2170-D-2	Unfiltered	7.5	5	81	550	29	81
2171-D-1	Unfiltered	7.5	5	78	545	29	88
2171-D-2	Unfiltered	7.0	5	81	520	29	87
2170-D-3	Unfiltered	7.0	5	85	525	29	158
2570-D-1	Filtered	7.3	2	81	480	25	57
3472-D-1	Filtered	7.3	2	88	540	26	109
3571-D-1	Filtered	7.3	2	88	560	26	135
2570-D-2	Filtered	7.3	0.2	82	500	27	203
3472-D-2	Filtered	7.3	0.2	88	490	25	188
3571-D-2	Filtered	7.0	0.2	86	530	29	158
3571-D-3	Filtered	7.0	2	98	695	29	55
3472-D-3	Filtered	7.0	2	101	645	26	55
2170-D-4	Filtered	6.6	2	96	690	29	55
2570-D-3	Filtered	6.6	2	93	655	29	55
2171-D-3	Filtered	6.2	2	95	680	29	55
3471-D-1	Filtered	7.7	2	99	700	29	55
2671-D-1	Filtered	7.7	2	93	680	30	55
3473-D-1	Filtered	7.7	2	92	650	29	55

The data from the 19 charges of slugs were treated in the following manner:

1. From operating records and measurement data, the slug surface temperatures, slug powers, exposure times and actual corrosion rates were determined.
2. From the slug surface temperatures slug powers and exposure times, the most probably corrosion rates the slugs would have experienced had they been exposed to pH 7.7 process water were determined from de Halas's correlation. (17, 18)

In evaluating the data, the three highest actual corrosion rates in a given charge were compared with the three highest expected corrosion rates as determined by step 2 above.

In most of the cases, the comparison of the actual rates with the rates expected in pH 7.7 water was taken to be a measure of the relative corrosivity of the water cooling the charge and pH 7.7 process water. In the case of charges 2170-D-4, 2171-D-3, 2570-D-3, 3472-D-3 and 3571-D-3, the actual maximum rates were compared to the maximum actual rates shown by the three control charges. This was done because all 8 charges were charged and discharged at the same time. Thus the 8 charges were subjected to essentially the same conditions except for the planned variables. Further there was a sharp increase in pile power level during the exposure, resulting in increases in slug powers and surface temperatures. Arithmetical averages of these values are used in de Halas' correlation to determine corrosion rates; however it is known that corrosion rates do not vary linearly with slug power and surface temperatures. This error is not important when slug powers and surface temperatures are nearly the same during an exposure; but the error will have a significant effect when the temperatures and powers are changed

(17) deHalas, D.R., "The Corrosion of Hanford Fuel Elements - Methods For Treatment and Analyses of In-Pile Corrosion Data," HW-34196, 9-21-54.

(18) deHalas, D.R., "Supplement to HW-34196, Slug Corrosion Rates in pH 7.6 Water," HW-36337-RD, 4-22-55.

considerably during an exposure. Because the error should effect the data on the five special charges and the three control charges in the same way, it is more realistic to compare the data on the eight charges by themselves.

A summary of the comparisons is shown in Table III.

In addition to these data, there are data on the in-pile corrosion of slugs cooled with pH 7.3 water under the terms of the half plant test at 100-F. ⁽¹⁹⁾ The data obtained on slugs cooled with pH 7.3 water at 100-F, when compared to deHalas' correlation indicate slug corrosion rates are reduced about 30% when the pH was lowered from 7.7 to 7.3. When the pH 7.3 data were compared to control data on slugs cooled with pH 7.7 water at 100-F at the same time, the apparent reduction became about 60%.

The in-pile corrosion data are graphically presented in Figure 3. In the figure the corrosion rates obtained at a given pH divided by corrosion rates at pH 7.7 are plotted against pH.

From the figure certain things are evident:

1. There is a steady decrease in slug corrosion rates as the pH is lowered from 7.7 to 6.2 with the rates at 6.2 being perhaps a factor of 15-20 lower than the rates at pH 7.7.
2. If anything, the reduction in dichromate concentration from 2 to 0.2 ppm tended to reduce slug jacket corrosion rates. Actually, the differences are probably not significant.
3. At a given pH, corrosion rates were somewhat increased when unfiltered rather than filtered water was used to cool the slugs. Corrosion of slugs in this unfiltered water will be discussed further in a later section.

Though it is apparent from the data that the in-pile test results confirm the importance of pH on corrosion rates, the data should not be over applied. To obtain the full value of jacket corrosion rate reduction,

(19) Miller, N. R., "Final Report, Production Test Number 105-526-E, Elimination of Lime as a Process Water Additive," HW-34530, 6-20-55.

TABLE III
SUMMARY OF CORROSION DATA OBTAINED FROM IN-PILE TESTING

Charge No.	Type of Water	pH	Dichro- mate Conc. ppm	Three max. Actual Rates		Three max. Expected Rates		Ratio of Actual to Expected Rates
				Mils/Month	Mils/Month	Mils/Month	Mils/Month	
2570-D-1	Filtered	7.3	2	0.64	0.63	0.87	0.87	0.73
3472-D-1	Filtered	7.3	2	0.86	0.85	1.2	1.1	0.76
3571-D-1	Filtered	7.3	2					
2570-D-2	Filtered	7.3	0.2	0.58	0.57	0.95	0.87	0.65
3472-D-2	Filtered	7.3	0.2	0.53	0.53	1.9	1.3	0.35
3571-D-2	Filtered	7.0	0.2	0.31	0.12	1.0	1.0	0.18
3472-D-3	Filtered	7.0	2	0.93	0.87	1.8	1.6	0.51(0.23)**
3571-D-3	Filtered	7.0	2	0.60	0.45	1.4	1.3	0.38(0.17)
2570-D-3	Filtered	6.6	2	0.40	0.38	1.1	1.0	0.38(0.17)
2170-D-4	Filtered	6.6	2	0.75	0.55	1.4	1.4	0.46(0.20)
2171-D-3	Filtered	6.2	2	0.15	0.14	1.2	1.1	0.14(0.06)
3471-D-1	Filtered	7.7	2	3.1	2.7	1.3	1.5	2.0
2671-D-1	Filtered	7.7	2	1.8	1.8	1.1	1.9	1.8
3473-D-1	Filtered	7.7	2	2.7	2.5	0.9	0.9	2.8
2170-D-1	Unfiltered	7.5	5	*				
2171-D-1	Unfiltered	7.5	5	0.81	0.76	0.73	0.67	1.1
2170-D-2	Unfiltered	7.5	5	0.60	0.25	0.73	0.66	0.51
2171-D-2	Unfiltered	7.0	5	0.56	0.54	0.90	0.88	0.68
2170-D-3	Unfiltered	7.0		0.68	0.63	0.95	0.90	0.59

* These charges operated under conditions insufficiently severe for deHalas' correlation to apply.

** Comparisons with the control tubes.

FIGURE 3
CORROSION OF 2-S ALUMINUM SLUG JACKETS FROM IN-PILE TESTING

it will be necessary to be able to predict corrosion rates under a given set of conditions. de Halas was able to do this for pH 7.7 water by having data on over 500 slugs which had operated at temperatures of 60 C or higher. A similar effort may be required for water at a lower pH.

It may seem that the corrosion rate experienced by a slug cooled with low pH water could be predicted by calculating the rate at which it would corrode in pH 7.7 water and applying the correction shown on Figure 3. Unfortunately, however, the rate reductions shown in the figure apply only to those particular charges. This fact can be illustrated by considering de Halas' correlation. The correlation is based on the assumption that corrosion rates are controlled by the temperature at the aluminum metal-corrosion product interface, i. e., the bulk water temperature plus the temperature gradient across the water film adjacent to the slug plus the temperature gradient across the corrosion product film on the slug. The bulk water temperature and the gradient across the water film can be calculated. de Halas was able to relate the gradient across the corrosion film on the slug to slug power and corrosion loss. From this he was able to express corrosion rates in terms of surface temperatures, slug powers and exposure times. With the low pH water, the temperature gradient across the film will not necessarily be related to previous corrosion loss and power in the same manner as it is in pH 7.7 water.

Thus, while it has been established that pH has a profound effect on in-pile slug jacket corrosion rates, it is evident more data are required to give a quantitative value to the effect under a given set of conditions.

The second point from the figure was that corrosion rates were not much changed by a reduction in dichromate concentration from 2 ppm to 0.2 ppm. It was believed, on the basis of experience at pH 7.7 that dichromate concentrations in the range 0.2 to 2 ppm would not affect corrosion.⁽²⁰⁾ The area of uncertainty was whether 0.2 ppm dichromate would inhibit pitting. This is discussed later.

(20) de Halas, D.R. and Miller, N. R., HW-30952.

The third point was the effect of using unfiltered cooling water on corrosion rates. One of the main differences between filtered and unfiltered water is the concentration of turbidity particles. Care is taken in the filtration process to maintain turbidity at 0.02 ppm or less. The turbidity of the unfiltered water supplied to the tubes during the test peaked at about 100 ppm, and averaged no less than 5 ppm during the test as is shown in Appendix IV. While the data from the four charges of slugs are somewhat contradictory (three charges corroded at rates higher and one at a rate lower than the line on the graph representing filtered water) one might justifiably be conservative and regard the higher rates as typical. A case can be made for the high turbidity concentrations increasing corrosion rates by an erosion process. Actually, no severe localized erosion was found.

Operating data for the slugs used in the in-pile testing are shown in Appendix IV.

2. Localized Corrosion Attacks.

The preceding discussion has been concerned with over-all corrosion losses, i. e. the total weight losses experienced by the slugs. Also of importance are localized corrosion attacks such as pitting and erosion-corrosion. One of the main purposes of conducting the in-pile tests was to determine localized corrosion characteristics under various conditions. It was probable that reducing pH would reduce over-all jacket corrosion attacks, but would it promote pitting? Would reduction of the amount of dichromate in the water from 2 to 0.2 ppm result in pitting and erosion as did the total elimination of dichromate? Would the slug jackets stand up under the erosive environment present when water containing up to 100 ppm of turbidity was pumped by the surfaces at velocities of 25 ft/sec or higher?

The post irradiation inspections of slugs give only a semi-quantitative estimation of the extent and severity of localized attack on the

slugs. (21) However, if a particularly severe localized attack occurred, it would be evident from the inspection reports.

A study of the inspection reports on the slugs showed that no more severe nor more frequent local attack occurred on the 16 special slug charges than occurs with slugs cooled with regular pH 7.7 water. On the other hand, no particular improvement was found over slugs cooled with the pH 7.7 water.

The chemical type pitting attack on the slugs cooled with low pH water did not occur. No unusual or severe attack was noted on slugs cooled with water containing only 0.2 ppm of dichromate. Further no erosion-corrosion was found on any of the slugs cooled with the unfiltered water. Some of these charges of slugs were exposed during the very peak in river water turbidity and yet no erosion occurred. Further, film patterns showed that one slug had been badly cocked in a tube. Such a condition leads to high local water velocities - a condition conducive to erosion, yet no erosion occurred.

