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Author(s): N. Li, X. He, A. Rusanov and A. P. Demishonkov

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Corrosion Test of US Steels in Lead-Bismuth Eutectic (LBE) and Kinetic Modeling of Corrosion in LBE Systems

N. Li, X. He
MSK764, Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A.
ningli@lanl.gov

A. Rusanov and A. P. Demishonkov
Institute of Physics and Power Engineering, Obninsk, Russian Federation

Abstract

We present the LBE corrosion test results of several US steels, and a preliminary analysis using a kinetic model for corrosion in LBE systems. Tube and rod specimens of austenitic steels 316/316L, D9, ferritic/martensitic steels HT-9 and T-410 and Russian martensitic steel EP823 were inserted in an LBE loop CU-1M at IPPE. The oxygen concentration in LBE was between $3\text{-}5\times10^{-6}$ wt% and the flow velocity in the test sections was 1.9 m/s. The tests were performed simultaneously at 460 and 550°C for 1000, 2000 and 3000 hours. We performed weight, optical, SEM and X-ray analysis of the specimen, obtaining results on oxide film thickness, corrosion depth, microstructure and composition changes. Protective oxide films formed on the surfaces of all steels. The oxides on austenitic steels are thin compared to the oxides on ferritic/martensitic steels, which have pronounced double layer structure. T-410 specimens suffered local corrosion.

Parallel to the experimental investigations, we developed a kinetic model for corrosion in oxygen controlled LBE systems. Our model incorporates the species distribution based on local thermodynamic equilibrium at the surface of structural materials into boundary conditions, and directly calculates mass transport through boundary layer diffusion and convection in the bulk flow. The model predicts drastic reduction of corrosion when oxygen in LBE is properly controlled. It also predicts complex profiles of corrosion and precipitation in flow loops that are dependent upon global conditions. This indicates that the straightforward test results may have limited applicable range if the configuration and conditions of the entire test loop are not carefully taken into account.

Introduction

Material compatibility and corrosion in lead-bismuth eutectic (LBE) systems present a critical challenge for using LBE as nuclear coolant and high-power spallation neutron target. There exists extensive Russian experience in its development of LBE coolant technology for nuclear submarine reactors, and extensive development and testing of special alloys and active control of oxygen activity in LBE to reduce corrosion and coolant contamination. There is scarcely any test data available for US materials in oxygen-controlled LBE systems.

From 1999 to 2000, the Accelerator-driven Transmutation of Waste (ATW) Program at Los Alamos National Laboratory and US DOE sponsored a corrosion test of several US steels in an oxygen-controlled LBE flow loop at the Institute of Physics and Power Engineering (IPPE) at Obninsk, Russia[1]. We present the test results from this experiment. The results are also consistent with other investigations**[4]**[**5**].

The process of the formation of a protective "self-healing" oxide film on the steel surface in oxygen controlled LBE can be roughly described as follows. Due to the higher chemical affinity of the steel alloying components (*Fe*, *Ni*, *Cr*) to oxygen than lead and bismuth, oxygen in LBE will "passivate" the steel surface with formation of an oxide film. The film will get thicker as oxygen and metallic elements diffuse across the oxide and continue to react. This oxide film is protective. Once a continuous film is formed, however, another process takes place in competition to the oxidation process. At the interface between the oxide and LBE, the oxide interact with LBE and the corrosion products, either reducing the oxide film, or receiving precipitation from LBE. At the high temperature parts of an LBE system, reduction of the oxide will occur and the film is "self-healing" in that it continues to grow into the substrate.

We developed a kinetic model of the corrosion process in LBE systems with oxygen control[2]. Our kinetic modeling attempted to incorporate chemical and mass transport kinetics near the surface of structural materials, with the hydrodynamic flow that transports oxygen and corrosion products in a simple loop to study the system corrosion effect. Key findings and some future development will be discussed here.

The model, with a few reasonable assumption and well-defined simplifications, and only one estimated transport property, predicts drastically reduced corrosion rates consistent with the test results.

