

# Performance of Tightly Coupled Linux Cluster Simulation using PETSc of Reaction and Transport Processes During Corrosion Pit Initiation

Eric Webb<sup>a</sup>, Jay Alameda<sup>b</sup>, William Gropp<sup>c</sup>, Joshua Gray<sup>a</sup>, and Richard Alkire<sup>a\*</sup>

<sup>a</sup> *Department of Chemical Engineering, University of Illinois at Urbana-Champaign, USA*

<sup>b</sup> *National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign, USA*

<sup>c</sup> *Mathematics and Computer Science Division, Argonne National Laboratory, USA*

## Abstract

The most dangerous forms of corrosion occur unexpectedly and often out of sight of ordinary inspection methods. Therefore, remote monitoring is increasingly installed on bridges, tunnels, waste repositories, pipelines and marine structures, for example. Predicting material failure based on field data, however, depends upon accurate understanding of corrosion processes, which involve phenomena that span more than ten orders of magnitude in time and distance scales. Consequently, the situation represents an extreme challenge.

In this work, we consider a seminal moment: the initiation of a small corrosion pit that possesses the ability to grow into a larger pit, and then to form crevices and cracks that may cause catastrophic failure. Improved understanding of mechanisms of pit initiation is needed. Direct laboratory measurement of local events during pit initiation is surprisingly difficult. The complexity of the system creates a situation where experiments seldom can be compared directly with

simulation results, not to mention with each other. Multiple scientific hypotheses therefore emerge. Simulations that accurately emulate experimental observations are essential in order to reduce the number of experiments needed to verify scientific understanding of the system, as well as to design corrosion monitoring technology. The role of sulfur-rich inclusions on pit initiation on a surface of stainless steel was simulated numerically as well as investigated experimentally. Mechanistic hypotheses suggested by the experimental data were simulated in numerical models in order to test their validity

In this work, we describe our experience in solving the mass balance and species transport relationships for an electrically neutral solution, in the form of a system of coupled, non-linear partial differential and algebraic equations. This system was solved numerically with the use of a finite difference method with second-order centered finite differences in two dimensions being used to transform the partial differential equations into a system of non-linear algebraic equations, and second-order forward- and backward-difference approximations were used on the boundaries. A fully implicit scheme was implemented to step forward in time. To solve the resulting system of equations, we used the Portable, Extensible Toolkit for Scientific Computation (PETSc), which provided a robust parallel computing architecture, numerical software libraries and data structures, and sparse matrix storage techniques. In particular, we describe our experience in moving our PETSc-based code from the NCSA Origin Array to the emerging linux cluster architecture, and the resulting code and solver performance that resulted from our work on the linux cluster.

Through this work, we will show that the dual strategies of taking strategic advantage of object oriented nature of C<sup>++</sup> to create chemistry and geometry classes, which simplified the task of testing hypotheses, as well as employing PETSc as our solver, allowed a straightforward transition to the linux cluster architecture, while enjoying good code performance to allow simulation of complex electrochemical phenomena. This approach provides an excellent starting point to more detailed computational investigations of electrochemical phenomena in the future.

## 1 Introduction

The initiation of pitting corrosion of metal involves numerous events that occur simultaneously over a wide range of length and time scales. In this paper, we report on the case of pit initiation on Type 304 stainless steel, which is arguably the most important corrosion resistant alloy in use today. In this system, the spontaneous dissolution of small sulfide inclusions that are present on the surface of the metal leads to a unique micro-environment that somehow triggers the corrosion process. As the dissolved species build up in the vicinity of the inclusion, they undergo rapid chemical equilibration through homogeneous reactions in the volume, and also participate in surface reactions simultaneously.

Direct experimental measurement of many features of local behavior during pit initiation can be difficult to impossible to perform. In certain windows of opportunity, however, sophisticated experimental procedures have recently emerged for investigating phenomena at very small length scales as well as very fast time scales. Nevertheless, there often remain key uncertainties in understanding behavior of the overall system. As a consequence, a variety of hypotheses of mechanism have been put forth in order to fill in missing details associated with pit initiation in stainless steels as well as many other alloys. Most such hypotheses involve a large number of chemical reactions and equilibria among a large of number of species that move to and from the reacting surface by transient diffusion, migration and convective transport processes.<sup>1 2 3, 4, 5, 6, 7, 8, 9, 10</sup> The situation is therefore complex from a modeling point of view, with the result that most models are relatively simple conceptual models and not rigorous treatments.

