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WATER TREATMENT PROGRAM - OLD REACTORS

by

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November 19, 1962

Classification Cancelled (Change to

Declassified

By Authority of

Feb 10 1973

5/4/92

SPECIAL RE-REVIEW

FINAL DETERMINATION

DECLASSIFICATION CONFIRMED

BY *JP Lenoir* DATE *10/20/81*

BY *MS Barker* DATE *10/27/81*

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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INTRODUCTION

The conclusions resulting from a recent corrosion study,⁽¹⁾ together with evidence of graphite damage possibly occurring during retubing operations (having obvious implications in regard to reactor life), initiated a critical assessment of the water treatment process. The study was undertaken to determine whether immediate or near-term process changes could be made at the older reactors to minimize aluminum corrosion without causing adverse effects in other areas.

CONCLUSIONS

All of the water treatment process changes considered have some disadvantages and involve areas of technology which have not been evaluated fully with respect to reactor operation. For this reason, no immediate process changes should be made.

However, so that sound decisions can be made in the future, the following test program should be carried out without delay:

1. Half-plant test at D Reactor to compare a pH of 6.6 with a pH of 7.0.
2. Half-plant test at F Reactor to determine the effect of high alum feed versus low alum feed on fuel element ledge corrosion.
3. Half-plant test at C Reactor to compare 1.8 ppm with 1.0 ppm sodium dichromate at a pH of 6.6.

Assessment of carbon steel and aluminum corrosion rates, as well as the effluent activity problems, should be completed by the end of July, 1963. If favorable over-all results are obtained and water treatment process changes are instituted at that time, 70 per cent of the tubes installed between December, 1962, and the end of CY-1963 would have the benefit of a less corrosive environment.

In order that water treatment process changes can be made without delay when test program results are available, the interim period should be used to complete the engineering work necessary for the changes. Specific emphasis should be placed on preparations for the addition of sulfuric acid at or downstream of the 190 Tanks.

DISCUSSION

A. Water Treatment Plant Operating Conditions

1. pH

The pH of process water was established at 7.0 ± 0.1 in 1956. The pH of the process water at KW was reduced to 6.6 on June 23, 1961, under

1) Clinton, M. A. Analysis of the Frequency of Ledge Corrosion Attack Observed on Fuel Elements, HW-75368. 10/24/62. (Secret)

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authorization of Production Test IP-380-A.(2) Supplement A to Production Test IP-380-A authorized the reduction of pH at KE to 6.6 on September 26, 1961.

2. Alum Feed

Prior to mid-1961, the amount of aluminum sulfate flocculant used in the water treatment process was that amount which would produce reactor quality water. This resulted in seasonal variations of alum feed rate. Average alum feed rates were:

January-March	5 ppm
April-June	9 ppm
July-September	5 ppm
October-December	3 ppm

In mid-1961, the high alum feed program was introduced at the direction of the Atomic Energy Commission to reduce the radioactivity in reactor effluent, particularly P³². The change in alum feed rate to 18 ppm was made as follows:

<u>Reactor</u>	<u>Date</u>
F	5/1/61
B, C	7/1/61
KE, KW	7/6/61
D, DR, H	7/15/61

With the exception of the K plants, alum feed rates have remained constant. The changes made at the K plants, in unsuccessful attempts to reduce the concentration of P³² in the effluent, were made in the following manner.

<u>Reactor</u>	<u>Date</u>	<u>Alum Feed Rate, ppm</u>
KW	9/6/61	18 to 8
KW	10/6/61	8 to 12
KW	12/6/61	12 to 18
KE, KW	3/9/62	18 to 10
KE	4/12/62	10 to 13
KW	4/30/62	10 to 18
KE	5/21/62	13 to 18
KW	5/21/62	18 to 20
KW	9/1/62	20 to 18

3. Sodium Dichromate

Sodium dichromate at a feed rate of 2.0 ± 0.2 ppm has been used for many years as a corrosion inhibitor. On September 26, 1960, a half-plant test