It is, however, illustrated in the model that corrosion in LBE systems depends globally on temperature and flow distributions, not merely local temperature and flow conditions. For instance, in the IPPE test loop where specimens were tested at 460 and 550°C, there are indications that the long-term corrosion behaviors may differ qualitatively. At 550°C, which is near the highest temperature in the loop, net loss of materials begins after 2,000 hours - the initial stage of building up the protective oxide layer. At 460°C, which is an intermediate temperature of the loop, the initial oxidation stage may not have completed after 3,000 hours due to the slowing of kinetics at lower temperatures. From the modeling of a simplified loop this test section may have been a neutral or even a precipitation site, further complicating the interpretation of the test results. This 460°C corrosion test result may not be applicable to another system (e.g. a test target) in which 460°C is the highest temperature.

Corrosion Test

We conducted corrosion tests for several US steels (316 (tube), 316L (rod), T-410 (rod), HT-9 (tube), and D-9 (tube)) in an oxygen controlled LBE environment. The Russian steel EP823 (rod) was included for comparison. The compositions of the steels are listed in Table 1.

These samples were inserted into IPPE's CU-1M non-isothermal loop at 460˚C and 550˚C. The oxygen level in LBE is controlled at 0.03 - 0.05 wppm. The velocity in the test section is around 1.9 m/s, typical of coolant flow in LBE-cooled reactor cores. Other details about the experimental setup can be found in the report[1].

The 316/316L steel specimens are made of standard tube (5/16"O.D. x 1/25") and rod (5/16") supplies that are dual certified for low carbon content. T-410 specimens are also made of standard rod (5/16") supply. D-9 (0.230" O.D. x 0.200" I.D.) and HT-9 (0.230" O.D. x 0.194" I.D.) specimens are cut from EBR-II driver fuel cladding stock from Argonne National Laboratory[3]. All specimens were put into the test loop without additional surface preparation.

The LBE in CU-1M has the initial composition of (wt%) 43.45 *Pb* - 56.5 *Bi* - < 3.2×10^{-3} *Ni* - < 1×10^{-3} *Fe* - < 3×10^{-4} *Cr* - < 3×10^{-4} *Al* - < 1×10^{-5} *Mn* - 1×10^{-3} *Ag*.

Steel	C	Si	Ni	Mn	Cr	Mo	other
316/316L	0.02	1	10-14	2	16-18	2	-
D-9	0.04	0.85	13.6	2.1	13.6	1.67	0.30Ti
T-410	-	1	0.34	1.0	12.5	-	-
HT-9	0.22	0.30	0.59	0.58	12.0	1.11	0.50W
EP823	0.18	1.21	0.72	0.59	10.97	0.73	0.64W, 0.33V, 0.1Ce, 0.34Nb

Table 1. Composition of the steels used in the corrosion test (wt%).

The CU-1M is a non-isothermal forced-circulation loop with 60L of LBE and flow capacity of 5 m^3/h. It has two test sections at 550°C and 460°C, with the nominal highest and lower temperature at 600 and 300°C (Figure 1). The oxygen content in the loop is monitored and maintained throughout the experiment.

After 1000 hours of testing, half of the test specimens were extracted and replaced with fresh specimens. Then testing continued for another 2000 hours. Therefore we have three sets of specimens for1000, 2000 and 3000 hours at two different temperatures.

After the testing, specimens were extracted and residual LBE cleaned. We performed weight analysis, optical microscopy, SEM and X-ray analysis (energy dispersive X-ray analysis (EDX) and X-ray diffraction for compound characterization). Some of the results are summarized in the next section. A more complete report will be published later.

