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SUMMARY AND CORRELATION OF WATER QUALITY TESTING RESULTS

AUTHOR

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SUMMARY AND CORRELATION OF WATER QUALITY TESTING RESULTS

INTRODUCTION

A considerable technical effort has been expended during the past two years in evaluating the effects of various process water qualities on the corrosion of aluminum tubes and slugs. Primary emphasis has been placed on four types of water: ferric sulfate coagulated water with and without dichromate addition, and alum coagulated water with and without dichromate addition. Both in-pile and flow laboratory data have been obtained on the corrosivity of these several water qualities.

It appears that a review of the available information will serve two useful purposes. First, a comparison of corrosion data from all available sources will provide a better overall understanding of the corrosive properties of the various types of water. Second, a knowledge of the applicability of small scale and mock-up tests to actual in-pile operating conditions will permit more efficient experimentation in current work aimed at raising outlet water temperatures, reducing water treatment costs, and reducing corrosion rates of pile components.

The purpose of this report is to present a summary and correlation of flow laboratory and in-pile corrosion data in various qualities of process water.

SUMMARY

Corrosion data obtained both with in-pile and out-of-pile tests with various types of process water have been summarized and correlated. The available data indicate that water coagulated with alum is less corrosive to the 2-S aluminum slug jackets

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than is water coagulated with ferric sulfate within the temperature range studied. Also, at some temperature about 65 C the addition of dichromate to the water increases the corrosion of the slug jacket as determined by weight loss measurements.

Comparisons of results obtained with flow laboratory and in-pile corrosion tests show that the data obtained with the flow laboratories are reliable in predicting corrosion trends experienced under in-pile conditions. This fact makes it highly desirable to continue using flow laboratory facilities to the fullest extent possible in the development of new water treatment processes, because flow laboratory testing is much less costly and hazardous and much more flexible than is in-pile testing. Results obtained in the flow laboratory should, however, be confirmed by multiple tube in-pile tests or full pile demonstrations, depending on the magnitude of the change, before definite decisions concerning a given problem are made.

PHILOSOPHY OF 100 AREA WATER QUALITY TESTING

In considering a water process developmental program, as with any developmental program, one should weigh the possible benefits to be derived from the program against the probable costs of the program. In general, the gains in improving the 100 area water treatment programs are:

1. Reduction of initial capital investment of new water plants. A 100-K water plant costs approximately \$50,000,000.
2. Reduction of shutdown time attributable to operational problems caused by water quality. Assuming a cost of \$15 per MWD and a power level of 650 MW, shutdown time costs about \$9,700 per day due to lost production alone.
3. Providing a water which could be heated to a higher temperature in a reactor without damaging pile components. Assuming a pile coolant flow of 50,000 gpm and a value of \$15 per MWD, production increases worth about \$150 per day per degree Centigrade of temperature increase would be realized.
4. Reduction of the present chemical treatment costs which now are \$3.00 to \$10.00 per million gallons.

From the above, it seems reasonable to state that significant gains might be realized by optimizing the process water treatment.

The original water treatment process specifications were based on work done by the CMX group during the early days of Hanford. This group did not have the time nor the facilities to develop an optimum water treatment process. Their aim was to develop a water process which would supply water suitable for use in cooling a reactor during an assumed short time of reactor operation under comparatively mild conditions. The CMX group was successful in developing a treatment which furnished water to meet the above criteria; but it is known that they did not develop an optimum treatment. During the years of pile operation, treatment costs have been decreased by eliminating the addition of sodium silicate to the water, and plant capacities have been increased by using alum and activated silica rather than ferric sulfate as the water coagulant. It is probable that further improvements can be made. It will be practical, then, to try to improve further the treatment if the cost of development is not excessive in comparison with the savings to be realized.

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Inasmuch as the possible benefits of an improvement are fixed, the problem resolves to minimizing the total cost of the developmental program and maximizing the probability of success of the developmental program. This objective can best be obtained by developing a given modification of treatment through a series of coordinated bench type experiments, out-of-pile mock-up tests, multiple tube in-pile studies and half or whole pile demonstrations. Two actual cases will be discussed to show the efficacy of the above method of attack.