The level of expertise required to carry out sophisticated experiments is in some respects comparable to the high level of skill required to create rigorous numerical simulations. Most experimentalists are not experts in writing code, and vice versa. As a consequence, a communication gap is growing between the communities of experts who perform experimental measurements and the experts who write numerical codes. What is needed is for code to be written in a manner that allows experimentalists to test more than one hypothesis of mechanism. Once a model has been successfully tested and verified, then estimation of important engineering design parameters, such as the ‘pitting potential’ and ‘induction time’, can be carried out with increased confidence.

In the future, the placement of codes in a location such as the Alliance Science Portal, will offer a collaborative environment where experimentalists can easily access code and test hypotheses, and where computational scientists can continually to improve the base codes. The development of efficient collaborative tools represents a major enhancement for simulation of corrosion processes.

## **2 Goal and Strategic Approach**

The goal of the development of the electrochemical transport and reaction model using PETSc is two fold. First, the model represents the first model to investigate the local phenomena occurring during the initiation of pitting corrosion at sulfide inclusions in stainless steel. The model includes both the chemistry due to sulfide inclusion dissolution as well as the chemistry due to stainless steel dissolution. Second, the code was developed to take advantage the PETSc numerical library to provide scalable parallel equation solvers, and was written in an object-oriented manner in that the hypothesis of mechanism is essentially placed outside the code such that it can be modified by an experimentalist who does not have complete knowledge of the source code.

A mathematical model represents a working hypothesis that can be compared with experimental data, improved as new knowledge is gained, and used to predict behavior where direct experiments may be difficult or impossible. The complexity of the computational aspects associated with initiation of pitting corrosion can be daunting. In the present work, we introduce an object-oriented computational approach in order to simplify the task of testing multiple hypotheses involving different chemical species and system parameters. In this approach, each entity in the model is created as an object, and the objects are placed outside of the solution to the model equations. In this manner, the objects can be easily modified and/or transferred to other solution algorithms. With use of the object-oriented approach, the sequence of reactions, the species, the parameters of the composition and geometry of the system all represents objects that can be altered without additional code modifications. In addition, the computational approach takes advantage of PETSc and its robust parallel computing architecture, numerical software libraries and data structures, as well as sparse matrix storage techniques. These enhancements significantly reduce real computation time and, in addition, make it easier for other corrosion scientists to use the model to test other hypothesis of mechanism than the one selected for investigation and demonstration in this work.

### 3 Technical Approach

In the present paper, a mathematical model of single sulfide inclusion was developed to test the hypothesis of mechanism of the dissolution of the sulfide inclusion, as well as to test the criteria that pit initiation occurs when critical concentration of thiosulfate and chloride ions build up during dissolution. The model was used to calculate the critical potential for the initiation of pitting corrosion at a single sulfide inclusion, and the numerical results were compared to experimental results. Modeling of the sulfide inclusion system provides a means for testing various hypothesis of mechanism for the initiation of pitting corrosion of stainless steel.

#### 3.1 Model Equations

A material balance for each chemical component,  $i$ , is given by

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + R_i \quad (1)$$

where the flux is

$$N_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i \quad (2)$$

and mobility,  $u_i$ , was estimated by the Nernst-Einstein equation.

$$D_i = RTu_i \quad (3)$$

The homogeneous chemical reactions terms,  $R_i$ , in Eq. 1 are eliminated by adding or subtracting the appropriate individual species balances. The equations for reaction equilibrium, as shown in Eq. 23, provide additional relationships for the concentrations of the chemical species.

$$\frac{c_i^\alpha c_j^\beta}{c_k^\delta} = K_{eq} \quad (4)$$

Elimination of the homogeneous reaction terms,  $R_i$ , in Eq. 1, resulted in the formation of elemental balances, which are the sum of the material balance equation of each species,  $i$ , containing the base species,  $k$ .

$$\sum_k \left( \frac{\partial c_i}{\partial t} \right)_k = \sum_k \left( -s_i^k \nabla \cdot N_i \right)_k \quad (5)$$

The set of equations was completed with the assumption that the solution was electrically neutral.

