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REDUCTION OF THE AMOUNT OF DICHROMATE ADDED TO PILE COOLING WATER FINAL REPORT, PT-105-542-E

BY

D. R. DE HALAS

PILE TECHNOLOGY SECTION
ENGINEERING DEPARTMENT

AUGUST 23, 1956

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REDUCTION OF THE AMOUNT OF DICHROMATE

ADDED TO PILE COOLING WATER

FINAL REPORT, PT-105-542-E Classification Cancelled And Changed To

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By

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Pile Materials Sub-Section

August 23, 1956

By Authority of RG-PR-2

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ABSTRACT

Sodium dichromate has been tested for use as a process water corrosion inhibitor at a concentration of 0.5 ppm. The test was conducted by operating one half of D Reactor with 0.5 ppm while the other half operated at the normal concentration of 2 ppm sodium dichromate. A concentration of 0.5 ppm was found to be as effective a corrosion inhibitor as the normal concentration of 2 ppm except under one very important set of circumstances. If the reactor process tube ribs were previously worn or corroded down, so that the water in the between-rib annulus became excessively hot; 0.5 ppm sodium dichromate was found to be non-effective in stopping corrosion at this location. From five to ten times as many slug ruptures and tube leaks occurred from this accelerated between-rib corrosion if the sodium dichromate concentration was 0.5 ppm rather than 2 ppm.

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REDUCTION OF THE AMOUNT OF DICHROMATE
ADDED TO PILE COOLING WATER
FINAL REPORT - PT-105-542-E

INTRODUCTION

Sodium dichromate is currently added to the reactor cooling water at a concentration of 2 ppm to inhibit pitting attack of aluminum.^(a) The chemical costs for adding sodium dichromate to the water at all reactors during FY 1955 was about \$285,000.⁽¹⁵⁾ When the other associated costs (salaries, maintenance, etc.) are considered the total cost was about \$440,000.⁽¹⁵⁾ If the costs are extrapolated to post CG-558 flows, the chemical costs alone for adding 2 ppm of sodium dichromate to the water will be about \$500,000 per year.

If the dichromate concentration in the reactor cooling water could be reduced without increasing the amount of aluminum corrosion, a substantial monetary saving would be realized. In addition to the economic incentive for reducing the dichromate concentration, there is the possibility that it may eventually become necessary to limit the amount of dichromate added to the river because of toxic effects on fish.⁽⁷⁾

With the above considerations in mind a series of laboratory tests were initiated in 1953 to investigate the possibility of adding sodium dichromate to the reactor cooling water in concentrations of less than 2 ppm. All of the laboratory tests indicated that sodium dichromate concentrations down to 0.1 ppm were as successful as 2 ppm in inhibiting corrosion of aluminum.⁽³⁾⁽⁴⁾⁽⁵⁾⁽⁸⁾ Based on these results a production test was started in June, 1954, to test 0.5 ppm sodium dichromate in the far side of D Reactor.⁽⁶⁾ This test continued until November, 1955,^(b) when it became apparent that the far side of D Reactor (0.5 ppm sodium dichromate) was suffering from an inordinate number of ruptures and tube leaks as compared

(a) Sodium dichromate concentrations are expressed as ppm of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.

(b) The duration of the test was from 6-30-54 to 11-5-55.

to the near side of the reactor (2 ppm sodium dichromate).⁽¹²⁾

The effectiveness of 0.5 ppm sodium dichromate has been analyzed, taking into account the relative degree of corrosion of the process tubes in both sides of the reactor before the test began. This document presents the results of this analysis.

SUMMARY

A test has been completed to determine the practicality of reducing the sodium dichromate concentration to 0.5 ppm in the process water. The use of 0.5 ppm sodium dichromate is generally not safe because excessive numbers of slug ruptures and tube leaks occur, if the reactor process tubes have reduced rib heights. The results of the test show that it would be safe, however, to reduce the dichromate concentration (at a process water pH of 7.6⁵) for reactors that do not have severely corroded process tubes. This procedure might be especially desirable during periods of low river flows to alleviate river pollution by dichromate if pollution becomes a problem. However, this step cannot be recommended until tests are conducted with reduced dichromate concentrations in pH 7.0 process water.^(a)

DISCUSSION OF DATA

The laboratory tests showed that dichromate added to the water does not affect the over-all uniform corrosion rates of aluminum, but does drastically inhibit pitting type attack of aluminum.⁽⁵⁾⁽⁸⁾ Before this production test was made, only two "types" of pitting attack in the absence of dichromate had been observed on slugs and tubes. These were:

1. "F-Type" pitting, which was exhibited as deep tear-drop pits on slugs and as similar deep pits on tubes, usually located at the slug junctions.^(b) The "F-Type" pitting was shown to be caused by erosion-corrosion in the absence of dichromate.⁽²⁾

(a) The pH during this test was 7.6⁵ for 10 months and 7.3 for 6 months.

(b) The term "F-Type" was adopted in 1952 when this type of pitting was thought to be particular to F Reactor.