Summaries of the inspection reports for each charge of slugs and turbidity concentrations of the unfiltered water cooling the slugs are given in Appendix IV.

C. Tube Corrosion - Out-of-Pile Tests

Recently quantitative data on tube corrosion rates in pH 7.7 plant process water have been obtained from two sources: actual measurements of the remaining 72-S aluminum cladding thicknesses on tubes and weight loss measurements on tubes exposed under out-of-pile conditions. The work on obtaining residual cladding thicknesses has been done primarily by W. C. Houck and the techniques of assembling sections of process tubes for obtaining corrosion loss data have been worked out by D. R. de Halas.

(21) de Halas, D.R., "Summary of Slug Pitting Data," HW-34430, January 12, 1955.

During this out-of-pile testing, tube corrosion data were obtained under various conditions as tabulated below:

TABLE IV
TUBE CORROSION TESTING CONDITIONS

<u>Temperature °C</u>	<u>pH's at Which Data Were Obtained</u>
70	7.7
95	7.7
110	7.7
120	7.7, 7.3, 7.0, 6.6, 6.2
140	7.3
150	7.0, 6.6, 6.2

Weight loss versus time curves are shown plotted in Figures 11, 12, 13, 14, 15, and 16, Appendix V. Corrosion rates calculated from the slopes of the curves are shown in Table VI, Appendix V. In Figure 4, corrosion rates are plotted against pH with temperatures as the parameter. From the figure several things are evident. Lowering the pH in the range 7.7 - 6.2 reduces tube corrosion rates to a similar degree as it does slug corrosion rates. The point representing pH 7.7 data was obtained from this test and from W. C. Houck and represents all available corrosion rate data on process tubes obtained at pH 7.7 under either laboratory or in-pile conditions.

At a given temperature and pH, tube corrosion rates are higher than slug corrosion rates by a factor of five or more. This is at least partially due to the fact that slugs are autoclaved before use.

It can be noted that the rates obtained with tubes exposed at pH 7.0 at 120 C and 150 C are equal. As was the case with slugs, the tubes exposed to pH 7.0 water at 150 C were covered with a crystalline oxide film and the tube exposed to 120 C were not. Apparently the crystalline film again proved to be a corrosion barrier.

The crystalline film was also found to some extent on tubes exposed to pH 7.7 water at 110 and 120 C but the data are not precise

FIGURE 4
CORROSION OF 72-S CLAD PROCESS TUBING FROM OUT-OF-PILE-TESTING

enough to show the film's effect on corrosion at this higher pH.

The tubes were inspected after exposure. No pitting was found in any tubing. However, the surface of the tube experiencing the highest corrosion losses were roughened after exposure. A more complete description of the tubes will be found in Appendix V.

D. Tube Corrosion - In-Pile Tests

Several of the 72-S clad process tubes were new at the beginning of the tests and were removed at the tests' conclusion. These tubes, on removal, were slit longitudinally and inspected. Small sections of the tubes were then obtained and wall thickness and cladding thickness measurements made.

Inspections of the tubes provided some of the most important data obtained from the in-pile testing. From information obtained from laboratory testing of slugs and tubes and in-pile testing of slugs it was rather well established that over-all tube corrosion rates would be reduced by lowering the pH. The main point of interest was whether pitting would occur on the tubing at the lower pH's. This was thought to be particularly possible on the front sections of the tubing where water temperatures are low. Such conditions have been found to be particularly conducive to pitting when the pH of dichromate free water was lowered.⁽²²⁾ Also, the main point of interest in the tests with unfiltered water was whether the turbidity in the water would cause erosion-corrosion.

Inspection reports showed that none of the tubes experienced a severe or extraordinary attack. Pitting of the front tube section was found only on the tube cooled with pH 7.5 unfiltered water. This pitting was limited and not severe. Some pitting was found in the hot rear sections of most of the tubes. However, the severity and extent of the attacks were no higher than is experienced by tubes cooled with pH 7.7 process water under similar conditions. A more detailed account of the inspection

(22) Miller, N.R., HW-30574.

reports is included in Appendix VI.

Table V shows the operating conditions of the tubes removed from the pile for inspection.

TABLE V
OPERATING CONDITIONS OF TUBES REMOVED
FROM PILE FOR INSPECTION

<u>Tube Number</u>	<u>pH</u>	<u>Type of* Water</u>	<u>Dichromate Concentration ppm</u>	<u>Time in Pile Months</u>
2570-D-A	7.3	Filtered	2	2
2570-D-B	7.3	Filtered	0.2	8
3571-D-A	7.3	Filtered	2	5
3571-D-B	7.0	Filtered	0.2	6
	7.0	Filtered	2	3.5
2170-D-A	7.5	Unfiltered	5	5
2170-D-B	7.0	Unfiltered	5	6
2170-D-C	6.6	Filtered	2	3.5
2171-D-A	7.5	Unfiltered	5	3
	7.0	Unfiltered	5	7
	6.2	Filtered	2	3.5

* Where more than one type of water was supplied to a given tube, the first type listed was the first type supplied; the second type listed was the second type supplied, etc.

Wall thickness and cladding thickness measurements were also made. These data showed that no extraordinary over-all corrosion attack occurred. Because of the uncertainty involved in original wall and cladding thicknesses and the short exposure times it was not possible to give a quantitative value to the corrosion rates experienced. However, the data show that it should be safe to operate in-pile tubes for much longer periods of time under the test conditions without likelihood of tube failure. These long term tests will give quantitative data.

E. Carbon Steel Corrosion

As discussed before, lowering the pH of process water reduces the corrosion rates of the aluminum slug jackets and process tubes. However, the literature shows that lowering the pH below 7.5 might have a deleterious effect on the carbon steel portion of the system exposed to hot

water. (23)

To study this, a number of corrosion tests were made with AISI -C1010 carbon steel. The first test was carried out to determine roughly the pH of hydrogen evolution where the corrosion rates are greatly accelerated. The results of this test indicated that with plant process water at 85-90C, hydrogen evolution would begin somewhere in the pH range 6.0-6.2.

It was realized that the hydrogen evolution test was not quantitative so further testing was carried out to determine steel corrosion rates at various pH's and dichromate concentrations. All the tests were carried out at 90C. The tests were run in open systems because it is impractical to pressurize the present pile effluent lines. Thus a test in an open system more nearly approximates plant conditions than would a test in a closed system.

The various testing conditions are tabulated below:

TABLE V
STEEL TESTING CONDITIONS

<u>pH of Water Used in Test</u>	<u>Dichromate Concentration in ppm Employed with Corresponding pH</u>
7.7	0 , 2.0
7.3	0.2
7.0	2.0, 5.0
6.6	0.0, 2.0
6.2	2.0
5.9	2.0

The detailed data from the corrosion tests are presented in Appendix VII. Figures 17, 18, 19, 20, 21, 22, 23, 24, and 25 in the appendix are plots of weight loss due to corrosion plotted against exposure time. Corrosion rates as determined from the slopes of the curves are listed in Table VII. Descriptions of the coupons are also presented in the Appendix.

(23) Uhlig, H. H., "Corrosion Handbook", John Wiley and Sons, N. Y., N. Y., 1948.

Corrosion rates, as determined by weight loss measurements, are plotted against pH in Figure 5. The data indicated three things:

- a. In the presence of 2 ppm of dichromate, corrosion rates were not severe at pH's of 6.6 and higher.
- b. Adding 2 ppm of dichromate to the water reduced corrosion from those experienced with water containing no or 0.2 ppm dichromate.
- c. Increasing the dichromate concentrations from 2 to 5 ppm did not have nearly the effect on corrosion rates as increasing the concentration from 0.2 to 2.0 ppm. In fact, the data are not precise enough to show for sure whether the increase in concentration from 2 ppm to 5 ppm had any effect.

The samples were examined after exposure. All samples were uniformly attacked with two exceptions: The coupons exposed to pH 7.3 water with 0.2 ppm dichromate and pH 6.6 water with 0 ppm dichromate. These coupons were pitted. The pitting on the coupons exposed to the pH 7.3 water with 0.2 ppm dichromate was quite severe and extensive. Whole areas of the coupons were attacked to depths of 15 - 25 mils. The pits on the coupons exposed to dichromate-free water at pH 6.6 were not as deep or as extensive.

The unexpected fact revealed by the tests was the effectiveness of 2 ppm of dichromate in inhibiting corrosion attacks. Dichromate acts to prevent corrosion of steel by forming a film preferentially at anodic areas on the surface and stops or slows further attack.

However, unlike aluminum, steel corrosion rates are cathodically controlled. Thus, decreasing the areas of the anodes (the sites where the metal is attacked) does not much affect the total corrosion occurring unless these anodes are practically completely polarized. Instead, decreasing the anodic areas simply concentrates the corrosion attack

FIGURE 5

CORROSION OF CARBON STEEL AT 90C

causing pitting. Apparently 2 ppm of dichromate were sufficient to lay down the protective layer at all anodic areas. However, apparently, 0.2 ppm at pH 7.3 were not sufficient. This appears to be true because the coupons exposed to this water were pitted more severely than coupons exposed to dichromate free water at either lower or higher pH's.

It should be pointed out that it is a large extrapolation from a test coupon to a pile effluent line. With further testing of low pH water, close attention should be paid to the effluent system. With plant sized piping employing different flows and having different surface area to volume ratios, it is possible that the deleterious effects of low dichromate concentration may not appear.

VI. FILM FORMATION

One of the important variables to be considered in developing a change in process water is the effect of the change on the deposition of film on slug and tube flow surfaces. This deposition film is composed primarily of hydrated iron oxides and may become thick enough to have significant effects on the hydraulic characteristics of the loaded process tubes.

A correlation has been made which enables one to relate effective film thicknesses on the slugs and tubes with coolant flow rate, pressure drop across the tube and inlet and outlet water temperatures.⁽²⁴⁾ By effective film thickness is meant the thickness of film which, if evenly deposited on tube and slug surfaces throughout the length of the tube, would produce the same hydraulic effect as does the deposition of the actual film. The actual film thickness no doubt varies along the length of the tube and is thicker on slugs than on tubes.

Previous experience indicated that lowering the pH of process water would increase the tendency for film formation.⁽²⁵⁾ Also, it seemed

(24) Miller, N.R. and Woods, W.C.A., "A Method for Precise Measurement of Pile Film Formation," HW-28304, November 19, 1953.

(25) Miller, N.R., HW-30574.

possible that unfiltered water containing high iron concentration might also cause film formation.

Experience from this test showed that essentially no film formation occurred with unfiltered water at pH 7.5 or 7.0. Apparently the turbidity in the water sufficed continually to purge the slugs and tube during all periods.

