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A kinetic model for corrosion and precipitation in non-isothermal LBE flow loop

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Abstract

A kinetic model was developed to estimate the corrosion/precipitation rate in a non-isothermal liquid lead–bismuth eutectic (LBE) flow loop. The model was based on solving the mass transport equation with the assumptions that convective transport dominates in the longitudinal flow direction and diffusion dominates in the transverse direction. The species concentration at wall is assumed to be determined either by the solubility of species in LBE in the absence of oxygen or by the reduction reaction of the protective oxide film when active oxygen control is applied. Analyses show that the corrosion/precipitation rate depends on the flow velocity, the species diffusion rate, the oxygen concentration in LBE, as well as the temperature distribution along a loop. Active oxygen control can significantly reduce the corrosion/precipitation of the structural materials. It is shown that the highest corrosion/precipitation does not necessarily locate at places with the highest/lowest temperature. For a material testing loop being constructed at the Los Alamos National Laboratory (LANL), the highest corrosion occurs at the end of the heater zone, while the highest precipitation occurs in the return flow in the recuperator. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Using liquid lead–bismuth eutectic (LBE) as coolant in nuclear systems has been studied for more than 50 years. LBE has many unique nuclear, thermophysical and chemical attributes that are attractive for nuclear coolant applications [1,2]. In addition, lead and bismuth can produce copious spallation neutrons when bombarded with energetic protons. This makes LBE one of the top candidates for a high-power spallation target in an accelerator-driven transmutation of waste (ATW) system [3].

One of the key obstacles to applying LBE in an ATW system or any other nuclear facilities is the corrosiveness of LBE to structural materials. The corrosion is primarily due to the relatively high solubility of the base and major alloying components of steels, such as Ni, Fe, Cr, etc., in lead–bismuth. Without some protective means, containment structures would be rapidly corroded via dissolution and mass transfer. Considerable efforts were devoted to finding ways of maintaining effective protective films on structural materials in the West before mid-1960s, without much success. This problem was first solved in the Russian nuclear submarine program using an active oxygen control technique [1].

The active oxygen control technique [1,4] exploits the fact that lead and bismuth are chemically less active than the major components of steels, such as Fe, Ni, and Cr. By carefully controlling the oxygen concentration in LBE, it is possible to maintain an iron and chrome oxide-based film on the surfaces of structural steels, while keeping lead and bismuth from excessive oxidization that can lead to precipitation contamina-

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tion. The oxide film, especially the compact portion rich in Cr, effectively separates the substrates from LBE. Once this oxide film is formed on the structure surface, the direct dissolution of the structural materials becomes negligible because the diffusion rates of the alloying components are very small in the oxides. In this circumstance, the only effective means of transferring structural materials into LBE is through the reduction of the oxide film at the interface of the film and LBE.

The reduction of the oxide film will reach a local equilibrium and the Fe concentration near the interface equals an equilibrium value. This equilibrium Fe concentration depends highly on the oxygen concentration in LBE. When the oxygen level is controlled within a certain range, this Fe concentration can be several orders of magnitude smaller than the Fe solubility in LBE. Subsequently, the depletion or corrosion of the structural material can be reduced to a tolerable level for long-term applications. This is the working mechanism behind the active oxygen control technique.

The concentrations of steel elements near surfaces, with the oxygen control or without any oxygen, are functions of temperature [4]. A sustained corrosion process can only happen in a non-isothermal system. Without temperature variation, species concentration would eventually reaches a homogeneous distribution and no further corrosion would occur. With a temperature variation, steel elements will be depleted from the hot structural wall, transfer to locations with lower temperatures, and precipitate there. It should be pointed out that the precipitation at cold walls is often more important because severe precipitation may lead to clogging of piping and degradation of heat transfer. Both diffusion and convection are important in a corrosion/precipitation process. Diffusion is usually the limiting process for transferring species from the wall surface to the bulk fluid, while convection effectively transfers the species from hot places to cold places. Clearly, a systematic study including convection and diffusion is necessary for a full understanding of the complete corrosion/precipitation process.

