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DATE: March 27, 1956

SUBJECT: HRP-CP: Corrosion of Decay-Storage Vessels
(C-1 and C-2) by H_2SO_4

TO: E. G. Bohlmann

FROM: W. L. Carter

CLASSIFICATION CANCELLED

DATE MAR 14 1957 *jet*

For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

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TO: E. G. Bohlmann

FROM: W. L. Carter

SUBJECT: HRP-CP: Corrosion of Decay-Storage Vessels (C-1 and C-2) by H_2SO_4

In recent discussions with the Design Review Committee for the chemical processing plant it was pointed out that a potentially serious H_2SO_4 corrosion problem exists for the decay-storage vessels in the low pressure system of this plant. These are the vessels which collect the weekly batches of fission and corrosion products removed from the reactor fuel system. This memorandum describes the operating conditions and gives pertinent data that will be helpful in evaluating the corrosion problem. It would be appreciated if the Corrosion Group would examine this information and advise the Process Design Section of their opinions. Of specific interest is a material of construction for the decay-storage vessels; the current plan is to fabricate these tanks from HRP grade SS 347. Probably sufficient data exists on the corrosion of stainless steel by H_2SO_4 that it will not be necessary to test specimens; however, if the tests are advisable, the Design Section would be pleased to have them made.

It has been calculated that the quantity of slurry drained into a decay-storage vessel will be as follows:

Fuel Solution Components (Soluble)

D_2O	8255	gm/week
(1) U (as UO_2SO_4)	85.9	gm/week
(2) $CuSO_4$	1.8	gm/week
(3) H_2SO_4	19.3	gm/week

Corrosion and Fission Product Components (Insoluble)

(4) ZrO_2	167.9	gm/week
(5) Fe_2O_3	153.9	gm/week
(5) Cr_2O_3	47.6	gm/week
$(FP)_2(SO_4)_3$	<u>32.9</u>	gm/week
Total	402.3	gm/week

- (1) Based on a fuel concentration of 10.4 gm U/kg D_2O .
- (2) Calculated from $CuSO_4$ concentration of 0.03% mole based on U.
- (3) Calculated from H_2SO_4 concentration of 35% mole based on U.
- (4) Based on Zr corrosion rate of 10 mils/year.
- (5) Based on stainless steel corrosion rate of 1 mil/year.

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The corrosion and fission product components are only those which are insoluble in the fuel solution. In addition to these, there will be small amounts of soluble nickel and fission product compounds. The quantities of these compounds will increase slightly each week as their concentrations build up in the reactor.

The operating plan is to collect in one decay-storage tank for a maximum of 20 weeks and then to allow radioactive cooling to take place for approximately 20 additional weeks. During this time the vessel would be boiling at 100° C. Since the vessel has a total capacity of only 5 gallons and since about 2 gallons of liquid are added each week, it will be necessary to concentrate the slurry by evaporating D₂O before each subsequent addition. It is not planned to evaporate at temperatures high enough to remove H₂SO₄ because of the adverse effect the acid vapor would have on some of the components of the vapor system; therefore, there would be an increase in H₂SO₄ concentration in the storage container. A convenient operating level appears to be 8 kg D₂O in the decay-storage vessel.

The accompanying chart, Figure 1, plots the H₂SO₄ concentration as a function of time for the condition where the level is maintained at 8 kg D₂O. The curve is not smooth because concentration is performed batchwise once each week. Included on the same graph are the concentrations of U and CuSO₄; these are included because they might have some bearing on the corrosion problem. The concentrations of these substances remains constant after 20 weeks because this is a cooling period and no further additions are made to the tank.

One literature reference * gives data for the corrosion of 18-8 stainless steels at 20° C by sulfuric acid solutions when CuSO₄ is present in varying concentrations. The data include curves for only two H₂SO₄ concentrations, i.e., 50 and 100 gm/liter. The indications are that at CuSO₄ concentrations above 10-15 gm/liter the corrosion rate is inhibited. Figure 1 shows that CuSO₄ concentration in the decay-storage vessel increases only to about 4.5 gm/kg D₂O which is considerably below the above figure. However, it would be possible to plant a heel of CuSO₄ in the vessel when it was put into service if this compound is proved to be an effective inhibitor for H₂SO₄ corrosion at these operating conditions and temperatures (> 100° C).