- 2) Nesselson, E. J. Production Test IP-380-A, Reduction of pH of Process Water, HW-67634. 12/2/60. (Secret)

was started at C Reactor, in which the sodium dichromate feed to the test side was reduced to 1.0 ppm.⁽³⁾ By mid-1961, sufficient data had been obtained from Production Test IP-321-A to indicate no adverse corrosion effects, and the dichromate feed was reduced to 1.0 ppm at B, F, H, and KE on July 1, 1961.⁽⁴⁾ The dichromate feed at KE Reactor was increased to 1.8 ppm on September 26, 1961, concurrent with the reduction in pH to 6.6. This was still considered a necessary step, since the combination of low pH - low dichromate had not been evaluated. On December 16, 1961, the dichromate feed at D and DR was reduced to 1.0 ppm under Supplement A to PITA-IP-17-AI.

B. Water Treatment Process Options

The potential water treatment process changes considered in this study are shown in Table I, with the advantages, disadvantages, and unknown aspects of each. There are additional options involving combinations and subcases of those considered. It is the intent, however, to confine attention only to the major cases. Costs and effluent activity estimates stated below are based upon water treatment changes being made at all of the older reactor plants.

1. Alum Feed

The corrosion study presented in HW-75368⁽¹⁾ concludes that a marked increase in the frequency of fuel element ledge corrosion occurred in July, 1961. Since July, 1961, was the date the high alum feed process for treating reactor coolant was initiated, it can be assumed to be responsible for the increased ledge corrosion. If it is further inferred that the frequency of ledge corrosion in process tubes has increased and that ledge corrosion in tubes is a potential cause of tube failure, a possible course of action might be to reduce alum feed rates from 18 ppm to whatever is required to produce reactor quality water. Such action could be carried out immediately with no capital expense, and would result in an operating cost savings of about \$100,000 per year. A general increase in effluent activity would result. The P₃₂ concentration in the effluent would be expected to increase by a factor of two. This would result in a net increase for the entire plant of 45 per cent. The effect of alum feed rate on fuel element ledge corrosion has not been clearly demonstrated, nor has the effect of alum feed rate on tube corrosion and/or failure.

2. pH

Reducing the coolant pH from 7.0 to 6.6 will decrease aluminum corrosion rates, although the amount of reduction has not been determined. There

3) Nesselson, E. J. Production Test IP-321-A, Reduction of the Amount of Dichromate Added to Reactor Cooling Water, HW-65189. 5/11/60. (Secret)

4) Nesselson, E. J. and R. D. Shimer. Production Improvement Transition Authorization IP-17-AI. Reduction of the Amount of Dichromate Added to Process Water.

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are several ways in which this can be accomplished. For all cases considered in this report, a reduction in pH requires an increase in sodium dichromate feed rate from 1.0 to 1.8 ppm.

a. H₂SO₄ Addition at 190 Tanks

In addition to an operating cost increase of nearly \$400,000 for additional chemicals, capital costs are required for this alternate. Detailed estimates have not been made, but an installation at D Reactor for this purpose is expected to cost \$13,000. Inasmuch as it was possible to obtain a tank not otherwise being used for the D installation, perhaps \$25,000 might be required at each of the other reactors, or a total of \$125,000. Time for procurement of equipment and to effect the installation would also be required. The lower pH will increase the rate of carbon steel corrosion.

Areas of uncertainty with this type of pH control involve the amount of increase in carbon steel corrosion rates, the effect on effluent activity, and the degree, if any, of increased film formation.

b. H₂SO₄ Addition at 183 Building

Lowering the pH to 6.6 by sulfuric acid addition at the 183 Building could be carried out immediately with no capital expense. Since the acid is added prior to filtration, no increased film formation potential will exist. Operating cost increase for chemicals would be somewhat higher than in the previous alternate, since more water must be treated. In this case, the water plant would be operated as the K-Area water plants are now, and a two-fold increase in the P³² concentration of the reactor effluent would be certain. This would amount to a net increase of 45 per cent for the whole plant. As in the previous case, carbon steel corrosion rates would increase somewhat, which might be of more concern in this case, since more carbon steel is exposed to the 6.6 pH water.