It is the purpose of this study to carry out such an analysis on corrosion/precipitation in a non-isothermal LBE flow loop. We will derive an analytic model for estimating the corrosion/precipitation rate in a loop flow. From this non-local analysis, we can determine what the maximum corrosion and precipitation rates are and where they locate. This information will be useful for helping to design and operate LBE cooled systems. The rest of the paper is organized as follows. In Section 2, we present the derivation of the model. The model is applied in Section 3 to analyze two non-isothermal LBE flow loops. Some discussions are presented in Section 4, with conclusions in Section 5.

2. Theory

As discussed in the last section, the corrosion of molten LBE to structural materials, steels in particular, usually occurs in two different ways. No matter in which way the corrosion proceeds, it is usually sufficiently fast that the component concentrations are always at their saturated or equilibrium levels. For a dissolution process, the surface component concentrations are equal to their saturated concentration [4]

$$\log(c) = \log(c_s) = A + \frac{B}{T}, \tag{1}$$

where T is the absolute temperature in Kelvin. Unless otherwise mentioned, all the concentrations are measured in wppm in this report. The values of parameters A and B vary for species and some of them are listed in Table 1 for common components in steels.

In the reduction process, the protective Fe_3O_4-based film can be reduced by Pb via the following chemical reaction:

$$\frac{1}{4}\mathrm{Fe_3O_4} + \mathrm{Pb} = \frac{3}{4}\mathrm{Fe} + \mathrm{PbO}. \tag{2}$$

The equilibrium concentration of Fe is [4]

$$\log(c_{\mathrm{Fe}}) = 11.35 - \frac{12844}{T} - \frac{4}{3}\log(c_{\mathrm{O}}), \tag{3}$$

where c_{O} is the oxygen concentration in LBE.

Eq. (3) should be used with caution. For a given temperature, it has an intersection with Eq. (1) in the c_{Fe} vs c_{O} plot (Fig. 1). This intersection determines the

Table 1
Solubility data

c_s	Ni	Fe	Cr	O
A	5.53	6.01	3.98	5.2
B	−843	−4380	−2280	−3400

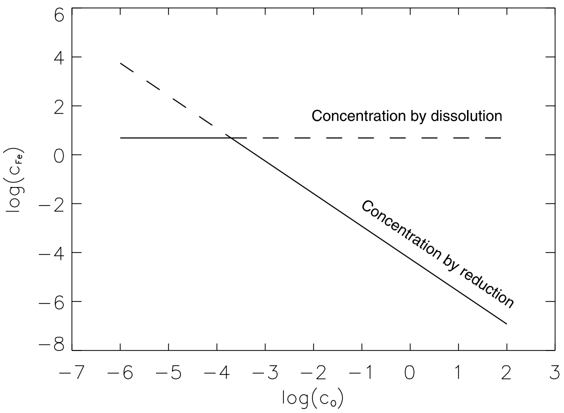

Fig. 1. Fe concentration at wall surfaces ($T = 550°\mathrm{C}$).

minimum oxygen level required for retaining a protective oxygen film. Below this oxygen level, no iron oxide-based film can exist and the Fe concentration at the surface is given by Eq. (1). Above this oxygen level, a continuous iron oxide film can form and the Fe concentration is given by Eq. (3). It is not clear how these two regions connect to each other, but in practice we can assume that the species concentration at surfaces is given by the minimum of the saturation concentration and the chemical equilibrium concentration. For Fe, we have

$$c_{\mathrm{Fe}} = \min(c_{\mathrm{O}}^{-4/3} 10^{11.35-(12844/T)}, 10^{6.01-(4380/T)}), \tag{4}$$

which is the thick solid line in Fig. 1. Notice that there is an upper limit for operating oxygen level in LBE beyond which Pb and Bi could be oxidized to contaminate the coolant. For further information on the upper limit of operating oxygen level, see [4].

It is important to notice that the species concentrations at wall surfaces are functions of temperature. In a closed isothermal system, species concentration is uniform on the wall surfaces. Although corrosion may initially proceed if there is a concentration difference between the wall and the bulk fluid, 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 legs, transported by diffusion and convection to cold legs, and precipitate at the walls there.