### 3.2 Boundary Conditions

Figure 1 shows the computational domain used in the model of single sulfide inclusions. Referring to line AH in Fig. 1, the concentrations of all species were ascribed their bulk values, and zero potential with respect to the reference electrode was specified.

$$\begin{aligned} c_i &= c_i^\infty \\ \Phi &= 0 \end{aligned} \quad (6)$$

On the insulating surface, GH, the normal fluxes of all species were zero, and electroneutrality was satisfied.

$$\begin{aligned} \underline{n} \cdot \underline{N}_i &= 0 \\ \sum_i z_i c_i &= 0 \end{aligned} \quad (7)$$

At the electrode surfaces, BG, the fluxes of the non-reactive ions were equal to zero.

$$\underline{n} \cdot \underline{N}_i = 0 \quad (8)$$

For the species reacting at the MnS inclusion surfaces, lines BC and CD, the fluxes were given by the appropriate reaction rates expressed by Eqs. (9) and/or (10). The boundary conditions at the inclusion surface were completed with the addition of the equation of electroneutrality.

$$j_{MnS} = j_{MnS}^o \exp(m(E_{appl} - E_{MnS} - \Phi)) \quad (9)$$

$$r_c = kc_{H^+} \quad (10)$$

$$\sum_i z_i c_i = 0 \quad (11)$$

For the stainless steel surface, lines DE, EF, and FG, the fluxes of the reacting species were given by

$$\underline{n} \cdot \underline{N}_i = \frac{j_{SS}}{n_{SS} F} \quad (12)$$

where  $j_{SS}$  is the current density of the passive stainless steel dissolution reaction (a constant). On the line of symmetry, AB, the gradients of the concentration of all species and the gradient of the potential were equal to zero.

$$\begin{aligned} \frac{\partial c_i}{\partial n} &= 0 \\ \frac{\partial \Phi}{\partial n} &= 0 \end{aligned} \quad (13)$$

In summary, the set of equations given by Eqs. (1) – (5) along with the boundary conditions given by Eqs. (6) – (13), form a system of coupled, nonlinear partial differential equations mixed with nonlinear coupled algebraic equations. The set of equations was solved simultaneously for the concentration field of each chemical species as well as the potential field.

### 3.3 Method of Solution

The system of coupled, non-linear partial differential equations and algebraic equations was solved numerically with use of a finite difference method. Second-order centered finite differences, in two-dimensions, were used to approximate the solution of the set of non-linear partial differential equations by transforming them into a set of non-linear algebraic equations. Second-order forward- and backward-difference approximations were used on the boundaries. The finite difference form of the partial differential equations was obtained from partial Taylor series expansion by using unequally spaced nodes, and a fully implicit scheme was implemented to step forward in time.

Owing to the large number of equations to be solved simultaneously, a substantial level of computational resources was required. PETSc<sup>11</sup> (Portable, Extensible Toolkit for Scientific Computation), a set of numerical subroutines

and data structures developed for the parallel solution of systems of equations resulting from the discretization of partial differential equations, was found to provide a powerful set of tools and procedures for the problems addressed here. In particular, PETSc provided an efficient set of tools to solve the system of linear- and non-linear equations and boundary conditions, an efficient storage method to reduce memory requirements associated with very large, very sparse matrix associated with the set of equations, and an efficient method to parallelize the structured grid with a distributed array.

### **3.4 Code Performance**

Simulations were performed on NCSA Silicon Graphics Origin 2000 supercomputer. Convergence of at each time step was achieved after 4-8 iterations. Figure 2 shows the speedup in the computation time as a function of the number of processors. The efficient parallelization resulted in a significant decrease in the computation time, which allowed for the completion of large transient simulations in a reasonable amount of time.. Subsequent work with the application has shown that the scalability extends well to 32 processors on the Origin.

