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March 19, 1953

SODIUM DICHROMATE AS A PROCESS WATER ADDITIVE; AN EVALUATIONINTRODUCTION

For several years after the start-up of the Hanford Piles, little concern was felt for the quality of process water. Techniques developed by CMX and improved in the course of operating experience were substantially successful for controlling and removing pressure drop film; (1,2) and corrosion rates at the early power levels were uniformly low and not a matter of concern, particularly since slugs were not exposed for more than 250 MWD/ton. As power and exposure levels were drastically increased, however, corrosion rates began to become serious and now threaten to limit future increases. The occurrence of slug ruptures became distressingly regular, and the possibility of tube leaks became a reality.

Whether or not corrosion was causing these latter problems, it was clearly imperative to seek ways to reduce the corrosivity of the water. Furthermore, the expense of the water treatment procedure made it highly desirable to seek simplifications and to critically examine the necessity of all parts of the process.

It was immediately recognized that substantial savings could be made by the elimination of sodium dichromate as a process water additive. Since the rather high pH of process water was necessary primarily to prevent dichromate reduction, the way would then be open for reducing the pH, and it was hoped that this would improve in-pile corrosion and materially reduce water treatment costs. Incidentally in the course of pH reduction, lime addition would be eliminated, but any saving might be offset by the acid which would be required if the pH adopted were low enough to require acid adjustment. Though flow laboratory experiments did not augur well for pH reduction, Production Test 105-453-P seemed to indicate that the elimination of dichromate would in itself lower corrosion, and so dichromate addition was stopped in April, 1952. Since that time operating problems and various experiments have cast doubt on the wisdom of dichromate elimination.

There is a large amount of data in the project literature pertaining to the dichromate problem, and it seemed urgent in view of recent experiences to re-evaluate this information to learn whether the issues might not be clarified and firm conclusions reached. This document presents such a re-evaluation and draws conclusions which, pending the completion of experiments now in progress, will serve as a primary basis for technical recommendations concerning dichromate addition to process water at all existing 100 areas and at the 100-K areas now under construction.

SUMMARY

A detailed review of the pre-start-up corrosion literature shows that an extremely strong empirical case for the use of 2 ppm sodium dichromate as a corrosion inhibitor was built up. The main advantage of dichromate was its ability to repress the strong pitting tendencies of Columbia River water in the pH range 6.5 to 8.0, where uniform corrosion rates were low. From the electrochemical point of view, the use of dichromate reduced the protective value of the 72-S aluminum cladding on 2-S aluminum tubes,

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but was very effective in reducing galvanic corrosion in general, including that to be expected from the thermogalvanic cell formed by hot slugs and cool tube wall.

Because the scope of the dichromate elimination test was limited, and because the results are not unequivocal, it is concluded that the actual elimination of dichromate was not altogether justified. Operating experience, since the elimination of dichromate, has been punctuated by a serious increase in front tube corrosion and by the appearance of a severe slug pitting attack at F Pile last summer. Laboratory work strongly suggests that both problems can be controlled by the addition of sodium dichromate at a concentration of 0.2 to 2 ppm.

The literature also contains strong indications that excessive reduction of dichromate will not occur at pH as low as 7.0, a pH which would be very desirable for the much lower uniform corrosion rate obtainable there, but which is definitely dangerous, in the absence of dichromate, due to the high probability of pitting.

It is concluded that the Works should return to the use of sodium dichromate, and that efforts be made to determine the minimum pH feasible for operation with dichromate, as well as the optimum concentration of dichromate to be used. At the same time, current experiments should be continued to determine the feasibility of a set of conditions under which operation without dichromate would be safe.

PART I

BASIS FOR THE ORIGINAL USE OF SODIUM DICHROMATE

The original specifications for Hanford process water were based on the recommendations developed from the intensive CMX pilot plant scale investigation. These recommendations, as presented in the CMX Final Report(3), were never intended to represent a true optimum; but they did provide a workable system which was presumably subject to improvement under continued plant operation(1). More recently, prevailing Hanford philosophy has tended to the position that the CMX findings might better be discounted(4,5,6,7).

In evaluating the findings of the CMX group, it is of some importance to recognize the objectives as well as the limitations of the program under which they worked(8). In general, the principal aim was to develop a water treatment method which would permit operation of the piles, and which would give a slug corrosion rate of one mil per month or less. Practically, cost was not a consideration; in the case of additives, for example, availability was a much more important factor. The work, of necessity, was done in an atmosphere of rapidly changing conditions, equipment and treatments. For example, the filtration procedure was constantly changing as information developed or as equipment became available: filtration without coagulation, no filtration, filtration with intermittent coagulation, filtration with alum or ferric sulfate coagulation were all used at one time or another. Whatever process was in use was subject to considerable manipulation of the process variables. Time, of course, was the most serious limitation: the first reactor was in operation less than a year after the actual start of CMX tests. As a consequence, there was no opportunity to make a thorough year round study of the effect of changing river water conditions on the final treatment method.

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The recommendations developed by CMX for process water treatment were as follows: (3)

1. Chlorination for algae control; free Cl_2 not to exceed 0.2 ppm, chloride not to exceed 2.0 ppm.
2. pH adjustment with lime, coagulation with a commercial ferric sulfate coagulant, settling and filtration. The final pH to be in the range 7.5 to 7.8.
3. Addition of 10 to 30 ppm sodium silicate for control of film growth.
4. Film removal by solids purge where necessary.
5. Addition of 2 ppm $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ to reduce corrosion.

An important limitation on CMX was the failure of their laboratory to duplicate exactly the 100 Areas water systems, a vital factor in the film problem*. This difference lies at the root of the subsequently observed failure of sodium silicate addition to inhibit film growth in the piles. Actual operating experience has also shown coagulation with filter alum to be more satisfactory in controlling film than ferric sulfate coagulation. This can be correlated with the CMX observation, that while film from alum treated water was the more severe, it formed in the cold, front part of the tubes (3,9), while with ferric sulfate treatment, film formed in the rear, heated sections. Coagulation is more rapid with alum treatment, and the much greater hold-up times in the 100 area plants allow a stable steady state to be attained before the water enters the piles.

No such difference existed in the corrosion investigation, with the single exception of the presence of radiation. According to the CMX final report, "acceptable" corrosion rates were observed in process water at a pH of 6.5 to 7.3, and in the presence of 2 ppm sodium dichromate, the rate was lower and pitting was nil. Recently, as a more cost conscious attitude towards water treatment developed, the necessity of the dichromate addition was subjected to considerable scrutiny, since sodium dichromate represented roughly one-half of the chemical cost of water treatment (10,11,12). Unfortunately, the attitude adopted was a priori that dichromate was certainly doing no good and might even be harmful (1,6). In the efforts to establish this position, frequent reference was made to such sources as the Corrosion Handbook (13) even though all the remarks in this work relative to dichromate inhibition are essentially irrelevant to the Hanford system. In the final analysis, the only system of interest at the Hanford Works is Columbia River water, more or less treated, flowing through the pile tubes at the operating velocities and temperatures**. Results on distilled water and other natural waters cannot be extrapolated to local conditions without considerable reservation.

* CMX was well aware of this problem. The final report states:

"It may not be possible to completely duplicate the laboratory results in the filter plants since the laboratory tests were made under entirely different conditions of mixing, flocculation and filtration. For these reasons the final evaluation of the coagulants probably will have to be made in the filter plants" (Ref. 3, page 26).

** From a memorandum from H. Worthington to C. P. Kidder, November 23, 1943:

"Mr. Williams has urged upon me the desirability of our taking the attitude that we do no water treatment, even flocculation, that is not of proved value. The experiments that you already have underway are in accordance with this".