Film formation occurred with filtered water at pH 7.3 and 7.0 part of the time. However there were periods when those waters did not cause film formation. pH 6.6 and 6.2 water caused heavier filming, with pH 6.2 water being worse than pH 6.6.

Operating experience has shown that film formation with pH 7.3 water produced on a plant scale can be controlled.⁽²⁶⁾ This is done by keeping turbidity low and by adding lime in dosages of about 0.5 ppm. The role of lime is discussed elsewhere.⁽²⁷⁾

In this test it was not possible to control the water quality to prevent filming. The water used in the test was regular filtered water produced by the 100-D Area filter plant. This water is produced to prevent film formation in regular pile tubes. It was not feasible to produce water of high enough quality or add additional chemical to prevent filming in a few special tubes when this film could be controlled by purging the individual tubes.

Thus, while film formation rates were prohibitive in the two tubes cooled with pH 6.6 water and the one tube cooled with pH 6.2 water, a plant scale test may be required to determine if the use of water at these pH's is feasible for pile cooling.

Film formation rates with the various water are shown plotted in Figure 26, Appendix VIII. Because of the film formation it was necessary to purge the special tubes to remove film. Purges were carried out when

(26) Miller, N.R., HW-34530 .

(27) Miller, N.R., HW-34530.

film formation had occurred to the extent that coolant flow rates dropped resulting in overly high outlet water temperatures or when the tube inlet pressure or venturi throat pressure increased to the degree that the "high" trip which scrams the pile was neared. The high pressure trip is so set that the pile will be shut down before flow can be sufficiently decreased in the tube to the point that unstable boiling might occur.

Between January 8, 1955, and March 6, 1955, a period of 57 days, it was necessary to purge the tube supplied with pH 7.0 water 13 times, the tubes supplied with pH 6.6 water 15 times and the tube supplied with pH 6.2 water 20 times. In contrast, during the eleven months unfiltered water was supplied to two tubes, no purges were required.

VII. BOILER SCALE FORMATION

If pH 7.7 filtered water is heated to some temperature a precipitate of calcium carbonate is obtained. The precipitation temperature at pH 7.7 has variously been reported as between 135 - 150 and at 135C. (28, 29) The later temperature is believed reliable. The reactions of interest from the standpoint of precipitation of carbonates are listed below:

(28) Goldsmith, S., "Laboratory Studies of 2-S Aluminum Corrosion at Elevated Temperatures," HW-24584, May 27, 1952.

(29) Wilson, C.D., "Flow Laboratory Comparison of pH 7.3 and pH 7.65 Process Waters". HW-33873, April 14, 1955.

When the water is heated, the bicarbonate-carbonate equilibrium is shifted to the right and carbonate precipitation occurs despite the fact that at higher temperatures the water further dissociates forming more H^+ , and tends to force the reaction to the bicarbonate side. From the reactions involved, it appears that at higher pressures carbon dioxide would be kept in solution better thus favoring carbonate formation. However in one experiment, this effect was not found. ⁽³⁰⁾

It is obvious from the law of mass action that reducing the pH should reduce the tendency for precipitation. To test this hypothesis, pH 7.3 water was supplied to a testing apparatus operated by C.D. Wilson of the Pile Coolant Studies Unit. Wilson found that with pH 7.3 water carbonate boiler scale formed at 145 C. ⁽³¹⁾

As discussed previously, out-of-pile corrosion tests were carried out at 150 C with pH 7.0, 6.6 and 6.2 water. No scale formation was found at any of these pH's.

To study further the effect, a special boiler scale study was conducted with pH 6.5 water. In the test, the water was preheated in a carbon steel heat exchanger and passed through a mock-up process tube charged with dummy slugs. In the first step, the apparatus was operated one week with the water preheated to 160 C. After the period of operation, the apparatus was shut down, the dummy slugs discharged and the slugs and tubes inspected for signs of scale deposition. This step was repeated at temperatures of 170 C and 190 C.

No sign of carbonate scaling was noted at any temperature, on slugs or tubes. Further, no decrease in the heat transfer coefficient in the heat exchanger was noted. Thus it is concluded that at pH 6.5, no carbonate scaling occurred at temperatures up to 190 C. The results show, then, the importance of pH in carbonate scale formation.

(30) Wilson, C.D., HW-33873.

(31) Wilson, C.D., HW-33873.

Though carbonate deposition did not occur at temperatures up to 190 C, another type of filming did occur at 190 C with pH 6.5 water. This film was found to contain calcium and magnesium as major constituents. It is not known whether or not this type film or scale could be prevented in practice or if it could be easily removed. It is thought probable that the film was composed of calcium and magnesium sulfates and hence might be prevented by the total or partial use of an acid other than sulfuric for pH control or the use of a pH higher than 6.5 .

The tests definitely show that temperatures of at least 170 C are possible without scale formation. In practice, maximum slug surface temperature may exceed outlet water temperatures by 5-15C. Thus, from a scale forming standpoint alone, it should be possible to operate at tube outlet temperature of at least 155 C.

VIII. ACID REQUIREMENTS

In designing acid addition facilities for reducing the pH to 7.0 or lower, it is important to know acid requirements. Also, the additional chemical costs required to obtain the lower pH's will be needed to determine the optimum decrease in pH. For this reason a titration of Columbia River water was carried out.⁽³²⁾ This titration is shown in Figure 6, where the amount of 93% sulfuric acid added in ppm is plotted versus pH.

In the treatment process, alum is added to coagulate the water in concentrations of 4-12 ppm. It has been noted that two ppm of alum have about the same acidic effect as one ppm of sulfuric acid.⁽³³⁾

IX. EFFLUENT ACTIVITY

The effluent water from the Hanford Piles is returned to the Columbia River after only a short retention period. Thus, a study of the effects of a change in a water treatment process on effluent activity must be made.

(32) Sharpelos, J.M. and Perey, R.E., Private Communication.

(33) Miller, N.R., HW-34530.

FIGURE 6

TITRATION OF COLUMBIA RIVER WATER

The main difficulty, from an effluent activity standpoint, foreseen in the adoption of low pH water was that the concentration of P^{32} in the return water might be markedly increased. This increase might come from the (n, p) reaction on sulfur.

Data obtained from the tubes cooled with pH 6.2 and 6.6 water showed that the P^{32} concentration was not increased over that experienced with pH 7.7 process water.⁽³⁴⁾ The fact that the tubes were frequently purged during the sampling period may cloud the results. The activity might be expected to decrease after a purge.⁽³⁴⁾

Data also were obtained from radiochemical analyses of the effluent from the tubes supplied with unfiltered water. These data⁽³⁵⁾ showed that unfiltered water activities were significantly higher than those obtained with filtered water. Gross beta and P^{32} activities were five times higher and the Mn^{56} activity was eight times higher than is experienced with filtered water.

These effects are quite serious. However, the complete interpretation of these results lies outside the scope of this report and is left to those who are expert in the field of biological effects of radioactive materials in river water.

X . CONCLUSIONS

From the data, it is possible to draw the following conclusions:

1. In out-of-pile tests with aluminum dummy slugs exposed to water at 120 C, corrosion rates were reduced from 0.60 mils/month to approximately zero as the pH was lowered from 7.7 to 6.2.

2. Out-of-pile tests at 120 C with pH 7.3 water showed that changing the concentration of dichromate in the water from 2 to 0.2 ppm had no significant effect on either over-all or localized corrosion attacks on dummy slugs.

(34) Matsumoto, W.Y., Private Communication.

(35) Etheridge, E.L., "Feasibility Study of a Full Pile Test Using Unfiltered Cooling Water", HW-34096, 2-24-55.

3. In out-of-pile tests with dummy slugs exposed to water at 150 C, over-all corrosion rates were reduced from 0.70 to 0.30 mils per month as the pH was lowered from 6.6 to 6.2. Slugs exposed to 150 C water at pH 7.0 initially experienced a corrosion attack of 5.4 mils/month. After a short period of time, about 10 days, a heavy adherent layer of alpha aluminum monohydrate appeared on the slugs and the rate was reduced to 0.42 mils/month.

4. Localized attacks on the dummy slugs at 120 C and 150 C were generally associated with weaknesses or damages in the autoclave film, often at rib marks. In general the severity of local attack was proportional to over-all corrosion weight losses. The heavy corrosion product film on the slugs exposed to pH 7.0 water at 150 C protected these slugs from local attacks.

5. Results from in-pile testing indicated that slug jacket corrosion rates may be reduced a factor of four by lowering filtered water pH from 7.7 to 7.0 and by a factor of 15-20 by lowering pH from 7.7 to 6.2.

6. No relation could be found between pH and localized attack on the slugs tested in-pile with filtered water. This may be due to the fact that inspection of irradiated slugs can yield only semi-quantitative data.

7. No significant differences could be found in the in-pile corrosion behavior of slugs cooled with filtered water containing 0.2 and 2 ppm of dichromate at a pH of 7.3 and 7.0.

8. The use of unfiltered instead of filtered water probably increases the over-all corrosion of slugs by as much as a factor of three at a given pH.

9. Turbidities as high as 100 ppm in unfiltered water containing 5 ppm of dichromate did not cause an erosion attack on the slug jacket.

10. No film formation occurred in tubes cooled with unfiltered water.

11. Out-of-pile tests with filtered water at 120 C showed that over-all tube corrosion attacks were reduced from 3.5 mils/month to

about 0.9 mils/month as the pH was lowered from 7.7 to 6.2. Rates obtained with filtered water at 150 C were 2.0 mils/month at pH 7.0, 2.4 mils/month at pH 6.6 and 1.7 mils/month at pH 6.2. A heavy adherent oxide film, similar to that described on slugs exposed to pH 7.0 water at 150 C, was found on tubes exposed to pH 7.0 water at 150 C, and to pH 7.7 water at 110 and 125 C.

12. No pitting was noted on any of the tubes exposed out-of-pile to 120 or 150 C water. The surfaces of the tube experiencing the highest corrosion rates were roughened after exposure.

13. Examination of the tubes used in the in-pile tests showed that no pitting occurred on the front sections of tubes cooled with filtered water at pH's of 6.2, 6.6, 7.0, or 7.3. This includes tubes supplied with pH 7.0 and 7.3 water containing 0.2 ppm dichromate. The hot, rear sections of the tubes experienced localized attack at the above pH's to a degree comparable to that experienced with pH 7.7 water.

14. The in-pile tubes supplied with unfiltered water showed no evidences of erosion-corrosion even at places where slugs had been cocked. At cocked slug areas, local water velocities are increased thus increasing the likelihood of erosion. A minor front tube section pitting attack was noted on tubes supplied with raw water. Localized attacks on the tube in the rear hot sections were no more severe than that encountered with filtered water.