At present, the Water Plant Development Sub-Unit is actively studying the possibility of reducing the pH of the cooling water supplied to the Hanford piles. The primary gains to be realized from this modification would be to decrease the corrosivity of the coolant to aluminum. Such a decreased corrosivity may be necessary to make increased pile power levels or metal exposure concentrations feasible. The general history of this program has been:

1. A search of the literature showed that the change was feasible⁽¹⁾.
2. Out-of-pile tests with water coagulated with ferric sulfate showed that overall corrosion losses were reduced by reducing the pH of the water in the range to 7.65 to 6.2, but that slug pitting was excessive⁽¹⁾.
3. Out-of-pile and in-pile tests with water coagulated with alum showed that reducing the pH from 7.65 to 7.0 reduced overall corrosion losses, but did tend to cause excessive slug and tube pitting⁽²⁾.
4. A four tube in-pile test showed that if 2.0 ppm dichromate were added to the water to suppress the tube pitting, film formation (caused by reduction of hexavalent chromium to trivalent chromium) would not be excessive at pH's above 7.2⁽²⁾.
5. Another two tube in-pile test showed that if the pH of process water were allowed to "float" at the post filtration value of 7.3 to 7.7, tube pitting would not be a problem. Corrosion effects have not yet been fully determined under these conditions but at the very least this type of water is no worse than pH 7.65 alum coagulated water with 2.0 ppm of dichromate addition⁽³⁾.
6. A half pile test is now being conducted to determine the economics of allowing the pH to "float" and also to give a final answer as to the effects of this type of water on pile operation⁽⁴⁾.
7. Another series of out-of-pile and in-pile tests are being planned to determine the effects of maintaining the pH of alum coagulated water with 2.0 ppm dichromate addition at 7.3⁽⁵⁾. If allowing the pH to "float" does not prove to effect a large enough reduction in corrosion, then this pH 7.3 water will probably be developed to the extent that a full pile demonstration would be feasible.

- (1) Atwood, J. M., "Process Water pH Effects", HW-24007, May 15, 1952.
- (2) Miller, N. R., "Interim Report Number 1, PT-105-509-E, The Effects of Low pH Alum Water on Pile Operation", HW-29954, November 11, 1953.
- (3) Miller, N. R., Personal Laboratory Notes, HW-4218-T, August, 1953.
- (4) Atwood, J. M., "PT-105-526-E, Elimination of Lime as a Process Water Additive", HW-28934, August 10, 1953.
- (5) Miller, N. R., "PT-105-525-E, The Effects of Water Quality on Pile Operation", HW-29406, September 21, 1953.

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As can be seen, the above program has been aimed at keeping the development tests on a small scale until the results have seemed promising enough to warrant a whole or half pile demonstration. By following this plan, risks and expenditures have been minimized and the program has been kept extremely flexible in order to permit modification of the procedure as more knowledge was gained. Thus, the approach maximized the possibility of success while minimizing costs and risks.

Another subject under active consideration is the possibility of using unfiltered water as a pile coolant. This evaluation could have been made by merely converting an entire area to this type of cooling. This approach did not seem technically feasible, however, because of the danger of damaging a reactor worth \$50,000,000 by the use of an untried and radically different type.

The program actually adopted has been outlined in detail by J. M. Atwood⁽⁶⁾. Briefly the approach has been this:

1. A series of bench type tests have been made. These tests, which are low in cost, show general trends to be expected by changing a variable such as chemical addition.
2. The bench type tests have been confirmed by conducting a fewer number of more expensive out-of-pile tests with mock-up process tubes and slugs.
3. A treatment suggested by the results of steps (1) and (2), is now to be studied further with a two tube in-pile test. This in-pile test will be considerably more expensive than the two preceding tests; but is justified by the favorable results thus far obtained.
4. When the results of the in-pile test are available and have been correlated, a sound decision can be made as to what further evaluations should be made. The results may indicate that a full pile demonstration is in order or may indicate that further preliminary studies should be carried out.

As can be seen, the above program is aimed at reducing total costs and risks and maximizing the ultimate success of the process. This approach can be followed only when sufficient laboratory facilities are available.

It is at once apparent that in actuality the above approach is sound only if the out-of-pile tests are reasonably reliable in predicting in-pile experience. This document discusses in some detail the reliability of out-of-pile tests made with mock-up process tube and slugs in predicting in-pile experience. A discussion of the equipment used in this type of testing and the particular merits and limitations of different techniques may be found in Appendix I.

REVIEW OF WATER TREATMENT PROCESSES AT HANFORD

Specifications for the original water treatment process at Hanford were based on recommendations made by the CMI project. Included in these recommendations were the use of ferric sulfate for coagulation of the water before filtration, the addition of 2.0 ppm of dichromate for inhibition of corrosion, and the addition of a

(6) Atwood, J. M., "A Program for Testing Raw Columbia River Water as a Pile Coolant", HN-28778, July 21, 1953.