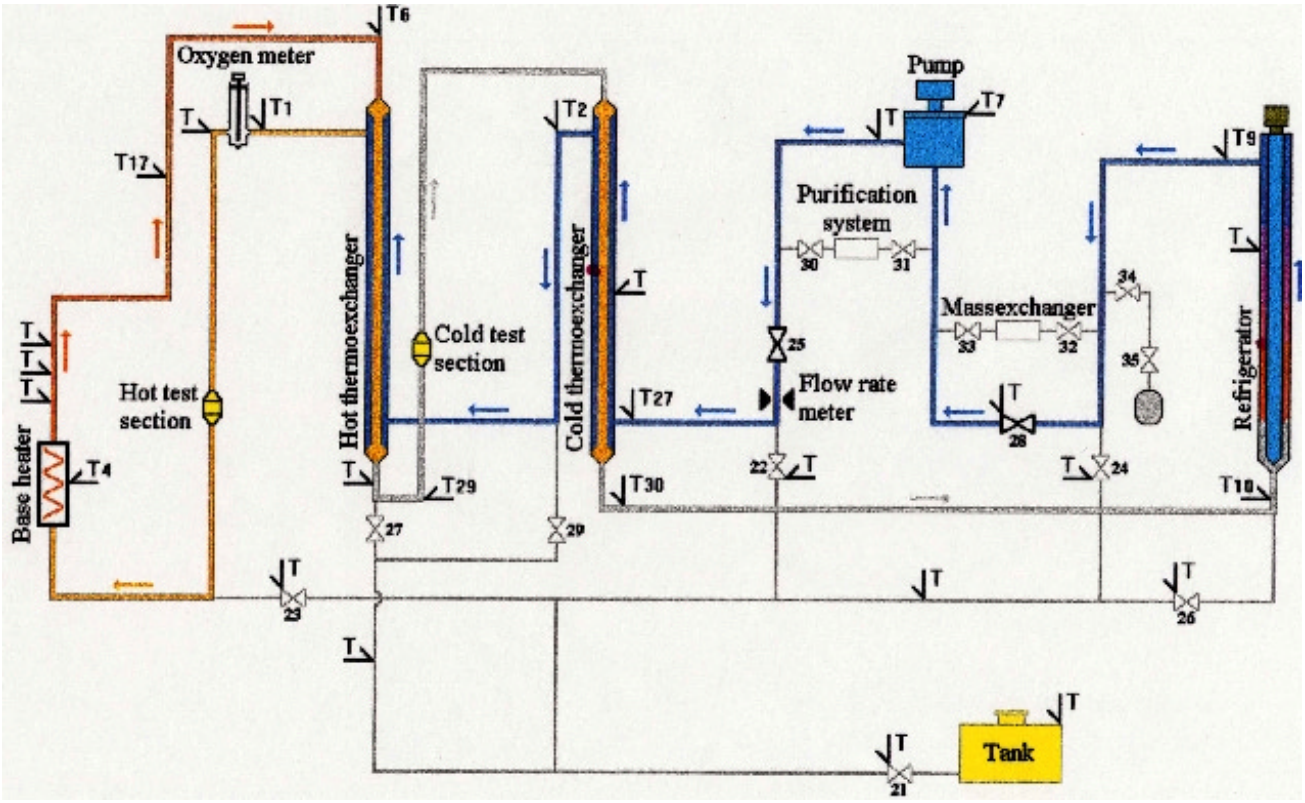


Figure 1. Principal scheme of CU-1M loop.

Corrosion Performance

In all cases, specimens were subject to oxidation to different extent. The oxide film thickness varies considerably on the same test specimens, and increases in time. In thicker oxide films, double layer structure is clearly seen, which can be roughly described as a porous Fe_3O_4 outer layer over a chrome-rich inner layer. No corrosion damage typical for “liquid metal” corrosion was found in the 316/316L, D9, HT-9 tube specimens, while local corrosion, mostly in the form of “slot”, was found on 316/316L and T-410 rod specimens.