In general, the transport of species in LBE satisfies the convection–diffusion equation

$$\frac{\partial c}{\partial t} + (u \cdot \nabla)c = D\nabla^2 c + q, \tag{5}$$

where c is the concentration, u the flow field of the fluid, D the diffusion coefficient, and q is the net mass production/depletion rate due to chemical reactions. In this study, we assume that the chemical reaction is much slower than the characteristic times of diffusion and convection. So chemical reaction contributes little to mass transfer in bulk fluids. The average time for coolant to complete a cycle in a typical testing loop is less than 1 min (loop length/average velocity), and the characteristic boundary layer diffusion time is on the order of minutes. To justify the above assumption, the characteristic time for the chemical reaction must be longer than tens of minutes, which appears to be reasonable. We are planning to carry out experiments to verify this.

For a loop flow, it is reasonable to assume that the convection is dominant in the longitudinal direction and the diffusion is dominant in the transverse direction. In addition, we assume the diffusion is confined in a thin layer near vessel walls. We will only focus on steady flow in this study. With these considerations, the governing equation for species transport can be simplified as

$$\gamma y \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}, \tag{6}$$

where x and y are coordinates in the axial and transverse directions, respectively; γ is the shear rate at the wall. (y is measured from walls.) Introducing

$$\xi = \frac{x}{L}, \quad \eta = \left(\frac{\gamma}{DL}\right)^{1/3} y,$$

where L is the length of a loop, Eq. (6) becomes

$$\eta \frac{\partial c}{\partial \xi} = \frac{\partial^2 c}{\partial \eta^2}. \tag{7}$$

Now we expand the concentration in a Fourier series

$$c(\xi, \eta) = \sum_k Y_k(\eta)\, \mathrm{e}^{2\pi \mathrm{i} k \xi}. \tag{8}$$

Each Fourier harmonics, $Y_k(\eta)$, satisfies the following ODE:

$$2\pi \mathrm{i} k \eta Y_k(\eta) = \frac{\mathrm{d}^2 Y_k(\eta)}{\mathrm{d}\eta^2}, \tag{9}$$

which has the general solution

$$Y_k(\eta) = a_k \operatorname{Ai}((2\pi \mathrm{i} k)^{1/2} \eta) + b_k \operatorname{Bi}((2\pi \mathrm{i} k)^{1/2} \eta), \tag{10}$$

where Ai and Bi are Airy functions. As for the boundary conditions, the concentration at the walls is given by Eq. (4) and the concentration in the bulk fluid is limited. Applying these boundary conditions yields

$$Y_k(\eta) = c_k \frac{\operatorname{Ai}((2\pi \mathrm{i} k)^{1/3} \eta)}{\operatorname{Ai}(0)}, \tag{11}$$

where c_k is the harmonics of the Fourier transform of the species concentration at the wall

$$c(y = 0) = \sum_k c_k\, \mathrm{e}^{2\pi \mathrm{i} k \xi}. \tag{12}$$

The species flux at the vessel wall, or the corrosion/precipitation rate, can be subsequently calculated as

$$\begin{aligned} q &= D \frac{\partial c}{\partial y} \\ &= 0.730 \left(\frac{2\pi \gamma D^2}{L}\right)^{1/3} \sum_k c_k k^{1/3} \exp\left(2\pi \mathrm{i} k \xi + \mathrm{i}\frac{\pi}{6}\right), \end{aligned} \tag{13}$$

where we have used $\operatorname{Ai}(0) = 0.355$ and $\operatorname{Ai}'(0) = 0.259$.

Eq. (13) can be easily implemented in a computer program.

3. Analysis results

The above model is applied to an ideal loop and a test loop under construction in our laboratory.

3.1. Loop with sinusoidal concentration profile

The corrosion/precipitation rate can be exactly calculated when the species concentration varied sinusoidally along a loop. Suppose that the species concentration has the following distribution:

$$c(y=0) = c_0 + c_1 \cos(2\pi x + \phi_0). \tag{14}$$

The corrosion/precipitation rate can be readily derived from Eq. (13):

$$q = D\frac{\partial c}{\partial y} = 0.730\left(\frac{2\pi\gamma D^2}{L}\right)^{1/3} c_1 \cos\left(2\pi x + \phi_0 + \frac{\pi}{6}\right). \tag{15}$$

This result indicates that the corrosion/precipitation rate also varies sinusoidally along the loop. However, it is important to note that the highest corrosion/precipitation do not occur at the highest/lowest temperature. Instead, there is a phase shift of one-twelfth of the loop length between the highest corrosion/precipitation rate and the highest/lowest temperature. Although this phase shift value is not generally applicable for all concentration distributions, as indicated in the later analysis, it shows that the highest corrosion/precipitation does not necessarily occur at places with the highest/lowest concentration or temperature.