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minimum of 5.0 ppm of sodium silicate for inhibition of film build-up⁽⁷⁾.

Operation of the 100 areas water plants continued on this basis until August, 1948. At this time tests were initiated to determine the effects of reducing and then eliminating the addition of sodium silicate^(8,9,10). The results of these tests showed that the elimination of sodium silicate addition did not increase film formation rates⁽¹¹⁾ and it was estimated that there was a 95 per cent probability that sodium silicate addition would never be required in the future⁽¹²⁾.

After the addition of sodium silicate was eliminated, attention was directed to the possibility of eliminating dichromate addition. Accordingly, a production test was initiated on June, 1951, to study the effects of dichromate elimination under in-pile conditions⁽¹³⁾. The results of this test indicated that elimination of dichromate addition would reduce the overall rates of slug corrosion and would not increase the rates of tube corrosion⁽¹⁴⁾. On the basis of this information, the addition of dichromate to process water was eliminated at the 100-B, 100-D, 100-DR and 100-H areas on April 18, 1952, and at 100-F on April 27, 1952⁽¹⁵⁾.

Because of the possibility that 100 areas filter plant capacities might limit future production increase, a study was made of the feasibility of increasing filter rates by using alum as the coagulant and activated silica as a coagulation aid⁽¹⁶⁾. Experience at other installations had shown that higher filtering rates are possible when the water is coagulated with alum-silica instead of ferric sulfate. In order to determine the effects of alum coagulated water on pile operation, a production test was issued authorizing the use of alum at 100-F⁽¹⁷⁾. The conversion of facilities at 100-F was completed and the use of alum started on October 10, 1951⁽¹⁸⁾.

- (7) Kidder, C. P., "CMX Final Report", 7-4444, July 31, 1946.
- (8) Conley, W. R., "PT-105-214-P, Silica Feed Reduction", HM-10734, August, 1948.
- (9) Alexander, W. K., "PT-105-214-P, Supplement A, Silica Feed Reduction", HM-12903, March, 1949.
- (10) Snoeberger, D. F., "PT-105-214-P, Supplement B, Silica Feed Reduction", HM-13275, May, 1949.
- (11) Conley, W. R., "Final Report, PT-105-214-P, Silica Feed Reduction", HM-15943, February, 1950.
- (12) Woods, W. K., "Silica Additions to Process Water", HM-16083, February, 1950.
- (13) Purcell, R. H., "PT-105-453-P, Sodium Dichromate Elimination Tests", HM-21355, June, 1951.
- (14) Purcell, R. H., "Final Report, PT-105-453-P, Sodium Dichromate Elimination Tests", HM-24009, April 10, 1952.
- (15) Fryar, R. M., "Technical Activities Report, Materials of Pile Cooling", HM-24323, May 5, 1952.
- (16) Atwood, J. M., "The Effects of Alum and Activated Silica on Process Water Treatment", HM-21756, July, 1951.
- (17) Fryar, R. M., "PT-105-473-P, The Use of Commercial Aluminum Sulfate for 100 Areas' Process Water Coagulation", HM-21924, August, 1951.
- (18) Woods, W. C. A., "Final Report, PT-105-473-P, The Use of Commercial Aluminum Sulfate for 100 Areas' Process Water Coagulation", HM-23163, January, 1952.

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During the winter months, it is desirable to add activated silica with alum to aid in coagulation. Accordingly, facilities for this addition were constructed and a production test authorizing the use of activated silica at 100-F was issued⁽¹⁹⁾. Addition of activated silica at 100-F was started on December 28, 1951⁽²⁰⁾.

It was desired to have alum coagulated water available for low pH in-pile tests at 100-D so alum-activated silica facilities were constructed at that area⁽²¹⁾ and the use of alum was started on July 18, 1952⁽²²⁾. The addition of activated silica was started on January 19, 1953⁽²³⁾.

Corrosion of the front sections of process tubes became increasingly serious at some of the 100 areas after dichromate elimination. In order to determine the best type of water from the standpoint of this front tube corrosion and from other factors, the water treatment processes at the different areas were specified so that the effects of various water quality variables could be studied⁽²⁴⁾. Accordingly, coagulation with alum was started at 100-DR on December 24, 1952⁽²⁵⁾, and the addition of activated silica at this area was started during January, 1953⁽²⁶⁾. The 100-C water plant was operated using alum for coagulation and dichromate addition for corrosion inhibition. Dichromate addition was reinstated at 100-D on November 5, 1952⁽²⁴⁾, at 100-DR on December 24, 1952⁽²⁵⁾ and at 100-B, 100-F and 100-H on April 10, 1953⁽²⁷⁾.