Initial studies of the same code applied to a much simpler two-dimensional simulation of diffusion and migration of  $\text{Cu}^{2+}$  on the Linux cluster “posic.ncsa.uiuc.edu” at NCSA were encouraging: 1 195MHz CPU of Origin performed the calculation in 47 s, while 1 500 MHz Pentium III Xeon CPU of the linux cluster took only 19 s. Similarly, for a simple two-dimensional Aluminum corrosion problem, solving the diffusion and migration problem, 16 processors of a 250 MHz origin took 139 s to solve the problem, while 16 processors of the same linux cluster consumed 58 s to perform the same computation. Clearly, there was reason for optimism for the MnS inclusion problem to perform well on the linux cluster, as only the chemistry has changed – albeit to a degree which makes the problem significantly more computationally challenging.

Since our initial results on the linux cluster for the MnS inclusion were not as we expected (the code slowed down for 2 processors and did not converge for 4 or more) we are working with the PETSc development group, to determine what is impeding convergence of the more challenging problem, and, subsequently, to improve the performance of the PETSc library and the finite difference application. Since this is an ongoing study, we will present our latest results at the conference..

## **4 Results of Sulfide Inclusion System**

Calculations were performed representing the system most commonly observed experimentally of a single, shallow sulfide inclusion (20  $\mu\text{m}$  diameter.) with a microcrevice, positioned at the center of a 100  $\mu\text{m}$  diameter microcapillary containing 0.1 M NaCl at a pH of 6 and polarized to an overpotential of 150 mV. The results of the model show only small changes in the local chemistry near a dissolving sulfide inclusion. That is, the simulation did not support an initiation mechanism based on significant accumulation of species, such as would be required for salt film formation, near a dissolving inclusion. In agreement with experimental data, the pH was computed to decrease to approximately 4.5 as a result of sulfide inclusion dissolution, a value that would not cause loss of SS passivity. The model supports a hypothesis of mechanism of pit initiation based on the accumulation of thiosulfate (in millimolar amounts) produced from inclusion dissolution in the presence of chloride ions to result in the depassivation of the stainless steel matrix.

Under the assumption of the existence of critical condition of thiosulfate and chloride ions near the stainless steel surface that prevents repassivation, critical potentials were predicted (at which the thiosulfate concentration in the microcrevice reached the critical value required for passivity breakdown) as a function of the bulk chloride ion concentration and sulfide dissolution kinetics for deep sulfide inclusions, as shown in Fig. 3. The predicted critical potentials compared well with experimentally determined values at deep sulfide inclusions, and thus supported the hypothesis that pit initiation occurs owing to the accumulation of thiosulfate near the exposed stainless steel surface as a result of inclusion dissolution.