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CMX OBSERVATIONS ON DICHROMATE INHIBITION

In the course of various discussions on the merits of dichromate addition, the suggestion was made that the actual CMX data did not justify the conclusions drawn in the final report. Finally, in reference 4, it was stated:

"There are no data in the CMX test runs which show that dichromate in the range of 1 - 20 ppm does reduce corrosion. The following table summarizes the results of CMX test runs of 100 or more hours duration in which uninhibited water, dichromate treated water, and sodium silicate treated water were tested" (see Figure 1).

On the other hand, CMX Final Report states:

Marked inhibition of corrosion was observed in all runs in which dichromate was used. The range covered was 1 - 20 ppm, although little correlation was obtained between the amount added and corrosion. Most data were obtained with a 2 ppm addition and showed an overall penetration of less than one-half that which non-inhibited water would show under similar conditions. A major advantage in using this inhibitor lies in the nearly complete absence of pitting-type corrosion when it is used even under conditions which normally would cause severe pitting, as for example, when aluminum is in contact with stainless steel, particularly at high pH (7.5 to 8.0).

In view of this disagreement, it seemed pertinent to review the CMW weekly reports⁽⁵⁴⁾ and the data therein. This analysis has led to a substantial verification of all of the statements made in the CMX final report concerning corrosion of 2-S aluminum. The corrosion rate did indeed decrease when dichromate was added; but what is far more important, the pitting frequently observed throughout the pH range 6.5 to 8.0 did not occur in the presence of dichromate. In any event, below 95 C the long time corrosion rate was below 1 mil/mo. in the range pH 6.5 to 8.0 with or without dichromate, and the only factor of any importance was the incidence of pitting. Since pitting occurred only in the absence of dichromate, the specification of dichromate addition was eminently reasonable and desirable.

In Figures 2 and 3 are presented the pertinent CMX data concerning the effect of dichromate on corrosion. It will be noted that the corrosion data are somewhat incomplete: this is associated with the early CMX recognition that obtaining low corrosion rates was not a problem. Most of the effort of CMX was devoted to solving the film problem and preventing pitting. Since it was thought that the reduction of dichromate by radiation would be excessive below pH 7.5, the decision to operate in the range 7.5 to 7.8 involved accepting an higher inherent corrosion rate in order to obtain the security given by dichromate against pitting.

The weekly inspections recorded in the CMX reports give the impression that pH 7.5 to 8.0 is more severe in general than any pH between 6.5 and 7.5, etching being more regularly observed. Though dichromate did prevent pitting, the appearance of slugs exposed to the higher pH water was less favorable than those exposed in dichromate water at pH 6.5 to 7.5. It should be pointed out that these weekly inspections convinced CMX that operation at any pH would be dangerous without some kind of

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Figure 1*

SUMMARY TABLE SHOWING THE EFFECT OF pH AND VARIOUS REAGENTS
ON ALUMINUM CORROSION RATES--IN CMX TEST RUNS

<u>pH</u>	<u>Number of Test Runs</u>	<u>Reagent Addition, ppm</u>		<u>Aluminum Corrosion Rate at 85 C (mils/month)</u>	
		<u>Na₂Cr₂O₇</u>	<u>Na₂Si O₃</u>	<u>Average of all Tests</u>	<u>Maximum Observed</u>
6.5	4	0	0	0.0002	0.0008
6.5	3	2.4 & 6	0	0.0002	0.0007
6.5	11	0	20 - 40	0.0004	0.0006
6.5	9	2 - 20	20 - 40	0.0002	0.0004
7.0	2	0	0	0.0003	0.0004 75 C
7.0	1	0	11	0.0002	0.0003
7.5 - 7.7	4	0	0	0.0007	0.0013
7.6	1	2 - 10	12	0.0033	0.0038
7.7	4	2	2 - 4	0.0010	0.0012
8.0	2		10 & 20	0.0015	0.002

* This table is reproduced exactly as it appears in Ref. 4. Figures 2 and 3 give a more complete summary of the actual CMX data. The table above gives no information about relative times, although the corrosion rate did not become constant till well over 200 hours in CMX experience.

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Figure 2

CMX RUNS AT pH 6.5^c

- Notes:
- Time of runs was usually less than 400 hours. Where the data show significant trends the time is broken into 2 periods: 0 to 200 hours and 200 hours and over.
 - Additive: D = 1 to 10 ppm $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, S = 5 to 40 ppm Na_2SiO_3 , T = Turbidity (sand or diatomaceous earth).
 - Numbers in the diagram indicate number of observations. Stars indicate the occurrence of pitting. All numbers are single digit numbers.
 - Circles indicate an extraneous condition, such as experimental additives for control of film.
 - Total number of runs is not necessarily equal to number of points, since corrosion rates were not measured in all runs, though all runs were inspected for pitting. Several sets of weight loss data were collected in some runs at different times.

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Figure 3

CMX RUNS AT pH 6.8 - 8.0

See notes, Figure 2.

a. Demineralized and deaerated.

b. pH unadjusted, averaged 7.7.

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inhibitor (cf 14). Of particular interest are the series of experiments in which continuous feeds of artificial turbidities were studied for their film removal properties. The use of such abrasive conditions resulted in very serious erosion-corrosion under all conditions except the presence of 1 to 10 ppm sodium dichromate. The latter completely stopped such attack, so much so that a continuous feed of 10 ppm diatomaceous earth was seriously considered as a reasonable treatment.

The CMX work did not include a systematic study of the variation with concentration of the efficacy of dichromate. What work was done did not show any substantial difference in behavior in the concentration range of 1 to 20 ppm. Though most runs were made with 2 ppm, the initial choice appears to have been arbitrary, although ample experience demonstrated the effectiveness of this particular concentration.

OFF SITE LABORATORY STUDIES

The extensive laboratory corrosion studies at the Metallurgical Laboratory in Chicago largely substantiated the CMX findings. According to the final report: (15)

"From the corrosion tests run in this investigation, it is considered that 2-S aluminum corrosion is slight enough so that the use of the material should be safe in Columbia River water at:

- (a) pH 6.7, temperature 70 to 90 C (and probably all lower temperatures) zero to 10^{-4} , normal H_2O_2 , zero to 25 ft/sec. flow rate, zero to 2 ppm Cl^- , with no other materials added to the water;
- (b) pH 7.8, other conditions identical to (a) as long as 2 ppm $Na_2Cr_2O_7 \cdot 2H_2O$ is present as a corrosion inhibitor, 2-S aluminum corrosion rates were minimum within the general pH range 5.5 to about 7.0 with the least danger due to corrosion at pH near 6.5, in the absence of corrosion inhibitors. When 2 ppm $Na_2Cr_2O_7 \cdot 2H_2O$ was present at pH 7 to 8, only very mild attack occurred, with danger of penetration of aluminum parts very slight, at temperatures from 70 to 95 C. In the absence of dichromate, areas of local attack were found in this pH range, believed due to local turbulence and other external factors. It must be emphasized that this does not necessarily predict that 2-S aluminum may be used according to plans at H.E.W. at the above conditions without any serious corrosion. No good simulation has been made of the effects of radiation and external factors such as the geometry or construction, presence of other construction materials, metal surface to volume ratio, etc".

Other results of interest from the Chicago investigation can be briefly summarized:

- (a) The corrosion rate in uninhibited water as a function of pH is shown in Figure 4.
- (b) The probability of pitting is a minimum at approximately pH 7.0, although pitting is more probable and more severe on the acid side. Though pitting at 6.5 apparently was not considered to be a problem, it was observed, particularly in longer runs.
- (c) Dichromate eliminates pitting in the range 7.0 to 8.0, reduces the steepness

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Fig. 4 *

CORROSION RATE OF 2S ALUMINUM AT 70C AND
95C IN SIMULATED COLUMBIA RIVER WATER
AS A FUNCTION OF pH.