A further step in chemical processing is to take the contents of the decay-storage vessel to dryness at the end of a cooling period before opening the cell and removing the vessel. By dryness it is meant that D₂O would have been evaporated from the slurry but H₂SO₄ would not have been evaporated. Therefore, the concentration of H₂SO₄ - as well as U and CuSO₄ - would quickly increase to a much higher value. For example, the temperature of the tank would have to be raised to only 123° C for the concentration to have reached 1000 gm H₂SO₄/kg D₂O. But in order to recover all D₂O in the system, the temperature would have to be increased to 340° C, the boiling point - or more correctly stated, the decomposition point - of pure H₂SO₄. No attempt will be made to raise the temperature to the decomposition point of H₂SO₄; however, it is desirable to recover as much D₂O as possible. Therefore, rather concentrated H₂SO₄ can be expected, but this concentration would only exist for a maximum time of two days. This would be the time required for removing the vessel from the cell and diluting the contents with dissolving solution.

*Uhlig, H. H., The Corrosion Handbook, page 152, Fig. 1, John Wiley and Sons, Inc., New York, 1948

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It might be pointed out that sufficient corrosion products in the form of iron and chromium are present to react all of the H_2SO_4 . If the reaction between iron and sulfuric acid takes place according to the equation

it would require only 10.5 gm Fe_2O_3 to react all of the acid collected each week. The calculated corrosion rate indicates that there will be considerably more Fe_2O_3 than this collected each week. It would be fortunate if H_2SO_4 were removed from solution by reaction with the corrosion products. Another thought has been that a heel of some alkaline compound be added to the decay-storage vessel to neutralize the acid. As mentioned above, the neutralizing agent could be added when the vessel was put into service. Some of the carbonates should be suitable; hydroxides are not desirable if they contain light hydrogen.

Another factor that will adversely influence the corrosion rate is the radiation level in the tank. Figure 3 presents a graph of accumulated solution activity as a function of time. Each step in the curve is a record of the activity change over one week's time; the downward trend represents decay and the upward trend shows the boost given by draining the next succeeding batch into the same vessel. When accumulation is discontinued, the activity falls off according to the smooth curve on the right portion of the graph.

The data and conditions described herein are representative of the operation of the decay-storage vessels in the HRT chemical processing plant. Proposed material of construction for these vessels is HRP grade SS 347. It would be appreciated if the Corrosion Group would examine and evaluate this information and advise us of their opinions. Specifically, the Design Section would like to know what is a suitable material of construction, whether it might be expected that the acid will be used up in reaction with the corrosion products and an expression concerning the use of additional $CuSO_4$ or an alkaline neutralizer to inhibit corrosion.

William L. Carter

W. L. Carter
Chemical Technology Division
Process Design

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FIGURE 1

BUILD-UP OF H_2SO_4 , U , & $CuSO_4$ IN
 CHEMICAL PROCESSING PLANT
 Decay-storage tank level
 maintained at 8 kg D_2O

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B.P. OF PURE H_2SO_4

H_2SO_4 CONC. gms/g H_2O

FIGURE 2
BOILING POINT CURVE
 H_2SO_4 - H_2O SOLUTIONS
 $P=1$ ATM

KEUFFEL & ESSER CO., N. Y. NO. 389-BIG
Semi-Logarithmic, 4 Cycles X 10 to the Inch.
MADE IN U. S. A.

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FIGURE 3

ACCUMULATION OF ACTIVITY
IN DECAY-STORAGE VESSELS

UNPUBLISHED CALCULATIONS
BY H.C. WELLEN

ACTIVITY, KW

TIME, days

FIGURE 4

HRT CHEMICAL PROCESSING
DECAY-STORAGE VESSEL