Numerical simulations verify the above analytical result. The simulations are based on solving the full mass transport equations using a lattice Boltzmann method [5]. Fig. 2 shows a sample concentration distribution and the consequent mass flux from the analytical solution, Eq. (15), and from the numerical simulation. The results agree with each other well.

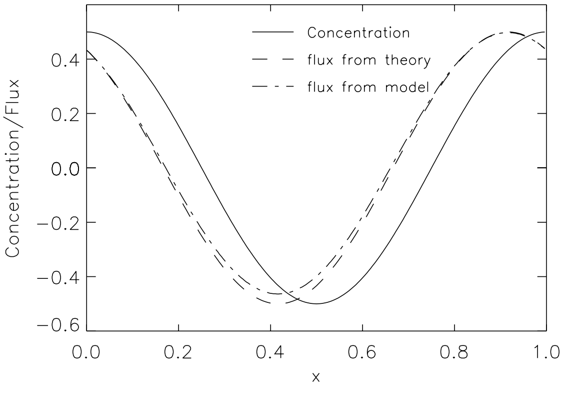

Fig. 2. Corrosion/precipitation rate for a sinusoidal concentration distribution. The concentration is scaled as $(c - c_{\min})/(c_{\max} - c_{\min})$; while the flux is scaled as $q/(\beta(c - c_{\min}))$ where $\beta = 0.730(2\pi\gamma D^2/L)^{0.333}$.

3.2. LANL materials test loop

To study the corrosion/precipitation phenomenon in LBE flow systems, a material testing loop is being constructed at the Los Alamos National Laboratory (LANL). The loop is designed to test corrosion/precipitation of various structural materials in LBE in a non-isothermal circulation system. It uses a heater, a recuperator, and a heat exchanger to set and control the temperature variations. LBE comes out of a pump at about 350°C. It is partially warmed up to 450°C when flowing through a recuperator and absorbing heat from LBE returning from the test section (hot leg of the loop). After that, a series of heaters bring the temperature to 550°C before LBE reaches the test section. In the course of returning, LBE first passes the recuperator that reduces the LBE's temperature to 450°C. A heat exchanger further reduces the temperature to 350°C. This temperature variation along the LANL material testing loop is shown in Fig. 3.

From the temperature distribution, we can calculate the species concentration at the wall along the testing loop based on Eq. (4). Fig. 4 shows such variations of Fe under various operating conditions. With proper oxygen control, the Fe concentration at the wall can be reduced several orders of magnitude. For example, by controlling the oxygen concentration at 0.01 wppm level in LBE, the highest Fe concentration is about 0.03 wppm, which is more than 100 times smaller than that without oxygen. With a further increase of the oxygen concentration to 0.1 wppm, the Fe concentration can be reduced to 0.001 wppm, which is more than 1000 times smaller than that without oxygen. It should be pointed out that oxygen concentration cannot be exactly zero in real systems, although it can be maintained below

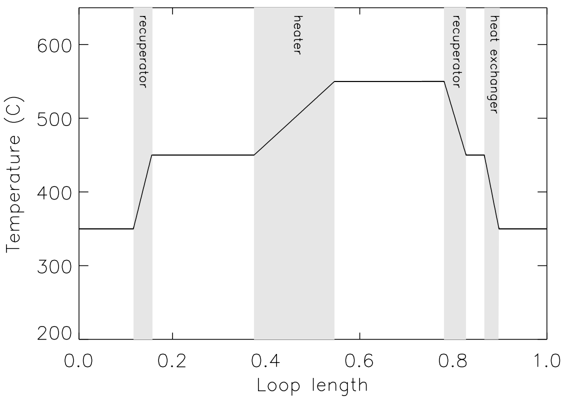

Fig. 3. Temperature distribution in the LANL material testing loop. The distance is scaled with the total loop length.