15. No important differences in the over-all corrosion rates of mild carbon steel samples exposed to filtered water containing 2 ppm of dichromate at 90 C were noted at pH's from 7.7 to 6.6. Rates at pH 6.2 were significantly higher than at higher pH's. Samples in dichromate-free water at pH 7.7 were corroded at a higher rate than samples in water containing 2 ppm of dichromate. Samples exposed to pH 7.3 with 0.2 ppm of dichromate experienced a rapid over-all rate of attack and a severe localized attack.

16. The addition of sufficient sulfuric acid to obtain pH's as low as 6.2 did not show, from the results of preliminary tests, an increase in the concentration of P^{32} in the effluent water.

17. The use of unfiltered water caused a marked increase in effluent activities.

XI. UTILIZATION OF TEST RESULTS

These tests were intended to be a first step in the improvement of pile cooling water from the standpoint of a corrosion, boiler scale formation and cost. It was expected that favorable results would be followed up by further laboratory and plant scale testing.

Such further testing is in progress. As has been mentioned previously, the reduction of the pH of process water to 7.3 has been evaluated on a plant scale and has been adopted for all reactors.⁽³⁶⁾ Further, a half plant test is now in progress to evaluate the use of pH 7.0 water.⁽³⁷⁾

The evaluation of lowering dichromate concentrations in process water is being approached more cautiously. The potential gains are limited and the potential hazards involved, if say pitting were initiated, are large. There are plans, however, to evaluate the use of pH 7.3 filtered water containing 0.5 ppm of dichromate.⁽³⁸⁾

An evaluation has been made on the desirability of immediately testing unfiltered water on a plant scale. The study showed that there are limited economic gains for converting present plants to the use of unfiltered water if 5 ppm of dichromate addition are required. Further, the

(36) Miller, N. R., HW-34530.

(37) Richman, R. B., "Production Test No. 105-554-E, Evaluation of 7.0 Process Water," HW-36481, April 19, 1955.

(38) de Halas, D. R., Private Communication.

(39) Etheridge, E. L., HW-34096.

effluent activity problem may prove to be a serious barrier. (39)

Plans have been made to study further the effects of using unfiltered water. It is planned to determine if 2 ppm of dichromate will inhibit erosion-corrosion as did the addition of 5 ppm. Plans also include a plant scale test with unfiltered water early in 1956. (40)

N. R. Miller

NRM:dt

(40) Richman, R. B., "Raw Water Test Program," HW-38012, 7-13-55.

APPENDIX I
REVIEW OF PREVIOUS TESTING

A. pH Studies

Until May 1955, water treatment specifications required that the pH of the process water supplied to the reactors be maintained in the range 7.5 - 7.8. This specification was based on a recommendation by the CMX group, who carried out early studies on water quality at Hanford. ⁽⁴¹⁾ The CMX group realized that the pH range 7.5 - 7.8 was not optimum from the standpoint of minimizing over-all rates of aluminum corrosion. Results from both CMX tests with actual Columbia River Water and tests previously carried out at Clinton Laboratories with simulated Columbia River water ⁽⁴²⁾ indicated that over-all aluminum corrosion rates would be minimized in the pH range 6.0 - 7.0. The range 7.5 - 7.8 was selected because it was decided to add dichromate to the water to inhibit localized attacks such as pitting, erosion-corrosion, and galvanic corrosion. It was feared that the dichromate might be reduced to trivalent chromium at pH's lower than 7.5. This reduction, it was postulated, might be caused by the hydrogen peroxide which is formed from the action of the pile fluxes. By keeping the pH at 7.5 or higher it was believed that the peroxide would not act as a reducing agent and the Cr^{+3} formation would not occur. Concern was shown over the possibility of the Cr^{+3} formation because the CMX group had shown that Cr^{+3} would deposit on slug and tube surfaces to form a tenacious pressure-drop film. ⁽⁴³⁾

Early in 1952 it appeared that dichromate addition could be eliminated. ⁽⁴⁴⁾ Thus, the question of optimum process water pH was reopened. pH tests were carried out using the facilities of the 105-D Flow Laboratory with plant process water treated with two different coagulants.

(41) Kidder, C. P. HW-7-4444.

(42) Draley, J. E., CT-3027.

(43) Kidder, C. P., HW-7-4444.

(44) Purcell, R. H., "Final Report 105-453-P, Sodium Dichromate Elimination Tests," HW-24009, 4-10-52.

The first tests were carried out with the out-of-pile facilities of the 105-D Flow Laboratory using dichromate-free, ferric sulfate coagulated water. Results showed that over-all aluminum corrosion rates were reduced by about a factor of ten as the pH was reduced in the range 7.7 - 6.2. However pitting attacks became increasingly severe at the lower pH's and it was concluded that the process water pH should not be changed.⁽⁴⁵⁾

At the conclusion of the first tests, the use of aluminum sulfate to coagulate plant process water was being considered. Early results had shown that water coagulated with aluminum sulfate exhibited significantly different properties than did water coagulated with ferric sulfate. The use of alum resulted in a sizeable reduction of the rate of pressure-drop film deposition⁽⁴⁶⁾ and apparently in a significant decrease in slug jacket corrosion rates.⁽⁴⁷⁾ Therefore it was decided to run tests to determine the aluminum pitting tendencies in low pH, dichromate-free alum treated water.

These tests were carried out using the out-of-pile and the newly available in-pile facilities of the 105-D Flow Laboratory. Results from these tests closely paralleled results obtained with the ferric sulfate coagulated water. Over-all corrosion rates were reduced as much as a factor of ten as the pH was lowered from 7.7 to 7.0. However, pitting of aluminum in cold water became very severe at the lower pH's. Thus the possibility of using low pH non-inhibited process water as a pile coolant was concluded to be nil.⁽⁴⁸⁾ Later, operating experience showed that the use of uninhibited water at pH 7.5 - 7.8 also led to severe localized attacks,^(49, 50) so dichromate addition was reinstituted.

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- (45) Atwood, J. M., "Process Water pH Effects," HW-24007, 5-15-52.
 - (46) Woods, W. C. A., "Final Report, PT No. 105-470-P, The Use of Commercial Aluminum Sulfate For 100 Area's Process Water Coagulation," HW-23163, January, 1952.
 - (47) Woods, W. C. A., HW-28011.
 - (48) Miller, N. R., HW-30574.
 - (49) Wilson, C. D., HW-28027.
 - (50) Lutton, J. M., HW-27158.

The development of a less corrosive water now depended on whether or not the formation of the trivalent chromium films did occur at lower pH's. The results of a test conducted in the spring of 1953 showed that the trivalent chromium definitely did not prove troublesome at pH's of 7.2 and higher.⁽⁵¹⁾ This finding opened up the field of pH testing once again.

The next logical step was to run a series of tests with inhibited, low pH water. This goal had to be compromised because of the need for obtaining data for the design of the water plants for two new reactors. For several reasons, it was undesirable to provide facilities for adding lime to the water for pH control at these new plants. The next tests at the 105-D Flow Laboratory, therefore, were designed to determine the feasibility of using caustic soda instead of lime for pH control and the feasibility of using no pH control, letting the pH "float" at the coagulation value. Without the addition of base, the pH of the water was obviously lower than otherwise. Unfortunately, the reduction in pH was small and no sizeable reductions in corrosion rates were evident from the test results. The data were promising enough, however, to test the elimination of base addition on a half-plant scale.⁽⁵²⁾ This half-plant test was initiated in the fall of 1953 at 100-F Area.

When the 105-D Laboratory facilities were freed from the lime-elimination testing, a new series of pH tests was started under the terms of this production test. The first tests utilized pH 7.3 water containing 2 ppm of sodium dichromate. The selection of the pH of 7.3 for testing was a compromise. It was known that this pH would not be optimum from the standpoint of reducing over-all aluminum corrosion rates. However, it was believed that film formation would become increasingly severe as the pH was lowered. Also it was known that the tendency towards pitting would increase as the pH was lowered. Inasmuch as the goal of the testing was to obtain data to provide the basis for a half-pile test, it seemed

(51) Miller, N.R., HW-30574.

(52) Miller, N.R., "Final Report Production Test No. 105-509-E, The Effects of Low pH Alum Water on Pile Operation," HW-32603, 7-30-54.

reasonable to select a water which probably would reduce corrosion rates without giving other ill effect even if the condition still were not optimum.

These pH 7.3 tests with water containing 2.0 ppm of dichromate were started in December, 1953. By April 1954, sufficient data were available to justify the reduction of the pH of water cooling half of a reactor to 7.3. This was done by writing a supplement modifying the plant-scale base-elimination test. ⁽⁵³⁾

The next step in pH testing was taken late in May, 1954, when water containing 0.2 ppm of dichromate at a pH of 7.0 was utilized to cool one charge of slugs in the 100-D pile with the facilities of the 105-D Flow Laboratory.

The final step taken at 100-D was made in November, 1954, when a series of tests to study the use of pH 7.0, 6.6 and 6.2 water for pile cooling. By this time, the data from the half-pile test were available in quantity to show that the use of pH 7.3 water at all piles was a very promising. ⁽⁵⁴⁾ In May, 1955, the process specification was formally changed to provide for the use of pH 7.3 water at all areas.

B. Reduction of The Amount of Dichromate Added to Process Water

As mentioned in the previous paragraphs, it was originally decided to add 2.0 ppm of sodium dichromate to the process water to inhibit localized corrosion attacks. When the water treatment process was reviewed early in 1951, the wisdom of this addition was not apparent. There were some thoughts that the addition of 2.0 ppm of dichromate not only might not be inhibiting localized attacks but actually might be promoting them. The dichromate acts to polarize anodic areas. If sufficient dichromate were added merely to polarize part of the anodes, and if the corrosion reaction were cathodically controlled, then the corrosion currents would be concentrated at the remaining anodic areas with a

(53) Miller, N.R., "Supplement A, Production Test No. 105-526-E, The Elimination of Lime As A Process Water Additive," HW-30487, 1-12-54.

(54) Miller, N.R., "An Evaluation of the Use of Sulfuric Acid in the 100 Areas, Water Treatment Process," HW-33142, 9-22-54.

subsequent high rate, localized attack or pit. On the basis of this line of reasoning, ferric sulfate coagulated dichromate-free water was supplied to two tubes in 100-H Pile. The data from this test showed a definite reduction in over-all slug jacket corrosion rates without an accompanying increased pitting attack. Examination of the tube used in the test showed no deleterious effects.⁽⁵⁵⁾ On the basis of this, dichromate addition at all areas was halted early in 1952.

Subsequent experience, especially at the areas which had adopted alum coagulation, showed that the cessation of dichromate addition was followed by erosion-corrosion attacks on slugs and tubes, pitting of process tubes, and galvanic corrosion attacks on aluminum components coupled to stainless steel.⁽⁵⁶⁾ By spring 1953, it became apparent that the difficulties would probably be alleviated by resuming dichromate addition. With the resumption of dichromate addition, the localized corrosion attacks disappeared. The reasons for the H-test not predicting the detrimental effects of dichromate elimination are discussed elsewhere.⁽⁵⁷⁾

Inasmuch as experience showed that 2.0 ppm of dichromate actually were sufficient to inhibit localized corrosion attacks, the logical question arose: "Would less than 2.0 ppm of dichromate suffice?"