Slug jacket corrosion data have been obtained under in-pile and flow laboratory conditions with the preceding types of water.

DISCUSSION OF SLUG CORROSION DATA

In the following pages, slug corrosion data obtained with both laboratory and in-pile facilities will be discussed. In order to make the discussions more understandable, there is included a short general description of the process of aluminum corrosion in water.

- (19) Fryar, R. M., "PT-105-503-E, The Use of Activated Silica as a Coagulation Aid for Aluminum Sulfate", HW-22755, November 19, 1951.
- (20) Woods, W. C. A., "Interim Report Number 1, PT-105-503-E, The Use of Activated Silica as a Coagulation Aid for Aluminum Sulfate", HW-27115, March, 1952.
- (21) Woods, W. C. A., "PT-105-508-E, The Use of Aluminum Sulfate as a Process Water Coagulant", HW-24761, June 23, 1952.
- (22) Atwood, J. M., "Technical Activities Report, Water Plant Development", HW-25057, August, 1952.
- (23) Atwood, J. M., "Technical Activities Report, Water Plant Development", HW-26901, February 10, 1953.
- (24) Atwood, J. M., "PT-105-513-E, 100 Areas Process Water Quality Evaluation Tests", HW-25976, November, 1952.
- (25) Atwood, J. M., "Technical Activities Report, Water Plant Development", HW-26619, January 12, 1953.
- (26) Atwood, J. M., "Technical Activities Report, Water Plant Development", HW-26273, December 10, 1952.
- (27) Skarpeles, J. M., Personal Communication, September, 1953.

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A. Aluminum Corrosion in Water

When aluminum covered with an appreciable oxide film such as is found on autoclaved slugs is exposed to water corrosion proceeds in three stages (28). First of all, there is an induction period during which time no or very little corrosion takes place. This initial period continues for a few days and is followed by a period of accelerated attack. Finally the corrosion rate decreases to an appreciably lower constant rate. The durations of periods and the magnitudes of the rates depend on the test conditions.

In general, the corrosion rate of practical importance is the final constant rate. This rate may be determined by exposing several samples under the same conditions, removing one or more samples periodically, and plotting corrosion loss versus time of exposure. The slope of this curve at any point is the instantaneous corrosion rate and the steady state corrosion rate is obtained directly. Figure 1 is a sketch showing this behavior of aluminum corrosion. An alternate method of determining the rate is by exposing the samples for a sufficiently long enough time that the major part of the corrosion loss is incurred during the period of constant rate. One then can assume that the average rate (the total weight loss divided by the time of exposure) is equal to the constant rate. In using this second method, care must be exercised to insure that the test is continued for a sufficiently long period of time. Otherwise, the calculated rates will be in error, generally higher than the actual rates.

B. Corrosion Data Obtained With Steam Jacketed Tubes

Corrosion data on dummy slugs have been obtained using steam jacketed tubes with three different types of water (25,29): ferric sulfate with dichromate addition and alum with and without dichromate addition. Curves obtained from the data are shown in Figure 2. These curves are of the type:

$$CR = Ae^{bt}$$

where:

CR = Corrosion rate
A, b = Constants
t = Temperature

as determined by the method of least squares. The bands show the 50 per cent confidence intervals as determined statistically. A description of the statistical methods used is outlined in Appendix II.

The results of the testing show that water coagulated with ferric sulfate is more corrosive than water coagulated with alum. The data also indicate that, at

- (28) Goldsmith, S., "Laboratory Studies of 2-S Aluminum Corrosion at Elevated Temperatures", HW-24584, May, 1952.
- (25) Atwood, J. M., LocCit.
- (29) Miller, N. R., "The Effects of Process Water on Three Types of 2-S Aluminum Slug Jackets", HW-23102, December, 1950.

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FIGURE 1
A TYPICAL CURVE OF ALUMINUM
CORROSION LOSS VERSUS TIME

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FIGURE 2
SLUG CORROSION RATES DETERMINED WITH STEAM-JACKETED PROCESS TUBES

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temperatures above 80 C, the addition of dichromate to alum coagulated water may increase slug corrosion rates.

The conditions of the three tests are shown in Table I.