* Ref. 15

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of the corrosion rate versus pH curve in this range, and reduces the temperature coefficient of the corrosion rate. Not studied was the effect of dichromate in the pH range 6.0 to 7.0.

Another important investigation was carried out at Chicago relative to Hanford pile problems, dealing with the electrical aspects of aluminum corrosion. This work, as reported by R. B. Hoxeng⁽¹⁶⁾, dealt mainly with the characteristics of the 2-S/72-S couple, which would be present if 72-S clad 2-S aluminum tubes were to be used. Primary effort was devoted to ascertaining under what conditions and to what extent 72-S would be anodic to 2-S, as must be the case if the 2-S is to be galvanically protected. Since a number of process variables, e.g. silicate concentration, peroxide concentration, dichromate concentration, pH and temperature have a marked and inter-related effect, attention was directed primarily to a series of specific conditions. In the case of dichromate, the net conclusion reached was that under all circumstances of interest, the solution potentials of 2-S and 72-S are very nearly the same. The precision of the data was such that the polarity of the 2-S/72-S couple in the presence of dichromate could not be predicted with certainty because of the small magnitude of the potential difference and the frequent fluctuations from one direction to the other. In view of these observations, it was suggested that the use of 72-S aluminum clad tubes was questionable.

Another important influence of dichromate can be seen in the effect of temperature on solution potentials and currents at pH 6.5, as shown in Figure 5. At room temperature, dichromate makes each electrode slightly more anodic, practically eliminating the potential difference between electrodes, whereas it reduces the temperature coefficient of the solution potential by a factor near five. The corrosion current is correspondingly reduced, and, in the presence of dichromate, there is no apparent temperature coefficient. This effect of dichromate is essentially the same at all concentrations in the range 0.5 to 10 ppm. Unfortunately, there are no data at higher pH's in the absence of dichromate, but those data at pH 7.0 to 8.0 with dichromate, while very erratic and complicated by other factors, suggest that values of the corrosion currents, at least, follow similar trends. In substance, the results suggest the use of 72-S cladding will do no great good and no great harm from the electrochemical point of view.

The most interesting aspect of the data in Figure 5 is the effect shown by dichromate on the corrosion currents, which were negligibly small at all temperatures measured in marked contrast to their appreciable increase with temperature when no dichromate was present. Though the potential differences were small, the failure of the currents to increase with temperature indicates that an important aspect of the effect of dichromate is anodic polarization. References 4 and 16 both list the following "possible effects of the use of sodium dichromate:

1. May change potential between cathode and anode.
2. Will increase conductivity of solution.
3. May form a film on the anode which will decrease the anodic area, thereby increasing the anodic polarization. This may result in local corrosion and

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Figure 5*

ELECTROCHEMICAL BEHAVIOR OF 2-S ALUMINUM - 72-S ALUMINUM COUPLE
AT pH 6.5 IN SIMULATED COLUMBIA RIVER WATER

Temp.	Metal	<u>No Dichromate</u>		<u>2 ppm Na₂Cr₂O₇ · 2H₂O</u>	
		<u>Pot. vs. SCE**</u> <u>volts</u>	<u>Short Circuit</u> <u>Current***</u>	<u>Pot. vs. SCE**</u> <u>volts</u>	<u>Current***</u>
28 C	72-S	0.57 ± 0.10	+ 0.013	0.66 ± 0.03	+ 0.009 ± 0.013
	2-S	0.42 ± 0.02		0.70 ± 0.03	
70 C	72-S	1.10 - 1.30	+ 0.061 ± 0.03	0.81 ± 0.02	- 0.012 ± 0.010
	2-S	0.82 - 1.00		0.81 ± 0.02	
80 C	72-S	1.00 - 1.23	+ 0.071 ± 0.06 - 0.03	0.84 ± 0.02	+ 0.009 ± 0.013
	2-S	0.87 - 0.99		0.83 ± 0.02	

* Ref. 16

** Saturated Calomel Electrode

*** Calculated to uniform corrosion in mils/mo. Positive sign indicates 72-S anodic.

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pitting*.

4. As an oxidizing agent will tend to depolarize the cathode.
5. May form a film on the cathode and increase cathodic polarization*.

Neither reference lists an obvious sixth effect:

6. As an oxidizing agent will tend to polarize the anode.

In commenting on items 1 to 5, ref. 4 states:

"The first four of these effects are all serious for their effect is to increase the galvanic attack of 2-S aluminum corroding in preference to 72-S aluminum when the solution potential of the 2-S aluminum is less** than that of the 72-S*.

Of course, this remark is not true of items 1 and 3. The word "change" implies neither direction nor magnitude. If the film mentioned in the third effect actually forms, and if the film is incomplete, the current density is increased at the anode, but the total current is unaffected, i.e., the galvanic attack is localized, but not increased. If the film is not perforated, then the only effect is to decrease the galvanic current. Since pitting is not observed in the presence of 2 ppm sodium dichromate, the latter effect must predominate.

Clearly, item 2 is irrelevant, since in waters of interest, where the ion concentration lies in the range of 75 to 100 ppm, the effect on the conductivity of adding 2 ppm $\text{Na}_2\text{Cr}_2\text{O}_7$ will be insignificant. (In the experimental work reported in ref. 16, the concentration of SO_4 ranged from 80 to 120 ppm, depending on the degree of pH adjustment with H_2SO_4 . The conductivity of the solution varied from 2 to 4×10^{-4} mhos.)

No work was done in the electrochemical studies to identify the specific polarization effects which were acting to produce the very low corrosion currents observed. Any depolarization either did not occur or was slight relative to the obvious polarization actually observed, as indicated by the very small currents. Therefore, the only important effects were 1, 3, 5, and 6, the observed decrease in the potential across the 72-S/2-S cell reducing the tendency for corrosion and the diminution in current representing a reduction in actual corrosion. Consequently, under the conditions of these tests***, 72-S aluminum has little value as protective anode for 2-S, but all galvanic corrosion due to aluminum couples is materially reduced because of the polarization.

* This list is quoted exactly from ref. 16. Ref. 4, which claimed to be quoting ref. 16, reworded item 3 as follows:

"May form a film on the anode which will decrease the anodic area, which would result in local pitting".

Neither reference makes clear that such local attack would be associated only with a lack of integrity of such a film if it forms.

** By less is presumably meant more electronegative, i.e., more anodic.

*** Stirred beakers, with simulated Hanford water.

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For all these reasons, the conclusions reached in ref. 4 relative to galvanic effects are incorrect and should be reversed. For example: "The result of this effect" is that, in all cases where 2-S aluminum is corroding to 72-S, the use of 2 ppm sodium dichromate will increase the rate of attack" should read ". . . decrease the rate of attack".

OFF SITE MOCK-UP STUDIES

As a matter of fact, the laboratory investigation of the galvanic effects in the 2-S/72-S system had very little application to the Hanford piles. That such was the case was well brought out in a concurrent series of experiments at Chicago in which an attempt was made to include the velocity effect⁽¹⁷⁾. In this study couples were exposed in a flow system at 15 ft./sec., the solutions and instruments being those used in the beaker study. The conclusions of interest were:⁽¹⁷⁾

1. "When couples of stainless steel and 2-S aluminum were tested in the beaker set-ups using simulated river water, pitting of the aluminum usually occurred within two to three days, whereas in the flowing systems there was no evidence of pitting after seven or eight days.
2. It appears that the flow and static test data can be correlated only to a limited extent. In solutions of simulated river water containing 10 ppm SiO_2 , 2 ppm $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, pH 7.5, temperatures of 70 and 90 C, increasing the H_2O_2 concentration from 5×10^{-5} to 10^{-2} N had very little effect on the single potentials of 72-S and 2-S aluminum in the flowing system, and over this range 72-S was slightly anodic to 2-S aluminum. In the beaker tests, increasing the H_2O_2 concentration above 10^{-4} N caused the 72-S to become cathodic to 2-S.