Studies showed that dichromate concentration as low as 0.1 ppm were effective in stopping pitting in the cold front tube sections.⁽⁵⁸⁾ Other studies showed that, at pH 7.7, dichromate concentration in the range 0.2 to 2.0 ppm had no effect on over-all aluminum corrosion rates at temperatures up to 120 C. Further, even 0.2 ppm of dichromate inhibited erosion-corrosion attacks.⁽⁵⁹⁾

(55) Purcell, R. H., HW-24009.

(56) Wilson, C. D., HW-28027.

(57) de Halas, D. R., and Miller, N. R., HW-30952.

(58) de Halas, D. R., "Final Report, Effects of Various Small Dichromate Concentrations on Front Process Tube Corrosion," HW-30884, 2-18-54.

(59) de Halas, D. R., and Miller, N. R., HW-30952.

In addition to the out-of-pile tests, the facilities of the 105-D Flow Laboratory were used to cool two charges of slugs in D-Pile with pH 7.7 water containing 0.2 ppm of dichromate. The results of this test indicated that 0.2 ppm of dichromate were as effective as 2.0 ppm.⁽⁶⁰⁾ On the basis of the above, a test authorizing the reduction of dichromate in the water cooling half of a pile to 0.5 ppm was authorized and initiated.

In this present test, dichromate concentrations of 0.2 ppm have been studied at pH's of 7.3 and 7.0.

C. Unfiltered Water Studies

During the period of original development work relatively little emphasis was put on work with unfiltered water. The incentive was to develop a water treatment process in the shortest period of time which would work; not necessarily to develop the least costly system. In fact, little thought was directed on the feasibility of using unfiltered water as a pile coolant until early in 1953. Early tests with unfiltered water in the absence of dichromate inhibitor had shown that excessive erosion-corrosion attack occurred. Mock-up process tubes used in the tests failed in as little as two weeks time. However, when the value of dichromate as an inhibitor of erosion-corrosion became so apparent in early 1953, the possibility of using unfiltered water was reopened. A survey document showed that under certain conditions, there was economic incentive in shutting down the filter plants if no deleterious effects occurred in the process.⁽⁶¹⁾ Further, if an additional plutonium producing pile without power recovery were to be built, significant savings in capital costs could be expected by elimination of the filter plant.⁽⁶²⁾ Because of these incentives, a program for unfiltered water testing was initiated.⁽⁶³⁾

(60) Miller, N. R., HW-32603.

(61) Lutton, J. M., and Woods, W. C. A., "Columbia River Water as a Pile Coolant," HW-28467, 6-23-53.

(62) Jaske, R. T. "Single Purpose Replacement Reactor Plant For Plutonium Production," HW-30175, 12-2-53.

(63) Atwood, J. M., "A Program For Testing Raw Columbia River Water as a Pile Coolant," HW-28778, 7-21-53.

Preliminary tests were made with the out-of-pile equipment of the 105-D Flow Laboratory. The results of these tests showed that river water with the addition of 5 ppm of dichromate and sufficient sulfuric acid to obtain a pH of 7.5 showed sufficient promise to warrant further study.⁽⁶⁴⁾ This further study was made with the in-pile facilities of the 105-D Flow Laboratory under the terms of this production test.

(64) Etheridge, E. L., "Preliminary Test Results of Unfiltered River Water as a Pile Coolant," HW-32664, 8-4-54.

APPENDIX II
CLEANING METHODS

A. Oxalic Acid Cleaning of Slugs and Tubes

This treatment was used to remove the amorphous iron oxide and corrosion product film from slugs and tubes.

A 10% solution of oxalic acid was prepared and heated to about 85 C. The slugs were totally immersed for about five minutes depending upon the tenacity of the film.

B. Electrolytic Cleaning of Slugs and Tubes

This method was used to clean the heavy alpha aluminum oxide monohydrate from the samples. Runs with "blank" slugs showed that very little metal was lost in the process as compared to the total corrosion loss.

A saturated boric acid solution in distilled water was prepared. The slug to be cleaned was made anodic, immersed in the solution, and about 250 volts D.C. were applied.

For slugs where the film was particularly tenacious, sufficient chromium oxide was added to obtain a direct current of 5 - 10 amperes.

As the process was continued for a number of samples, the temperature of the solution was allowed to increase from the ambient to about 85 C.

An interlock was provided to prevent the application of the voltage unless the electrode holder was seated on the vessel containing the solution. This step was taken to prevent electrocution of the operator.

C. Electrolytic Cleaning of Steel Samples

The method used for cleaning the steel samples was similar to that outlined in Uhlig's "Corrosion Handbook."

A five per cent solution of sulfuric acid was prepared and 2 ml of

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Rodine (an organic inhibitor) per liter of solution added. The solution was then heated to 75 C.

The sample was made the cathodic to a steel anode and a direct current of 1.0 ampere/sq in. of sample applied.

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APPENDIX III

DATA ON DUMMY SLUGS USED FOR OUT-OF-PILE TESTING

A. Graphical Data on Weight Measurements

Plotted in Figures 7 and 8 are weight loss versus time data on the out-of-pile corrosion of dummy slugs in 120 C water. Figure 9 is a similar plot of data obtained with 150 C water.

Figure 10 is a plot of film weights removed from slugs exposed to pH 7.0 water at 150 C. The weight of film removed in oxalic presumably is iron oxide or soluble, amorphous aluminum oxide. The differences between the total weights removed and the weights removed with oxalic acid represents the weights of the crystalline alpha aluminum oxide monohydrate. No certain explanation is available for the large amount of film removed from the 40 and 53 day slugs by oxalic acid.

B. Inspection Data

The slugs used for the out-of-pile testing were inspected after cleaning. These inspections are summarized as follows:

1. pH 7.7 filtered Water With 2 ppm Dichromate at 120 C

<u>Time of Exposure Days</u>	<u>Inspection</u>
7	Light ledging* at rib marks.
21	Surface was dark gray after cleaning. Ledging more severe than after 7 days. Jacket of one slug shiny around weld bead indicating preferential corrosion.
28	Ledging more severe. Attack found on jacket near weld bead.
35	Severe ledge attack.
44	These slugs were less severely ledged than those exposed 28 days. A ring of pits were found around the jacket associated with the

* By ledging is meant a localized attack in which a whole area corrodes uniformly leaving a "ledge" between the attacked and unattacked areas.

Exposure Time-Days

FIGURE 7

CORROSION OF 2-S ALUMINUM SLUG JACKETS AT
 120C AND pH 7.3 - 7.7 (OUT-OF-PILE-TESTS)

FIGURE 8
CORROSION OF 2-S ALUMINUM SLUG JACKETS AT
120C AND pH 6.2 - 7.0 (OUT - OF - PILE - TESTS)

FIGURE 9

CORROSION OF 2-S ALUMINUM SLUG JACKETS AT 150C AND pH 6.2 - 7.0
(Out-of-Pile Tests)

FIGURE 10
FILM WEIGHT ON SLUGS EXPOSED TO pH 7.0 WATER AT 150C
(Out of File Test)

62

end of the cap inside jacket.

Very severely ledged and attacked near weld bead. Maximum depth of ledge attack estimated to be about 7 mil. Can corroded 4-8 mils below weld bead.

Summary

The slugs exposed to this type water experienced ledge type attack at areas associated with damages to the autoclave film and local attack at weld beads. As time progressed, the ledging became more extensive and penetrated about 7 mils into the jacket wall.

2. pH 7.3 water with 2 ppm Dichromate at 120 C

Time of Exposure Days

Inspection

7	Light ledging. Unaffected areas newer looking than unaffected areas on slugs exposed to pH 7.7 filtered water for 7 days.
28	Looks good. Are in much better condition than exposed to pH 7.7 water for 28 days.
35	Ledging more extensive than after 28 days. Much better looking than those exposed to pH 7.7 water 28 days.
42	Similar in appearance to those exposed 35 days.
49	Ledging more extensive than that noted after 42 days.
56	Similar to slugs exposed for 49 days. Maximum depth of attack about 7 - 10 mils.

Summary

These slugs experienced a ledging attack associated mainly with rib marks. The depth of the ledging compared with that experienced by slugs exposed to pH 7.7, filtered with 2 ppm dichromate at 120 C but was not nearly so extensive. The local attack at the weld bead was not found on these slugs.

3. pH 7.3 Filtered Water with 0.2 ppm Dichromate at 120 C

Summary

These slugs were attacked similar to those exposed to pH 7.3 water with 2 ppm dichromate. Ledging was found associated with rib marks and no local attack was experienced next to weld bead.

4. pH 7.0 Unfiltered Water with 5 ppm Dichromate at 120 C

Exposure Time Days

Inspection

7

Some scratches at rib marks. Definitely better appearing than slugs exposed to pH 7.7 water 7 days.

24

Some ledging. More shallow than experienced with 7.7 or 7.3 water with 2 ppm dichromate for 21 days. Unaffected surfaces look new. Shallow pits on jacket associated with end cap.

Summary

These slugs were lightly ledged. Unaffected areas appeared new.

5. pH 7.0 Filtered Water with 2 ppm Dichromate at 120 C

Time of Exposure Days

Inspection

4

Shallow corrosion at rib scratches.

10

Similar to 4 days slugs. Scratches perhaps 2 mils deep.

34

Corrosion at scratches less than 4 mils deep.

53

Corrosion at scratches.

Summary

These slugs were in excellent condition after 53 days. Some corrosion was evident at scratches associated at rib marks. With slugs in pH 7.3 and 7.7 water at 120 C this corrosion widened out, but at 7.0 was confirmed to original scratches. The depth of the scratches estimated to be 2-4 mils.

6. pH 6.6 Filtered Water with 2 ppm Dichromate at 120 C

Exposure Time Days

Inspection

4	Look good. Very little corrosion at scratches.
10	Slugs look almost new. Very few "corrosion" scratches. Depth less than 2 mils.
34	Few light corrosion scratches. A ring of very shallow pits around slug at place associated with end of end cap inside jacket.
52	Slugs in excellent condition. Better looking than slugs exposed to pH 7.0 water at 120 C for 52 days.

7. pH 7.0 Filtered Water with 2 ppm Dichromate at 150 C

Time of Exposure Days

Inspection

4	After cleaning, surface of slug was dark gray. There was no local attack.
10	Surface was silvery gray after cleaning. No local attack.
34	No local attack. On one slug, the can had corroded way around a rib mark leaving a ridge.
52	One slug experienced ledge attack. This was the only slug in this type water which showed this attack.