TABLE I

CONDITIONS OF CORROSION TESTS WITH STEAM JACKETED TUBES

<u>Coagulant</u>	<u>Dichromate Addition</u>	<u>Flow Rate</u>	<u>Duration of Test</u>
Ferric Sulfate	2.0 ppm	20 gpm	120 days
Alum	2.0 ppm	10 gpm	54 days
Alum	0.0 ppm	20 gpm	63 days

Other tests have shown that variances in tube flow rates in the range of 10 to 20 gpm have no significant effect on corrosion rates⁽³⁰⁾. Also, after 54 days at the temperatures maintained, the average corrosion rate should be nearly equal to the constant rate. In view of these two facts, the conclusions drawn above should be valid despite the minor differences in test variables.

C. Discussion of Data Obtained With Preheated Water

Data on the corrosion rates of dummy slugs in alum and ferric sulfate coagulated water with and without dichromate addition have been obtained in the 105-D Flow Laboratory^(1,31). These data were obtained at a temperature of 95 C and a flow rate of 20 gpm.

Figure 3 is a plot of these laboratory data. In this figure the corrosion losses are plotted against the times of exposure. The average corrosion rates at 95 C are presented in Table II.

TABLE II

CORROSION OF 2-S ALUMINUM IN PREHEATED (95 C) WATER
UNDER FLOW LABORATORY CONDITIONS

<u>Type of Water</u>	<u>Corrosion Rate</u>	<u>Days of Exposure</u>
Ferric sulfate with dichromate	0.067 mg/cm ² /day	74
Ferric sulfate without dichromate	0.061	93
Alum without dichromate	0.035	128
Alum with dichromate	0.028	195

It is evident from the above data that tests with preheated water also indicate that slugs exposed to water coagulated with alum corrode at lower rates than slugs exposed

(30) Wilson, C. D., "The Effect of Water Velocity on 2-S Aluminum Slug Jacket Corrosion", HW-26033, October, 1952.

(1) Atwood, J. M., LocCit.

(31) Hayden, K. D., "Water Quality Studies", HM-4991-T, April, 1953.

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FIGURE 3
SLUG CORROSION DATA WITH PREHEATED WATER

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to water coagulated with ferric sulfate. Also, the data indicate that dichromate addition to ferric sulfate coagulated water slightly increases slug corrosion rates, but that dichromate addition to alum coagulated water slightly decreases slug corrosion rates. However, the effect of the dichromate is not nearly so pronounced as is the effect of the coagulant.

It can be noted that the plots do not plainly show induction periods or periods of accelerated attack. This fact is probably caused by the lack of data taken during the first few days of exposure.

D. Discussion of Corrosion Data Obtained by In-Pile Testing

In-pile corrosion data have been obtained with the four types of process water (32, 33, 34). These data are plotted in Figure 4, and show the following:

1. Dichromate addition to water coagulated with ferric sulfate increases slug corrosion rates.
2. Alum coagulated water is less corrosive than ferric sulfate coagulated water.
3. Dichromate addition to alum coagulated water tends to increase corrosion rates at higher temperatures.

The above comments apply with certainty only to the temperature range covered.

The corrosion data obtained for the alum coagulated water with dichromate addition were obtained from 100-DR. Some additional data obtained with this type water are not shown in the plot. These data are discussed below:

1. Data have been obtained with a tube of slugs discharged from 100-F at an exposure of 175 MWD/T (35). These data showed corrosion rates ranging from 0.011 mg/cm²/day at 15 C to 0.022 mg/cm²/day at 62 C. A plot of the data on semi logarithmic paper is a straight line. Because of the low exposure, it is believed that these data are not representative.
2. Data from the 100-C Pile with a tube partially charged with enriched uranium slugs also are available (36). At 90 C, the corrosion rates exhibited by these slugs were 0.45 mg/cm²/day—considerably higher than one would expect on the basis of previous experience. These data were not included in the plot because the enriched slugs operated at higher power levels than slugs used in previous in-pile tests. Goldsmith shows that power level is an

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- (32) Woods, W. C. A., Unpublished corrosion data obtained with alum water with dichromate addition.
- (33) Woods, W. C. A., "Summary of In-Pile Corrosion Data at Hanford", HM-28011, May, 1953.
- (34) Purcell, R. H., "Final Report, PT-105-453-P, Sodium Dichromate Elimination Tests", HM-24009, April, 1952.
- (35) Woods, W. C. A., "Interim Report Number 1, PT-105-503-E, The Use of Activated Silica as a Coagulation Aid for Aluminum Sulfate", HM-27115, April, 1953.
- (36) Lang, L. W., "Interim Report Number 2, PT-105-532-A-2, Irradiation of Enriched Uranium Slugs", HM-28713, August, 1953.