The galvanic currents developed between the 72-S and 2-S aluminum also showed that the 72-S aluminum was anodic, which would indicate that the clad 72-S would tend to prevent pits from penetrating into the 2-S core".

In none of the reports discussed above is there a consideration of the probably decisive influence of the temperature gradient across the water annulus on the direction of galvanic current flow in process tubes. Because of the low conductivity of process water, it is unlikely that the cell made up of the couple between slugs and tube wall is responsible for the major corrosion process. However much this particular galvanic corrosion occurs, it is quite clear that 2 ppm sodium dichromate would tend to reduce its extent and to assist the temperature effect to maintain the highly desirable polarity situation in which the slugs are anodic".

* (i.e., the decreased protection of the 2-S due to the decrease in potential difference and corrosion current in the 2-S/72-S cell.)

** Ref. 4 gives the impression that such a polarity is highly undesirable, which amounts to a preference for tube leaks instead of ruptured slugs, or at least a periodic complete tube replacement program, a difficultly tenable position. The primary function of the sacrificial 72-S layer on the tube wall is not to protect the slugs, but to protect the tube; and, in order to perform this function, the 72-S must be anodic relative to the 2-S tube wall. There is certainly not enough 72-S aluminum present to render protection to the slugs for any extended period. Clearly then, if the cladding layer is corroding to the slugs, the net effect is to diminish the protection afforded the tube in favor of providing a more or less useless protection to slugs which, in any event, have a relatively short life.

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One other corrosion research, carried on at Chicago, was a pilot plant project, on a somewhat more modest scale than CMX(18,19). Rather short prototype tubes and prototype fittings were exposed to simulated Columbia River water under conditions of internal heating and actual proposed velocities. Principal conclusions did not differ materially from those discussed above, i.e. below 95 C uniform corrosion is very small up to pH 7.0, pitting frequency is minimal in the region pH 7.0 to 8.0 and increases with increasing rapidity on the acid side. Sodium dichromate at 2 ppm gave some reduction in overall corrosion in the neighborhood of pH 8.0 and maximum security from pitting.

CORROSION AND RADIATION

In all of the investigations discussed above, the effect of H_2O_2 on aluminum corrosion was studied in an attempt to simulate the effect of radiation. The only clear result, considering all of the various data, is that in the concentration range of interest, 10^{-4} to 10^{-5} N, peroxide has no deleterious effect. Some indications were obtained that H_2O_2 could act as a general corrosion inhibitor or as a pitting corrosion inhibitor or both. Although the presence of H_2O_2 simulated one condition which it was expected would be produced by radiation, it was not known to what extent corrosion would be affected by the in situ formation of peroxide or by associated radiation effects.

Aside from the indirect effect on the corroding medium, it was expected that the main action of pile radiation would consist in a considerable lowering of the activation energies of reactions occurring at the solution metal interface(20). In the case of metals which tend to form films, the result would be an accelerated initial corrosion, due to this depolarization, until a strongly adherent oxide coat had been established. It was thought that this film should have high integrity and good protective qualities, because of its accelerated in situ formation.

A number of experiments were carried out using high intensity specific sources, such as cyclotrons, and the relatively weak sources provided by the piles in operation prior to the Hanford piles(21,22,23). In general, these tests gave a good simulation of pile conditions, with the major exception of a high neutron flux. (Any conjoint action due to the coincidence of high intensity beta, gamma and neutron radiations, was not possible either). In all such investigations, the same conclusion was apparent, namely, that the effect of radiation on aluminum corrosion was beneficial or nil, i.e., corrosion rates, as measured by weight losses, tended to be lower in the radiation field. One very interesting aspect was observed in an electrical study of the 2-S/72-S couple in the Clinton Pile(22). It was shown that the pile radiation made the 72-S more protective, (the current and potential increased several fold) and greatly increased the galvanic corrosion due to the cell. The addition of 2 ppm dichromate more than offset the radiation effect as shown in Figure 6.

CONCLUSIONS FROM EARLY CORROSION INVESTIGATIONS

Considering all of these data together, the following conclusions logically might have been drawn:

1. Corrosion predictions from out-of-pile experiments probably would not be greatly in error for actual pile operation.

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Figure 6*

INFLUENCE OF $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ON THE EFFECT OF
PILE RADIATION ON THE 2-S - 72-S COUPLE

Legend

- Potential Difference, Shield Cell
- Potential Difference, Pile Cell
- Corrosion Current, Shield Cell
- Corrosion Current, Pile Cell

♥ Reference 22

Temperature = 70 C
Pile Power = 3,000 KW
pH = 7.0

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2. Hanford water under practical operating conditions would have somewhat greater corrosive tendencies than higher purity waters.
3. For security from pitting, the minimum pH which could be considered would be in the range 6.5 to 7.5, possibly on the low side.
4. The uniform penetration rate would reach an excessive level in the range pH 7.7 to 8.0.
5. 2 ppm sodium dichromate would give greatly enhanced security from pitting throughout the pH range 6.5 to 8.0.
6. In the presence of 2 ppm sodium dichromate, uniform penetration would not be excessive below pH 8.0.
7. In the presence of 2 ppm sodium dichromate, or above a pH somewhere in the range 7.0 to 7.5, the use of 72-S clad tubes would have questionable value, however, with dichromate, little danger, either.
8. In the presence of sodium dichromate, galvanic corrosion in general would be minimized.
9. While sodium dichromate at a concentration of 2 ppm is satisfactory, some other concentration, probably in the range 0.5 to 5.0 ppm, might be better.

RADIATION AND SODIUM DICHROMATE

Towards the end of March, 1944, the status of the CMX study could be summarized as follows: (24)

"It was found at CMX that about 20 ppm SiO_2 dissolved in water as sodium silicate is sufficient to inhibit the formation of a film deposit at pH 6.5. This undemineralized water is, however, not ideal for passage through aluminum tubes containing aluminum-coated slugs. Pitting-corrosion and impingement-erosion are observed. These effects are in turn inhibited by the addition of 2 ppm of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$. The problem of handling this water was consequently considered well in hand until Wigner pointed out that the reduction of dichromate under irradiation had already been reported (CN-467 and Fricke, J. Am. Chem. Soc. 55, 2358 (1933))."

Starting in May of 1944, CMX ran a series of studies on the film forming tendencies of chromic ions (25). Shortly, it was discovered that Cr^{+++} at a concentration of 0.1 ppm or lower produced a heavy pressure drop film at a very rapid rate. The most serious aspect, however, was that the film could not be removed readily by purging with solids, the only effective purge for Cr_2O_3 films involving the use of high concentrations of H_2O_2 , a dubiously practical material. It was finally concluded that the maximum tolerable concentration of Cr^{+++} would be in the neighborhood of 0.02 ppm (26). While the extrapolation of this result to the pipes is somewhat more certain than the results on Fe_2O_3 - Al_2O_3 films, there is a possibility that the figure should be revised either up or down.