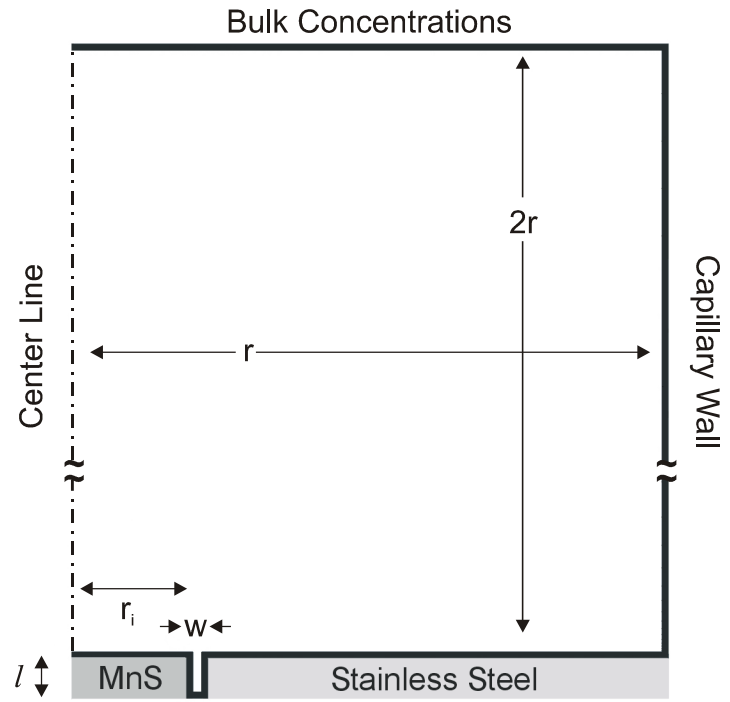
## 5 Conclusions

A mathematical model was developed for simulating the pitting potential based on the local chemical environment produced by dissolution of a sulfide inclusion on stainless steel. The key hypotheses were that pit initiation occurs by depassivation of stainless steel as a result of accumulation of thiosulfate ions above a critical concentration in the presence of chloride, and that the rate of inclusion dissolution was catalyzed by chloride. The model consisted of unsteady-state equations for reaction and transport in a 2-D circular cylindrical geometry that corresponded to the electrochemical microcell used here. Simulations used a combination of inputs that included experimental measurements of system behavior (that suggested mechanistic details) as well as experimental and literature data for values of system parameters. Simulations were carried out to obtain current-voltage data and concentrations of critical species at key locations. An object-oriented computational method was used so that additional hypotheses of mechanism could be tested now as well as in the future, when new understanding emerges in areas such as solution chemistry, mechanism of inclusion dissolution, and mechanism of pit initiation.

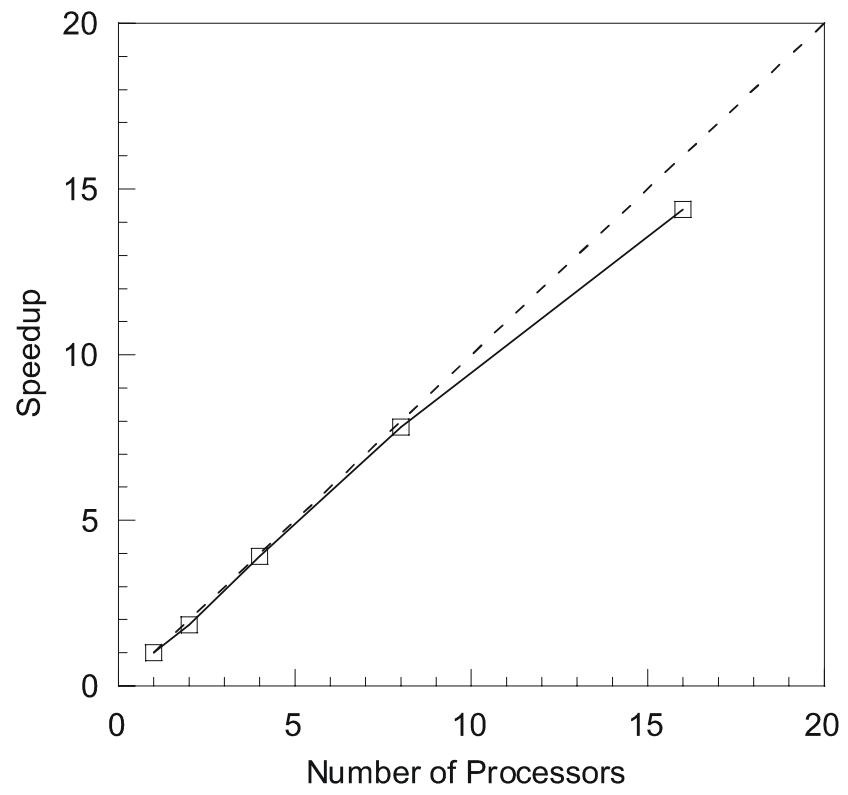
While this code is currently not performing as hoped on the Linux cluster, we are working to identify roadblocks preventing good parallel performance, and remain optimistic that we will see good parallel performance on the cluster.