Summary

After the heavy crystalline film was stripped from the slugs, the surfaces were found to be quite smooth and unattacked. Of interest was the fact that on some slugs there were ridges associated with rib marks; the can had uniformly corroded around the area touching the rib.

8. pH 6.6 Filtered Water with 2 ppm Dichromate at 150 C

<u>Time of Exposure Days</u>	<u>Inspection</u>
4	Superficial local attack at weld bead.
10	Shallow ledging at rib marks.
34	Ledging deeper than after 10 days.
52	Ledging progressing to depth of about 5 - 10 mils.

Summary

These slugs experienced a local attack somewhat worse than the slugs exposed to pH 7.0 water at 150 C. The depth of attack was about that experienced by slugs exposed to pH 7.0 water at 120 C; but the attack was limited to smaller area.

9. pH 6.2 Filtered Water with 2 ppm Dichromate at 120 and 150 C

The slugs at 120 C were virtually unattacked. The slugs at 150 C had shallow corrosion scratches. It should be noted that the pH 6.2 tests continued for only 21 days.

APPENDIX IV
DATA ON SLUGS USED FOR IN-PILE TESTING

In the first part of the appendix are listed tube operating conditions, slug powers, temperatures and corrosion rates. The second part of the appendix summarizes inspection data.

Tube Number. 2570-D-1
Time of Operation, Days 57
Average Tube Power, KW. 480
Average Tube Outlet Temperature, C. 81
Average Tube Inlet Temperature, C. 8
Average Coolant Flow Rate, GPM. 25
pH. 7.3
Dichromate Concentration, ppm 2
Type of Water Filtered

<u>Slug Number</u> <u>From Rear</u>	<u>Surface</u> <u>Temperature, C</u>	<u>Slug Power</u> <u>KW/8⁰⁰ Slug</u>	<u>Corrosion</u> <u>Rate, Mils/Month</u>
1	86	4	0.10
3	86	7	0.13
5	85	9	0.15
7	85	10	0.21
9	84	12	0.18
11	83	14	0.20
13	83	15	0.64
15	81	16	0.17

Tube Number 3472-D-1
 Time of Operation, Days 109
 Average Tube Power, KW 540
 Average Tube Outlet Temperature, C 88
 Average Tube Inlet Temperature, C 8
 Average Coolant Flow Rate, GPM 26
 pH 7.3
 Dichromate Concentration, ppm. 2
 Type of Water Filtered

<u>Slug Number</u> <u>From Rear</u>	<u>Surface</u> <u>Temperature, C</u>	<u>Slug Power</u> <u>KW/8⁰⁰ Slug</u>	<u>Corrosion</u> <u>Rate, Mils/Month</u>
1	92	7	0.18
3	92	9	0.24
5	92	10	0.32
7	90	11	0.42
9	89	13	0.43
11	88	14	0.56
13	87	15	0.63
15	87	17	0.64
17	85	19	0.58
19	83	20	0.52
21	82	22	0.54
23	79	23	0.41
25	78	24	0.37
27	75	25	0.28
29	72	26	0.28
31	70	27	0.23

Tube Number 3571-D-1
 Time of Operation, Days 135
 Average Tube Power, KW 560
 Average Tube Outlet Temperature, C 88
 Average Tube Inlet Temperature, C 8
 Average Coolant Flow Rate, GPM 27
 pH 7.3
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	90	3	0.16
3	92	6	0.28
5	92	10	0.38
7	91	12	0.48
9	91	14	0.66
11	90	16	0.85
13	89	18	0.86
15	88	20	0.70
17	86	22	0.69
19	84	23	0.70
21	82	24	0.61
23	79	25	0.50
25	77	36	0.37
27	74	26	0.46
29	71	26	0.30

Tube Number 2570-D-2
Time of Operation, Days 203
Average Tube Power, KW 495
Average Tube Outlet Temperature C 82
Average Tube Inlet Temperature, C 13
Average Coolant Flow Rate, GPM 27
pH 7.3
Dichromate Concentration, ppm 0.2
Type of Water Filtered

<u>Slug Number From Rear</u>	<u>Surface Temperature, C</u>	<u>Slug Power KW/8" Slug</u>	<u>Corrosion Rate, Mils/Month</u>
1	88	9	0.34
3	87	11	0.31
5	86	12	0.38
7	85	13	0.46
9	85	15	0.45
11	83	16	0.51
13	82	17	0.57
15	81	19	0.58
17	79	20	0.29
19	77	21	0.38
21	75	21	0.24
23	73	21	0.35

Tube Number 3472-D-2
 Time of Operation, Days 188
 Average Tube Power, KW 490
 Average Tube Outlet Temperature, C 88
 Average Tube Inlet Temperature, C 14
 Average Coolant Flow Rate, GPM. 25
 pH 7.3
 Dichromate Concentration, ppm 0.2
 Type of Water Filtered

<u>Slug Number</u> <u>From Rear</u>	<u>Surface</u> <u>Temperature, C</u>	<u>Slug Power</u> <u>KW/8" Slug</u>	<u>Corrosion</u> <u>Rate, Mils/Month</u>
1	91	6	0.23
3	92	8	0.27
5	90	8	0.36
7	90	10	0.45
9	90	12	0.53
11	89	14	0.53
13	90	18	0.52
15	87	18	0.51
21	81	22	0.42
23	80	22	0.32
25	77	22	0.30
27	74	22	0.21
29	71	22	0.18

Tube Number 3571-D-2
 Time of Operation, Days 158
 Average Tube Power, KW 830
 Average Tube Outlet Temperature, C 86
 Average Tube Inlet Temperature, C 16
 Average Coolant Flow Rate, GPM 29
 pH 7.0
 Dichromate Concentration, ppm 0.2
 Type of Water Filtered

<u>Slug Number</u> <u>From Rear</u>	<u>Surface</u> <u>Temperature, C</u>	<u>Slug Power</u> <u>KW/8" Slug</u>	<u>Corrosion</u> <u>Rate, Mils/Month</u>
1	90	10	0.07
2	90	12	0.06
3	89	13	0.07
4	88	15	0.08
5	87	16	0.12
6	86	18	0.31
7	84	19	0.04
8	83	20	0.12
9	81	22	0.13
10	79	22	0.20
11	77	23	0.25
12	75	24	0.29
13	72	25	0.08

Tube Number 3571-D-3
 Time of Operation, Days 55
 Average Tube Power, KW 695
 Average Tube Outlet Temperature, C 98
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 27
 pH 7.0
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
3	101	12	0.36
5	99	16	0.39
7	96	20	0.45
9	94	25	0.60
11	87	27	0.42
13	84	29	0.36
15	78	31	0.28
17	72	31	0.34

Tube Number 3472-D-3
 Time of Operation, Days 55
 Average Tube Power, KW 645
 Average Tube Outlet Temperature, C 101
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 26
 pH 7.0
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	103	6	0.33
3	104	12	0.36
5	103	17	0.93
7	100	21	0.42
9	97	25	0.87
11	92	26	0.82
13	85	28	0.58
15	80	30	0.32
17	74	30	0.30

Tube Number 2570-D-3
 Time of Operation, Days 55
 Average Tube Power, KW 655
 Average Tube Outlet Temperature, C 93
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 29
 pH 6.6
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	97	9	0.11
3	96	14	0.14
5	95	18	0.30
7	91	21	0.25
9	87	24	0.40
11	83	26	0.38
13	79	28	0.36
15	73	29	0.27

Tube Number 2170-D-4
 Time of Operation, Days 55
 Average Tube Power, KW 690
 Average Tube Outlet Temperature, C 96
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 29
 pH 6.6
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	101	11	0.40
3	99	16	0.75
5	97	20	0.55
7	94	26	0.54
9	88	23	0.39
11	84	28	0.40
13	80	22	0.45
15	70	28	0.65

Tube Number 2171-D-3
 Time of Operation, Days 55
 Average Tube Power, KW 680
 Average Tube Outlet Temperature, C 95
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 29
 pH 6.2
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	97	6	0.08
3	98	10	0.11
5	97	17	0.14
9	90	22	0.12
11	86	24	0.11
13	83	28	0.14
15	77	30	0.13
17	71	30	0.15

Tube Number 3471-D-1
 Time of Operation, Days 58
 Average Tube Power, KW 700
 Average Tube Outlet Temperature, C 99
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 29
 pH 7.7
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	102	7	0.66
3	101	12	0.80
5	100	16	1.32
7	98	20	2.67
9	94	24	3.06
11	89	26	2.61
13	85	28	1.85
15	79	30	1.11
17	73	30	0.61

Tube Number 2671-D-1
 Time of Operation, Days 55
 Average Tube Power, KW 680
 Average Tube Outlet Temperature, C 93
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 30
 pH 7.7
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	94	6	0.77
3	95	12	0.80
5	93	17	1.82
7	91	22	1.88
9	88	26	1.82
11	83	27	1.31
13	75	27	0.63

Tube Number 3473-D-1
 Time of Operation, Days 55
 Average Tube Power, KW 650
 Average Tube Outlet Temperature, C 92
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 29
 pH 7.7
 Dichromate Concentration, ppm 2
 Type of Water Filtered

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	94	7	0.59
3	93	10	0.72
5	91	14	1.94
7	89	19	2.54
9	86	22	2.68
11	82	25	2.42
13	78	27	1.24
15	73	28	0.91

Tube Number 2170-D-1
 Time of Operation, Days 36
 Average Tube Power, KW 540
 Average Tube Outlet Temperature, C 78
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 30
 pH 7.5
 Dichromate Concentration, ppm 5
 Type of Water Unfiltered
 Turbidity Concentration, ppm 2 - 5

<u>Slug Number</u> <u>From Rear</u>	<u>Surface</u> <u>Temperature, C</u>	<u>Slug Power</u> <u>KW/8⁰⁰ Slug</u>	<u>Corrosion</u> <u>Rate, Mils/Month</u>
1	82	10	0.58
5	82	16	0.61
9	81	22	0.68
13	79	26	0.52
17	75	30	0.34
21	70	32	0.15

Tube Number 2171-D-1
 Time of Operation, Days 88
 Average Tube Power, KW 545
 Average Tube Outlet Temperature, C 78
 Average Tube Inlet Temperature, C 7
 Average Coolant Flow Rate, GPM 29
 pH 7.5
 Dichromate Concentration, ppm 5
 Type of Water Unfiltered
 Turbidity Concentration, ppm 2 - 90

<u>Slug Number</u> <u>From Rear</u>	<u>Surface</u> <u>Temperature, C</u>	<u>Slug Power</u> <u>KW/8⁰⁰ Slug</u>	<u>Corrosion</u> <u>Rate, Mils/Month</u>
1	82	7	0.40
3	84	9	0.63
5	82	12	0.76
7	82	14	0.74
9	82	17	0.81
11	81	20	0.74
13	81	23	0.66
15	79	24	0.93
17	76	22	0.41
19	72	20	0.23

