

Theoretical Study of Corrosion of Corrosion-Resistant Alloys in Chemical Processes Environments including Mixed Acids and Salts using a Mechanistic Model

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ABSTRACT

Corrosion-resistant alloys (CRAs) are often employed in aggressive environments including pure acids as well as their mixtures with or without salts to mitigate corrosion risks. However, corrosion behavior of such alloys in wide ranges of process conditions needs to be reliably predicted. In this work, a previously developed model database is extended and refined to study the corrosion behavior of a group of nickel-base alloys (22, 28, 276, 625, 825, and 2550) and a martensitic stainless steel (S13Cr) in systems relevant to chemical processes, particularly in acids and their mixtures. The computational framework comprises a thermodynamic model for predicting speciation and an electrochemical model for predicting alloy dissolution due to anodic and cathodic processes. The framework also includes a repassivation potential model for localized corrosion. A comprehensive database of relevant experimental data from the literature has been collected in order to refine the parametrization of the model. The same modeling framework has been used to evaluate localized corrosion of the alloys in systems relevant to oil and gas production by calculating corrosion rate, corrosion potential, and repassivation potential as a function of environment speciation, temperature, pH, and partial pressure of gases including CO₂ and H₂S. The results show acceptable accuracy of the model in representing the literature data.

Key words: Corrosion resistant alloys, acid corrosion, salts, nickel-base alloys, electrochemical modeling, chemical processes environments, localized corrosion

INTRODUCTION

Chemical process environments often contain corrosive multicomponent systems including acids, salts and their mixtures¹ accompanied by various types of gases. Similarly, the oil and gas industry experiences corrosion caused by acid gas species in brine environments encountered during well development and stimulation, oil production, and refining.^{2,3} In order to prevent corrosion problems, selection of appropriate corrosion-resistant alloys (CRAs) is usually guided by their reported corrosion rates and applicability domains at specific operating conditions.⁴ However, this information is rarely available for corrosion in multi-component systems at varying fluid compositions or acid gas partial pressures, especially at higher temperatures. Localized and general corrosion of CRAs can be evaluated

by analyzing electrochemical characteristics of the alloys, including the corrosion potential (E_{corr}), repassivation potential (E_{rp}), and depassivation pH (pH_d). In particular, E_{corr} and E_{rp} can be used together to predict the onset of localized corrosion and to estimate its propagation rate⁵ for different types of CRAs. However, the electrochemical parameters such as E_{corr} or E_{rp} are usually obtained from laboratory tests in relatively simple corrosive environments and are not available at complex operational conditions. Therefore, there is a need to establish predictive models that could quantify the behavior of CRAs in complex process environments. This need has motivated the development of practical models that not only explain the corrosion mechanisms but also simulate the effects of environmental parameters on the corrosion properties of CRAs in complex environments.

In earlier studies,^{1,5-11} a mechanistic model was developed in order to predict the general and localized corrosion of CRAs in various environments including mixed acids and salt systems. In the present work, this model is applied to simulate and explain the corrosion behavior of several nickel-base and martensitic alloys in complex environments containing both oxidizing and non-oxidizing acids and their mixtures with salts in wide ranges of pH and chloride concentration. The effects of CO_2 and H_2S on corrosion rates and corrosion potential are also studied for a selected CRA. The model is validated against experimental corrosion rates, corrosion potentials, recommended applicability domains, and critical crevice corrosion temperature data.

COMPUTATIONAL MODEL

A computational framework was previously developed to calculate the corrosion potential and corrosion rate on the basis of the mixed-potential theory, and to compute the repassivation potential using a localized dissolution model.^{1,5-11} The combined framework is able to explain the corrosion behavior of various CRAs as a function of the aqueous environment composition, temperature, pH, and partial pressures of gases. The details of the model have been described elsewhere.^{1,2,5-11} Here, we summarize the key parts of the model:

I. Computation of the thermodynamic properties of the aqueous environment in the bulk and at the surface constitutes the foundation of the model. For this purpose, an aqueous thermodynamic model is used to predict the properties of the system at equilibrium including the speciation, activity of species and other thermophysical and transport properties. The thermodynamic model also makes it possible to compute phase equilibria (including solid solubilities and vapor-liquid and liquid-liquid equilibria) based on the equality of the chemical potential for each species in the phases at equilibrium.^{12,13} An ion solvation-based equation of state is used for calculating the standard-state properties of individual species and an electrolyte excess Gibbs energy model is used to compute activity coefficients of each species in the solution at finite concentrations.^{12,13}

