ASSUMPTIONS, UNCERTAINTIES, AND LIMITATIONS IN THE PREDICTIVE CAPABILITIES OF MODELS FOR SENSITIZATION IN 304 STAINLESS STEELS

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ABSTRACT

A review of literature on sensitization in 304 stainless steels has been made from what we believe would be the regulatory framework evaluating the claim that there is reasonable assurance that predicts the absence of sensitization for the times (300-1000 years) and temperatures (below about 200°C) associated with a high-level waste (HLW) repository at Yucca Mountain.

We conclude that such a claim would be indefensible.

## 1. INTRODUCTION

The DOE Contractors have selected metal containers to achieve long-term isolation of HLW.

The answer to whether or not metal degradation and metal failure is sufficiently well understood to predict performance over hundreds to thousands of years at temperatures between 250° to 60°C is critical to deciding if claims made by the DOE Contractors on long-term performance of metals in their present designs can be defended in the existing regulatory framework.

Over the past years, the DOE Contractors have produced a great deal of work that has been extensively reviewed and criticized by the Nuclear Regulatory Commission (NRC), the Materials Review Board (MRB) of the DOE, the Advisory Committee on Reactor Safeguards (ACRS), and the technical support group at Brookhaven National Laboratory (BNL). Common aspects of the reviews and criticisms have provided information on the level of evidence required by the regulatory agencies and the scientific community to defend performance claims.

From "Peer Reviews" of waste isolation programs, it has become clear that the standards for defending a claim or a model for performance of metals needed to satisfy repository licensing requirements is significantly more stringent than the peer reviews associated with publication of journal articles.

Although a very large volume of literature dealing with the requirements to demonstrate a claim with "Reasonable Assurance" has been produced by the NRC and its Contractors, a representative summary of the problem can be inferred from a recent statement by the NRC on the contents of the important





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Site Characterization Plans (SCP) which include major sections on predicting metal performance

"Should the range of uncertainties and alternative interpretations and assumptions that can be reasonably supported by the existing data not be considered in the SCP development, the SCP could be deficient ..........."

Since more and more of the metallurgical community is becoming involved with peer review of waste management programs, we have selected, as an example, what we believe would represent part of a regulatory review and analysis of a claim made by a DOE Contractor that, based on reference [12], models exist or will be developed that can be used to predict the absence of sensitization in AISI 304 stainless steels over periods of hundreds to thousands of years at temperatures between 250°-60°C. The claim is being made to support the statement

> "For intergranular stress corrosion cracking, the process of sensitization, crack initiation, and crack propagation will be characterized so that the likelihood of occurrence of failure by this process can be predicted."

The statement appears in the original, and in the revised draft version UCRL-53765, Virginia M. Oversby, "The Nevada Nuclear Waste Storage Investigations Project Strategy For Showing Compliance Of Waste Performance With Regulations Governing The Post-Emplacement Period", p. 53, October 1986, and again in the recent draft versions of the forthcoming NNWSI Site Characterization Plan.

We wish to stress, that we are unaware that such a claim has been made by any of the authors of the papers reviewed. On the other hand, the paper by T. Kekkonen, P. Aaltonen and H. Hanninen [1], claims that sensitization at temperatures below 288°C can develop during the relatively short lifetimes of BWRs. Because of the significantly large number of pipe cracking events in BWRs below 200°C associated with sensitization, a great deal of work exists that is directly or indirectly pertinent to prediction of sensitization at low temperatures.

The objective of this review is to relate the approximations, uncertainties, and inconsistencies in data and models on sensitization, to regulatory guidelines for performance predictions in systems affecting the health and safety of the public.

In the existing regulatory framework, the burden of proof is on the applicant for the repository license. The logic for justifying a performance claim requires the explicit description of the temporal changes in the environment and in the physical and chemical conditions affecting the expected performance. The regulatory agencies evaluating the adequacy of this evidence invoke analyses of the uncertainties in the data and in the models, and require the applicant to provide analyses of the consequences of both favorable and unfavorable predicted performance. Implicit in every claim for favorable performance is the assumption that adverse processes do not occur.