Tube Number 2170-D-2
 Time of Operation, Days 81
 Average Tube Power, KW 550
 Average Tube Outlet Temperature, C 81
 Average Tube Inlet Temperature, C 8
 Average Coolant Flow Rate, GPM 28
 pH 7.5
 Dichromate Concentration, ppm 5
 Type of Water Unfiltered
 Turbidity Concentration, ppm 4 - 90

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8" Slug	Corrosion Rate, Mils/Month
1	87	12	0.23
3	87	13	0.22
5	86	14	0.23
7	86	16	0.25
9	84	18	0.60
11	84	20	0.22
13	80	20	0.16
15	77	21	0.22
17	76	22	0.17
19	75	23	0.16
21	73	24	0.14
23	71	24	0.10

Tube Number 2171-D-2
 Time of Operation, Days 87
 Average Tube Power, KW 520
 Average Tube Outlet Temperature, C 81
 Average Tube Inlet Temperature, C 13
 Average Coolant Flow Rate, GPM 29
 pH 7.0
 Dichromate Concentration, ppm 5
 Type of Water Unfiltered
 Turbidity Concentration, ppm 10 - 30

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8" Slug	Corrosion Rate, Mils/Month
1	84	7	0.21
3	86	14	0.42
5	86	22	0.56
7	85	26	0.54
9	80	25	0.54
11	76	26	0.45
13	73	28	0.38
15	71	30	0.26

Tube Number 2170-D-3
 Time of Operation, Days 158
 Average Tube Power, KW 515
 Average Tube Outlet Temperature, C 85
 Average Tube Inlet Temperature, C 16
 Average Coolant Flow Rate, GPM 29
 pH 7.0
 Dichromate Concentration, ppm 5
 Type of Water Unfiltered
 Turbidity Concentration, ppm 5 - 30

Slug Number From Rear	Surface Temperature, C	Slug Power KW/8 ⁰⁰ Slug	Corrosion Rate, Mils/Month
1	90	11	0.54
3	88	12	0.68
5	87	15	0.63
7	84	17	0.52
9	81	19	0.34
11	76	21	0.31
13	72	23	0.31

The following pages summarize the inspection reports of the irradiated metal slugs. Localized attacks are classified as pits and rib marks. Rib marks are mechanical damage or corrosion attacks along the length of the slugs where the slugs rested on the tube ribs. This type attack is probably caused by mechanical damage to the autoclave film on the slug -- thus presenting unprotected aluminum to the environment.

Tube operating conditions are found in the preceding pages of this appendix.

TUBE NO. 2170-D-1

Temperature	Number of Slugs	Number of Slugs Pitted	Number of Slugs With Rib Marks
80 - 89	12	7	12
70 - 79	12	6	12
60 - 69	4	2	4
10 - 59	28	11	27

TUBE NO. 2171-D-1

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
80 - 89	7	4	7
70 - 79	3	1	3
60 - 69	6	4	6
10 - 59	11	4	10

TUBE NO. 2170-D-2

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
80 - 89	7	1	0
70 - 79	5	1	0
60 - 69	2	0	0
10 - 59	13	4	0

TUBE NO. 2171-D-2

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
80 - 89	4	0	0
70 - 79	4	2	0
60 - 69	1	1	0
10 - 59	19	7	3

TUBE NO. 2170-D-3

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
90 - 99	2	1	2
80 - 89	8	4	7
70 - 79	4	0	3
60 - 69	4	0	2
10 - 59	0	1	4

TUBE NO. 2570-D-1

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
10 - 59	22	8	21
60 - 69	6	4	6
70 - 79	10	4	9
80 - 89	18	12	17

TUBE NO. 3472-D-1

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
10 - 59	9	6	9
60 - 69	3	3	3
70 - 79	5	3	5
80 - 89	7	7	7
90 - 99	4	4	4

TUBE NO. 3571-D-1

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
10 - 59	10	1	1
60 - 69	3	0	0
70 - 79	4	0	1
80 - 89	5	0	1
90 - 99	6	5	2

TUBE NO. 2570-D-2

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
10 - 59	24	7	15
60 - 69	8	8	4
70 - 79	8	8	8
80 - 89	16	12	13

TUBE NO. 3472-D-2

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
10 - 59	8	1	3
60 - 69	5	0	2
70 - 79	3	0	3
80 - 89	6	2	2
90 - 99	6	1	4

TUBE NO. 3571-D-2

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
10 - 59	9	4	0
60 - 69	5	5	0
70 - 79	5	5	0
80 - 89	7	5	1
90 - 99	2	1	0

TUBE NO. 3571-D-3

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
100 - 109	4	1	4
90 - 99	6	2	6
80 - 89	4	1	4
70 - 79	4	0	4
10 - 69	10	2	10

TUBE NO. 3472-D-3

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
100 - 109	8	5	8
90 - 99	4	0	4
80 - 89	4	1	4
70 - 79	4	1	4
10 - 69	8	1	8

TUBE NO. 2570-D-3

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
90 - 99	8	3	8
80 - 89	4	0	4
70 - 79	4	1	4
10 - 69	12	4	12

TUBE NO. 2170-D-4

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
100 - 109	2	2	2
90 - 99	6	5	6
80 - 89	6	1	6
70 - 79	2	1	2
10 - 69	12	3	12

TUBE NO. 2171-D-3

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
90 - 99	10	5	10
80 - 89	4	2	4
70 - 79	4	0	4
10 - 69	10	5	10

TUBE NO. 2671-D

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
90 - 99	4	3	4
80 - 89	2	2	4
70 - 79	1	0	1
60 - 69	2	0	2

TUBE NO. 3473-D

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
90 - 99	3	3	3
80 - 89	3	3	3
70 - 79	2	2	2
60 - 69	1	0	1

TUBE NO. 3471-D

<u>Temperature</u>	<u>Number of Slugs</u>	<u>Number of Slugs Pitted</u>	<u>Number of Slugs With Rib Marks</u>
100 - 109	3	3	3
90 - 99	2	2	2
80 - 89	2	2	2
70 - 79	2	1	2

APPENDIX V

DATA ON TUBING USED FOR OUT-OF-PILE TESTING

The first part of the appendix presents plots of weight loss versus time data obtained by out-of-pile test with process tubing. Next, corrosion rates as determined from the plots are tabulated.

The final item in the appendix is a tabulation of inspections of the tubing used in the out-of-pile tests.

A. Weight Loss Versus Time

Figures 11 - 16 show plots of weight loss versus time data obtained by out-of-pile test with process tubing.

B. Tabulation of Out-of-Pile Tube Corrosion Rates

TABLE VI
CORROSION RATES AS DETERMINED FROM WEIGHT LOSS
VERSUS TIME CURVE

<u>Temperature, C</u>	<u>pH</u>	<u>Corrosion Rate</u> <u>Mils/Mo</u>
70	7.7	0.15
95	7.7	0.56
110	7.7	2.8
125	7.7	2.8
120	7.3	2.2
140	7.3	2.9
120	7.0	2.0
150	7.0	2.0
120	6.6	1.2
150	6.6	2.4
120	6.2	0.87
150	6.2	1.7

C. Inspection Results

1. pH 7.7 at 70 C.

After 37 days at 70 C the samples were new looking except at areas next to the Van Stone flanges. At these places, the metal was very shiny and polished appearing - possibly indicative of preferential corrosion.

FIGURE 14

CORROSION OF 72-S CLAD PROCESS TUBING
EXPOSED TO pH 7.3 WATER AT 120C AND 140C

Weight Loss - Mg/cm²

Weight Loss - Mg/cm²

Time of Exposure - Days

2. pH 7.7 at 95 C.

After 37 days at 95 C, the samples were very smooth and were covered with a thin gray oxide coat. There was no evidence of local attack.

3. pH 7.7 at 110 C.

After 16 days, the sample, after cleaning, was covered with a light gray oxide film. After 20 days the oxide layer was darker and there small mounds above the general surface on part of the samples. It appeared that the mounds were aluminum metal covered with oxide. A typical mound measured 30 mils in diameter and was a few mils high.

After 36 days, the heavy adherent oxide, similar to that noted on slugs exposed to pH 7.0 water for 50 days, was found and stripped electrolytically. The surface under the film was quite smooth.

4. pH 7.7 at 120 C.

After 16 days exposures the sample was covered with a light gray oxide film except at areas adjacent to Van Stone flanges. These areas were shiny as noted for samples exposed to pH 7.7 water at 70 C.

After 20 days the oxide film was darker appearing but was not of the thick heavy type removable by electrolytic stripping. There were some small mounds on the samples as described in samples exposed to the pH 7.7 water at 110 C.

After 36 days, the sample was covered with the heavy oxide film which was removed by electrolytic stripping. Some mounds were apparent after stripping.

5. pH 7.3 at 120 C.

After 14 days the sample, after cleaning, was covered with a light gray oxide film. The surface of the sample was smooth and no local attack was noted.

Two samples were exposed for 22 days. After cleaning, one of these samples was light gray except at the areas adjacent to the Van Stone Flanges which were shiny. The other sample had a dark gray oxide

film with the mounds described previously. The later sample lost approximately twice as much weight as the other.

6. pH 7.3 at 140 C.

After 14 days the samples, after cleaning, were covered with a light gray oxide film. The areas adjacent to Van Stone Flanges were shiny.

7. pH 7.0 Water at 120 C.

After a total of 52 days exposure, the sample was smooth and covered with a light gray oxide film.

8. pH 7.0 Water at 150 C.

After 19 days, the surface of the sample was roughened. The sample exposed 34 days had a few mounds on the sample. After 53 days, there was a layer of the thick adherent oxide film which was removed electrolytically. After electrolytic stripping the sample surface was rough.

9. pH 6.6 Water at 120 C.

After 19 days, the sample was quite smooth and covered with a gray oxide film. The sample exposed 32 days was still smooth but the gray film was somewhat blotchy or mottled in appearance.

After 53 days, the sample was covered with a dark gray film and was slightly rough in appearance. The roughness was in patterns corresponding to the mottled spots in the 34 day sample.

10. pH 6.6 Water at 150 C.

After 19 days, the sample was quite smooth and covered with a dark gray oxide layer. After 34 days the sample was still quite smooth. Of interest is the fact that on one area about two inches long by one inch inside the gray oxide was absent leaving a shiny metallic surface.

APPENDIX VI

DATA ON TUBING USED FOR IN-PILE TESTING

Some of the tubes used for various of the in-pile testing were removed and inspected. Also, measurements of the wall and cladding thickness were made.

When the tube is installed in the pile, the rear 120 inches are in the rear shielding and reflector and, hence, flow through this section is nearly isothermal at outlet water temperature. The next 290 inches contain the metal slugs and the remaining tubing is in the front shield and reflector. The nominal wall thickness of a tube is 67 mils at the top and 61 mils at the bottom. The nominal cladding thicknesses are 8.5 mils at the top and 7.5 mils at the bottom. The thicknesses of walls and cladding on tube sides of the tubes range between the value for the top and bottom.