II. Alloy dissolution in the active state is modeled by the Butler-Volmer equation, which takes into account the adsorption of electrochemically active species and their surface coverage to calculate the metal dissolution current density.^{1,6,10,11} The computational framework also includes expressions for the cathodic reactions taking place at the surface of the metal. The exchange current density in the active dissolution expression is correlated with the activity of species on the surface of the metal.^{1,6,10,11}

III. The active-passive transition and, consequently, the total anodic dissolution current (i.e., the active dissolution and passive dissolution) are expressed by solving an equation that considers the change of the passive layer coverage fraction with time in the steady-state limit.^{1,6,10} The critical current density, Flade potential, and passive dissolution range are also represented by applying this formulation.¹ Active-passive transition as well as passive dissolution are related to solution chemistry through surface reactions between the oxide film and solution species including aggressive ions (e.g., halides) and inhibitive ions (e.g., NO_3^-).^{1,6,10} The products of these surface reactions can then undergo dissolution. In addition, the impact of flow conditions on the mass transfer to and from the interface (and consequently on the surface activities of species and limiting current densities) is modeled by computing mass transfer

coefficients using the diffusion coefficients, viscosity, and density obtained from the thermophysical module (cf. part I above) as functions of temperature and composition.¹⁰

IV. The repassivation potential is calculated by solving, in the limit of repassivation, the expression for the current density in an occluded localized corrosion environment. This expression takes into account the effects of competitive adsorption of active species (such as Cl^- and H_2S) on anodic dissolution.⁵ Adsorption of various aggressive species (e.g. Cl^-) and inhibitive species (e.g., NO_3^- or SO_4^{2-}) has an effect on alloy dissolution and the formation of metal oxide (or sulfide) layer, which are modeled to accompany the repassivation process.^{5,8} The repassivation potential model also returns an estimate of the maximum rate of propagation of localized corrosion, which is based on the current density vs. potential relationship in the occluded solution environment.

By combining steps I through III as described above, the corrosion potential (E_{corr}) and the general corrosion rate are computed by calculating a synthesized polarization curve based on the mixed-potential theory. Taking into account that localized corrosion cannot occur at potentials below the repassivation potential,⁵ the calculated E_{rp} value (resulting from step IV) is then compared with the E_{corr} value to predict the occurrence of localized corrosion and to estimate the maximum propagation rate of localized corrosion as a function of environmental conditions.

Although all the elements of the combined model have been described before, this study is the first application of the model to simultaneously represent multiple corrosion phenomena in a fully consistent way, including corrosion of CRAs in both oxidizing and non-oxidizing acids and acid-salt mixtures, passive dissolution and active-passive transition in moderately acidic environments containing corrosive components such as H_2S and CO_2 , and localized corrosion induced by both oxidizing (e.g., FeCl_3) and sulfur-bearing species.

MODELING RESULTS

Table 1 shows the chemical composition of the alloys studied here. These alloys include several nickel-base alloys with different Cr and Mo contents as well as a martensitic stainless steel. They provide a wide range of alloy compositions to verify the performance of the model in various classes of environments, i.e., (a) single inorganic or organic acids, (b) mixed acids, (c) brines with or without oxidizing agents and (d) brines in the presence of acid gases such as H_2S and CO_2 .

Table 1
Nominal compositions of the alloys studied in this work (weight percent)

UNS No.	Common name	Ni	Fe	Cr	Mo	C (max)	W	Other (wt% max>1)
N06625	625	Bal.	2.93	21.97	8.9	0.01	0.0	Nb 3.52
N08825	825	Bal.	29.91	22.72	3.3	0.05	0.0	Cu 1.7
N06022	22	Bal.	3.0	22	13.0	0.015	3.0	Co 2.5
N10276	276	Bal.	5.5	16.0	16.0	0.01	4.0	Co 2.5
S41425	S13Cr	5.9	Bal.	12.1	1.9	0.03	0.0	
N08028	28	31.0	Bal.	27.0	3.5	0.03	0.0	Mn 2.0
N06255	2550	49.8	1.7	24.5	7.5	0.03	0.0	Cu 1.2