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2. Front tube pitting, which was evidenced by deep pits in the cold front sections of the process tubes. These pits were normally covered with small mounds of corrosion product, or barnacles, that made them readily apparent by viewing them from the front end of the tube.

During the time that this production test was being run a third type of accelerated attack appeared.⁽¹⁶⁾ This attack occurred only in process tubes that have reduced rib heights because of corrosion occurring during their long length of time in service. In these tubes the water between the tube ribs became excessively hot because of the restriction of the water annulus in this region. This hot water caused rapid corrosion and failure of both tubes and slugs at the between-rib location.⁽¹⁴⁾ This attack occurred even when the dichromate concentration was 2 ppm, but it is of special interest to this test, since essentially all of the slug and tube failures during this test at D Reactor were of this type.

Observation of Slug Corrosion

A total of eleven tubes of weighed metal were charged into D Reactor during the test. As predicted from the laboratory experiments, there was no significant difference in the overall uniform slug corrosion rates between the near and far sides of the reactor.^(a) The conditions under which the eleven control tubes were run are listed in the appendix.

There was no noticeable difference between the amount and degree of pitting on the slugs from both sides of the reactor. In particular, no slug pitting resembling the characteristic "F-Type" pitting was observed.

During the test and until the end of 1955, a total of thirty-seven ruptures occurred at D Reactor that could be attributed to corrosion. Of these, all but six were identified as being caused by excessively hot water between the ribs (between-rib ruptures). Twenty-eight of the thirty-one between-rib ruptures occurred on the 0.5 ppm side of the reactor. This subject

(a) A more detailed discussion of the measured corrosion rates is given in the interim report of this production test.⁽¹⁷⁾

will be discussed in some detail in the section titled 'Cause of Tube Leaks and Between-Rib Ruptures'.

Observations of Tube Corrosion

One of the most noticeable ways in which dichromate affects tube corrosion is by the prevention of front tube pitting or 'barnacle formation'. Frequent inspections of the condition of the front tube sections were made during the test. Some tubes that were new at the beginning of the test were included in these inspections along with many older tubes. There was no significant amount of front tube corrosion observed, nor was there any apparent difference in the corrosion behavior of the front tube sections on either half of the reactor.⁽⁹⁾

During the test and throughout the remainder of 1955, 30 tubes were removed from D Reactor and subjected to visual and metallographic examination. Twenty-one of these tubes were removed from the far side (0.5 ppm sodium dichromate) of the reactor. Within the accuracy of tube corrosion measurements, no difference could be found between the uniform tube wall corrosion rates occurring on both sides of the reactor. One tube that was examined, 2779 D, had been in the reactor for only 15 months, and exposed for 13 months to 0.5 ppm sodium dichromate at an average outlet temperature of 90 C. The corrosion rate of this tube was equal to, or perhaps somewhat less than, that calculated for a tube exposed to normal process water (2 ppm sodium dichromate) under the same conditions. There was no unusual attack observed in this tube.

Tube 3980-D that leaked on December 26, 1954, exhibited a hole that was quite similar to those that have been found when no dichromate is in the water ("F-Type" pit). However, similar holes have occasionally been found in tubes exposed to 2 ppm sodium dichromate water, and may possibly be a carryover from the period when the reactors operated with no dichromate in the water.^(a) No other examples of this type of attack were found.

(a) From Spring 1952 to Spring 1953.

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Essentially all of the tubes examined that had been in the reactor for a long period of time exhibited accelerated corrosion attack between the ribs. The most severe cases discovered were from the 0.5 ppm sodium dichromate side of the reactor; however, only nine tubes from the near side of the reactor were examined. Further evidence as to the relative prevalence of between-rib corrosion was furnished by the occurrence of tube leaks; because tube leaks (not including Van Stone failures, mechanical damage, etc.) are almost always caused by between-rib corrosion.^(a) During the test and the remaining two months in 1955 there were twenty-eight tube leaks at D Reactor; twenty-six of these were on the 0.5 ppm sodium dichromate side.

Cause of Tube Leaks and Between-Rib Ruptures

Between-rib ruptures and tube leaks both result from excessively hot water between the tube ribs. The large preponderance of these ruptures and tube leaks on the far side of D Reactor indicated either:

1. That essentially all of the tubes at D Reactor with reduced rib heights were located on the far side of the reactor because of some peculiarity in the past operation of the reactor (which caused that side to have hotter average temperatures); or
2. That the tubes with reduced rib height were more susceptible to rapid corrosion attack on the reduced dichromate side (far side) of the reactor than on the normal dichromate side.

Until June, 1956, there were not sufficient data compiled on the past operating history of D Reactor to choose between possibilities 1 and 2 listed above. In June, 1956, the maximum amount of corrosion expected to occur on each tube, the corrosion index,^(b) was calculated from complete tube temperature histories.⁽¹³⁾ It was found that essentially all tube leaks at D Reactor have occurred only when the corrosion indices of the tubes were greater than 37 mils.

