Preliminary Corrosion Model in Isothermal Pb and LBE Flow Loops

†Sung Ho Lee, Choon Ho Cho, and Tae Yung Song

Korea Atomic Energy Research Institute, Daejeon 305-600, Korea

HYPER(Hybrid Power Extraction Reactor) is the accelerator driven subcritical transmutation system developed by KAERI(Korea Atomic Research Institute). HYPER is designed to transmute long-lived transuranic actinides and fission products such as Tc-99 and I-129. Liquid lead-bismuth eutectic (LBE). Has been a primary candidate for coolant and spallation neutron target due to its appropriate thermal-physical and chemical properties, However, it is very corrosive to the common steels used in nuclear installations at high temperature. This corrosion problem is one of the main factors considered to set the upper limits of temperature and velocity of HYPER system. In this study, a parametric study for a corrosion model was performed. And a preliminary corrosion model was also developed to predict the corrosion rate in isothermal Pb and LBE flow loops.

Keywords : HYPER, lead-bismuth eutectic, corrosion, model, corrosion test loop

1. Introduction

HYPER(Hybrid Power Extraction Reactor) is the accelerator driven transmutation system developed by KAERI (Korea Atomic Energy Research Institute). HYPER is designed to transmute long-lived transuranic actinides and fission products such as Tc-99 and I-129. Lead-Bismuth eutectic(LBE) alloy was determined as a spallation target and coolant material of HYPER due to its high production rate of neutrons and its effective heat removal, However, LBE has a great corrosion problem at high temperature.[1]-[2] Thus, the problem has been considered as a important design-factor that limits the operational temperature and flow velocity of the ADS system.[2]-[3]

KAERI recently finished the fabrication of isothermal LBE and Pb corrosion test loops(KPAL I and KPAL II) to predict the corrosion rate of HYPER materials in flowing liquid LBE and Pb. They consist of an electromagnetic pump (EMP), two electromagnetic flow meters (EMF), a teat section, an oxygen control tank (with an expansion tank), a calibration tank, a magnetic and a mechanical iron trap, and an argon or an argon with 5% hydrogen gas control system, The oxygen concentration was controlled by adjusting the H_2 and H_2O vapor ratio.[1] Fig. 1 show the schematics of the isothermal Pb corrosion test loop recently installed at KAERI.
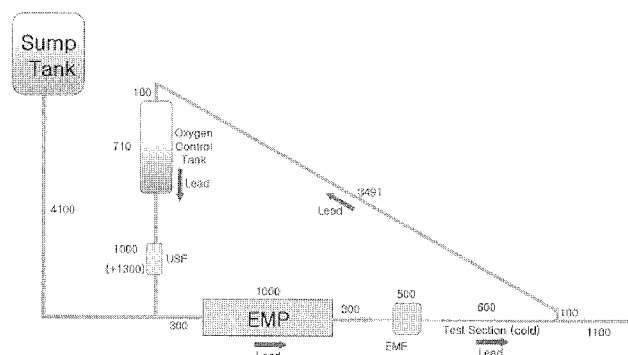

Fig. 1. Schematics of the isothermal Pb corrosion test loop recently installed at KAERI.

Corrosion in liquid Pb and LBE systems is primarily due to the relatively high solubility of the base and major alloying components of steels, such as Fe, Ni, Cr, etc. Liquid metal corrosion can proceed via dissolution at very low oxygen concentration, and through surface oxidation and reduction of surface oxides at higher oxygen concentrations. Without some protective means, the selective dissolution of materials would destroy the containment structure. Corrosion rate is typically a function of local temperature and flow velocity. However, corrosion and precipitation rates and distributions can depend strongly on the global temperature distribution, limiting the applicability of many corrosion models.

Several method have been considered to prevent the

†Corresponding author: shlee6@kaeri.re.kr

corrosion problem in liquid Pb and LBE.[4)-5)] One of the method is to form and keep the protective oxide film on the structure to reduce the corrosion rate through the control of active oxygen concentration in the liquid metals. When a protective layer of oxide can be maintained on the surface of stainless steel pipe exposed to liquid LBE, the corrosion resistance of piping can be greatly enhanced.[3)] Another one is to modify the surface of the material or the material compositions.