Single inorganic/organic acids

In this section, we apply the model to general corrosion in aqueous solutions of a non-oxidizing inorganic acid (H_2SO_4) and a non-oxidizing organic acid (HCOOH). Figure 1 shows the calculated and experimental corrosion rates for UNS N06625 in sulfuric acid solutions in the concentration range from 0 to 30 molal and in the temperature range from 311 to 435 K. In this system, the main cathodic reaction is the reduction of protons while the anodic metal dissolution depends on the acidity (pH) of the solution, which affects the active-passive transition of the alloy. In sufficiently concentrated sulfuric acid solutions, the alloy

corrodes in the active state. Therefore, the corrosion rate data in H_2SO_4 solutions are used to determine the model parameters that express the pH-dependence of the active-passive transition (including the critical current density) and the cathodic reaction of proton reduction (including the activation energy of the reaction). The model is equally applicable to organic acids. In the latter case, additional cathodic reactions need to be taken into account to represent the reduction of undissociated acids at high concentrations. As shown in Figure 2, the model accurately represents the corrosion rate data for UNS N08825 in formic acid solutions at various temperatures and in a wide range of acid concentration. Reduction of neutral formic acid as a proton donor and a direct proton reduction are the dominant cathodic reactions in such systems.

Mixed inorganic acids

The main advantage of a mechanistic model is being able to predict the behavior of alloys in multicomponent mixtures using parameters generated from simpler, building-block systems. In the case of acids, we reproduce the corrosion behavior of alloys in individual acids by adjusting the relevant model parameters (i.e., exchange current densities in Parts II and III of the model as described above). Then, we apply the model to predict the corrosion behavior in mixed acids. Here, we analyze the behavior of UNS N06022 in mixtures of hydrochloric and nitric acids.

First, the available experimental corrosion rate data in single-acid, HCl and HNO_3 solutions have been used to develop the relevant model parameters. Figures 3 and 4 show the calculated and experimental corrosion rates for UNS N06022 in HCl and HNO_3 solutions, respectively. Corrosion in these acids proceeds according to different mechanisms. HCl is a non-oxidizing acid, in which the chloride ions (Cl^-) have a considerable effect on the active-passive transition. On the other hand, HNO_3 is an oxidizing acid, in which the corrosion potential is elevated due to a strong additional cathodic reaction of HNO_3 reduction. In single-acid HCl solutions, anodic dissolution is in the active state whereas the presence of HNO_3 leads to the passive dissolution of the metal.