-
- (a) Between-rib corrosion is the primary cause of corrosion tube leaks at all reactors regardless of dichromate concentration in the cooling water.
- (b) The method of calculating the maximum expected amount of corrosion, which is defined as the corrosion index of the tube, is explained in Reference 13.

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This calculation was used to determine the position of all tubes in the reactor susceptible to leaking because of corrosion that occurred previous to the time that the leaks and ruptures started. (corrosion index greater than thirty-seven in June, 1955)^(a)

Figure 1 shows the position of the tubes in D Reactor with corrosion indices greater than 37 mils in June, 1955. The same figure also shows the location of all the corrosion tube leaks and between rib ruptures occurring during the test and until the end of 1955. The same data as shown in Figure 1 are tabulated in Table 1.

TABLE 1 - LEAKS AND RUPTURES

	Number of Tubes with Corrosion Index greater than 37 in June, 1955	Number of Between- Rib Rup- tures	Number of Corrosion Leaks	Between- Rib Rup- ture Frequency (b)	Leak Frequency (b)
0.5 ppm Sodium Dichromate (Far Side)	166	28	26	0.169	0.156
2 ppm Sodium Dichromate (Near Side)	114	3	2	0.026	0.018
Ratio: (Far Side) (Near Side)	1.5	9.3	13.0	6.5	8.7

(a) The corrosion index was calculated for the tubes in June, 1955, rather than June, 1954, (the start of the test) because it was at this time the tube leak and slug rupture rate sharply increased at D Reactor.

(b) Frequency is defined as the average number of leaks or ruptures per tube with corrosion index greater than 37.

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- ◩ Tubes susceptible to leaking in June 1955; corrosion index greater than 37.
- Corrosion tube leaks during test until end of 1955.
- ◩ Between-Rib ruptures during test until end of 1955.

FIGURE 1
LEAKS AND BETWEEN-RIB RUPTURES

The data in Table I show that the badly corroded tubes (corrosion index greater than 37) had a much greater tendency to leak or to contain ruptures if they were on the far side rather than on the near side of the reactor. Apparently reducing the dichromate concentration increases the rate of between-rib corrosion of both slugs and tubes.

CONCLUSIONS

The sodium dichromate concentration cannot safely be lowered to 0.5 ppm at any reactor where there is an appreciable chance for between rib corrosion to occur (i.e. at any reactor containing highly corroded process tubes). If the reactor process tubes are in good condition the sodium dichromate concentration could be lowered to 0.5 ppm without creating any harmful effects. (in pH 7.6⁵ process water) However, this procedure is not recommended for the reactors with good process tubes (e.g. the K's) until testing in pH 7.0 water can be conducted. (The specified pH for process water has recently been changed to 7.0) It appears highly probable that it will prove safe to lower the process water dichromate concentration, in reactors with good tubes, during intervals of low river flow, if such a step is necessitated by river pollution problems.

FUTURE TESTING

During this test the process water pH was nominally at 7.6⁵. (a) It is unsafe to extrapolate the results of the test at this pH to lower pH's, since the dichromate principally affects the pitting attack, and lowering the pH increases pitting attack on aluminum. It is not known whether half the normal dichromate concentration (i.e., 1 ppm) would have proved satisfactory in preventing extensive between-rib corrosion. There is still considerable economic incentive to reduce the dichromate concentration by this amount. It can also be speculated that increasing the sodium dichromate concentration to greater than 2 ppm would have stopped between-rib corrosion completely. This result would very easily pay for the increased cost of dichromate addition.

(a) The process water pH at D Reactor was changed to pH 7.3 on May 20, 1955, and remained at this pH for the remainder of the test.

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The future testing program for sodium dichromate should be designed so that flexible process standards can be developed. These new process standards would ideally allow for reducing the dichromate during low river flow, and for adjusting the dichromate concentration to suit the conditions of the process tubes in the individual reactors. Such a program would:

1. Test the reduced dichromate concentrations at pH 7.0 (or lower if a lower pH is specified).
2. Start the testing at reactors known to have good tubes, and test the usefulness of 1 ppm before testing 0.5 ppm sodium dichromate.
3. Experiment with raising the dichromate concentration of the affected reactors, if between-rib corrosion cannot be solved by other means (e.g., flow mixing pieces,⁽¹⁷⁾ or the tube replacement program).

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APPENDIX

TUBES CONTAINING WEIGHED METAL DURING TEST

Tube Number	Dichromate Concentration, ppm	Average Outlet Temperature, C	Metal Concentration MWD/T
1178	0.5	82	510
3288	0.5	85	620
3682	0.5	87	800
4280	0.5	75	570
4285	0.5	70	570
4387	0.5	70	500
2671	2	86	270
3471	2	99	330
3668	2	87	650
2473	Questionable (a)	85	680
3473	Questionable (a)	92	280

(a) The concentration in these tubes is questionable because mixing of water from the far sides and near sides of the reactor occurs near the (vertical) center line.

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