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FIGURE 4

SLUG CORROSION RATES DETERMINED BY IN-PILE TESTS

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important variable in aluminum corrosion⁽³⁷⁾, therefore these data are not believed to be comparable to data obtained in the other in-pile tests.

3. Goldsmith has also obtained preliminary data with slugs discharged at low exposures and operating at higher than normal power levels. These data also showed higher corrosion rates at higher temperatures than previous experience would have led one to expect⁽³⁸⁾. These data were not included on the plot because of the short exposures and high slug powers.

Because of the differences in testing variables discussed above, it seems reasonable that the three sets of data should not be compared with other testing results. The data which are shown came from slugs exposed in tubes operating at average powers of from 355 KW to 390 KW. It is not believed that power variations of this order will greatly affect corrosion rates.

In order to make the corrosion picture more complete, it would be very desirable to have additional data on slugs exposed to alum coagulated water with dichromate addition. This information would be of particular value if obtained from slugs operating with higher surface temperatures but with specific slug powers comparable to those encountered in previous data. Such data should soon be available from tests conducted during the parts of the year when inlet water temperatures were at a maximum. These results should resolve the yet unanswered question of how alum coagulated water with dichromate addition compares in corrosivity with other types of water at the more extreme conditions.

E. Comparisons of Flow Laboratory and In-Pile Corrosion Data

Tabulated in Table III are the relative corrosion rates of slugs obtained with in-pile and out-of-pile tests. In each case, the corrosion rate obtained with ferric sulfate coagulated water with dichromate addition is arbitrarily taken as "100". In every case, the actual rates determined in the flow laboratories were lower than the rates found by in-pile tests, but the tabulation shows trends in the data.

TABLE III

RELATIVE CORROSION RATES OF ALUMINUM IN DIFFERENT PROCESS WATERS

<u>Type of Water</u>	Relative corrosion rate as determined with		
	<u>Steam Jacketed Tubes*</u>	<u>Pre-heated Water**</u>	<u>In-pile Tests*</u>
Ferric sulfate with dichromate	100	100	100
Ferric sulfate without dichromate	—	90	45
Alum with dichromate	35	50	30
Alum without dichromate	50	40	30

* Determined at 65 C

** Determined at 95 C

(37) Goldsmith, S., "Interim Report, PT-105-510-E, Determination of Pile Irradiation Effects on Corrosion of 2-S Aluminum", HW-27531, July, 1952.

(38) Private communication with S. Goldsmith, August 17, 1953.

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From Table III it can be seen that the three sets of data are in reasonably good agreement. Both pile and flow laboratory results show that water coagulated with ferric sulfate is more corrosive to aluminum than water coagulated with alum. Also, both pile and flow laboratory results show that dichromate addition to water coagulated with ferric sulfate will increase overall slug corrosion rates.

Results obtained from in-pile tests and from steam-jacketed flow laboratory tubes show that dichromate addition to alum water will decrease slug corrosion rates at temperatures of 65 C or less. However, the data also show that at some temperatures between 65 and 80 C the addition of dichromate will cause an increase in the corrosivity of alum coagulated water. The data obtained with preheated water at 95 C showed that dichromate addition reduced slug corrosion even at this higher temperature. Evidently the corrosion rate versus temperature curves obtained by the different methods are somewhat displaced from one another; the trends, though, are the same for the three sets of data.

LOCALIZED SLUG AND TUBE CORROSION

Other very important aspects of aluminum corrosion at Hanford are localized attacks on process tubes and slugs. Wilson has reported the results of intensive laboratory studies of localized attacks on slug jackets⁽³⁹⁾.

The results obtained from these tests agree well with in-pile experience and showed that flow laboratory studies of this nature can be of considerable value.

The pitting type of corrosion of the empty, front sections of process tubes was also studied with flow laboratory equipment in conjunction with in-pile studies. The conclusions drawn from flow laboratory tests^(23,25,26) agreed with in-pile experience^(40,41,42) and the problem was mitigated by resuming the practice of adding dichromate to process water.

