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SUBJECT: POSSIBILITY OF OXYGEN DEPLETION IN STAGNANT URANYL SULFATE LINES

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POSSIBILITY OF OXYGEN DEPLETION IN STAGNANT URANYL SULFATE LINES

Abstract

The possibility of oxygen depletion in the stagnant uranyl sulfate containing lines of the HRT has been investigated. With 100 ppm oxygen in the line at the time of stagnation, the time required to effectively consume the oxygen by corrosion has been estimated in Figure 1 as a function of pipe diameter. (This calculation neglects the effect of oxygen diffusion from the circulating stream and the possible thermal convection in the lines. The diffusion contribution should be quite small. The convection contribution is highly dependent on geometry, being a maximum for verticle lines.)

Since the time required to consume this oxygen is short the possibility of an oxygen source due to radiolytic decomposition of D_2O by fission product gammas and betas was considered. Enough copper was assumed to be in the solution to insure 80% gas recombination at a reactor power of five Mw. Under these conditions the oxygen concentration was found to range from one to 0.01 ppm depending on the temperature of the solution. This is shown in Figure 2. Oxygen concentrations as low as these are probably not effective in prohibiting corrosion.

Operations of the HRT mockup have shown that for circulating oxygen concentrations of 100 ppm there are high corrosion rates in dead end lines. Similarly for circulating oxygen concentrations of 500 ppm no excessive corrosion has been observed in the dead end lines.

Since the HRT is expected to operate with 20% gas letdown the fuel solution leaving the gas separator will be saturated with D_2 and O_2 at their partial pressures. Using recent data³, the solubility of D_2 and O_2 in uranyl sulfate solutions has been estimated for the reactor conditions of 2000 psi and 1700 psi with no excess oxygen added. These are shown in the following table:

Pressure	Oxygen Concentration (ppm)	
	After Separator	Average in Loop
1700	1230	1200
2000	1870	1820

Excess oxygen will probably be added at a rate of 500 cc/min to 1000 cc/min. In the circulating stream this would correspond to additional oxygen concentrations of 7 and 14 respectively. These oxygen concentrations are high enough so that excellent corrosion protection should be afforded the entire circulating loop.

This protection is not available to the dead end lines since oxygen is not as soluble in uranyl sulfate solution as the D_2 . At 2000 psi the

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deficiency of oxygen for complete recombination is 192 ppm, and at 1700 psi, the deficiency is 98 ppm. When the oxygen is recombined in the dead end lines, there will be an appreciable excess of deuterium and essentially zero oxygen present. The time required for this recombination is about 10 minutes at 250°C.

Thus it is seen that an excess of oxygen must be added to the circulating stream in amounts sufficient to recombine all the D_2 which will be in the dead end line and to serve as an adequate corrosion protection. Figure 3 shows the relationship between the excess oxygen charged to the solution and the actual amount available for corrosion protection in the dead end lines. It is seen that at least 200 to 250 ppm of excess O_2 must be added to the solution before any oxygen will be available for corrosion protection in the dead end lines. To insure against rapid corrosion in such lines it may be necessary to add 500 ppm or more of oxygen to the solution.

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POSSIBILITY OF OXYGEN DEPLETION IN STAGNANT URANYL SULFATE LINES

Introduction

Many of the uranyl sulfate containing lines in the HRT will normally be expected to contain stagnant solution for long periods of time. (Examples of this situation are the dump lines, sample lines, hydroclone lines to chem. tech. cell and many by-pass lines.) Such lines can be expected to suffer from oxygen depletion and thus high corrosion rates.

The corrosion rates of nonfissioning solutions (gammas and betas seem to have little effect on the corrosion rate) in static tests have shown about 5 mpy as bare metal attack and 0.3 or 0.4 mpy for conditioned surfaces in the presence of about 25 ppm or greater of oxygen. In the absence of oxygen the corrosion rate may be increased to hundreds of mils per year.

With oxygen in solution the corrosion proceeds through the following series of reactions to leave a relatively stable metal oxide on the metal surface¹.