Thereafter a number of experiments were undertaken to assess the extent of radiation induced reduction to be expected (24, 27, 28, 29), and the influence of various conditions. The following points were elucidated:

1. In one passage through the pile the equilibrium:

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- will reach a steady state. Under any water quality contemplated for pile use, the value of the ratio (CrO_4^{2-}/Cr^{+++}) equilibrium will be finite.
2. The magnitude of (CrO_4^{2-}/Cr^{+++}) eq. increases with pH, with temperature, with silica concentration, and, up to a point, with oxygen concentration.
 3. The magnitude of (CrO_4^{2-}/Cr^{+++}) eq. decreases with CO_3^{2-} concentration, with the amount of H_2O_2 produced, and perhaps with the presence of minor impurities.
 4. The magnitude of (CrO_4^{2-}/Cr^{+++}) eq. increases with radiation intensity.

Because of its unexpectedness, considerable effort was spent in firmly establishing this last relationship.

The earliest conclusion reached was that no appreciable reduction would be expected in Hanford water at pH 7.5⁽²⁴⁾. This was later modified somewhat on the basis of early experiments in the CP-3 Pile⁽²⁷⁾. It was felt that, due to the uncertainty in extrapolating to the Hanford piles and to a discouraging experiment with real Hanford water, "a pH of 7.8 should be safe as far as chromate reduction is concerned, and a pH of 7.5 or less may well prove practicable"⁽²⁷⁾. Later work, however, was more encouraging, further experiments on real Hanford water proving more satisfactory than those on simulated water⁽²⁸⁾ and the earlier sample of Hanford water. Finally, on the basis of the temperature and intensity effects:⁽²⁹⁾

"It appears that a pH of 7.5 will certainly be safe for W operation as far as formation of trivalent chromium is concerned. It is quite probable, but not absolutely certain, that a pH of 7.0 or even lower may be used without exceeding the prescribed tolerance level of fresh trivalent chromium in the W cooling water".

Apparently because of suspicions of the intensity effect and to allow for uncertainties in extrapolation, it was decided to operate above pH 7.5, if this proved otherwise feasible. Ample experience, of course, has shown that operation above pH 7.5 is safe from the point of view of dichromate reduction, but nothing appears to have been done to ascertain the safe minimum pH. Presently, however, experiments are being conducted along this line⁽³⁶⁾. (It should be pointed out that this minimum would drop approximately 0.15 pH unit between summer and winter, corresponding to the 15 C decrease in river water temperature. The position of this pH minimum would perhaps show a seasonal variation due to changing river water impurity content.)

Actually the extrapolation to the higher intensities expected at Hanford was rather short, as can be seen in Figure 7. Probably the main reason for not wishing to extrapolate the intensity effect was its rather unbelievable nature. Clearly as the intensity becomes smaller and smaller, the amount of chromate reduction cannot increase without limit (in terms of Figure 7, the curves shown there must somewhere bend back to the X-axis, ultimately becoming asymptotic as the reciprocal of the intensity increases without limit.)

The fact that the ratio (CrO_4^{2-}/Cr^{+++}) eq. increases with intensity may be justified theoretically. The reduction of chromate is probably a secondary effect, arising from the reaction with H_2O_2 or more probably, OH radical, which is the primary product of radiation. Since the equilibrium concentration of H_2O_2 can be expected to increase with intensity, and since the extent of dichromate reduction is observed to be an inverse function of the equilibrium concentration of H_2O_2 , the observed

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Fig. 7*

EFFECT OF PILE RADIATION INTENSITY ON
CHEMATE REDUCTION IN COLUMBIA RIVER WATER AT 25°C.

*Data From Reference 29
(a) Dose, at The Indicated Intensity, Equivalent to Dose Received On The Passage Through A Hanford Pile

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increase in the ratio ($\text{CrO}_4^{=}/\text{Cr}^{+++}$)eq. is not unreasonable.

SUMMARY

If, for safe operation of the piles, it is assumed that:

1. It is essential to provide maximum security against pitting type corrosion,
2. It is highly desirable to have a low, uniform corrosion rate, and
3. It is essential that film formation be controllable, and highly desirable that it be prevented altogether,

then certain conclusions are inescapable.

1. The evidence from the pre-start-up literature is overwhelmingly in favor of the use of sodium dichromate at a concentration of 2 ppm, though the possibility of some other concentration or even some other inhibitor is not precluded.
2. Any pH in the range 7.5 to 7.8 is probably safe. From the corrosion point of view, any pH in the range 6.5 to 7.5 would be more desirable and is not precluded by other pile operation considerations. The safe minimum would be determined either by the pitting probability or by the reduction of dichromate. The protection rendered by dichromate against pitting probably begins to fail as the pH is reduced below a value near 6.5; there is an excellent chance that the reduction of dichromate is not prohibitive at least at pH 7.0 and possibly below.
3. From the point of view of the literature discussed above, operation should have begun, as it did, at pH 7.5 - 7.8 and with the addition of 2 ppm sodium dichromate. The next logical step would have been in-pile experimentation directed to lowering the pH, with the hope that operation at pH 7.0 would be feasible, while still leaving a margin of error of a few tenths of a pH unit.

PART II

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DICHROMATE ELIMINATION

Because of the unique stringency of process water specifications, the original water treatment method was subject to considerable critical review, both from the standpoint of cost and of operability⁽²⁾. In the course of this program, a number of improvements and simplifications of the CMX process were effected by the Power Division culminating in the elimination of sodium silicate additions⁽³⁰⁾. An obvious further step was the re-evaluation of the need for sodium dichromate. Because of a lack of suitable laboratory facilities, information from unclassified sources, which had only a limited relevance, was cited in an effort to show that dichromate should be eliminated, although no complete study of the early project literature appears to have been made.

The corrosion literature makes frequent reference to the use of chromate inhibitors in a variety of service conditions. As typified by the "Corrosion Handbook",⁽¹³⁾ such situations involve the use of steel or aluminum in rather corrosive environments. The "Corrosion Handbook", when mentioning particular uses of chromate or dichromate, always does so with reference to a highly specific system. Unfortunately, this point has sometimes been overlooked. Reference 4, for example, states:

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"G. G. Eldredge and J. C. Warner in the 'Corrosion Handbook' state on page 913 that, in recirculation systems, from 500 to 1,000 ppm dichromate are necessary".

On page 913 of the "Corrosion Handbook" the only metal mentioned is steel, and the recommendation of the above amounts is only for closed, recirculating systems where the inhibitor depletion may be high. For recirculating systems with losses and make-up, as little as 100 ppm can be used, with the possible exception of a short initial period. Further points brought out on page 913 are that:

1. The amount of inhibitor needed decreases when contact with open air is maintained.
2. The amount of inhibitor needed increases with a decrease in the "degree" of agitation.
3. The amount of inhibitor increases with the salinity of the water.

In the case of aluminum, handling recirculating water, 1,000 ppm are recommended on page 914; but with reference to brines:

"The Aluminum Research Laboratories recommends one percent as much sodium dichromate as there is chloride ion present". @

In such recirculating systems the problem is not preventing a low overall concentration, but in preventing a very low concentration at some specific site, due to local depletion through use. In the Hanford reactors, where turbulence is very high, and overall depletion impossible, the only requirement is that the bulk water concentration exceed the maximum local instantaneous requirements, which, in this relatively pure water, is probably very low. The older literature, of course, is very clear on the dangers of anodic inhibitors at insufficient concentrations⁽³¹⁾. If insufficient inhibitor is present, the area of attack is diminished more rapidly than the total attack, leading to a high rate at a small site, i.e., pitting.

In 1951, several offsite consultations^(6,32,33,34) led to conclusions substantially similar to those drawn from the "Corrosion Handbook"; that 2 ppm was doing no good and possibly some harm, on the grounds that this concentration was too small. Alcoa, for example, did not approve of chromate inhibition, suggesting sodium nitrate instead; but felt that if used, the concentration of sodium dichromate should be at least 1,000 ppm⁽⁵⁾.