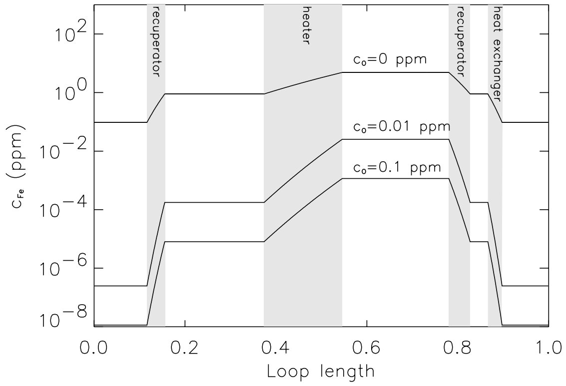

Fig. 4. Fe concentration at wall surface with different operation conditions.

10^{-4} wppm through application of a reducing cover gas (e.g., hydrogen). 'Without oxygen' or $c_O = 0$ is used here to simplify calculation.

Before proceeding to calculate the corrosion/precipitation rate, it is useful to estimate the parameter

$$\beta = 0.730\left(\frac{2\pi\gamma D^2}{L}\right)^{1/3}. \tag{16}$$

This parameter, in the unit of m/s, depends on the shear rate, γ, the loop length, L, and the diffusion rate, D. The loop is designed to run at an average flow velocity of 0.6 m/s and most of the vessels' diameter is $d = 0.05$ m. This yields a Reynolds number ($Re = Vd/v$) around 200,000, which is well within the full turbulent regime. Thus the shear rate can be calculated by

$$\gamma = \frac{\lambda\rho V^2}{2\mu}, \tag{17}$$

where the coefficient of resistance, λ, is given by [6]

$$\frac{1}{\sqrt{\lambda}} = 2.01\,\log(Re\sqrt{\lambda}) - 0.8. \tag{18}$$

For $Re = 200,000$, $\lambda = 0.0156$ and subsequently, $\gamma = 1.9 \times 10^4\ \mathrm{s}^{-1}$.

We are unaware of any direct measurements of the diffusion coefficient of iron in LBE. However, there exists an extensive body of data suggesting that it is in the range of [7]

$$1 \times 10^{-10}\ \mathrm{m^2/s} \leqslant D \leqslant 1 \times 10^{-8}\ \mathrm{m^2/s}.$$

In this study, we choose $D = 1 \times 10^{-9}\ \mathrm{m^2/s}$. Combining these data of γ and D with the loop length of 27.8 m, we obtain $\beta = 1.2 \times 10^{-5}$ m/s.

The calculated corrosion/precipitation rates in the loop are shown in Fig. 5 for different operating conditions. At very low oxygen ($c_O = 0$ for calculation), the corrosion or precipitation can reach as high as several millimeters per year. This rate is not acceptable. Active oxygen control can significantly reduce the corrosion/precipitation. With the oxygen level maintained at a level of 0.01 wppm, the maximum corrosion/precipitation rate is about 0.015 mm/yr, which is more than 100 times less than that at very low oxygen. When the oxygen level is increased to 0.1 wppm, the corrosion/precipitation rate can be further reduced to 0.0007 mm/yr. These rates appear to be consistent with the preliminary corrosion tests currently carried out by LANL and IPPE [8].

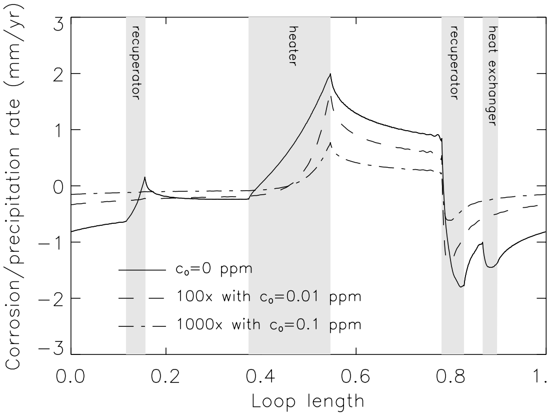

Fig. 5. Corrosion/precipitation rates in LANL material testing loop under three operating conditions.

The highest corrosion occurs at the end of the heater zone where the temperature reaches the maximum. The highest precipitation, however, does not occur at the end of heat exchanger where the temperature is the lowest. Instead, it occurs at the return end of the recuperator where the temperature is at the middle range. The reason is that the corrosion/precipitation depends more on the gradient of surface concentration rather than on the concentration itself.