After formation of the oxide film, further corrosion is believed to proceed by the film developing fine cracks, due to thermal and mechanical stresses, in which corrosion proceeds on the bare metal thus exposed.

If no oxygen is present the corrosion of stainless steel by uranyl sulfate solution is believed to occur through the following series of reactions:

The reduction of the UO_2^{+4} to U^{+4} has the effect of increasing the hydrogen ion concentration near the surface of the metal, thus greatly increasing the corrosion rate. Uranium is precipitated as U_3O_8 in these cases.

The corrosion rate can be measured as a function of the oxygen consumption rate. For stainless steel the oxygen consumption rate has been determined as 7.8 gr. O_2 /mil-year-ft².

There was also the possibility that radiolytic gamma and beta decomposition would give a high enough O_2 concentration to insure that the oxide film would remain stable.

Oxygen Consumption Due to Corrosion

In stainless steels having the nominal composition of 18% Cr, 10% Ni, and 72% Fe, the rate of oxygen consumption due to metallic oxide formation is 7.8 gr. O_2 /mil-year-ft². Assuming that at the time of stagnation the fuel solution has 100 ppm of O_2 and that all of the O_2 in the pipe is available for oxide formation (that the reaction is not diffusion controlled) the time required to consume the O_2 can be calculated as a function of pipe diameter.

The surface area of the pipe is given as: $S_A(\text{ft}^2) = \pi DL$. The weight of soup in the pipe is: $W(\text{lb}) = \frac{\pi D^2}{4} \rho L$. The consumption rate of O_2 in the pipe:

$$C_{O_2} \left(\frac{\text{gr } O_2}{\text{day}} \right) = \frac{7.8}{365} S_A$$

Assuming a corrosion rate of one mil/year in these stagnant pipes (the actual corrosion rate may range from 0.3 to 5.0 mpy depending on the surface conditioning of the metal) the time required to consume the oxygen is:

$$t(\text{days}) = 5.31 \times 10^{-3} \rho DC$$

ρ = Density of solution, lb/ft³
 D = Inside diameter of pipe, ft
 C = Oxygen concentration, ppm

This curve is plotted in Figure 1 for an initial oxygen concentration of 100 ppm.

Oxygen Available from Radiolytic Decomposition

The D_2 concentration in the soup solution (and thus the O_2 concentration) due to radiolytic decomposition of the D_2O by fission product gammas and betas

can be adequately represented by¹:

$$\frac{dD_2}{dt} = 0.00622 \text{ GW} - k C_{\text{cu}} D_2$$

C_{cu} = Copper concentration, $\frac{\text{gr mols}}{\text{liter}}$

(For 80% recombination and 5 Mw reactor power, $C_{\text{cu}} = 0.0019 \frac{\text{gr mols}}{\text{liter}}$)

W = Energy absorbed by solution, kw/liter.
(Assume equal to total fission product energy of both gammas and betas)

k = Recombination rate constant, $\frac{\text{liters}}{\text{gr mol Cu}^{++} - \text{sec}}$
 $= ae^{-b/T} \quad (2)$

$$a = 2.37 \times 10^{10}$$

$$b = 12,200$$

T = Temperature, $^{\circ}\text{K}$

G = Yield, (For betas and gammas, $0.45 \frac{\text{molecules } D_2}{100 \text{ ev abs}}$)

D_2 = gr mols D_2 /liter solution

t = minutes .

The equilibrium value of the D_2 concentration may be estimated by,

$$\frac{dD_2}{dt} = 0 = 0.00622 \text{ GW} - k C_{\text{cu}} D_2$$

Substituting the values of the constants;

$$D_2 = \frac{0.00622}{0.0019} \cdot \frac{0.45}{100} \cdot \frac{W}{k} = 1.47 \times 10^{-2} \frac{W}{k}$$

With W as a function of time (by the Wigner-Way equation) and k as a function of temperature, the O_2 concentration is plotted in Figure 2. Since the stoichiometric ratio of D_2 to O_2 is 2 to 1 the oxygen concentration due to radiolytic decomposition is one-half of the deuterium.

