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May 20, 1963

EFFECT OF 6.6 pH PROCESS WATER
ON PROCESS TUBE AND FUEL ELEMENT CORROSION

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May 20, 1963

EFFECT OF 6.6 pH PROCESS WATER
ON PROCESS TUBE AND FUEL ELEMENT CORROSION

Reduction of the reactor process water pH from 6.9 to 6.6 at 100-B, D, DR, F, and H currently is proposed in order to reduce the aluminum corrosion rate and the resultant outage time for water leaks, fuel ruptures, and process tube replacement. This document reviews the current knowledge of the effect of reducing the pH to 6.6 on aluminum corrosion. An estimate of the expected costs and benefits is included.

SUMMARY

Insufficient in-reactor data is available to show the actual reduction of aluminum corrosion rate in the reactors when the process water pH is reduced from the current 6.9 to the proposed 6.6. Comparison of corrosion rates at different reactors operating at 6.6 and 6.9 to 7.1 pH indicates that reduction of the pH will reduce the corrosion rate from fifty to ninety percent. Laboratory experiments indicate that a fifty percent lower corrosion rate can be expected. A fifty to eighty-three percent reduction of the aluminum corrosion rate when the pH is reduced from 6.9 to 6.6 appears to be a reasonable estimate. The current 100-D Reactor half-plant low pH test is expected to show the actual reduction of corrosion rate within the next year.

The estimated benefits from reducing the pH to 6.6 are (1) a five to eight percent production increase because of less outage time for tube replacements, water leaks, probologging, and ruptures, and (2) reduced reactor maintenance costs of \$100,000 per year per reactor.

The costs of reducing the pH to 6.6 are estimated to be (1) \$80,000 per reactor per year for additional chemicals, and (2) an unknown increase in maintenance costs because of additional corrosion of carbon steel components in the reactor water systems.

DISCUSSION

Laboratory Data

Numerous laboratory experiments have been made to determine the effect of water quality on uniform corrosion of aluminum. The most recent published work at Hanford at reactor coolant temperatures was a series of experiments by V. H. Troutner in 1957 investigating the effect of various water qualities (pH and impurities) on aluminum corrosion at 92C.¹ The results generally are believed to be representative of uniform aluminum corrosion in the reactors.

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1. HW-50133, "Uniform Aqueous Corrosion of Aluminum - Effects of Various Ions", V. H. Troutner, June 10, 1957.

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Troutner concluded that the most important water quality variable that affects uniform corrosion of aluminum was the pH. He found that the corrosion rate was dependent only on pH in 300 Area tap water, reactor process water, distilled water, and distilled water containing up to 100 ppm chloride, nitrate, sulfate, bicarbonate, hydrogen peroxide, acetate, arsenate, silicate, dichromate, molybdate, and mixtures of these ions. Phosphate inhibited the corrosion and citrate increased corrosion.

The relationship of corrosion rate to pH found by Troutner is shown on Figure 1. This relationship shows a rapid decrease in corrosion rate as pH is reduced from 9 to 7. From pH's of 7 to 5, there is a transition in corrosion mechanisms, and below a pH of 5, the corrosion rate increases rapidly as the pH is reduced.

Because of normal scatter of the experimental data and because insufficient data points were obtained at pH's between 5 and 7, the exact location of the correlation line between pH's of 5 and 7 is uncertain.

If one assumes that the corrosion transition of Figure 1 occurs at a pH of less than 6.6, straight-line extrapolation of the corrosion correlation from 8.0 to 6.9 pH shows that the corrosion rate at 6.6 pH is approximately one-half the corrosion rate at 6.9 pH.

Laboratory data should be considered only to be indicative of the general relationship between pH and in-reactor corrosion rates. Several important variables that could influence the relationship of the corrosion rate of aluminum in the reactor to the process water pH have not been included in the laboratory investigations. Such variables are the reactor radiation flux, thermal stresses during reactor startups and shutdowns, coolant velocity, and differences in water quality. Whether or not such variables are significant is not known. As a result, it is best to interpret the laboratory data as being indicative of the general change in corrosion rate as pH is changed, but not as an exact representation.

In-Reactor Data

To date, only qualitative data has been obtained to show the relationship of pH to corrosion rate for aluminum in the reactors at 6.6 versus 6.9 pH. Quantitative data will not be obtained until the current 100-D Reactor half-plant low pH test² has operated long enough to permit comparison of the corrosion rates on the two sides of the reactor.

The qualitative data for 6.6 pH results from comparison of the process tube corrosion rates at the various reactors and from a small number of single tube reactor tests. Exact comparisons are not possible because differences in tube geometry, water quality, tube powers, and numerous other variables result in differences in corrosion environment for different reactors.

2. HW-71141, "Production Test IP-442-A, Half-Plant Reduction in Process Water pH, 105-D", F. W. Van Wormer, May 8, 1962.

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Two qualitative reactor comparisons are available: (1) comparison of the 100-K Reactor corrosion to the old reactor corrosion, and (2) comparison of corrosion rates of the five old reactors.