CONCLUSIONS

Comparisons of in-pile and flow laboratory data give rise to the following conclusions:

1. Water coagulated with ferric sulfate is more corrosive than water coagulated with alum.

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- (39) Wilson, C. D., "Flow Laboratory Investigations of 'F-Type' Pitting of Slugs and Tubes", HW-28207, June, 1953.
- (23) Atwood, J. M., LocCit.
- (25) Atwood, J. M., LocCit.
- (26) Atwood, J. M., LocCit.
- (40) DeHollander, W. R., "In-Pile Process Tube Examinations—A Program for the Examination of the Front Portion of Process Tubes", HW-27549, March, 1953.
- (41) DeHollander, W. R., "Interim Report from Tube Corrosion Problems", HW-26537, December, 1952.
- (42) DeHollander, W. R., "Interim Report Number 2, Front Tube Corrosion Problem, The Correlation Between Chloride Ion Concentration and Front Tube Corrosion", HW-27503, March, 1953.

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2. At some temperature above 65 C, dichromate addition to alum coagulated water increases slug corrosion rates.
3. Flow laboratory tests have been reliable in predicting trends in corrosion rates caused by varying water quality, although the actual rates determined in the laboratory are consistently lower than rates determined in-pile with a given water quality and at a given surface temperature.
4. Both flow laboratory techniques, the use of steam jacketed tubes and pre-heated water, may be used conjointly with good results in studying corrosion trends.
5. Flow laboratory investigations of localized slug and tube corrosion give results which agree with in-pile experience.

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APPENDIX I

MOCK-UP TESTING EQUIPMENT USED FOR OUT-OF-PILE STUDIES

Flow laboratory testing has, in general, been performed by passing hot water over dummy slugs in standard process tubes. There have been two primary methods by which this has been accomplished. First of all, preheaters have been used. In this method water is pumped through some type of tubular heat exchanger and the preheated process water is introduced to the process tube containing the dummy slugs. Secondly, steam jackets have been placed around the process tubes, and in this case the water is heated as it passes through the tubes. Figures 5 and 6 are flow diagrams of the facilities used for the methods.

Both of the techniques described above have certain advantages and limitations. There are certain practical advantages in using preheated water in corrosion testing. First of all, preheating reduces steam costs because the effluent water from the tube may be passed through a waste heat recovery exchanger to heat the cold inlet water somewhat before it is heated to the final temperature with steam. Also, with this system, temperature control is simplified. Another advantage arises from the fact that all the slugs are at the same known temperatures and one may easily determine a corrosion loss versus weight plct.

However, with the preheater the water is heated a finite time before it reaches the slugs. This heating has an effect on the colloidal particles in the water and, therefore, the quality of the water is changed before it reaches the slug surfaces. Also, there is a certain amount of metal ion pick-up by the water as it passes through the exchanger, and the water may be partially deaerated by the preheating. The preheating may cause a shift in the carbonate-bicarbonate equilibrium and effect a change in the pH by driving off CO₂. Furthermore, at a given time a heat exchanger produces water at one temperature. Therefore, with one experimental system it is possible to study aluminum corrosion at only one temperature. The data thus obtained give no information on the temperature coefficient of corrosion. Attempts to improve this situation have been made by bleeding off a part of the heated water, adding cold water to this stream, and passing the combined stream through another tube. In some cases, however, data obtained in this manner have proved to be different from data obtained by heating the water directly to the desired lower temperature⁽²⁸⁾. Evidently the quality of the water is different when it is heated directly to a given temperature than when it is heated to some higher temperature and then cooled to the desired temperature. Another limitation of this method evolves from considerations of the temperature effects on the galvanic potentials of 2-S and 72-S aluminum. At the same temperature, 72-S aluminum tends to be anodic to 2-S aluminum when coupled together in process water. In general, the galvanic potential of a metal tends to increase with increasing temperature⁽⁴³⁾. Therefore, under in-pile conditions, where the 2-S aluminum slug jackets are at a higher temperature than the 72-S tubes, the potential relationships are probably reversed and the slugs may be

(28) Goldsmith, S., LocCit.

(43) Hoxeng, R. B., "Corrosion of Construction Materials, Bonding Materials and Uranium—an Electrochemical Investigation", CT-3023, May 2, 1945.

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FIGURE 5
PREHEATED WATER TESTING SYSTEM

FIGURE 6
STEAM-JACKETED TUBE TESTING SYSTEM

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corroding sacrificially to the tubes. With preheated water, the slug jackets and tubes are at the same temperature and therefore pile conditions are not simulated.

The use of steam-jacketed tubes has certain advantages. The water is heated in the tube, simulating pile conditions. Hot water does not come into contact with steel or other metallic heat exchanger tubes and foreign ion pick-up is minimized. Also, original construction costs are reduced.

