Algorithms and Computing Architectures for Solving Differential-Algebraic Equation Systems Typically Encountered in Models of Corrosion Pit Initiation

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Models of pitting corrosion typically include transport by diffusion, migration, and convection, heterogeneous surface reactions, and homogeneous solution equilibria among many other events. Simulations that include these phenomena typically result in a set of coupled nonlinear differential-algebraic equation systems. One of the principal difficulties in solving such models arises from the extreme chemical environments associated with hydrolysis reactions, which are of central importance to many hypotheses of mechanism[1,2,3]. The resulting computational difficulties include numerical stiffness, ill-conditioned Jacobian matrices, and large data-storage requirements. Thus, simulations can be quite computationally intensive. In addition, most sophisticated codes are uniquely adapted to the particular local computing environment they run on with the result that, too often, they are difficult or impossible for other users to modify and re-use. Moreover, there are multiple reasonable mechanisms for pitting corrosion, and the experimental data are extremely diverse. In the present work, improved computational procedures are reported for addressing these difficulties.

The physical system selected as a testbed was that of single sulfide inclusions on stainless steel during early stages of pit initiation. The system was recently analyzed by numerical simulation of reaction and transport in the vicinity of single sulfide inclusions[4] which used the Portable Extensible Toolkit for Scientific Computing (PETSc)[5] from Argonne National Laboratory. The PETSc numerical suite provides a set of data structures and programming routines to assist the user in developing general, scalable application codes. The equations were solved with second-order finite differences in combination with a line-search Newton Method / Preconditioned GMRES Krylov algorithm. The model was used to test the hypothesis that pit initiation is based on a critical concentration of thiosulfate ions in the presence of chloride ions, which results in depassivation of the stainless steel beginning in a small trench at the periphery of sulfide inclusions. An object-oriented programming method was used so that additional hypotheses of mechanism could be tested by modification of the code.

The new computational platform uses the DASPK3.0[6,7] numerical software. DASPK is a well-known package[8,9] designed for efficient solution of general mixed DAE systems on a single processor, employing adaptive time-stepping algorithms. This package incorporates the use of automatic differentiation[10] to compute both an approximate Jacobian for the linear solves, as well as to compute the parameter sensitivities. environment.

The objectives of the testbed simulations were to predict critical conditions under which pit initiation occurs for 304-type stainless steel in chloride solutions, the pitting potential, and the induction time for the onset of pitting corrosion.

Based on the approach in Ref. [1], we carried out the following modifications.

- Implemented the corrosion model in DASPK,
- Obtained consistent initial conditions for both original and derived constraints for index-2 variables,
- Designed pre-conditioners to optimize the numerical algorithms,

The improved numerical platform reported here provides techniques to solve the equations more rigorously as well as to carry out sensitivity analysis of the parameters by the forward method. This work also lays the foundation for additional enhancements obtained by suturing DASPK into the PETSc environment in order to extract valuable information from the solution and to make available the full range of PETSc's capabilities including parallelization. In addition, the implementation of this approach will facilitate the evaluation of additional mechanistic hypotheses that have been described in the literature.

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