Excess Oxygen Required in Solution

Since gas letdown is expected in the HRT, the fuel solution leaving the gas separator will be saturated with D_2 and O_2 at their respective partial pressures. The solubility of D_2 and O_2 in uranyl sulfate solutions has been measured³ and found to follow Henry's law for the partial pressures of interest here. The vapor pressure of D_2O is found in CF-56-11-135. With these values and the recombination equations as given in CF-56-4-4, the concentration of D_2 and O_2 can be calculated for any point of the high pressure system.

At 2000 psi the D_2 concentration is thus found to range from 2.52×10^{-3} to $2.39 \times 10^{-3} \frac{\text{lb mol } D_2}{\text{lb mol sol}}$ with an average of $2.45 \times 10^{-3} \frac{\text{lb mol } D_2}{\text{lb mol sol}}$. Similarly the oxygen concentration ranges from 1.17×10^{-3} to 1.105×10^{-3} with an average concentration of $1.138 \times 10^{-3} \frac{\text{lb mol } O_2}{\text{lb mol sol}}$. At 1700 psi the averages are $1.619 \times 10^{-3} \frac{\text{lb mol } D_2}{\text{lb mol sol}}$ and $7.485 \times 10^{-4} \frac{\text{lb mol } O_2}{\text{lb mol sol}}$. These yield oxygen concentrations in the circulation stream of 1820 ppm at 2000 psi total pressure and 1200 ppm at 1700 psi.

Since the oxygen is less soluble in the solution than the deuterium there is for these temperatures and pressures a net deficiency of oxygen. At 2000 psi the deficiency for complete recombination is 192 ppm O_2 and at 1700 psi the deficiency is 98 ppm. Such deficiencies are of no consequence in the circulating portion of the loop but in the stagnant piping these deficiencies are real and will cause complete oxygen depletion with a very short time. The time required can be estimated:

$$\frac{dy}{dt} = -k y x$$

y = mole fraction D_2

k = rate constant, $\frac{\text{liters}}{\text{mol } Cu^{++} \cdot \text{sec}}$

x = copper concentration, $\frac{\text{mole } Cu^{++}}{\text{liter}}$

t = time, sec.

This integrates to:

$$y = y_0 e^{-k x t}$$

The D_2 required to completely recombine all the O_2 in solution at 2000 psi is

$$2.276 \times 10^{-3} \frac{\text{mol } D_2}{\text{mol sol}} \text{ leaving an excess of } D_2 \text{ in solution of } 0.174 \times 10^{-3}$$

$\frac{\text{mol } D_2}{\text{mol sol}}$. Assuming 80% total recombination and 250°C temperature in the

dead-ended lines:

$$k = 2.29 \frac{\text{liters}}{\text{gr mol Cu}^{++} - \text{sec}}$$

$$x = 0.0019 \frac{\text{gr mol Cu}^{++}}{\text{liter}}$$

$$y_o = 2.45 \times 10^{-3} \frac{\text{gr mol } D_2}{\text{gr mol sol}}$$

$$y = 0.174 \times 10^{-3} \frac{\text{gr mol } D_2}{\text{gr mol sol}} .$$

From which the time required to effectively recombine all the oxygen present is 10 minutes.

Thus it can be seen that for the dead-end lines, an excess of oxygen will be required in the circulating stream. Figure 3 shows the relationship between the excess oxygen charged to the solution and the actual amount available for corrosion protection in the dead-end lines.

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- 2 Aven, R. E. and Lawrence, M. C., CF-56-4-4, "Calculation of Effects of Copper Catalyst in the HRT".
- 3 Stephen, E. F., et al, BMI-1067, "The Solubility of Gases in Water and in Aqueous Uranyl Salt Solutions at Elevated Temperatures and Pressures".

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Figure 1

Inside Diameter of Pipe
vs.
Time Required to Consume
100 ppm O_2 in a Stagnant
Pipe

Inside Diameter
of Pipe, inches

(1 mil/year corrosion rate
and 2.8×10^{-2} as
 O_2 Consumption Rate)

Days.

7

Days of Cooling

8

Figure 3

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1-8