c. HNO₃ Addition at 190 Tanks

A third method for reducing pH would be to add nitric acid at the 190 Tanks. The disadvantages of such a proposal are similar to those expected when using sulfuric acid at the 190 Tanks. The capital costs would be higher, since stainless steel equipment is required. The operating cost increase for acid would be three times as high if nitric acid is used. Although it cannot be stated with certainty, the use of nitric acid for pH adjustment at the 190 Tanks would not be expected to aggravate the P³² release to the extent that sulfuric acid would.

3. Sodium Dichromate

Sodium dichromate feed rates offer a third variable in the water treatment process.

a. Increase to 1.8 ppm at pH 7.0

There has been no evidence uncovered in the tests carried out or in the 15 months of operation at a pH of 7.0 with 1.0 ppm sodium dichromate to indicate that this condition is detrimental in terms of aluminum corrosion. Thus, there is no justification for the increased operating costs.

b. Use 1.0 ppm at pH 6.6

The use of 1.0 ppm sodium dichromate with coolant at a pH of 6.6 would make reduced pH more attractive from an operating cost standpoint. Initial results from single-pass tube tests are encouraging, but there is not enough information to insure that the combination of low pH - low dichromate will not result in increased aluminum corrosion.

TEST PROGRAM

In order to provide information in those areas of water treatment where data are sparse or completely lacking, the following test program should be undertaken without delay. In this manner, changes can be made with assurance that, while beneficial in some respects, the changes will not be detrimental in others. This approach will also, in the long run, maximize the return from any required expenditures.

A. The Effect of Low pH

Production Test IP-442-A, (5) authorizing the use of pH 6.6 water to half of D Reactor, has been approved. Test conditions will be as follows:

	<u>Test Side</u>	<u>Control Side</u>
pH	6.6	7.0
Alum Feed	18 ppm	18 ppm
Dichromate Feed	1.8 ppm	1.8 ppm

Sulfuric acid for pH control will be added at the 190 Tanks. Tube and fuel element corrosion will be monitored by probologging, tube examination, and the use of weighed fuel elements. The effect of low pH on carbon steel corrosion will be assessed by coupons and corrosometer probes in both the influent and effluent lines of each side of the reactor. Each effluent riser will be sampled to determine the effect on effluent activity, and film forming potential will be determined by careful monitoring of Panellit gages.

The test is scheduled to start on December 1, 1962. The effect on effluent activity will be defined within three months. Corrosion effects will require six to nine months for definition.

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B. Low Alum Test

In order to determine definitely the effect of high alum feed on the frequency of ledge corrosion of fuel elements, Production Test IP-549-A(6) is planned for F Reactor, in which half of the coolant will be treated with high alum feed and the other half with low alum feed. Operating conditions would be:

	<u>Test Side</u>	<u>Control Side</u>
pH	7.0	7.0
Alum Feed	6 ppm	18 ppm
Dichromate Feed	1.0 ppm	1.0 ppm

The alum effect will be determined by the visual examination of fuel elements from each side of the reactor. This test can be implemented by December 1, 1962; and conclusions concerning fuel element ledge corrosion frequency will be obtained in four months.

C. Low Dichromate Test

A half-plant test (Production Test IP-321-A) has been in effect at C Reactor, in which 1.8 and 1.0 ppm sodium dichromate have been compared at a pH of 7.0. It is proposed to extend this test to afford a similar comparison at a pH of 6.6. Operating conditions would be:

	<u>Test Side</u>	<u>Control Side</u>
pH	6.6	6.6
Alum Feed	18 ppm	18 ppm
Dichromate Feed	1.0 ppm	1.8 ppm

As in the D-Reactor test, aluminum corrosion will be monitored by probologging, tube examination, and weighed fuel elements. It is estimated that the test can be started by January 1, 1963, and that from six to nine months will be required to obtain the corrosion data.