Since T-410 suffered rather severe local liquid metal corrosion[1], the data on T-410 is usually excluded. 316/316L rod specimens showed much less severe local liquid metal corrosion so that the test data still appears meaningful. The micro-hardness in the areas of corrosion damage in both steels is significantly lower than that of the bulk. It should be noted that both T-410 and 316L rod specimens were cut directly from rod supply without surface treatment. Further study of the possible contributions from micro-inclusions and other variations is needed to determine the exact cause.

Weight Changes

The weight changes of the steel samples after their corrosion tests provide direct information about the gross corrosion effect. Figure 2 shows the specific weight changes over time for all steel samples tested at 460 and 550°C. Although the data points are scattered, we can draw some qualitative information from the results.

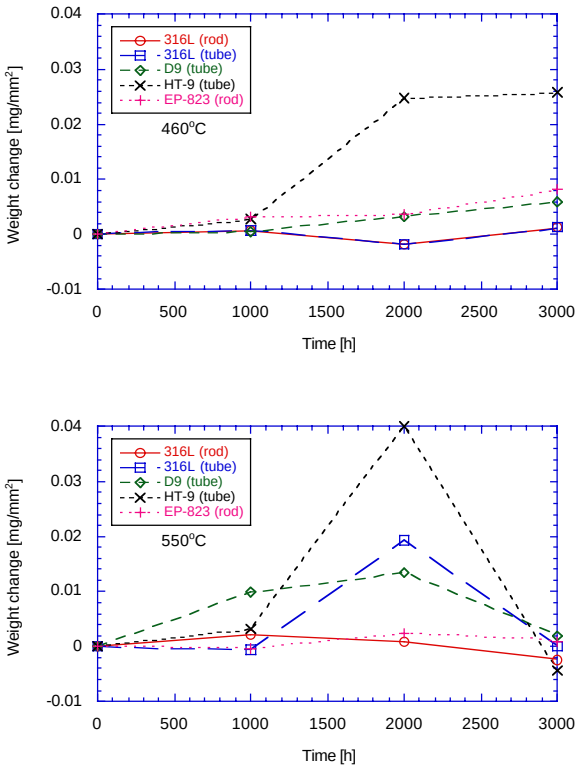


Figure 2. Specific weight changes of the steels tested in an LBE loop.

First, the characteristics of the overall weight change in the first 2,000 h testing period is different from that in the testing period after 2,000 h at 550°C. This difference indicates that there is an initial stage of oxidization that lasts about 2,000 hours. In this stage, an oxide film forms on the sample surface and the bound oxygen contributes to the increase in sample weights. This initial oxidization reaches a turning point around 2,000 h. After that, the weight change turns downward when the oxide layer becomes thick enough to balance the transport of oxygen into the substrate with the gradual reduction of oxide layer from the surface (which is ongoing all the time after the formation of the oxide film). In the meantime, the oxidization continues into the substrate steel and the oxide layer is "self-healing". At 460°C, the initial oxidation stage may not have completed in 3,000 h due to the much slower kinetics.

Secondly, the nature of the weight change at 460˚C may be even different from that at 550˚C in this loop, especially beyond the initial oxidization stage. According to our corrosion model of a simple loop, the 460˚C section may be a neutral or even a precipitation site in this loop. *Fe* as corrosion product carried over from hot upstream may precipitate and form new oxide on the sample surface here.

Thickness of oxide films

We measured the oxide film thickness on the steel samples. Figure 3 shows the oxide films thickness at three corrosion test intervals, at 460 and 550˚C.