In this study, a parametric study for a corrosion model was performed, and a preliminary corrosion model in isothermal Pb and LBE flow loops was also developed to predict the corrosion rate.

2. Theory

Mass transfer is the process of transporting corrosion products from the liquid-solid interface to the bulk flow. In a mass transfer controlled regime, the corrosion rate is limited by a diffusion. The corrosion rate, q in isothermal flow loop is calculated using the following expression.[3),6)]

$$\text{Corrosion rate } q = k(C_s - C_b) \tag{1}$$

Where k is mass transfer coefficient (m/s) dependent on the flow velocity, C_s is the corrosion product concentration at the solid-liquid interface dependent on the local temperature, and C_b is the corrosion product concentration in the bulk flow.

2.1 Governing equation for corrosion model

It is important to notice that the species concentration at wall surface are functions of temperature. Ina closed isothermal closed system, species concentration is uniform on wall surface. Although corrosion may initially proceed if there is a concentration difference between the wall and bulk fluid, however, it will eventually stop once the solution becomes saturated. This saturation, however, can never be reached in a non-isothermal system. In that situation, the structural materials are dissolved or reduced into LBE at hot legd, transport by diffusion and convection to cold legs, and precipitate at the wall there. In general, the following convection-diffusion equation is used to calculate the mass transport of corrosion products in flowing liquid system:[3),4),7)]

$$\frac{\partial C}{\partial t} + (u\nabla)C = D(\nabla^2 C) + q$$

Where C is the concentration of the corrosion product,

u is the flow velocity, D is the mass diffusion coefficient, and q is a net production/depletion rate due to chemical reactions in the liquid metal, In the present study, we neglect the reaction of corrosion product in the bulk of the liquid and q=0.

For a fully turbulent flow, it is reasonable to assume that the mixing flow homogenizes the bulk concentration and one only needs to solve the transport problem inside the boundary layer, where convection is dominant in the longitudinal direction and diffusion is dominant in the transverse direction, The corrosion model is based on solving the mass transport equation in the boundary layer. For the steady state case, the governing equation in the boundary layer can be written as,[7)]

$$u\frac{\partial C}{\partial x} = D(\frac{\partial^2 C}{\partial y^2})$$

Where X and y are coordinated in the axial and transverse directions, respectively.

3. Parametric study of a corrosion model

3.1 Modeling the mass transfer coefficient

According to the equation (1), modeling mass transfer coefficient, k exactly is very important for the corrosion model in the isothermal loops. Previous studies indicate that mass transfer coefficient, k depends on the hydrodynamic parameters and material transport properties. For a closed loop flow, the rate is constant, Neglecting the effect of the transition sections, several mass transfer coefficient expressions have developed in an aqueous media based on experimental data follows:[8)-10)]

- Berger and hau:[8)]
$$k_{B-H} = 0.0203\nu^{-0.53}D^{0.67}Q^{0.86}d^{-1.86} \tag{2}$$

- Silverman:[9)]
$$k_{Silverman} = 0.0219\nu^{-0.579}D^{0.704}Q^{0.875}d^{-0.1875} \tag{3}$$

- Harriott and Hamilton:[10)]
$$k_{H-H} = 0.021\nu^{-0.567}D^{0.654}Q^{0.913}d^{-1.913} \tag{4}$$

Where ν is the kinematic viscosity (m²/s), D is the diffusion coefficient (m²/s), Q is the volume flow rate (m³/s), and d is the hydraulic diameter (m).

For liquid metals, the kinetic viscosity is much larger than the diffusion coefficient, which indicated that the mass transfer boundary layer is submerged in the hydraulic boundary layer.

The concentration governing equation in the boundary

layer can be written as:[3]

$$\gamma \frac{\partial C}{\partial x} = D(\frac{\partial^2 C}{\partial y^2})$$

When x and y are coordinated in the axial and transverse directions, γ is $\lambda V^2/2u$ and λ is fanning friction factor.