D. Integrated Program

Figure 1 illustrates the over-all test program in terms of timing and decision dates. It is apparent that effluent activity effects will be established early in 1963. Assuming favorable results, the use of pH 6.6 process water at B, F, DR, and H could be undertaken at that time, if desired. Evaluation of corrosion data by the end of July, 1963, would permit a more complete assessment of the variables, including the economics involved.

- 6) Geier, R. G. and M. A. Clinton. Production Test IP-549-A, Half-Plant Low Alum Feed Water Treatment at F Reactor, HW-75541. To be issued. (Secret)

E. Test Program Effluent Activity Effects

If the concentration of P^{32} in the effluent from the test sides of F and D Reactors and all of C Reactor were to increase by a factor of two, the net P^{32} output of the plant would increase by about 15 per cent. In view of the technology to be gained and the fact that P^{32} is less of a problem between now and July, 1963, the modest increase should be no cause for concern.

F. The Effect of the Test Program on Tubes to be Installed through CY-1963

The latest tube replacement schedule⁽⁷⁾ indicates that 5,100 tubes will be installed in the older reactors from December 1, 1962, through CY-1963. As shown in Figure 1, 2,800 are scheduled prior to August, 1963, and 2,300 are scheduled after that date. If the test schedule delineated above is carried out, the 800 tubes scheduled for C Reactor, one-half of the initial block of 500 tubes scheduled for D Reactor, and one-half of the initial block of 400 tubes scheduled for F Reactor will be exposed to an environment presumably less corrosive to aluminum. By August 1, 1963, the aluminum and carbon steel corrosion data and the effluent activity data from the tests will have been evaluated, and the water treatment process at the older reactors can be firmly established. If one of the alternatives favorable to aluminum corrosion is found to be desirable, the 2,300 tubes to be installed late in CY-1963 will be protected. Thus, 3,550 of the 5,100 tubes, or 70 per cent of the tubes scheduled for installation, will receive the benefits of a less corrosive environment.

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TABLE I
POTENTIAL WATER TREATMENT PROCESS CHANGES

1. Alum Feed

- a. Reduce to quantity required to produce reactor quality water.

Advantages	Disadvantages	Unknown
Immediately carried out. Operating cost economies. No capital expense. Possible decrease in aluminum corrosion.	Increased effluent activity.	Effect on fuel element ledge corrosion. Effect on tube corrosion.

2. pH

- a. Decrease to 6.6 by H_2SO_4 addition at 190 Tanks.

Advantages	Disadvantages	Unknown
Reduced aluminum corrosion.	Capital expense. Installation time. Operating cost increase. Accelerated C-steel corrosion.	Aluminum corrosion rates. C-steel corrosion rates. Effluent activity. Film formation potential.

- b. Decrease to 6.6 by H_2SO_4 addition at 183 Building.

Advantages	Disadvantages	Unknown
Reduced aluminum corrosion. Immediately carried out. No capital expense. No film formation.	Operating cost increase. Effluent activity increase. Accelerated C-steel corrosion.	Aluminum corrosion rates. C-steel corrosion rates.

- c. Decrease to 6.6 by HNO_3 addition at 190 Tanks.

Advantages	Disadvantages	Unknown
Reduce aluminum corrosion.	Capital expense. Installation time. Operating cost increase. Accelerated C-steel corrosion.	Aluminum corrosion rates. C-steel corrosion rates. Effluent activity.

3. Sodium Dichromate

- a. Increase to 1.8 ppm at pH 7.0.

Advantages	Disadvantages	Unknown
	Operating cost increase.	

- b. Operate at 1.0 ppm at pH 6.6.

Advantages	Disadvantages	Unknown
Operating cost saving.		Effect of 1.0 ppm at pH 6.6 on aluminum corrosion.

FIGURE 1

INTEGRATED WATER TREATMENT TEST PROGRAM

Legend:

- ① Effluent activity effect established.
- ② Fuel element ledge corrosion established.
- ③ Aluminum and C/S corrosion rates established.
- ⬡ Tube replacements.

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