JUSTIFICATION OF THE DICHROMATE ELIMINATION TEST

It should be recalled that, in 1951, slug corrosion rates were rising drastically as power levels and temperatures were increased*. Simultaneously, a slug rupture problem

* The intermingled effects of simultaneously changing several variables produces subtle pitfalls. Reference 4 tried to show that the elimination of silicate additions in 1949 led to an increase in corrosion rates. Figure 2 in that document is a plot of corrosion rate versus time, and it shows that in 1949 the rate more than doubled after silicate elimination. Unfortunately, it is not pointed out that the 1949 points are from the elevated temperature production test⁽³⁵⁾ and that the tube outlet temperatures for these points were about 25 C higher than for the earlier data.

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arose, and various efforts were made to justify the elimination of dichromate on the grounds that it was responsible for most corrosion problems. Since there were neither laboratory nor pile data of recent vintage to support or refute this notion, the case had to be made on grounds such as those discussed above. Thus, J. E. Draley, ANL Corrosion Chemist commented⁽⁶⁾:

"It is quite possible that no improvement leading to higher corrosion resistance of the slugs or tubes would be necessary if the water treatment were changed to give a less corrosive medium. There is no apparent reason for adding the dichromate and there are several indications that it is harmful. With dichromate absent, the only known reason for operating at a potentially dangerous pH corrosion-wise, is that it is believed that a slightly higher rate of film formation would be observed at lower pH".

Even though the slug rupture problem had been practically non-existent before 1951, i.e., for over five years, attempts were made⁽⁴⁾ to explain the high frequency of ruptures, which came with increased power levels, as being due to pitting, caused by insufficient inhibitor. This is inconsistent with the well known fact^(15,36) that pitting tendencies decline with increasing temperature. Another approach^(4,12,10) to the same problem was the following argument:⁽¹²⁾

"It can be shown that the normal polarity relationships between the two metals (2-S and 72-S aluminum) may be reversed by the heating of the alloy with the lower potential; the polarity relationships may also be reversed by adding sodium chromate to the water. Since the slug jackets are hotter than the tube wall, it would be expected that the slug jacket would corrode sacrificially, and the presence of sodium dichromate may accelerate this corrosion rate".

Here the conclusions of reference 16 are being partially drawn upon. While the presence of dichromate may indeed reverse the normal polarity, it does this by "leveling" the differences between the separate anodic potentials to the point where minor fluctuations determine the actual polarity. Further, the temperature coefficients are reduced, so that dichromate, as pointed out earlier, would tend to offset greatly the magnitude of this thermogalvanic effect.

Another approach is to consider that 2 ppm sodium dichromate is grossly inadequate for anodic inhibition, so that the only effect would be cathodic depolarization. On the basis of reference 16, such an effect would be very unlikely; though, if it occurred, the result would be an increased uniform corrosion rate. This effect is presumably what Draley had in mind, though his major criticism was the high pH occasioned by the use of dichromate.

Probably the most serious charges leveled against the use of dichromate were in connection with the problem of front tube corrosion. There are two important aspects of this problem. The first was the pitting of Van Stone flanges, due to the couple between stainless steel nozzles and tube walls. CMX had found that dichromate

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prevented this type of attack*, but apparently their runs were not of sufficient length to show that dichromate only decreased the probability of this attack, but did not prevent it. This phase of the front tube program was solved by replacement of stainless steel with galvanized or aluminum nozzles.

The second aspect of the problem did not appear until the elimination of the front dummy pattern. It was then found that a pitting attack developed in the low velocity sections at the front of the tubes, characterized by the growth of mounds, or barnacles, of white corrosion product over the pits. This attack was not particularly threatening since it did not involve more than a fraction of the tube surface⁽³⁷⁾ and since the 72-S cladding was giving complete protection to the 2-S tube wall⁽³⁸⁾, as predicted by reference 17. This, however, constituted a pitting attack which sodium dichromate was not preventing, and so the whole ability of dichromate to prevent pitting was rightly questioned. Since the presence of lead had been detected in pressure drop films, it was further conjectured that particles of the insoluble lead chromate were settling in the low velocity sections and possibly causing this barnacle attack⁽¹⁰⁾.

THE DICHROMATE ELIMINATION TEST

The cost of adding sodium dichromate was about \$300,000 per annum,⁽¹¹⁾ and enough considerations, as outlined above, having been advanced to raise serious questions regarding the desirability of its use, a production test was initiated to study the feasibility of stopping dichromate addition. This test⁽¹¹⁾ was run using the recirculation equipment at H Pile to pass filtered water without dichromate through two reactor tubes, one of which was newly installed for the test. The charge consisted of 58 regular metal slugs and six dummies. Two normal tubes, one of which was new, were similarly charged and operated on process water as controls. The actual test ran for five months, and the slugs were carried to 65 percent of normal exposure. At the conclusion of the experiment, it was found that there was little or no evidence of pitting in either the test or control systems. (Some front tube pitting was observed in both old tubes, but this was probably not incurred during the test.) On the other hand, above 35 C, slug corrosion rates for the dichromate-free system were found to be 40 to 50 percent lower than in the regular process water tubes. (The corrosion data for the control tubes were in good agreement with the values predicted from corrosion rate monitoring.) Since every second slug was weighed, these data correspond to that which would be obtained from one full tube. Largely on the basis of the slug corrosion data obtained, dichromate was eliminated at all areas⁽³⁹⁾. (At F Area, and later at D, where the change from Ferrifloc to alum coagulation resulted in a 50 percent decrease in slug corrosion rates, it was assumed that a further reduction would occur when dichromate was removed.)

* CMX Final Report says:

"A major advantage of using this inhibitor lies in the nearly complete absence of pitting type of corrosion when it is used under conditions which normally would cause severe pitting, as for example when aluminum is in contact with stainless steel, particularly at higher pH (7.5 - 8.0)".

This statement, taken alone, appears to have given the impression that the main reason for using sodium dichromate was to prevent corrosion due to the stainless steel aluminum couple⁽¹²⁾. There are, however, a number of other remarks in reference 3 relative to the ability of dichromate to prevent pitting in general.

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In evaluating the results of the dichromate elimination test, there are two important points which must be considered.

1. During the course of the test, 22 hours of the 4418 hours of total operating time were spent on process water with dichromate, since the test system was tripped to process water during the bi-weekly pile purges. It has been established by Alcoa that the effects of adding or removing inhibitor may persist for some time, even running into months, after the actual change is made⁽³⁴⁾. This intermittent addition of dichromate could well have had a profound influence on the occurrence of pitting, though it is less obvious that the corrosion rate would be affected.
2. Since the conclusions of the test were effectively based on one tube, eliminating dichromate throughout the plant amounted to extrapolating from one tube to over 10,000.

LOW pH EXPERIMENTS

Concurrently with the dichromate elimination test, a series of experiments were run in the new water quality flow laboratory to study the effects of lowering the pH of dichromate-free water⁽³⁶⁾. In these experiments, filtered water at pH's 6.2, 6.7, 7.2, and 7.7 was passed through mock-up tubes at temperatures of 65 C and 95 C after preheating in a heat exchanger*. The results of this work agreed very well with what would have been predicted from the CMX data and the Chicago laboratory work. As the pH was decreased, the corrosion rate fell off rapidly to a very low value at pH 6.2 with no sign of a minimum at 95 C, and with a broad minimum in 65 C water, the rates for 7.2, 6.7, and 6.2 being substantially the same. The virulent pitting tendencies of Columbia River water found by CMX were also very apparent, showing all predicted tendencies. The percentage of pitting, dangerous even at pH 7.2, increased fairly rapidly with decreasing pH, and decreased by about 50 percent on increasing the temperature from 65 C to 95 C. No actual pitting was observed at pH 7.2 at 95 C or at pH 7.7 at 65 C or 95 C after 90 days of operation, but an extrapolation of the trends would indicate that even at pH 7.7, at least at 65 C, there is a small, but real, probability of pitting after more lengthy exposures.