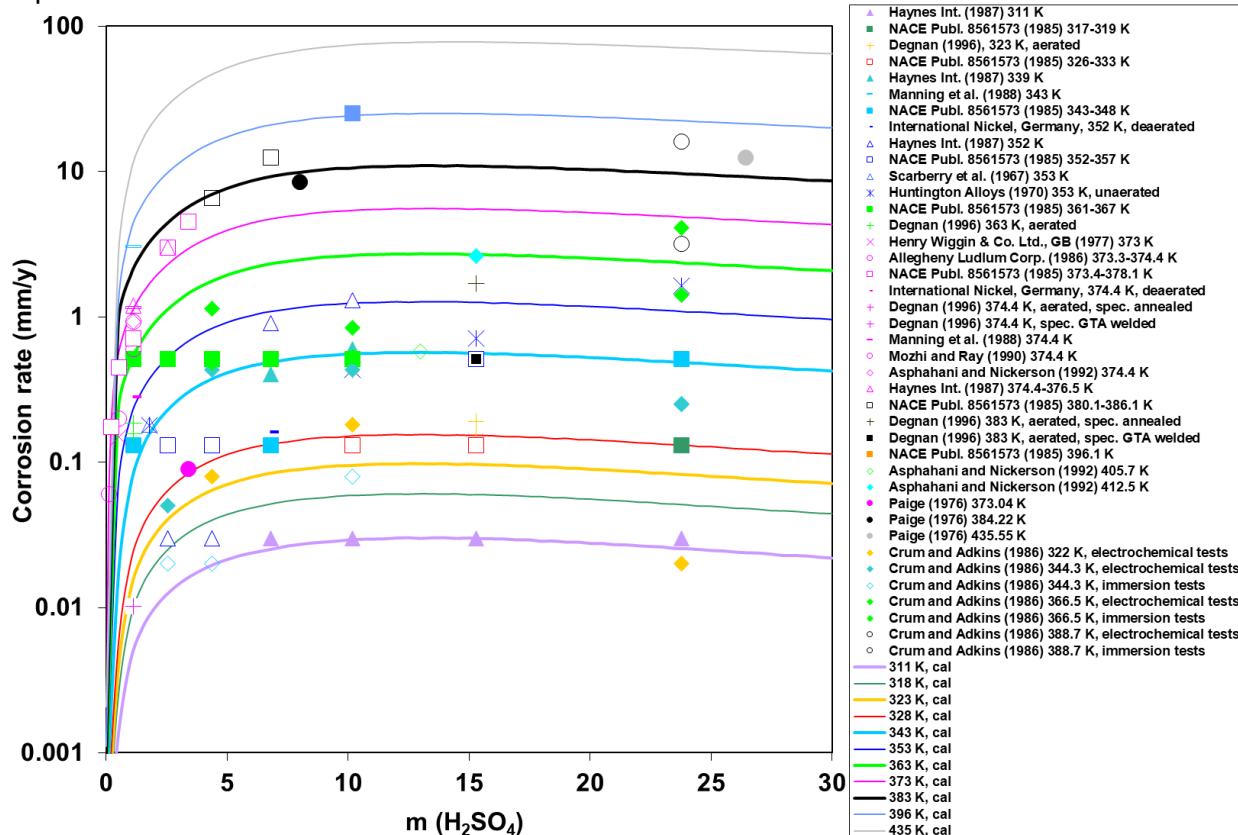


Figure 1: Calculated (lines) and experimental (symbols) corrosion rates of UNS N06625 in H_2SO_4 aqueous environments as a function of acid concentration at temperatures from 311 to 435 K.