Upper equation can be solved by the similarity method when is no concentration variation in the axial direction.[11] An analytical expression of the mass transfer coefficient is obtained:

$$k = \frac{3}{2\Gamma(1/3)}(\frac{3}{1740})^{\frac{1}{3}} \upsilon^{\frac{-2}{3}} D^{\frac{2}{3}} V(\frac{\lambda}{2})^{\frac{1}{2}}$$ (5)

Where Γ is the Gamma function.

For the expression of the friction factor, one of the simplest correlation is the Blasius equation.[6] $\lambda = 0.079 Re^{-0.25}$ Re is the Reynolds number, Re=VD/υ). Then, equation (5) becomes as follows:

$$k = 0.0133\upsilon^{-0.542} D^{0.667} V^{0.875} d^{-0.125}$$ (6)

Equation (6) shoes that the analytical expression is similar to the experimental expression. The diffusion coefficient for modeling the mass transfer coefficients can be calculated as following equation:[3],[12]

$$D(m^2/\sec) = 4.97x10^{-7} \exp[\frac{-Q}{RT(K)}]$$ (7)

Where Q:10500$\pm$1500cal/gmol, R: gas constant, 1.987cal/gmol°K.

Diffusion coefficient values calculated in liquid Pb and LBE at 450 °C and 550 °C, respectively are as follows,

- $D_{Fe.Pb}$ and $D_{Fe.Pb-Bi}$ = 3.28 $x10^{-10}$m^2/sec(450°C)

- $D_{Fe.Pb}$ and $D_{Fe.Pb-Bi}$ = 7.97 $x10^{-10}$m^2/sec(550°C)

The kinematic viscosity(υ) for modeling the mass transfer coefficients is calculated as following equation:[3]

$$\upsilon = 61.423 \times 10^{-7}(T(K)-273.15)^{-0.61106}$$ (8)

The values of the kinematic viscosity calculated in liquid Pb and LBE at 450 °C and 550 °C, respectively are as follows,

For liquid Pb-Bi:
$\upsilon = 1.4 \times 10^{-7}$m^2/sec(450°C), $\upsilon = 1.3 \times 10^{-7}$m^2/sec(550°C)

For liquid Pb:
$\upsilon = 1.9 \times 10^{-7}$m^2/sec(450°C), $\upsilon = 1.65 \times 10^{-7}$m^2/sec(550°C)

In our isothermal loops, the hydraulic diameter, d is 0.0254 m, loop/pipe length is 13 m, and flow velocity, u is 2.0 m/sec, The values for the mass transfer coefficients calculated in Pb and LBE loops by the using three mass transfer coefficient expressions, equations(2)-(4) are as follows, respectively:

-Pb loop:
· k_{B-H} = 1.56 x 10^{-4} m/sec
· $k_{Silverman}$ = 1.69 x 10^{-4} m/sec
· k_{H-H} = 8.87 x 10^{-5} m/sec

-LBE loop:
· k_{B-H} = 2.2 x 10^{-4} m^2/sec
· $k_{Silverman}$ = 1.94 x 10^{-4} m^2/sec
· k_{H-H} = 1.0 x 10^{-4} m^2/sec

3.2 Modeling bulk concentration(c_b) in loops

The bulk concentration of the corrosion product is another important factor in corrosion problem. For an open pipe flow concentration can be assumed to be zero to the inlet concentration. But for a closed loop flow, the fluid is no replenished, and the bulk corrosion product concentration increases with time due to corrosion at the liquid-solid interface until it reaches a steady state. The bulk concentration in a closed loop flow needs to be modeled.

For a fully turbulent flow, it is reasonable to assume that the mixing flow homogenizes the bulk concentration, the bulk concentration of the corrosion product stays constant along the axial direction of the loop, then the following equation is obtained,[3]

$$\beta \frac{\partial c_b}{\partial t} \int s(x)k(x)\{c_s(x) - c_b(t)\}dx$$ (9)

Where L is loop length(m), β is liquid volume in the entire loop(m^3), t is time(s), s is circumference of the pipe(m), and k is local mass transfer coefficient.