In the face of the experiments discussed above, it would appear that the following conclusions can be drawn:

1. Though it is possible that, because of the heat exchanger effect, the pH tests gave an overly pessimistic view, removing the sodium dichromate from process water would reduce security from pitting even if no change in the pH was made.

* Numerous experiments in the last year have given indications that it can be dangerous to draw absolute conclusions about the corrosivity of water that has been heated in a heat exchanger. Such water occasionally has its turbidity increased by the introduction of scale, producing a higher rate of erosion-corrosion. Water at some intermediate temperature which has been produced by mixing cold and hot water is somewhat different than water heated directly to the intermediate temperature. The concentrations of dissolved gases may be seriously disturbed; in particular the pH may increase due to the expulsion of CO₂. A general discussion of the relation between flow laboratory and in-pile results is given in reference 55.

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2. In the absence of dichromate, no change to lower pH's could be contemplated without extensive corroborating experimental data.
3. Though the results of the dichromate elimination test are not unequivocal, it was probable that removing dichromate would lower the corrosion rate.
4. Since the over-riding corrosion consideration is the prevention of pitting, it would have been desirable to have more conclusive data to justify the complete elimination of dichromate from process water.

PART III

THE EFFECTS OF DICHROMATE ELIMINATION

The water plants have now operated for over ten months without dichromate, and laboratory work dealing with several aspects of the effects of dichromate has been greatly expanded; much new information has thus become available. In interpreting the behavior of the piles, it must be remembered that, in the period immediately following the elimination of dichromate, the film of adsorbed chromate ions, previously built up, was slowly being removed. Consequently, any inhibiting action of dichromate might be retained in part for some time, and there would be a short period during which the dangerous effects of having insufficient inhibitor might be expected.

FRONT TUBE CORROSION

Some months after the elimination of dichromate, it became apparent that the front tube corrosion problem was approaching an acute stage. Routine inspections, instituted by S. Goldsmith⁽⁴⁰⁾ and currently being continued by W. R. DeHollander⁽⁴¹⁾, indicate that the attack is proceeding at a much faster rate than before dichromate was taken out. Unfortunately no information is available on the state of front tube attack at the time of dichromate elimination, so a detailed comparison is not possible. In fact, the only previous study of this problem was an examination of 123 tubes at B Pile, 26 at F, 30 at H and 50 at D⁽³⁷⁾. At the time of this inspection, mid-1950, the attack was negligible compared to what it is now; the worst tubes in the 1950 survey would all fall well within the lowest range on the scale used by DeHollander⁽⁴¹⁾, i.e., where the number of barnacles is countable during a quick look. The consensus seems to be fairly definite that the attack has been proceeding at a much faster rate in the last ten months than was ever the case before the elimination of dichromate^(40,41,42,43). It is certainly true that the corrosion occurring on the cap supported shielding pieces is much worse⁽⁴²⁾. The 72-S cladding is still protecting the tubes, so that there is no immediate danger, but at the present rate the cladding will soon be gone. D Pile, for example, has already lost what may be as much as 50 percent of the 72-S layer in the first eight feet of some of its tubes⁽⁴¹⁾.

Since this corrosion is occurring in the cold, inactive portions of the tubes, pile operating variables, such as power level, have no effect^(43,44). The flow laboratory has been able to reproduce barnacle formation very well^(43,44) and a number of the characteristics of the process have been elucidated.

1. It has been conclusively demonstrated that the probability of barnacle formation is very greatly decreased in the presence of 2 ppm sodium dichromate^(44,45). Preliminary data indicate also that this effect persists down to a concentration of 0.1 ppm and that intermittent dosages of 2 ppm are

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also effective, particularly if a pretreatment of continuous feed is applied⁽⁴⁵⁾.

2. Barnacles may possibly be initiated by small foreign particles in the water, though this is certainly not a major source⁽⁴⁴⁾.
3. The probability of barnacle formation increases with decreasing pH, with decreasing temperature, and with decreasing flow rates^(44,46).
4. The presence of graphite powder in a tube section greatly increases the probability of barnacle formation.
5. There is a marked tendency for barnacles to develop in mechanically produced defects and in axial lines in the tubes which apparently are associated with the extrusion process.
6. Pits under barnacles usually penetrate the 72-S layer but stop at the 72-S - 2-S interface. The character of the pits is typical of oxygen cell corrosion⁽⁴¹⁾.

A fully satisfactory description of the barnacle formation process has not yet been developed, but certain phases are clear. The development of a barnacle presumably begins with the establishment of a local cell, with a very small anode. In slowly moving water, the corrosion product builds up over the anodic spot, but not sufficiently close to prevent some access of water. Once started in this manner, the corrosion product built up protects the solution bathing the anode so that the oxygen concentration is rapidly reduced and maintained well below that of the bulk water: an oxygen concentration cell is set up and the mound grows rapidly to its equilibrium size. The means by which the original cell is set up are obscure, though several mechanisms have been suggested:

1. Inhomogeneities in the oxygen concentration, arising from the flow patterns.
2. A galvanic cell, arising from heavy-metals plating out of the process stream.
3. A differential oxygen concentration cell, arising from inhomogeneities in the deposition film.
4. A galvanic cell arising from graphitic streaks in the tube surface introduced in the fabrication process where graphite is employed as an extrusion lubricant.
5. Local anodes developed by selective local attack on the oxide coat by the chloride ions in the water.

Any or all of these mechanisms, or some other unsuspected impurity in the water could be responsible. One might predict that any of the effects listed would be repressed by sodium dichromate. Finally, it must be pointed out that dichromate does not completely prevent front tube corrosion, but does greatly decrease the severity, to the point where the attack does not appear to be dangerous.

The most recent front tube inspections show that the sampling procedure used heretofore does not give a quantitative picture of whole piles, consequently it is impossible to make summarizing statements concerning the overall status of the damage due to front tube corrosion. It is certainly true, however, that many specific tubes have been damaged to a dangerous extent and that some of the piles are in bad state.

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SLUG CORROSION

In the case of the slug rupture problem, the situation is not nearly as straightforward as it is for the barnacle problem. Information developed in the last year, makes it appear that much of the slug rupture problem may be unrelated to corrosion, but may arise from variations in the quality of the heavy metal and variations in the canning process⁽⁴⁷⁾. These factors make it extremely difficult to determine what connection there is between ruptures and corrosion; consequently correlations with water quality cannot, in general, be established. However, it must be assumed that corrosion is an important factor. Preliminary conclusions from a survey of information concerning the actual distribution of thickness in can walls indicate that there may be a regular increase in rupture frequency with corrosion rate, although this frequency, at present corrosion rates, is very much less than the overall rupture rate⁽⁴⁸⁾. This conclusion is based on the occurrence and degree of Al-Si penetration into the can wall. Further, the probability that a pit will develop over any particular area of penetration is slight, but the probability that a pit and an Al-Si penetration site will run into each other increases rapidly with pit depth, due to the increased frequency of Al-Si spots of lesser depth. This again supports the proposition that it is vital to prevent even relatively mild pitting.

As far as the uniform corrosion rate is concerned, there are as yet no data available from PT-105-9-P to confirm or deny the results of the dichromate elimination test, at least for ferric sulfate coagulated water. The extrapolation of the test results to alum water does not, however, appear to have been justified, since no appreciable difference has been observed to date in the corrosion rate in alum water with or without dichromate⁽⁴⁶⁾. The corrosion rate for alum treated water with or without dichromate is substantially below that for Ferrifloc water either with or without dichromate.