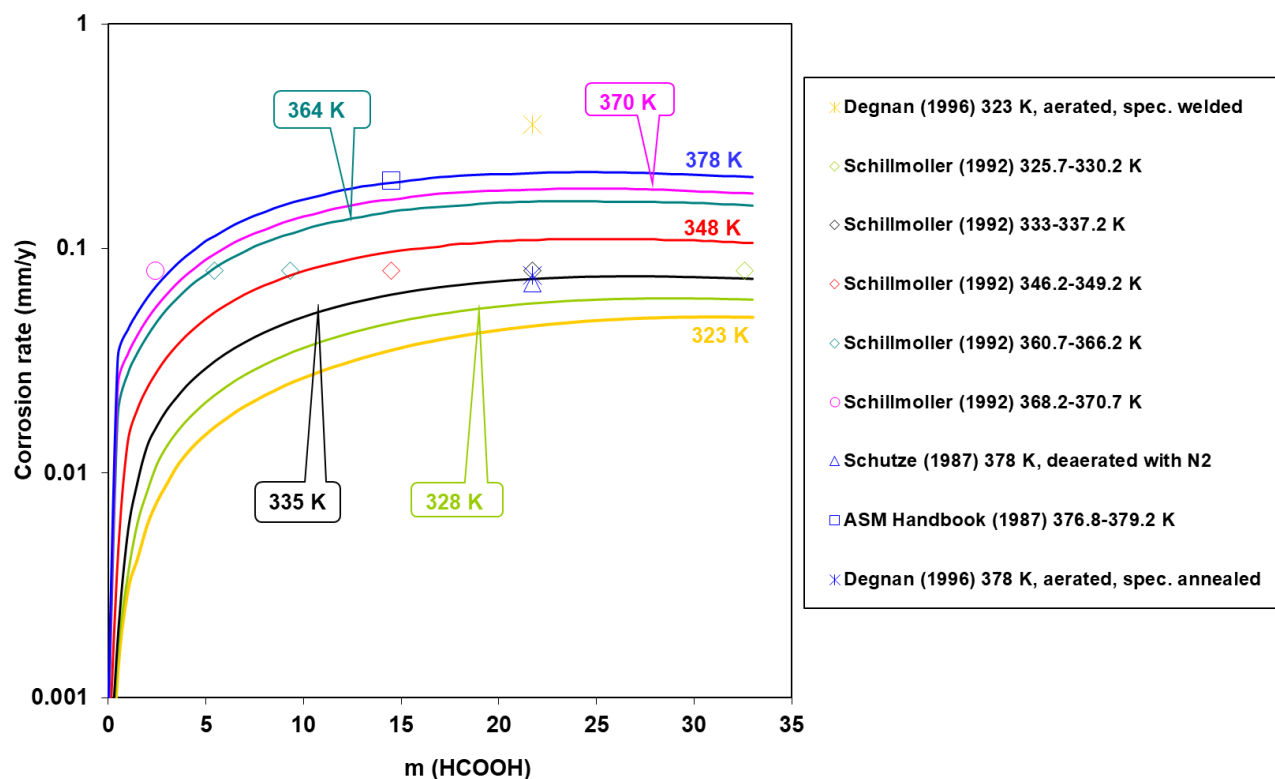


Figure 2: Calculated (lines) and experimental (symbols) corrosion rates of UNS N08825 in formic acid solutions at temperatures from 323 to 378 K.

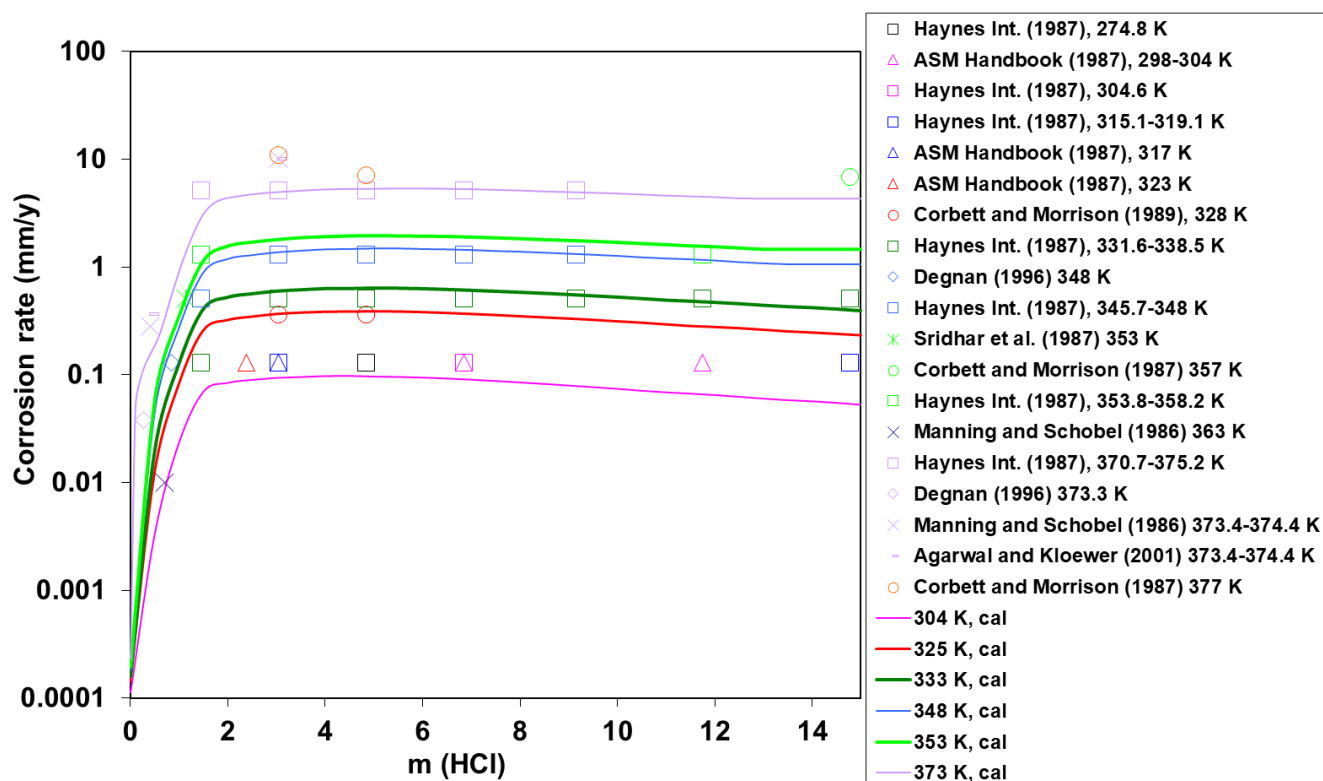


Figure 3: Calculated (lines) and experimental (symbols) corrosion rates of UNS N06022 in HCl aqueous environments at temperatures ranging from 304 to 373 K.