The initial condition is

At t = 0, c_b = 0

The solution of upper equation is

$$c_b(t) = \frac{\int s(x)k(x)c_s(x)dx}{\int s(x)k(x)}(1 - e^{-\frac{1}{\beta}t\int s(x)k(x)dx})$$ (10)

For steady state, the bulk concentration, c_b becomes

$$c_b(t) = \lim_{t \to \infty} c_b(t) \frac{\int s(x)k(x)c_s(x)dx}{\int s(x)k(x)} \qquad (11)$$

For an isothermal loop, the surface concentration, c_s does not vary along the loop axis. Therefore, although there is corrosion initially, after a short time, the bulk concentration reaches the value of surface concentration and no more corrosion occurs at the steady state foe an isothermal loop flow. The following parameters are used in the calculation of bulk concentration,
- Flow velocity, $u = 2$ m/s, and-Loop diameter and length, $d = 0.0254$ m, $L = 13$ m.

According to equation,[11] The values of the bulk concentration, c_b obtained for the corrosion model in the isothermal Pb and LBE loops are obtained as follows, respectively:[3]

- Pb loop
 · C_b B-H $= 9.784$ g/m^3 · C_b Silverman $= 9.189$ g/m^3
 · C_b H-H $= 9.768$ g/m^3

- LBE loop
 · C_b B-H $= 0.153$ ppm   · C_b Silverman $= 0.154$ ppm
 · C_b H-H $= 0.154$ ppm

3.3 Estimation of surface concentration(C_s) does not vary along the loop axis.

For an isothermal loop, the surface concentration, C_s does not vary along the loop axis.

The corrosion product concentration at the liquid-solid interface for Pb loop is calculated by the following equation,[3],[13]

$$\log C_s(ppm) = 4.34 - \frac{3450}{T(K)}$$

In oxygen control LBE loop, we calculate corrosion product concentration at the liquid-solid interface by the following equation,[4],[13]

$$. \log C_s(ppm) = 46.01 - \frac{4380}{T(K)}$$

· C_s (ppm, Fe) $= C_o^{-1.333} \, 10^{11.35-12844/T}$

Where C_o is the oxygen concentration in LBE and T is the absolute temperature in Kelvin.

The calculated valued of C_s are 1.41 ppm (14.5 g/m^2)

for Pb loop and 4.88 ppm(49.04g/m^2) for LBE loop, respectively.

4. Results and discussion

4.1 Preliminary corrosion model of steels in liquid heavy metals

For a isothermal closed loop, the bulk concentration reaches the value of the surface concentration after a short time. Therefore, there is a corrosion initially and no more corrosion occurs at the steady state for an isothermal loop flow, Under a constant temperature, the wall corrosion product concentration stays constant along the loop axis, thus, $C_W = \hat{C}$, where $\hat{C}$ is constant.. The corrosion rate for this case is estimated by the following equation.[14]

$$\frac{q}{C} = \frac{\sqrt{D}}{\pi t} \qquad (12)$$

The corrosion rate for an isothermal loop flow is in dependent of the hydraulic factors, such as the flow velocity, the hydraulic diameter, and the loop length. The solution is 1-dimension diffusion problem. When $t \to \infty$, the concentration approaches a uniform distribution, and the mass flux of the corrosion product stops because there is no concentration gradient between wall and bulk flow. Fig. 2 shows corrosion rate for an isothermal loop flow vs time. Based on the result in Fig. 2, the required time for the steady state($C_b = C_s$) is assumed as 1×10^6 sec(11.57), it will eventually stop once the solution becomes saturated with the corrosion product.

