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SUBJECT: Relationship Between the Rate-Controlling Step of the Mass-Transfer Process and Distribution of Corrosion Attack
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ABSTRACT

Equations are derived which relate the distribution of corrosion attack or cold-zone deposits with the rate-controlling step of a system which exhibits a thermal-gradient mass transfer. Characteristic distributions of attack and deposition are illustrated for thermal-gradient mass-transfer processes which are: 1) hot-zone controlled, 2) cold-zone controlled, and 3) both hot-zone and cold-zone controlled and the limitations of the method are discussed. It is concluded that both the hot-zone and cold-zone processes must be understood before the conditions leading to the least undesirable distribution of attack can be specified.

- 1 -

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It is possible with certain restrictions to determine the rate-controlling step of the thermal-gradient mass-transfer process in a liquid-metal or fused-salt loop by examining the distribution of hot-zone attack (or of cold-zone deposition). The basis for determining the rate-controlling step is a series of material balances on the transferred material at localized regions around the loop. In this report, equations will be derived which can be used to infer the rate-controlling step from the distribution of attack. Characteristic distributions of attack and deposition will be illustrated for thermal-gradient mass-transfer processes which are: 1) hot-zone controlled, 2) cold-zone controlled, and 3) Both hot-zone and cold-zone controlled.

Mass Balance on a Loop Element

Consider the element of length dZ in a mass-transfer loop of diameter D shown below:

Let

w = mass-flow rate - g/sec

x = mass fraction of solute - g solute/g total

D = pipe diameter - cm

Z = distance along the pipe - cm

t = time - sec

R = rate of solution at pipe wall - g/cm²sec

The solute entering the element dZ in the time interval dt comes from two sources, the solute in the liquid flowing into the element and the solute which dissolves at the wall. Expressed in terms of the above definitions the input is

$$wxdt + \pi DdZ \cdot R \cdot dt$$

At the low concentrations of solute encountered in mass-transfer loops, the total mass-flow rate does not change appreciably, and the material leaving the element dZ in time dt is

$$w(X + dX)dt$$

and the accumulation is

$$\frac{\pi}{4} D^2 dz \rho \frac{dX}{dt}$$

Since the input is equal to the output plus the accumulation, the above expressions may be equated and solved for R to give:

$$R = \frac{w}{\pi D} \frac{\partial X}{\partial Z} + \frac{D \rho}{4} \frac{\partial X}{\partial t} \quad (1)$$

Equation (1) is the general mass-transfer equation for solution in a circular pipe and expresses the rate of mass transfer in terms of the solute concentration in the liquid. Unfortunately, (1) has limited applicability in the analysis of practical systems, because the rate of mass transfer is so low in such systems that $\frac{\partial X}{\partial Z}$ and $\frac{\partial X}{\partial t}$ are smaller than the limits of experimental measurement, although they by no means vanish. Some simplification of (1) is achieved under steady-state conditions where $\frac{\partial X}{\partial t} \rightarrow 0$.

At steady state

$$R = \frac{w}{\pi D} \frac{\partial X}{\partial Z} \quad (2)$$

The rate of mass transfer at the wall in the element dZ may also be expressed by the equation:

$$R = K \rho (X^* - X) \quad (3)$$

where

K = the local mass-transfer coefficient - cm/sec
 ρ = density of the liquid - g/cm³
 X^* = equilibrium solubility at the wall temperature,
 expressed as mass fraction

By equating (2) and (3) one obtains the expression

$$K \rho (X^* - X) = \frac{w}{\pi D} \frac{dX}{dZ} \quad (4)$$

If it is assumed that radial-concentration gradients are small, it can be seen that solution can only occur in those areas of the loop in which $X^* > X$, and deposition of solute can only occur when $X^* < X$. It should be noted that the value of K for the hot-zone process is in general quite

different than K for the cold-zone process.

If one had accurate information on the values of X^* , ρ , and K as a function of Z , he could integrate (4) and obtain values of X as a function of Z . These values of X would permit the calculation of $R(Z)$ from (3). The amount of material, Q , per unit area removed or deposited at point Z in a time interval Δt could be computed at steady state by the expression:

$$Q = R(Z)\Delta t \quad (5)$$

so that the mass-transfer process at each location in the loop would be analytically described. In actual practice, however, the integration of (4) is very difficult. The quantities X^* , ρ , and K all vary with temperature, which in turn varies with the position in the loop. In addition insufficient data are available in most cases to permit the computation of the function $X^*(T)$ and $K(T)$.