During the last eighteen months, the 100-K Reactors have operated with a process water pH of 6.6, and the old reactors have had a pH of 6.9 to 7.1. During this period, the observed average corrosion rate of the 100-K central process tubes has been one-and-a-half mils per year. Corrosion rates of over three mils per year have been observed for only eleven percent of the tubes, and the maximum observed rate was six mils per year.³ In contrast, the corrosion rate of the old reactor central tubes has averaged six to fifteen mils per year for comparable tube outlet temperatures and minimum wall thicknesses near 40 mils, and corrosion rates of twenty to thirty mils per year frequently are observed (approximately twenty-five percent of the central tubes).⁴ Comparison of the average corrosion rates by use of the corrosion index calculation also shows that the old area tubes have been corroding at six to ten times the rate of the 100-K tubes for the same tube outlet temperatures.

The corrosion rates of process tubes in the B, D, F and H Reactors can be compared by calculating the rc values* of tubes with apparently the same operating histories. Recent mass probologging of the central tubes installed early in CY-1962 has provided enough data for such a comparison. The results of this comparison are as follows:

Table I
Old Reactor Tube Corrosion Rate - January, 1962, to February, 1963

<u>Reactor</u>	<u>Calculated Average Process Water pH</u>	<u>Mixer Location</u>	<u>Average rc</u>
B	7.10	None	4.0
D	7.04	One in tenth position from rear	3.0
F	6.91	None	2.1
H	6.99	None	5.0

The observed wall thicknesses of the tubes are plotted on Figures 2 to 6.

Several comments concerning interpretation of the above table are necessary before one forms conclusions.

* The rc is defined as the measured corrosion divided by the change in corrosion index.

3. HW-77466, "100-K Reactor Process Tube Corrosion", J. R. Young, April 30, 1963.

4. HW-75903, "Third Generation Central Tube Life, 100-B, D, DR, F and H Reactors", J. R. Young, December 17, 1962.

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The average rc for operation with a pH between 7.0 and 7.1 and without mixers in the fuel charges appears to be about 4.0. The rc for 100-D is lower than for B and H because of use of a mixer in each fuel charge at D. The mixer is known to reduce the coolant temperature in the top annulus and consequently the observed corrosion rates. The observed 100-H rc is believed higher than actually occurred because the 100-H tube outlet temperature thermocouples are believed to indicate temperatures 3 to 5 degrees below the actual temperatures.⁵ As a result, the calculated corrosion indices may be lower than actually occurred and the observed rc's may be higher than actual for 100-H.

The process tubes being compared on Table I are identified as uniform wall tubes with 80 mil ribs at 100-B, D, F and H. Tubes installed at 100-DR during early 1962 are identified as eccentric wall tubes with 86 mil ribs. Because of this difference in design, the 100-DR data should not be used in a comparison of the rc values to determine the effect of pH.

Sodium dichromate and alum feed rates appear to have been essentially the same at all five old reactors and are not believed to have influenced the rc values. The calculated average process water pH for each reactor was determined from acid used and a standard titration curve.⁶

Comparison of the rc values of Table I after consideration of the above comments shows that a significantly lower corrosion rate has existed at 100-F than at 100-B, D and H. The only apparent difference in operation at 100-F has been the lower process water pH. However, one cannot ignore the possibility that other differences in the 100-F operation may have contributed to the lower corrosion rate. The variables affecting aluminum corrosion rates in the reactors are not known well enough that one can say that none other than pH are influencing the comparison of 100-F corrosion to that of the other reactors. Analysis of Figure I indicates that a pH of 6.91 should result in about a twenty-five percent lower corrosion rate than would a pH of 7.05 - not an approximately fifty percent reduction as indicated by Table I.

Single tube reactor experiments comparing pH's from 6.2 to 7.5 were made in 1954 at tube outlet temperatures approximately 15C lower than current maximum temperatures and at approximately one-half the current average tube powers. Comparison of the corrosion rates for ten charges of fuel elements irradiated at various pH's from 6.2 to 7.5 showed that the corrosion rate at 6.6 pH is approximately one-half the corrosion rate at 7.0 pH.⁷ The small number of data points and the usual scatter makes quantitative conclusions of questionable accuracy.

The net conclusion from the above qualitative analyses is that lowering the pH from 6.9 to 6.6 is expected to reduce the corrosion rate by 50 to 83 percent (a factor of 2 to 6). The actual effect will not be known until the 100-D Reactor

5. "Interim Report, PT IP-479-I", B. R. Cremer, December 17, 1962.

6. Personal Communication, L. D. Gustafson, April, 1963.

7. HW-34544, "The Effects of Water Quality on Pile Operation, Final Report, Production Test No. 105-525-E", N. R. Miller, September 23, 1955.

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half-plant test has operated long enough that a significant and provable difference in the corrosion rates on the two sides of the reactor is observed to have resulted from the difference in pH.

Benefits From 6.6 pH

The actual benefits from reducing the process water pH to 6.6 cannot be calculated until quantitative data is obtained showing the resultant reduction in corrosion rate. The above discussion indicates that the corrosion rate probably will be reduced 50 to 83 percent. Three cases will be analyzed showing the benefits expected from reducing the corrosion rate by 50, 75, and 83 percent. The actual benefit probably lies somewhere in the range covered by these cases.