A. Tube 2570-D-A (pH 7.3 Water with 2ppm Dichromate)

This tube had no pitting or other local attack throughout its length. After the film was removed, faint grey rings were visible at slug junctions.

B. Tube 2570-D-B (pH 7.3 filtered Water with 0.2 ppm of Dichromate)

There was a shallow pitting attack and a light ledging attack in the rear sections of the tube. By ledging is meant a local type of attack where an area is uniformly corroded away leaving a ledge at the boundary of the attacked and unattacked portions. The attacks noted are similar to those ordinarily found in tubes cooled with pH 7.7 process water under similar conditions for like amounts of time.

Measurements:

<u>Longitudinal Position of Samples, Inches From Rear Flange</u>	<u>Radial Position of Sample</u>	<u>Cladding Thickness Mils</u>	<u>Wall Thickness Mils</u>
23	Bottom	4.8	54
49	Side	4.2	53
79	Top	6.0	59
112	Side	5.9	52
148	Side	4.0	55
186	Top	8.5	52
228	Side	4.2	54
334	Top	7.1	53
461	Bottom	8.6	53

C. Tube 3571-D-A (pH 7.3 Filtered Water with 2 ppm Dichromate)

Some pitting was found in the 72 S cladding in the rear sections of the tubes. The pitting was not severe nor extraordinary.

Measurements:

<u>Longitudinal Position of Samples, Inches From Rear Flange</u>	<u>Radial Position of Samples</u>	<u>Cladding Thickness Mils</u>
45	(This data not taken for this tube)	7.0
86		5.7
129		4.0
170		6.5
212		7.3
255		7.2
297		7.4
340		8.4
380		8.3
422		7.3
465		6.6

D. Tube 3571-D-B (pH 7.0 Filtered Water with 0.2 and 2 ppm Dichromate)

Some shallow pitting was found in the rear sections. Pitting was not severe or extraordinary.

Measurements:

Longitudinal Position of Samples, Inches from Rear Flange	Radial Position of Sample	Cladding Thickness Mils	Wall Thickness Mils
0 -- 100	Bottom	---	62
100 -- 200	Bottom	6	62
200 -- 300	Bottom	---	62
300 -- 400	Top	---	68
400 -- 500	Bottom	8	62

E. Tube 2170-D-C (pH 6.6 Filtered Water with 2 ppm of Dichromate.
Shallow pits in rear section of tube.

Measurements:

Longitudinal Position of Samples, Inches from Rear Flange	Radial Position of Sample	Cladding Thickness Mils	Wall Thickness Mils
0 -- 100	Bottom	---	60
100 -- 200	Side	7	---
100 -- 200	Bottom	---	60
200 -- 300	Bottom	---	61
300 -- 400	Side	7	66

F. Tube 2170-D-A (pH 7.5 Unfiltered Water with 5 ppm of Dichromate)

There were a few light pits in the rear section of the tube on the tube ribs and in tube wall. There were also a few pits along the ribs in the cold front section. Pitting was not serious or extraordinary.

Measurements:

Longitudinal Position of Samples, Inches from Rear Flange	Radial Position of Sample	Cladding Thickness Mils
44	(This data	7.3
126	Not taken	4.8
172	For This	6.0
223	Tube)	6.9
269		5.9
319		5.0
365		6.1
415		4.8
442		4.6
481		4.2

G. Tube 2170-D-B (pH 7.0 Unfiltered Water with 5 ppm of Dichromate)

This was an unclad 63-S aluminum tube. Light ledging attack was found on the rear section of the tube. The film pattern showed that one slug had been cocked in the tube. This behavior causes local high water velocities conducive to erosion. No erosion was found. After the area had been de-filmed a light ledging attack was noted in the cocked slug area.

Measurements:

Longitudinal Position of Samples, Inches from Rear Flange	Radial Position of Sample	Cladding Thickness Mils	Wall Thickness Mils
21	Side	*	62
49	Side		61
79	Side		62
111	Bottom		62
147	Top		62
187	Top		64
228	Side		61
273	Top		66
333	Top		66
372	Top		67
439	Side		62
478	Bottom		62

* This was an unclad tube

H. Tube 2171-D-A (pH 7.5 and 7.0 Unfiltered Water with 5 ppm of Dichromate and pH 6.2 Filtered Water with 2 ppm Dichromate)

No serious nor extraordinary attack was noted in this tube.

Measurements:

Longitudinal Position of Samples, Inches from Rear Flange	Radial Position of Sample	Cladding Thickness Mils	Wall Thickness Mils
0 -- 100	Bottom	---	60
100 -- 200	Bottom	9	60
200 -- 300	Bottom	---	61
300 -- 400	Bottom	---	61
400 -- 500	Top	10	71

APPENDIX VII
DATA ON THE CORROSION OF CARBON STEEL SAMPLES

Weight loss versus time plots obtained from the various tests are shown in the following figures. In comparing these plots it is very important to notice the change in the ordinate scale on different plots.

As will be noticed, the runs with water at pH 6.6 with no dichromate and pH 5.9 with 2 ppm dichromate are quite short term. These tests were of limited time because the laboratory facility was shut down due to the completion of new facilities at another area. The tests were run to gain a picture of the initial rates of attack which, as expected, were quite severe.

Table VII shows the rate of corrosion as statistically determined from the data. In determinations, the rates were taken to be the slope of the straight lines on the weight loss versus time plots.

Descriptions of the samples are given in the last part of the appendix.

A. Weight Loss Versus Time

Figures 17 - 25 show weight loss versus time for various tests.

B. Tabulation of Rates

TABLE VII
CARBON STEEL CORROSION RATES

pH	Dichromate Concentration ppm	Corrosion Rate Mils/Month	Std. Deviation Mils/Month
7.7	2	0.069	± 0.029
7.7	0	0.56	0.19
7.3	0.2	1.94	1.12
7.0	5	0.065	0.032
7.0	2	0.095	0.053
7.0	2	0.23	0.035
6.6	2	0.13	0.059
6.2	2	1.68	0.26

FIGURE 20

CORROSION OF CARBON STEEL EXPOSED TO
pH 7.0 WATER WITH 5 ppm DICHROMATE AT 90C

FIGURE 21

CORROSION OF CARBON STEEL EXPOSED TO
pH 7.0 WATER WITH 2ppm DICHROMATE AT 90C

FIGURE 22

CORROSION OF CARBON STEEL EXPOSED TO pH 6.6
WATER WITH 2ppm DICHROMATE AT 90C

1. pH 7.7, 2 ppm Dichromate

After 29 days, parts of the coupon surfaces were somewhat roughened but pit-free. Total average penetration after 29 days was 0.13 mils.

2. pH 7.7, 0 ppm Dichromate

The samples exposed for a short period, 5 days, appeared blotchy. Part of the original shiny surface remained but there were dark blotches over the sample; the surface of this five day sample was smooth to the touch. After 25 days the blotchy areas were more extensive and the sample was rough to the touch. Apparently the corrosion was occurring preferentially but there were no actual pits.

The total average penetration after 25 days was about 0.65 mils.

3. pH 7.3, 0.2 ppm Dichromate

After a few days exposure the coupons began experiencing a pitting type of attack which became more severe with time. After 48 days, pit depths of 25 mils were not uncommon. The area of the samples enclosed by the plastic spacers were less effected by corrosion, both uniform and pitting, than the rest of the sample surface. Total average penetration, as determined by weight loss, was 3.5 mils.

4. pH 7.0, 5 ppm Dichromate

After about 25 days exposure the samples were still smooth to the touch and the sample area still retained much of the original finish. Total average corrosion penetration after 25 days was about 0.18 mils.

5. pH 7.0, 2 ppm Dichromate

After 35 days exposure, some of the samples were slightly rough to the touch but pit-free. Some of the samples experienced local attack at the place where the plastic spacer touched the sample indicating a possible oxygen cell attack. Total average penetration after 33 days was 0.32 mils.

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6. pH 6.6, 2 ppm Dichromate

After 21 days the samples were smooth to the touch and pit-free. A few samples experienced local attack where the plastic spacer touched the sample indicating an oxygen cell attack.

7. pH 6.6, 0 ppm Dichromate

After four days exposure, the sample was covered with numerous pits about 1/16 inch in diameter and a few mils deep. After ten days, numerous pits 15-20 mils deep were observed. Total average penetration as determined by weight loss after ten days was about 1.9 mils.

8. pH 6.2, 2 ppm Dichromate

After 27 days exposure, the samples were quite smooth to the touch and pit-free. On a few coupons, there was local corrosion where the plastic spacer touched the coupon suggesting an oxygen cell attack. Total average penetration after 27 days was 1.9 mils.

9. pH 5.9, 2 ppm Dichromate

After six days exposure the samples were smooth and pit-free. Total average penetration after six days was 0.52 mils.

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APPENDIX VIII

FILM FORMATION DATA

Film formation rates were calculated for tubes cooled with each type of water. These rates are plotted in Figure 26. A negative rate indicates that film was sloughing off. Many of the tubes were purged numerous times but the purges are not reflected in the plots; rates were calculated for periods between purges.

Experience has shown that one of the important water quality variables is the lime addition dosages. Daily average lime dosages are plotted in Figure 27.

Some connection can be seen between lime dose on film formation rates. When the lime dose was increased from 0 to 1-3 ppm in the later part of February film formation rates in filtered water dropped markedly. When the dose was dropped from 5 to 1.5 ppm at the end of July, 1954, the rates experienced with water containing 2 ppm of dichromate increased.

In these tests where no two waters at a given low pH have different lime dosages, the importance of lime addition is not so marked as has been shown in other tests where there was this control. It is obvious from the data that other water quality variables have important effects on film rates which may overshadow the effect of lime if there are not sufficient comparison conditions.

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FIGURE 26

LM FORMATION RATES

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FIGURE 27

DOSAGE TO FILTERED WATER

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ABSTRACT

Tests have been made to study the effects of lowering process water pH from pH 7.7 to the range pH 6.2 - 7.3; of reducing the amount of sodium dichromate inhibitor added to the water; and of eliminating the filtration step in the water treatment process.

The results on the pH testing showed that reducing the pH of the cooling water would reduce aluminum corrosion rates. The plant specification has been changed to lower process water pH from 7.7 to 7.3 and plant scale testing of pH 7.0 water is in progress.

Reducing the dichromate concentration in the water from 2 to 0.2 ppm had no deleterious effects on the aluminum pile components but might cause pitting of the carbon steel pile effluent lines.

The use of unfiltered water is technically feasible from the standpoints of corrosion and film formation but probably would cause a sizable increase in the radioactivity of the pile effluent water.

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