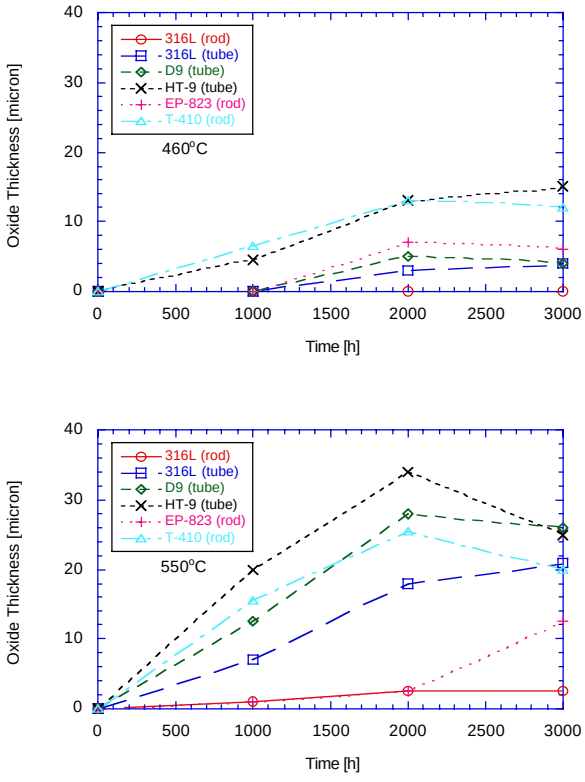


Figure 3. Measured average oxide film thickness.

We observe the initial oxidation stage and the beginning of perhaps the asymptotic oxide film "self-healing" process. Overall, the oxide films are thicker at 550˚C than at 460˚C but all of them are thinner than 40

microns. There is substantial variation among different steel samples. Since the formation of the oxide film is key to controlling LBE corrosion, future study is needed to identify all contributing factors and how they affect the oxide film formation and regeneration mechanisms.

Combined with the weight change data, it is evident that HT-9 (and T-410) suffers more oxidation than the other steels. The Russian alloy EP823 appears to have very good performance at both temperatures. While 316/316L steels showed different performance depending on whether they are in rod or tube form - they have different surface conditions, with rod form specimens having microscopically smoother surfaces. At 550°C, D9 also appears to be susceptible to high level of oxidation, suggesting possible effects from surface treatment since D9 tubes and HT-9 tubes were prepared very similarly.

Corrosion depth

An important index for corrosion is the corrosion depth, *i.e.* the loss of original substrate materials. We can calculate it by combining the weight change and oxide film thickness data. This is done by comparing the initial weight of a specimen

$$W_0 = \pi(d_o^2 - d_i^2)L\rho_{steel}/4,$$

with the final specimen weight

$$W_1 = \pi(\bar{d}_o^2 - d_i^2)L\rho_{steel}/4 + \pi\bar{d}_o hL\rho_{oxide},$$

where d_o and d_i are the initial outer and inner diameters of a coupon, L is the coupon length, and ρ_{steel} is the density of steels, h is the thickness of the oxide film, $\bar{d}_o$ is the final outer diameter of the coupon, and ρ_{oxide} is the density of oxide Fe_3O_4 (the main oxide component).

The weight change equals:

$$\Delta W = W_1 - W_0$$
$$= \pi(\bar{d}_o + d_o)(\bar{d}_o - d_o)L\rho_{steel}/4 + \pi h\bar{d}_o L\rho_{oxide}$$

From the weight change and oxide thickness, we can calculate the corrosion depth:

$$\delta = \frac{\bar{d}_o - d_o}{2} = \frac{\rho_{oxide}}{\rho_{steel}}h - \frac{d_o^2 - d_i^2}{4d_o}\frac{\Delta W}{W_0}.$$

Figure 4 shows the average corrosion depth versus time for different steels at both 460 and 550˚C.

It thus appears that, except for T-410 and perhaps 316L rod with surface imperfections leading to local corrosion, 316L, D9 and HT-9 steels are suitable for short to medium term applications in LBE systems for up to 550°C. In comparison, Russian steel EP823, although similar to HT-9 in composition other than the addition of *Si*, has much improved corrosion resistance. The role of *Si* should be investigated further.

