

### *Background*

Since 1995, OLI has been developing corrosion simulation technology to address the needs of the chemical process industry. This effort has resulted in the development of the Corrosion Analyzer, a unique, comprehensive software tool to study the effects of various chemical environments on both general and localized corrosion of engineering alloys. This work has been made possible by the support of the members of the CSP I – IV consortia as well as the funding provided by the U.S. Departments of Energy and Commerce (through the Advanced Technology Program).

In parallel with the development of corrosion simulation technology, OLI has been developing the Mixed-Solvent Electrolyte (MSE) model, a universal framework for predicting the thermophysical properties of electrolyte systems without limitations with respect to concentrations. At this stage of development, we are in a position to make a quantum leap by combining these two technologies to create a mixed-solvent corrosion model. However, this is not merely a matter of combining two software modules. More importantly, we will need to address new physical phenomena to create an MSE corrosion model that reflects the complexity of electrochemical behavior in systems that may or may not be dominated by water.

We are proposing to seize this exciting opportunity by continuing the CSP Consortium in a Phase V. The consortium will provide support and steer the development of the MSE corrosion simulation technology.

This document outlines the work that will need to be performed to ensure the successful completion of this project, which will be pursued within the framework of Phase V. This work will be discussed in the context of the technology that has been already developed. Also, this proposal outlines the proposed business terms of the consortium. Your participation in Phase V of the Consortium will make it possible to create the MSE corrosion model in a way that addresses the needs of the participating companies.

### **Objectives**

In Phase V of the CSP Consortium, we are proposing to develop a model for general and localized corrosion for mixed-solvent electrolyte systems. This model is intended to achieve the same range of applicability as the MSE thermodynamic model, i.e.,

- (a) With respect to electrolyte concentration, it will be applicable for systems ranging from infinite dilution to the limit of pure solutes or fused salts or solid-liquid saturation, whichever applies
- (b) With respect to chemistry, it will be designed to work for any combinations of electrolytes and nonelectrolytes

- (c) With respect to temperature, it will work up to 0.9 times the critical temperature of the mixture. For most dilute and moderately concentrated aqueous systems, this translates into approximately 300 °C although recent research indicates that the upper temperature limit can be significantly extended closer to the critical point for some systems
- (d) With respect to metallurgy, the model will encompass the same alloys that are currently supported by the aqueous corrosion model. Also, selected alloys may be added to the databank to meet the needs of the consortium members.

## Technical challenges

### *Integration with the MSE thermophysical models*

The existing OLI corrosion models rely on the thermodynamic speciation calculations obtained from the aqueous model. Also, they utilize the aqueous model transport properties to predict the mass transport effects. The MSE corrosion model will be integrated with the MSE thermodynamic and transport property models, which already cover the range of applicability that is envisaged for the MSE corrosion model.

The MSE thermodynamic model will immediately provide information on the activities of aggressive species and stability of corrosion products. However, the development of the MSE corrosion model goes well beyond the integration of the MSE thermodynamic model with electrochemical models. It also requires a complete reformulation of several aspects of the electrochemical models. This primarily includes the treatment of passivity in nonaqueous and mixed-solvent systems, the formation of salt films, and the effect of solvent composition on cathodic and anodic reactions.

### *Modeling passivity*

The current aqueous corrosion model assumes a water-dominated medium. Therefore, passivity is modeled on the assumption that water is always available to react with the underlying metal to form an oxide/hydroxide layer. The model further considers the interactions of various solution species with the oxide/hydroxide layer but the fundamental structure of the layer is assumed to remain unchanged. While this is a reasonable assumption for water-dominated systems, it breaks down in non-aqueous or water-depleted environments. In such environments, a passive film may not exist in the absence of oxygen donors such as water. Therefore, in a general case, the reactions between the metal and oxygen donors that lead to passivity need to be modeled explicitly rather than being implicitly assumed as in the aqueous corrosion model. This requires a complete reformulation of the passivity model.

The problem of stability of passive films as a function of the availability of oxygen donors is ubiquitous in systems dominated by organic components in the chemical process industry. Typically, corrosion rates in water – organic mixtures drop as the water content decreases and the organic component's content increases. This is usually due to a decrease in the activity of electrochemically active ions that participate in corrosion reactions. However, corrosion rates may then strongly increase as the non-aqueous limit is

approached, especially in the presence of oxidizing species. This is due to the loss of passivity in the absence of a sufficient supply of oxygen donors. When combined with the presence of oxidizing agents, a metal without a stable passive layer may show high corrosion rates. The MSE corrosion model will be designed to model such phenomena in addition to modeling passivity in aqueous solutions.