Calculated production benefits for the three cases are as follows:

<u>Table II</u> <u>Summarized Production Benefits From 6.6 pH</u>				
Percent Reduction of Corrosion Rate	0	50	75	83
Reactor TOE	73	76.8	78.6	79.3
Percent Production Increase	0	5.2	7.7	8.6

The detailed calculations are attached as Table III.

Reduction of the corrosion rate reduces outage time for tube replacements, probollogging, water leaks and ruptures. The outage time for tube replacements, probollogging, and water leaks probably would be reduced directly in proportion to the reduction in corrosion rate until the tube residence exceeds eight years. The integrity of the tubes after eight years central residence is questionable because of increased probability of Van Stone flange and transverse crack failures. An eight year residence corresponds to the seventy-five percent reduction of corrosion rate*. Table II shows that the benefits from 6.6 pH probably will not exceed eight percent production increase and probably will be between five and eight percent production increase (i.e., in the range of a 50 to 75 percent reduction of the corrosion rate).

In these calculations, it has been assumed that only six ruptures per reactor per year are caused primarily by corrosion and that the number of ruptures is proportional to the corrosion rate. These assumptions are believed conservative because most ruptures are caused primarily by corrosion, there usually are more than twelve ruptures per year per old reactor, and most ruptures result from cladding penetration at exposures over fifty percent of discharge concentration. A fifty percent reduction in corrosion rate should essentially eliminate all ruptures because the cladding no longer would be penetrated.

* It is assumed that the average central tube life at 6.9 pH will be two years. This corresponds to the eighteen month average life observed for pH's from 7.0 to 7.1. See reference 4.

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It should be noted that a seventy-five percent reduction of the corrosion rate reduces the related outage time to about seven days per year. The tube replacement, water leak, and rupture problems could become minor problems, and the incentive for further reduction in corrosion rates could be small.

Reactor maintenance costs will be decreased as a result of less tube replacements, water leaks, and ruptures. Less tube replacements probably would reduce costs by \$50,000 to \$80,000 per reactor per year (see Table III). Less leaks and ruptures probably would reduce maintenance costs by \$20,000 to \$50,000 per reactor per year. The total reduction of reactor maintenance costs probably is \$100,000 per reactor per year.

Costs of 6.6 pH

The significant costs of 6.6 pH are increased chemical costs and carbon steel corrosion.

The estimated additional annual chemical costs are \$80,000 per reactor per year, composed of \$40,000 for sulfuric acid and \$40,000 for sodium dichromate. The extra sodium dichromate cost may be proved unnecessary by the current half-plant low dichromate production test at 100-C.

The extra maintenance cost because of additional corrosion of carbon steel piping is not known. A significant increase in the uniform corrosion rate is not expected, but increased pitting attack may be important. Considerable effort currently is being expended to determine the current condition of the carbon steel piping and the corrosion rate at both 6.9 and 6.6 pH.

Reducing the pH to 6.6 is not expected to increase the total effluent radioactivity. Preliminary results from the 100-C and D low pH production tests show no significant increase in effluent activity when the pH is reduced from 7.0 to 6.6 and the additional acid is added downstream of the filters.⁸

J. R. Young, Senior Engineer
Plant Equipment Engineering
Applied Reactor Engineering

JRY:bd

8. Personal Communication, R. G. Geier, May, 1963.

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Table III
Benefits From 6.6 pH Process Water

BASIS: One year.
One old reactor.
Two year average central tube residence, at 6.9 pH.
Each tube probologged twice during residence.
Eight leaks per year at present because of internal corrosion.
Six ruptures per year caused primarily by aluminum corrosion.
Thirty tubes replaced per day of outage time.
Three minutes extra outage time per tube probologged.
Twelve hours extra outage time per water leak.
Twelve hours extra outage time per rupture.
73 percent TOE at 6.9 pH.
\$200 maintenance cost per tube replaced.

<u>CASE</u>	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
Process Water pH	6.9	6.6	6.6	6.6
Assumed Percent Reduction of Corrosion Rate	0	50	75	83
Average Central Tube Residence (Years)	2	4	8	12
No. Tube Replacements Per Year Because of Internal Corrosion	540	270	135	90
Number of Tubes Probologged Per Year	1080	540	270	180
Number of Internal Corrosion Water Leaks	8	4	2	1
Number of Corrosion Ruptures	6	3	2	1
Related Outage Time Per Year (Days)				
a. Tube Replacement	18	9	4.5	3
b. Probologging	2.3	1.1	0.6	0.4
c. Water Leaks	4	2	1	0.5
d. Ruptures	3	1.5	1	0.5
e. Total Related Days	27.3	13.6	7.1	4.4
f. Total Related TOE	7.5	3.7	1.9	1.2
Increased TOE	0	3.8	5.6	6.3
TOE	73	76.8	78.6	79.3
Percent Production Increase	0	5.2	7.7	8.6
Reduction of Maintenance Cost For Tube Replacement	0	54,000	81,000	94,000

Figure 1
Aluminum Corrosion Rate At 92C

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Probolog Wall Thickness - Mils

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