In spite of its limitations equation (4) may be used to analyze a system qualitatively. Consider the plot of X versus Z for the idealized loop shown in Fig. 1. For the purposes of this discussion X^* is assumed to be a saw-toothed function of position in this loop. If the saturation concentration of solute varied linearly with temperature, the plot of X^* versus Z could correspond to the temperature distribution in the loop. In the more common situation in which X^* varies exponentially with reciprocal absolute temperature according to the expression

$$X^* = X_0^* e^{-\frac{\Delta H}{RT}} \quad (6)$$

the temperature distribution along the wall would have to fit an expression of the type

$$Z = A + B e^{-\frac{\Delta H}{RT}} \quad (7)$$

where A and B are constants. However, over the temperature ranges encountered in loop-operation, this exponential may frequently be replaced by a linear approximation and the temperature distribution would then be linear also. It should be noted that this assumption of a linear temperature distribution has been made for purposes of illustration alone and in no way affects the validity of subsequent arguments.

Mass Fraction of Solute in the Liquid - X

Fig. 1 Liquid Concentration Profiles in Mass-Transfer Loops.

The concentration distribution in the loop for a hot-zone controlled process is shown by curve 1 of Fig. 1. The liquid would leave the cold zone ($Z = 0$) essentially saturated with respect to the minimum loop temperature. As the liquid passed through the heated area, the relatively slow process of solution would occur so that X would increase very gradually. Even after the liquid enters the cooled section ($Z > \frac{L}{2}$) X^* would remain much greater than X so that solution would continue until the temperature again approached the minimum loop temperature. At point P, X^* would be equal to X so that neither solution nor deposition would occur. Between P and L the rapid cold-zone process would permit X to drop quickly back to X^* min. Thus the mean-liquid composition would vary only slightly above X^* min. For a hot-zone controlled process the deposition in the cold zone would occur in a relatively narrow region where $X^* < X$ and the solution process ($X^* > X$) would occur over most of the length of the loop. The greater the rate of the cold-zone process relative to the hot-zone process, the more restricted is the area of deposition. It should be pointed out, however, that a broad distribution of deposits in the loop would not preclude a hot-zone controlled process, because the precipitate may be mechanically removed from the region of original deposition or redeposited in another area. Since, in this case, the solution process is so slow, this precipitate may not redissolve even though a potential exists for it to do so.

A cold-zone controlled process would be the exact reverse of the hot-zone controlled process and would correspond to curve 2 of Fig. 1. In this case the liquid would leave the hot zone ($Z = \frac{L}{2}$) saturated with respect to the maximum wall temperature. As the liquid enters the cooled region, deposition in the form of precipitation or inward diffusion would occur over the entire length of the cooled area. Even after the liquid re-enters the heated region of the loop X would exceed X^* so that deposition would continue to occur. Finally at point Q, X would equal X^* and beyond Q the liquid would quickly become saturated with respect to the maximum loop temperature. The mean-liquid composition X would vary only slightly below X^* maximum. For the cold-zone controlled process, then, the region in which solution occurs ($Q < Z < \frac{L}{2}$) would be very restricted and deposition would occur over most of the length of the loop. The more rapid the hot-zone process, the more restricted would be the solution-attacked region and for the same over-all mass transfer, the greater would be the depth of attack.

Curve 3 of Fig. 1 corresponds to the case in which the over-all rate of the hot-zone process is just equal to the over-all rate of the cold-zone process. Here solution attack would occur over half the length of the loop and deposition would occur over the other half. The mean-liquid composition would be intermediate between X^* maximum and X^* minimum.

The above discussion may be summarized as follows:

Hot-Zone Controlled Mass Transfer

$$\bar{X} \text{ (liquid)} \approx X^* \text{ min}$$

$$M = \frac{\text{length of loop where solution is occurring}}{\text{length of loop where deposition is occurring}} \rightarrow \infty$$

Cold-Zone Controlled Mass Transfer

$$\bar{X} \rightarrow X^* \text{ max}$$

$$M \approx 0$$

Both Zones Controlling the Mass Transfer

$$\bar{X} \approx \frac{X^* \text{ max} + X^* \text{ min}}{2}$$

$$M \approx 1$$

Thus by a study of the distribution of hot-leg attack or the cold-zone deposition, the rate-controlling step in the mass-transfer process may be inferred.

One rather interesting conclusion falls out of the above analysis. To reduce the rate of the controlling step of mass transfer in a loop could well have adverse effects on the system. It is quite possible that while the over-all rate of mass transfer could be decreased, the depth of attack in a localized region in the non-controlling region could be increased due to a shift in the parameter M . In many cases it would be beneficial to decrease the rate of the non-rate-controlling process to spread the area of attack. In any case it is important to understand the mechanisms and rates of both the hot-zone and cold-zone processes in order to improve the operating lifetime of any practical system.

The above discussion applies only in the analysis of loops which have operated under steady-state conditions for a long time. If the non-steady-state condition prevails over a reasonable fraction of the operating time, solution will have occurred at every point in the loop for this fraction of the time and the effects of the solution step could mask the steady-state effects. Thus the above analysis can be used safely only when the system in question has operated under steady-state conditions for the major fraction of the test period.

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