There are, however, certain disadvantages involved in using steam heated process tubes. First of all, the heat flux passes through the tube instead of the slug, and therefore the tube surface temperature is higher than the corresponding slug surface temperature. This effect is disadvantageous from the standpoint of galvanic potentials since the tubes would be more anodic than normal with respect to the slugs. Furthermore, the water is heated as it flows down the tube. It is therefore necessary to calculate the slug surface temperatures. Temperature traverses of a steam jacketed tube have been made⁽⁴⁴⁾. Unfortunately, however, film formation on the tube flow surfaces increases the resistance to heat transfer and may cause the temperature distribution along a tube to change during progress of a test.

Throughout the history of Hanford Works corrosion testing, both of the above methods have been used. The original work done at Hanford by the CMX project was carried out using both preheaters and steam jacketed tubes.

After the completion of CMX work, flow laboratory testing was not emphasized until early in 1951. At this time, a Water Quality group was formed in Pile Technology to study the effects of water quality on slug and tube corrosion and film formation⁽⁴⁵⁾. To accomplish this aim, facilities were erected in the 105-D Flow Laboratory where the quality of plant filtered water could be varied by chemical addition. This water was then used in mock-up tubes and in-pile tubes for testing. Because of the advantages noted previously, it was decided to use preheated water for the testing.

While construction of these facilities in the 105-D Flow Laboratory was underway, a limited number of tubes in the 105-F Flow Laboratory were fitted with steam jackets, primarily because the steam-jacketed tubes would be available for use in a comparatively short time. It was planned to use these tubes for obtaining certain preliminary data which were needed before the 105-D Flow Laboratory was completed. Originally, it was planned to dismantle the 105-F Flow Laboratory facilities when the 105-D Flow Laboratory was completed.

It soon became apparent, however, that the laboratory at 100-F was a unique, if limited, tool for use in corrosion testing. For this reason, the facilities at 100-F have been gradually expanded and at present the laboratory is proving to be of considerable value.

(44) Lewis, M., "Technical Activities Report, Pile Coolant Effects, December 1952", HM-26620, January 12, 1953.

(45) Fryar, R. M., "The Process Water Experimental Program", HM-19815, January 2, 1951.

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The 105-D Flow Laboratory, with more versatile facilities for the control of water quality variables, has proved to be an even more valuable tool in studying corrosion effects. This laboratory is now of particular value when used in conjunction with in-pile facilities in evaluations of water quality effects on the operation of present type piles.

It is now proposed to erect an additional flow laboratory at 100-K Area. This laboratory would have facilities for filtering water under various controlled conditions and therefore would be of considerably more value as an experimental tool than either the 105-F or the 105-D laboratory facilities. Also, the results of studies which could be made in this laboratory would apply to newer piles where tube flow rates and power levels will be higher than experienced in the older piles.

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APPENDIX IICALCULATION OF DATA OBTAINED WITH STEAM JACKETED TUBES

The original data for the curves shown in Figure 2 are plotted in the reference documents. These plots showed a considerable scattering of the points, so it was decided to determine statistically the best curves for the data.

In such a statistical treatment it is first necessary to select a type of equation. In general, the best correlation from the standpoint of theoretical considerations is obtained by plotting the log of the corrosion rate versus the reciprocal of the absolute temperature. If a straight line is obtained the data fit the equation:

$$CR = Ke^{\frac{-E}{RT}} \quad (1)$$

where

CR = Corrosion rate
K = Constant
E = Activation energy
R = Gas constant
T = Absolute temperature

This above expression is the familiar Arrhenius equation showing the influence of temperature on reaction velocities.

Practical experience has shown that in the limited temperature range of 30 to 90 C, if a plot of the logarithm of the corrosion rate versus the reciprocal of the absolute temperature is a straight line, then so also is a plot of the log of the corrosion rate versus temperature. This latter correlation has no theoretical basis but is of practical use in illustrating corrosion data. This second correlation was chosen for the data and the task evolved to evaluating the constants in the following equation:

$$CR = Ae^{bt} \quad (2)$$

where

A & b = Constants
t = Temperature

In the method of least square, one may assume error in either or both of the variables. In the case at hand, it was evident that error in the independent variable (the temperature) could not explain the scattering of the data. This is true because the data were obtained from slugs charged into a steam jacketed tube and adjacent slugs, which were necessarily at nearly equal temperatures, often exhibited widely different corrosion rates.

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