The corrosion/precipitation in the testing loop can be better understood from the concentration distribution near the structural walls. Fig. 6 shows the Fe concentration distribution in the near-wall region with the oxygen level maintained at 0.1 wppm. The concentration along the wall has a considerable variation due to the

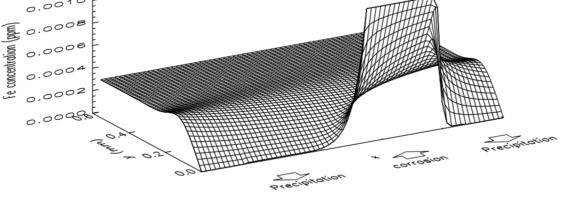

Fig. 6. Fe concentration distribution in the near-wall regions (the oxygen level is maintained at 0.1 wppm).

temperature changes. In the bulk fluid, however, the Fe concentration is quite uniform. Adjacent to the wall exists clearly a concentration boundary layer where the Fe concentration changes sharply from its wall value to the bulk value. The thickness of the concentration boundary is about 0.2 mm. Corrosion occurs when the concentration at the wall is higher than that in the bulk fluids. Precipitation occurs when the concentration at the wall is lower than that in the bulk fluids.

4. Discussion

First, if we use $\lambda = 0.184Re^{-0.2}$ to replace Eq. (18) [9], we have

$$\begin{aligned} q &= D\frac{\partial c}{\partial y} \\ &= 0.608(D/d)Re^{0.6}Sc^{1/3}(d/L)^{1/3} \\ &\quad \times \sum_k c_k k^{1/3} \exp\left(2\pi i k\xi + i\frac{\pi}{6}\right), \end{aligned} \tag{19}$$

where $Sc = \nu/D$ is the Schmidt number. This equation can be compared with the formula proposed by Epstein [7]

$$q = 0.023(D/d)Re^{0.8}Sc^{0.4}\frac{dS}{dT}\Delta T. \tag{20}$$

Epstein's equation only gives the average corrosion rate while our model gives the local corrosion/precipitation rate along the whole loop. Nevertheless, the dependence of the corrosion rate on the Reynolds number ($Re^{0.8}$ vs $Re^{0.6}$) and Schmidt number ($Sc^{0.4}$ vs $Sc^{0.33}$) is reasonably consistent for both models. Notice that Epstein's formula is based on a heat-transfer analogy, while in our analysis we solve the full convection–diffusion equation.

In terms of physical quantities, our model predicts that the corrosion/precipitation rate is proportional to $V^{0.6}$, $d^{-0.067}$ and $L^{-0.33}$. This implies that the corrosion/precipitation increases with flow velocity, decreases with the length of flow path, but depends little on the tube dimension. These predictions are consistent with the experimental observations.

One of the important assumptions in deriving the current model is that the velocity profile is linear in the concentration boundary layer. This is valid only when the thickness of the concentration boundary layer is very small. In addition, since we neglect the effect of the turbulence on the diffusion coefficient, the model is valid only when the concentration boundary layer is submerged in the laminar sub-layer of the turbulent channel flow. In the last section, we have seen that the thickness of the concentration boundary is about 0.2 mm. According to turbulence theory, the thickness of the laminar sub-layer in a smooth tube can be estimated by

$$\delta = \frac{70d}{Re}\sqrt{\frac{8}{\lambda}} \approx 0.4\ \text{mm}. \tag{21}$$

Hence, the concentration boundary layer is indeed submerged in the hydraulic boundary layer. This condition, of course, will change in more complicated geometric configurations such as elbows, gauge, etc. More sophisticated models are necessary for analyzing corrosion/precipitation in those configurations.

In case the chemical reaction (Fe and oxygen in LBE forming oxide that is insoluble) in the bulk, then the mass transport equation must be expanded to include the additional species and reaction kinetics. We will investigate this possibility in the near future.

5. Conclusions

We have developed a kinetic model for analyzing corrosion/precipitation in a non-isothermal LBE convection loop. It was found that the highest corrosion/precipitation does not necessarily occur at places with the highest/lowest temperature. In the LANL materials test loop, the highest corrosion occurs at the end of the heater zone and the highest precipitation occurs at the low temperature end of the return flow in the recuperator. The active oxygen control technique can significantly reduce the corrosion rate. The current model provides a useful tool for designing and operating LBE cooling systems.

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