### ***Modeling salt film formation***

Formation of salt films as a result of anodic dissolution or other phenomena is a ubiquitous phenomenon that strongly affects corrosion behavior. The formation of such films may or may not lead to passivity and is frequently dependent on factors such as solubility of corrosion products and hydrodynamic conditions that influence their dissolution. The current aqueous corrosion model includes the effects of selected sparingly soluble solids such as carbonates and sulfides. However, corrosion in concentrated solutions frequently leads to the formation of salts and other corrosion products that are not sparingly soluble but still influence the corrosion behavior.

A classical example of such behavior is provided by corrosion of steels in concentrated sulfuric acid. Corrosion rate in sulfuric acid initially increases rapidly with acid concentration, reaches a maximum at intermediate concentrations and rapidly decreases due to salt film formation. In the concentrated solution range, the corrosion rate has been observed to parallel the solubility of ferrous sulfate, including maxima that are due to transitions between the hydrated and anhydrous solid ferrous sulfate phases. The rates of dissolution mediated by the presence of sulfate films strongly depend on hydrodynamic conditions due to mass transfer effects. It is expected that the MSE corrosion model will be able to provide a quantitative representation of such phenomena.

### ***Effects of solvent on electrochemical reactions***

The partial cathodic and anodic processes that are simulated in the aqueous corrosion model depend on the activities of electrochemically active solutions species. The thermodynamic aspects of the effect of solvents on electrochemical reactions (i.e., the dependence of the activities of species on the system composition) will be handled by the thermodynamic model. However, in many cases, additional specific effects may be introduced by a different solvent environment. Such effects may include the electrochemical effects of solvated species or ion pairs that can be found in nonaqueous or water-depleted or simply concentrated aqueous electrolyte environments.

Also, the repassivation potential model will be reformulated to take into account the effect of other solvent species on the transition between active corrosion within a localized environment and the formation of an oxide layer. The model already accounts for the effect of water on the formation of oxide and will be extended to account for other possible solvents.

### ***Typical corrosive environments***

The MSE corrosion model will make it possible to simulate the general and localized corrosion behavior of metals in various environments that cannot be studied using the aqueous corrosion model. Such environments include:

- (1) **Concentrated acids** (e.g., sulfuric acid/oleum) as well as more dilute acids. It can be expected that the model will be able to account for the strong changes in corrosivity due to the changes of acid speciation with composition and the formation of surface layers.
- (2) **Systems related to gas processing.** Here, the model is expected to be applicable to systems containing amines and alkanolamines.
- (3) **Systems related to CO<sub>2</sub> capture and sequestration.** Recently, there has been great interest in materials performance in CO<sub>2</sub>-dominated systems that are related to processes for reducing global warming. In such systems, small amounts of dissolved water and various ionic and non-ionic solutes control the corrosion behavior. The model will be able to simulate electrochemistry in CO<sub>2</sub>-dominated environments.
- (4) **Organic and mixed organic – water systems.** Such environments provide classical applications for mixed-solvent electrolyte models and are frequently encountered in the chemical industry. The organics include here organic acids, alcohols, esters, phenols, polyacids and many other components. The behavior of such systems strongly depends on the protic character of the solvent and on the availability of oxygen donors to maintain passivity as briefly outlined above.
- (5) **Various systems related to oil and gas processing.** Such systems may involve hydrogen fluoride (e.g., in alkylation processes), amines and amine hydrochlorides (in refinery overhead systems), glycols and methanol in conjunction with acid gases and ionic components (e.g., in natural gas processing), etc.

The above list is tentative and may be revised to reflect the actual needs of the consortium members.

### **Deployment in Software**

The primary vehicle for the deployment of the technology outlined above will be OLI's Corrosion Analyzer software. The Corrosion Analyzer will be continually updated as progress is made in the development of the model. The latest versions of the Corrosion Analyzer will be immediately made available to the consortium members so that feedback can be timely provided to the researchers and software developers.

OLI's corrosion simulation technology is also available via Honeywell's UniSim Design platform. The MSE corrosion model will also become available through this platform, typically with a certain delay with respect to the Corrosion Analyzer due to UniSim's different development lifecycle.