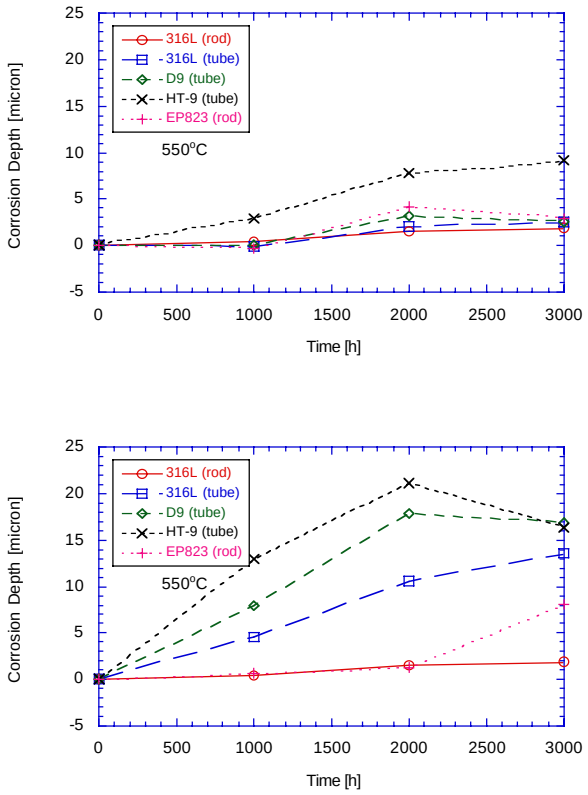


Figure 4. Estimated average corrosion depth.

Most differences between the test results at the two temperatures may be attributed to temperature dependent kinetics. It is unfortunate that the tests were not long enough to reveal much after the initial oxidation stage. Thus we can not conclude from these tests the long-term corrosion rates of the steels. However, our kinetic modeling of the corrosion/precipitation process reveals another aspect that limits the applicability of the test results.

Kinetic Modeling of Corrosion

We derived a kinetic model for the corrosion and precipitation rates in an oxygen-controlled LBE loop[2]. 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 interpreting the corrosion test result and for helping design and operate LBE cooled systems.

Our model incorporates the species distribution based on local thermodynamic equilibrium at the surface of structural materials into boundary conditions, and directly calculates mass transport through boundary layer diffusion and convection in the bulk flow.

We assumed that the mass transport through a boundary layer is by diffusion only, while in the bulk of the flow turbulent mixing and convection ensure uniform oxygen concentration along the loop. To simplify the model we neglected any chemical reactions in the bulk of the flow. With this assumption, the corrosion products in the form of reduced metallic elements (*Fe*, *Cr* and *Ni*) in LBE do not oxidize, although enhancing the condition for this to happen can facilitate the removal of the corrosion products via filters.

To summarize the prediction of our kinetic modeling, the following two features are important. First, the corrosion and precipitation rates depend on global flow and temperature distribution in an LBE loop, not just the local conditions. Second, precipitation takes place shortly after the temperature in the flow direction begins to decrease, and maximum precipitation may occur long before the flow reaches the minimum temperature.

To illustrate these conclusions, we use the example of a simple flow test loop that has a constant cross section.

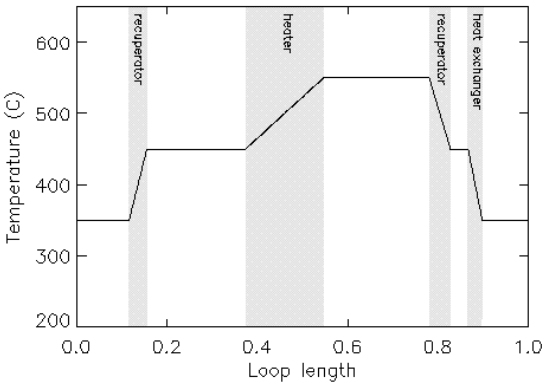


Figure 5. Temperature profile of a simple LBE flow loop.

The temperature profile of this loop is shown in Figure 5. The flow starts from the lowest temperature, gets heated in a counterflow recuperator and the main heater. It then gets cooled in the return path of the recuperator and the main heat exchanger. The loop has four sections of constant temperatures. CU-1M loop at IPPE is conceptually similar to this configuration.