The present conservative regulatory tenor has imposed a severe handicap on the applicant by requiring evidence for the absence of potentially adverse processes and by limiting the use of experiments in which the adverse process was not observed. The absence of potentially adverse phenomena must be defended by theoretical arguments which are supported by such confirmatory null experiments. Because of the inordinately long times over which performance predictions are required, null experiments by themselves bear little weight.

## 2. BACKGROUND

Stainless steels which are thermodynamically unstable with respect to their chromium and carbon activities, show an enhanced susceptibility to intergranular corrosion after specific types of heat treatment in the temperature range of 550°-800°C. In 1933, Bain [2] suggested that this sensitization to intergranular corrosion resulted from chromium depletion in matrix regions adjacent to grain boundaries in which chromium-rich carbides have precipitated. In 1969, Stawstrom and Hillert [3] postulated a model based on a kinetic-pseudo thermodynamic approach in which time-temperature-sensitization diagrams were calculated assuming that the rate determining step in developing a sensitized microstructure was chromium diffusion from the matrix into the grain boundary. With the additional assumptions that the kinetics of chromium carbide nucleation and precipitation in the grain boundaries are fast, and that the carbon activity is uniform and the same in both matrix and grain boundary, they proposed that the time to develop sensitization can be approximated by

$$t = \frac{m^2}{4D} \frac{(X_o - X_{eq})^2}{(0.13 - X_{eq})^2} \qquad (1)$$

where m is an empirically determined dimension (about 200 Angstroms) associated with the minimum region needed for the chromium to fall below the value of 13 at%. X(eq) was estimated from unpublished thermodynamic data of T. Nishizawa.

In 1971, Tedmon et al [4], showed that 304 steels with less than 13 at% Cr exhibit enhanced corrosion rates and suggested that these materials are not fully passive in the Strauss solution. They attributed susceptibility to intergranular attack to the continuity of the zone in which the local chromium concentration is below 13 at%. Stawstrom and Hillert ascribed the susceptibility to the width of the region with chromium below the same value. Tedmon et al. also suggested that X(eq) should be obtained from the equilibrium constant for the reaction

$$23Cr + 6C = Cr_{23}C_6$$

using Wagner's method to calculate the carbon activity. The chromium activity coefficient was obtained empirically by using an adjustable parameter force fit to data. Typical values of the time to sensitization occurring between 500°-700°C vary from tens of minutes to thousands of minutes.

In 1982 Fullman [5] proposed a method for including the effects of some alloying elements by calculating changes in the chromium activity and in the carbon activity. Briant et al., [6], in 1982, reviewed work showing evidence that the degree of sensitization as measured by a specific test depends upon variables that can affect intergranular corrosion by changing the corrosion susceptibility of the material without invoking microstructural mechanisms. The authors note a second group of variables such as cold work, the presence of martensite, the grain size, and the addition of elements which can segregate to the grain boundaries and retard carbide nucleation and growth.

The authors state

"Both of these effects have made it difficult to predict the occurrence of sensitization, and they contribute to the heat-to-heat variability that has plagued industrial applications [7,8]."

Since Equation (1) requires that the kinetics of carbide nucleation and growth are not the controlling factors in determining the time to develop a sensitized microstructure, this equation can not account for many of the variables known to affect sensitization.

Briant et al. [6], in recognizing this, invoked the empirical concept of effective chromium content originated by Cihal [9] and developed by Fullman [10] to correlate the effect of nitrogen in changing the time to initiate sensitization.

They claimed there was considerable evidence from their oxalic acid test data that nitrogen retards nucleation and/or growth of the carbides. They stated that in steels containing about 0.06 wt % carbon

"We found in the modified Strauss test a small improvement from nitrogen additions at 600°C, a significant one at 650°C, but none at 700°C."

In further discussing the effect of nitrogen they claimed

"All these results are consistent with the metallographic data of Eckenrod and Kovack [11] which showed that nitrogen additions delayed carbide precipitation."

More recently, Mozhi et al. [12] and Mozhi et al. [13] described work where nitrogen additions below 0.16 wt % retarded sensitization kinetics but an addition of 0.25 wt % nitrogen did not.

The authors used Equation (1) to estimate the bottom portion of TTS curves for the samples with nitrogen below 0.16 wt % by making assumptions of the effect of nitrogen on the activities of chromium and carbon. To explain the difference in behavior between 0.16 and 0.25 wt % nitrogen, they suggested that $Cr_2N$ precipitates at the high value but not at the low values.