Some time after the elimination of dichromate, the most serious corrosion problem yet observed in the piles appeared in the form of a severe slug pitting attack, accompanied by a very high rupture rate, at F Pile⁽⁴⁹⁾.

Three causes have been suggested as being responsible for this attack:

1. Mercury Corrosion. While sources of mercury contamination have been detected both in the 100 and 300 Areas, it is difficult to account for the F Pile specificity on such an hypothesis. Mercury has, however, been detected in pitted areas. Preliminary investigations have shown that it is unlikely that mercury can cause F type pits under pile flow conditions⁽⁴⁵⁾, and that 2 ppm dichromate inhibits mercury attack on aluminum in any event⁽⁴²⁾.
2. Cavitation. Considerable work has been done by the Pile Coolant Effects group on the production of cavitation in process tubes. Conclusions to date are that unreasonably high restrictions of the annulus and improbably low pressures are required for cavitation to occur in the pile⁽⁴⁵⁾.
3. Erosion-corrosion. Recently there has come to light a picture from one of the CMX reports⁽⁵⁰⁾ depicting slugs which show pitting similar in all respects to that produced in F Pile. This attack occurred during runs which had added turbidities, e.g. diatomaceous earth, Columbia River sand, etc. CMX, at the time, early 1944, was contemplating the use of a continuous feed of artificial turbidity for control of film, and a detailed study was made of this erosive

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attack. It was found that the attack was strongly temperature dependent, indicating that the corrosion was chemical and that the function of the abrasive was the removal of any protective oxide coat. It was also found that 2 ppm sodium dichromate completely inhibited the attack at any pH between 6.5 and 8.0. Recently a series of jet impingement tests have completely verified the conclusion that dichromate at 2 ppm inhibits erosive attack⁽⁵¹⁾, and have shown that down to a concentration of 0.5 ppm dichromate retains this inhibiting power. Currently, mock-up tube tests are in progress to study the phenomena further. A number of tests which were run in the cavitation study gave evidence of F type pitting, but it now appears that, in every case where the attack was observed, it was due to turbidity from heat exchanger scales. Although it has been possible to make some correlation of the attack with F Pile turbidity⁽⁴⁵⁾, it cannot be said that the nature of F Pile attack is known. It is, for example, possible that air bubbles can produce the same effect as turbidity. In any event, the disappearance of the attack at F Pile seems to be associated with the lower prevailing river water temperature, so this particular type of attack would not be expected again until next summer. On the other hand, there is no good reason for not expecting it again at F Pile or at the other areas currently not using dichromate. As a matter of fact, slugs with F type pits have shown up in both the B and H reactors⁽⁵²⁾.

CONCLUSIONS

The decision to abandon dichromate was based on an experiment of limited scope that provided data only for a restricted set of conditions. There was a large amount of data from early experiments indicating that, under certain circumstances, which well might arise in a Hanford pile, pitting would occur in uninhibited water. Operational experience, since the elimination of dichromate, has shown that pit-producing conditions can and do occur in the actual piles with present methods of operation, as predicted by the early data. All of the available information strongly indicates that dichromate will alleviate the severity of this pitting. Until such time as the piles can be operated strictly within the confines of a set of conditions which are known to be safe from pitting, the insurance provided by dichromate will probably be necessary.

Within the framework of a dichromate inhibited system it should be possible to effect significant improvements in water quality and at least some reductions in cost. In all of the information reviewed there is nothing to suggest that a concentration of 2 ppm of sodium dichromate is the optimum, and there are strong indications that good inhibition will be obtained at concentrations in the tenths of parts per million range. In view of the fact that the actual concentration is largely arbitrary, there is clearly no reason for requiring the close limits of 1.8 to 2.2 ppm previously in effect, and it is likely that considerable savings in operating costs could be made if these limits were broadened. So long as the composite daily average rate of addition falls in the range 1.8 to 2.2 ppm, the instantaneous limits need be no narrower than 1.0 to 3.0 ppm.

In addition, there is a good possibility that dichromate will not undergo radiation reduction at a pH as low as 7.0. If experiments currently in progress show this to be the case, and provided it can be shown that dichromate will successfully inhibit pitting tendencies at the lower pH under actual operating conditions, then the need

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for pH adjustment will be obviated, lime additions can be eliminated, and the resulting water should produce a significantly lower corrosion rate.

It is clear that dichromate is not a completely satisfactory inhibitor, though it is far better than no inhibitor under present conditions. This means that the specific causes of the corrosion problems in the pile should be sought and eliminated where possible. If such causes cannot be eliminated, there is always the chance that there are more effective ways of living with them in safety than by adding sodium dichromate. But the importance of knowing the dangers is no greater than the importance of knowing precisely how to deal with them.

The current operation of the piles under PT-105-513-E⁽⁵³⁾ represents the most hopeful expedient for defining the conditions which will be safe without the addition of dichromate and for isolating the effects of the variables which are important in the corrosion processes now occurring in the piles.

Specific conclusions are as follows:

- a. Water process specifications should be changed to include the addition of 2 ppm $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ to process water. Control limits should be 1.0 to 3.0 ppm so long as the average rate is within the range 1.8 to 2.2 ppm.
 - b. With the restrictions noted in c, d, and e, PT-105-513-E⁽⁵³⁾, which now has D, DR, and C Piles operating with dichromate addition and B, H, and F without, should be permitted to continue, since it will provide reasonable data for a decision concerning the actual value of dichromate under present conditions.
 - c. Before the return of high river water temperatures, the desirability of continuing PT-105-513-E unchanged will have to be re-evaluated in the light of laboratory data then available concerning the nature of the attack noted at F Pile in the summer of 1952. Upon any prior recurrence of this type of attack, immediate consideration should be given to adding dichromate at all areas.
 - d. Due caution should be exercised in interpreting the results of PT-105-513-E with reference to the use of dichromate; in particular:
 1. The minimum time that the test must run to produce meaningful results is one year; even then account must be taken of variations in the character of the river from year to year.
 2. The effects of changing other variables in the process must be given a full and detailed consideration. For example, the recent change in the control of chlorine feed rates⁽⁵⁷⁾ marks the actual date on which the year should be considered to have begun.
 - e. The purging not necessary to remove film, currently being carried out under PT-105-513-E*, should be stopped immediately, at least in the areas where dichromate is not being added. Such purging serves no useful purpose and is potentially very dangerous.
- * When PT-105-513-E was initiated, there were meagre indications that purging diminished front tube corrosion. C, DR, and F Piles are presently being purged on a regular schedule, though essentially no pressure drop film is ordinarily formed from the alum coagulated water in use in these reactors. Experiments in the flow laboratory have demonstrated that purging is not a significant variable in the front tube corrosion process.

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- f. From the point of view of corrosion, the best available water appears to be alum coagulated, pH unadjusted or adjusted to somewhere in the range 6.5 to 7.5, and sodium dichromate added at a concentration in the neighborhood of 2.0 ppm or less. Vigorous efforts are presently being expended to determine:
1. The optimum concentration of sodium dichromate to be added.
 2. The minimum pH which will be safe for pitting attack and for dichromate reduction.
- g. An investigation of the polarity relationships in operating pile tubes should be made with the end in view of evaluating the overall desirability of 72-S clad tubes, with particular reference to water quality.
- h. Future research should also include:
1. An investigation to determine the effect of the fabrication process on front tube corrosion.
 2. An investigation to determine the feasibility of preventing front tube corrosion by the use of sacrificial perfs.
 3. An investigation of the effects of velocity on the minimum inhibitor concentration.
 4. An investigation of the feasibility of new inhibitors.
 5. A study of the corrosive effect of specific impurities in the water, e.g., is the chloride ion now being added responsible for front tube corrosion.

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