The data used for a corrosion model in isothermal Pb and LBE flow loops are the following:

- temperature, $T = 550°C$,
- kinematic viscosity,
  $v = 1.3 \times 10^{-7}$ m^2/sec(LBE), $v = 1.65 \times 10^{-7}$ m^2/sec(Pb),
- corrosion product concentration (C_s) at the surface,
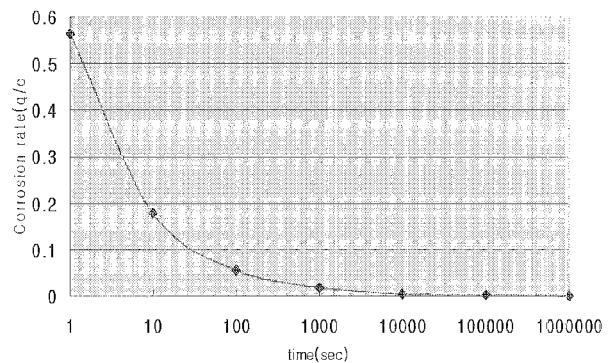 1.41 ppm (14.5g/m^2) for Pb and 4.88ppm (49.04g/m^2)for LBE

Fig. 2. Corrosion rate for an isothermal loop flow vs. time.

- the required time for the steady state ($C_b = C_s$), t = 1 x 10^6 sec (11.57day)
- hydraulic diameter, d = 0.0254 m,
- loop/pipe length, L = 13 m
- liquid velocity, V = 2.0 m/sec,
- oxygen concentration = 0.001 ppm(LBE).

By the using the estimated input parameters for the corrosion model, corrosion rates, q in the isothermal Pb and LBE loops are modeled preliminarily as follows, respectively:

- Pb loop:
  - q_{B-H} = 7.35 x 10^{-4} g/m^{2}s = 92 μm
  - $q_{Silverman}$ = 8.98 x 10^{-4} g/m^{2}s =112.4 μm
  - q_{H-H} = 4.2 x 10^{-4} g/m^{2}s =52.6 μm

- LBE loop:
  - q_{B-H} = 8.82x 10^{-4} g/m^{2}s = 110.4 μm
  - $q_{Silverman}$ = 7.74 x 10^{-4} g/m^{2}s = 96.9 μm
  - q_{H-H} = 4.0 x 10^{-4} g/m^{2}s =50.2 μm

5. Conclusions

A parametric study for a corrosion model was performed. And corrosion rate in isothermal Pb and LBE flow loops is modeled preliminarily. Using the present corrosion model, we predict the corrosion rates in the test section of Pb and LBE test loop under isothermal condition. Based on the results, the corrosion rate increases with an increase of flow rate and temperature. The present study provides important tool to predict the corrosion rate of steels and to interpret the corrosion experimental data obtained from the isothermal Pb and LBE corrosion loop. We are performing the corrosion experiments of Hyper materials in isothermal Pb and LBE loop. In future studies, by comparing the metal corrosion rate between the corrosion experiment result and modeled results, we will modify mass transfer coefficient expressions, and determine best expression to predict the corrosion rate for our isothermal loops.

References

1. W. S. Park, T.Y Song, and C. K. Park, *Nuclear Engineering Design*, **219**, 207 (2002).
2. G. Mueller, *J. of Nuclear Materials*, **278**, 85 (2000).
3. J. Zhang and N. Ni, *Nuclear Technology*, **144**, 379 (2003).
4. B. X. he, N. Li, and M. Mineev, *J. of Nuclear Materials*, **297**, 214 (2001).
5. N. Li , *J. of Nuclear Materials*, **278**, 85 (2000).
6. F. Balbaud-Celerier and F. barbier, *J. NUcl. Mater.*, **289**, 227 (2001).
7. J. Zhang and N. Ni, *Nuclear Technology*, **321**, 184 (2003).
8. F. P Berger and K. F .F. 1. Hau, *J. Heat Mass Transfer*, **20**, 1185 (1977).
9. D. C. Silverman, *Corronsion*, **40**, 220 (1984).
10. P. Harriott and R. Hamiton, *Chem.Eng.Sci.*, **20**, 227 (2001).
11. W. V. Pinczewski and S. Sideman. Chem. Eng. Sci,. **29**, 1959 (1974).
12. W. M. Robertson, Trans. TMS-AIME, **242**, 2139 (1968).
13. J. R. Weeks and A. J. Romano, *Corrosion*, **25**, 131 (1969).
14. J. Zhang and N. Ni, *Corrosion*, **60**, 331 (2004).