### **Acknowledgment**

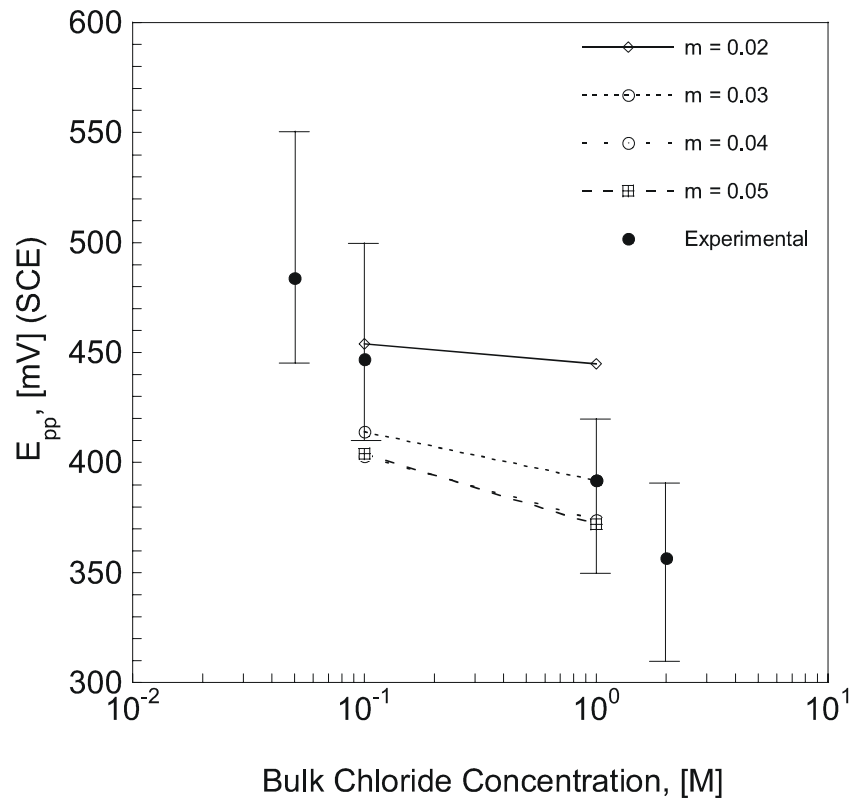
This work was supported by the U. S. Department of Energy, Division of Materials Science, Grant DEFG02-96ER45439 through the University of Illinois, Frederick Seitz Materials Research Laboratory, Urbana, Illinois 61801, and by the National Science Foundation, Grant 9619019 through the University of Illinois, National Computational Science Alliance, Urbana, Illinois, 61801.



**Figure 1:** Domain of single shallow MnS inclusion within microelectrochemical cell.



**Figure 2:** Computational speedup versus the number of processors.



**Figure 3:** Experimentally determined pitting potentials as a function of chloride concentration at individually selected deep MnS inclusions, and numerically predicted critical potentials for pit initiation for various MnS dissolution kinetics.

- 
- <sup>1</sup> D. E. Williams, T. F. Mohiuddin and Y. Y. Zhu, *J. Electrochem. Soc.*, **145**, 2664 (1998).
  - <sup>2</sup> J. R. Gavele, *J. Electrochem. Soc.*, **123**, 464 (1976).
  - <sup>3</sup> R. C. Alkire and S. E. Lott, *J. Electrochem. Soc.*, **136**, 3256 (1989).
  - <sup>4</sup> S. P. White, G. J. Weir, and N. J. Laycock, *Corros. Sci.*, **42**, 605 (2000).
  - <sup>5</sup> S. M. Sharland and P. W. Tasker, *Corros. Sci.*, **28**, 605 (1988).
  - <sup>6</sup> S. M. Sharland, *Corros. Sci.*, **28**, 621 (1988).
  - <sup>7</sup> J. C. Walton, *Corros. Sci.*, **30**, 915 (1990).
  - <sup>8</sup> S. M. Sharland, *Corros. Sci.*, **33**, 183 (1992).
  - <sup>9</sup> G. Englehardt, M. Urquidi-Macdonald and D. D. Macdonald, *Corros. Sci.*, **39**, 419 (1997).

- 
- <sup>10</sup> N. J. Laycock and S. P. White, in *Critical Factors of Localized Corrosion III*, R. G. Kelly, G. S. Frankel, P. M. Natishan, and R. C. Newman, Editors, PV 98-17, p. 469, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
- <sup>11</sup> S. Balay, W. D. Gropp, L. C. McInnes, and B. F. Smith, <http://www.mcs.anl.gov/petsc> (2000).