The data and analyses described in reference [12] do not appear to be consistent with the data observed by Briant [6]. Although both sets of steels have similar compositions, the model used in reference [12] shows a large effect of nitrogen at 700°C while the observations described in reference [6] show no effect of nitrogen at 700°C. The model requires a monotonic variation with temperature while the data are non-monotonic.

Recently, the LLNL staff of the NNWSI program, in support of the quote from UCRL-53765 which is repeated in drafts of the forthcoming SCP, claimed that they intended to expand the model used in reference [12] to support the claim that sensitization will not occur at temperatures below 200°C for time periods from 300-1000 years.

In direct conflict with this claim is a great deal of work reviewed by and including the work of, Kekkonen et al. [1]. These authors have shown the development of sensitization in 304 stainless steel in 1500 days at 350°C. The authors also show from analyses of six references, that five of the references predict the development of sensitization below 288°C at times ranging from less than one year to less than 40 years.

Povich [14-16] found that if non-sensitizing carbides precipitate at grain boundaries at high temperatures, sensitization could occur with subsequent exposure at temperatures lower than those used in the standard single isothermal heat treatment.

Fullman [17] suggests two mechanisms that could overestimate the rate of sensitization when extrapolated from high temperatures, and one which could underestimate the rate. He attributed possible overestimation to

"1. Reduction of dislocation 'effective area' as a result of impurity adsorption at dislocations.

2. A shift from diffusion-limited to interface-limited kinetics."

Underestimation through a low activation process was attributed to chromium depletion by enhanced diffusion along dislocations.

Kekkonen et al. [1], claim that nucleation occurring at high temperatures allows increases in the degree of sensitization at lower temperatures through low activation processes of carbide growth and grain boundary migration. They state

> "The thermodynamic and kinetic considerations of LTS have not taken into account the proposed growth mechanism. The carbide growth may be faster than predicted by kinetic calculations. The major consequence of the carbide growth involving grain boundary migration is the increase in the width of the Cr-depleted region and thus enhanced DOS, compared with the results given by thermodynamic models or extrapolations from high temperature data.

"The (T,t) dependence of LTS suggests a change in the activation energy as the temperature decreases. A possible reason for the observed departure from linear Arrhenius dependence of a reaction rate is the transition from one mechanism to another.... In this case extrapolation from high temperature data will underestimate the low temperature reaction rate."

3. COMMENTS

The temperature dependence of the equation giving the time for sensitization is in principle determined by a large number of factors, some of which are empirical and poorly understood. In addition to the various temperature dependences of the diffusion coefficient of chromium in austenite, in the grain boundaries, along dislocations, and how temperature changes in Cr activity change diffusion, a large number of temperature dependent factors determine X(eq), the equilibrium chromium concentration. These include the temperature dependent factors affecting the carbon activity and activity coefficient as well as the temperature dependent factors affecting the nitrogen activity and activity coefficient. In all, some 30-40 temperature dependent processes, variables, constants, and crossterms have been postulated for use in explaining changes within the metal. Additional uncertainties are associated with environmental parameters and with questions of the limitations of the tests demonstrating sensitization.

Much of the modeling of sensitization is based on "adjustable parameter" force fits to experimental data. Although several papers allow that sensitization can occur at low temperatures, none of the work reviewed claims that the model can be used to predict the absence of sensitization at lower temperatures than those used.

No overview exists that deals with either a sensitivity analysis or an uncertainty analysis that addresses the predictive capabilities of the model. Such analyses are required in the existing regulatory framework. We believe the wide variation in results and explanations, the large number of poorly understood phenomena that have been invoked to explain observations, and the explicit published work contradicting the prediction that low temperature sensitization will not occur, do not support the claim that Equation (1) can be developed to defend prediction of the absence of sensitization at low temperatures for hundreds of years.