In this kinetic model the surface concentration of *Fe* (the main corrosion element under consideration) is determined by the oxygen concentration in the LBE, or at saturation if there is no oxygen (or very low concentration in practice). Our model predicts the corrosion and precipitation rate shown in Figure 6 with only one parameter estimated from literature – the mass diffusion coefficient of *Fe* through LBE (1×10^{-9} m^2/s).

In terms of physical quantities, our model predicts that the corrosion/precipitation rate is proportional to $V^{0.6}$, $d^{-0.067}$ and $L^{-0.33}$ (V is the bulk turbulent flow velocity, d is the diameter of the pipe, and L is the length of the loop). This implies that the local rate of corrosion and precipitation increases with flow velocity and decreases with the length of flow path, but depends little on the cross section dimension.

It is evident that the corrosion and precipitation rates are drastically reduced with increasing levels of oxygen in LBE (before saturation). At the 0.01 wppm level and flow of 0.6 m/s, the peak corrosion rate is approximately 0.015mm/yr. Adjusted to the velocity of 1.9m/s with the $V^{0.6}$ scaling, the rate would be about 30 micron per year at 550°C. This is consistent with the experimental results.

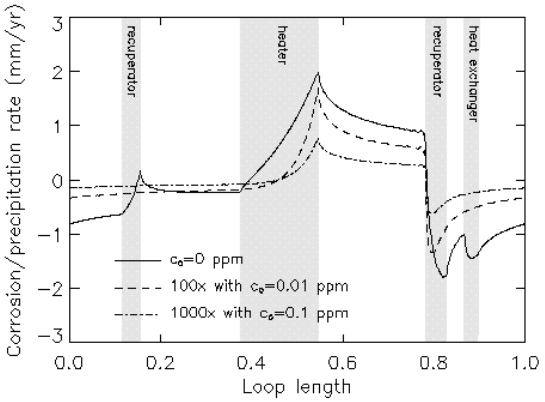


Figure 6. Predicted corrosion and precipitation rates with different levels of oxygen concentrations in a simple LBE flow loop.

It is also demonstrated that precipitation takes place shortly after the temperature begins to decrease in the flow direction. This is very important for properly interpreting the test results at 460°C in CU-1M: that test section could be a neutral or precipitation site. Materials

being tested in that section could have weight increases as corrosion products from upstream precipitate from the LBE flow and deposit onto the surfaces.

This implies that the corrosion test results obtained from a flow loop can not be directly applied to other systems in which the temperature profiles are different. The initial oxidation rates, however, may be applicable if it is significantly higher that the rate of losing oxide by reduction at the surface.

There is also some degree of variation in corrosion and precipitation rates in sections of constant flow velocity and temperature. More importantly, the peak precipitation may occur long before the flow reaches the coldest section, making it more challenging to implement cold traps.

In future studies, the model should incorporate the chemical kinetics of reactions of corrosion products and oxygen in the bulk of the flow. It should be validated with a set of experiments in test loops where corrosion and precipitation behaviors are examined in several locations, rather than relying on the test coupons in one or two test sections. At 550^{o}C, the test should last longer than 3000 hours. Better understanding of the system corrosion and precipitation mechanisms will lead us to more complete and efficient test programs, and more accurate interpretation of the valuable but costly test results.

Conclusion

The corrosion tests of several US steels revealed the differences in corrosion resistance due to differences in compositions, surface conditions and secondary treatment. The kinetic modeling of corrosion cautions us to use the corrosion test results carefully when their applicability limits can be determined. Interpreting the test results within the framework of the model, we suggest that the corrosion test need to exceed 3000 hours, preferably to above 6000 hours, for temperatures below 550^{o}C. The model also suggests that testing in one test loop do not necessarily predict corrosion performance in systems with different temperature profiles. The model illustrates the drastic reduction of corrosion and precipitation in oxygen-controlled the LBE systems, consistent with the test results.

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