## 4. CONCLUSIONS

We believe it is, and has been for many years, obvious that it is not possible to defend prediction of the absence of sensitization in 304 steels for hundreds of years at the temperatures expected in an HLW repository through use or extension of Equation (1). Using Equation (1), or an equivalent algorithm, to predict time for sensitization at repository temperatures implies several extrapolations. Extrapolation on the composition of the carbide to low temperatures. Extrapolation of the free energy of formation of the carbide to low temperatures. Extrapolation of the activity coefficients of carbon and chromium to low temperatures. Extrapolation of the diffusion coefficients of carbon and chromium to low temperatures. And finally, extrapolation of the chemical kinetics assumptions on which the model is based must be valid at low temperatures.

Our evaluation of the uncertainties, the theoretical limitations and the inconsistencies lead us to conclude that it virtually would be impossible to defend an argument that the existing understanding of sensitization in stainless steels can be used to predict its absence at temperatures between 250° and 60°C over time periods of hundreds of years.

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Mr. R. Stein
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Dear Mr. Stein:

The purpose of this letter is to alert you to the accumulation of a significant quantity of independent and consistent information that seriously contradicts the central philosophy of the NNWSI licensing strategy.

As you are aware NNWSI has stated repeatedly:

"The central point of the NNWSI Project licensing arguments will be the near absence of liquid water in contact with the waste package during the containment period and the limited quantities of liquid water available to contact, enter, and exit from breached waste packages during the controlled release period."

"The limited amount of water available to contact waste packages results in limited ability for transport of radionuclides from the waste packages even if the packages contain breaches through the metal barrier. Thus, for a site in the unsaturated zone, 'substantially complete containment' can be achieved without having to show that a substantial fraction of the waste package containers are intact."

Ever since the early 1980's, NNWSI, DOE-WMPO, NRC, USGS, SAIC, Los Alamos, Sandia, State of Nevada representatives, and DOE headquarters staff have been involved in trying to identify the origin of the calcite-silica deposits in a trench located between the east slope of Yucca Mountain and Exile Hill which cross-cuts the Bow Ridge fault.

From 1984 to the present, a series of workshops and reviews have not been able to determine whether the deposit was formed from surface water running down (pedogenic), or springwater ascending (hydrothermal). The problem has received a great deal of publicity through NRC comments on the EAs, through a recent (6/13/87) letter from NRC Chairman Zech to Senator B. Johnston, through stories in a series of publications such as the Nevada Nuclear Waste Newsletter, through NRC trip reports and memoranda, and through the recent GAO report "Status of DOE's Nuclear Waste Site Characterization Activities."

From an NRC memorandum "Appendix 7: Attendance At DOE Peer Review Committee Meeting For Veins Deposits" (6/17/87) it appears that as of April 1987 no convincing evidence has been obtained identifying the source of the deposit. The additional work proposed is expected to take 30 to 39 months with no guarantee that the problem will be resolved.

By this time it is well known that almost all parties agree that the existence of "hydrothermal activity" causes serious problems in determining groundwater travel times and precludes acceptable defense of controlled release.

I wish to emphasize the following points:

1. The potential existence of hydrothermal activity is sufficiently serious so that the consequences of the deposit originating through pedogenic processes have been mentioned only superficially in these workshops. Nevertheless, it has been recognized that even under the most favorable conditions of origin of the deposits (i.e., surface water running down), "substantial quantities of water may be involved."*

2. If hydrothermal activity cannot be excluded, the regulatory significance will likely be determined by the NRC, the DOE, the USGS, etc. You may recall from comments on the draft EAs that the NRC stated that the Wahmonie NTS site was eliminated because

   "local surface deposits from recent warm springs indicate upward seepage of groundwater, possibly from great depths."

   At present, I believe the DOE can do little in the geology-hydrology portions of the draft SCP other than explicit acknowledgement of the problem.

3. Under the more favorable assumption that eventually it may be possible to show that the calcite-silica deposits have pedogenic origins, the NNWSI claims on limited water over 10,000 years still will be considered indefensible.

*DOE-WMPO presentation quoted in a letter from LLNL to the NRC (3/6/86).

In summary, I believe the evolution of information over the past several years has made defense of controlled release more and more difficult for all the projects. In the case of NNWSI, these particular problems may require that 10,000-year containment is the only acceptable alternative.

Since the NNWSI SCP states that its licensing strategy will be based on "near absence of water" and "limited water" you may wish to consider how these claims will be received in view of the recent highly publicized events.

Sincerely,

Don Schweitzer

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