

## MECHANISTIC BASIS FOR EXTRAPOLATION OF CORROSION RATES FOR WASTE OVERPACKS

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### ABSTRACT

The need to ensure the containment of the nuclides placed in a waste repository for essentially an indefinite time period, 1,000 years, is a key issue in the design of high level nuclear waste packing. The corrosion processes acting in the waste package during the containment period must be well understood. In particular the corrosion rates during this long exposure period must be determined. An "Interrupted Oxidation" method for the characterization of corrosion rates over long term exposure is discussed herein.

### INTRODUCTION

The purpose of this paper is to present a methodology used in oxidation research that can be applied to qualifying overpacks where corrosion resistance up to 1000 years is needed. Assurance that a metallurgical system can resist complete degradation is difficult to demonstrate over these long lifetimes even by extrapolation. This methodology allows one to understand the oxidation mechanism at progressing stages of oxidation without waiting for a 1000 year time span. Its use would enhance the confidence that overpack systems can meet licensing regulations.

### WHAT IS INTERRUPTED OXIDATION?

The technique of interrupted oxidation relies on a measurement system sufficiently sensitive to detect uptake of oxygen molecules while a defect gradient is being established across a rate controlling, adherent film of oxide. Most oxidation experiments measure the gross uptake of oxygen which over time follows an averaged rate law. Because sufficient buildup of oxide film is required for measurement the subtle changes in mechanism are lost or obscured. Often it is more instructive to discern what mechanism is operating after certain levels of oxidation have been achieved (different scale thickness) than to know the total uptake particularly if extrapolation to the desired life is required. Some scales spall and generate new films which may change the mechanism due to buildup of impurities in the film.

The interrupted oxidation method allows for controlled measurement of oxygen uptake at two levels. First the gross level where the total uptake is measured to determine the extent of oxidation after a significant fraction of the overpack system has been degraded (oxidized). At each of these stages the gross oxidation process is interrupted and the second level of oxidation is measured at high sensitivity to determine defect mobility and defect concentration which govern the controlling process of oxidation at each stage. Trends in the mobility and concentration terms give insight to subtle changes in oxidation mechanisms not evident in the gross oxidation measurements. Gross oxidation to a particular stage can be accelerated by using stronger corrosion media or higher temperatures or a combination of both. After interruption each stage is returned to a standard condition for the high sensitivity oxidation measurements.

### WHY SHOULD INTERRUPTED OXIDATION BE USED?

The principal degradation mechanism in determining the life of overpacks stored in repositories is oxidation of the alloy container. The oxygen supply in sealed repositories may range from very low oxygen activities to ambient atmospheric conditions. Qualification of the selected overpack material depends on a reliable method for predicting the rate of attack and the nature of the attack. Research on candidate overpack alloys is being done to understand the broad corrosion aspects and to provide a sound basis for selection. When an overpack is selected then a follow-on quality assurance program is required. Oxidation uptake measurements conducted over short periods are difficult to extrapolate since the accuracy is not sufficient. Consequently an oxidation measurement that determines the rate of uptake after significant stages of oxidation gives a greater assurance of knowing the trends.

### HOW IS INTERRUPTED OXIDATION USED?

Measurements of oxygen uptake offer greater sensitivity than conventional weight gain measurements of metal coupons. Oxygen uptake involving gas phase manipulation is difficult particularly if oxidation is done at very high temperatures. Fortunately repository conditions operate at low enough temperatures such that one may use conventional precision glass equipment. After interruption of the oxidation process highly sensitive pressure changes at reduced pressures of oxygen give extremely sensitive measurements of the uptake to determine key data involved in the diffusion process through the oxide scale.

If  $V$  is the rate of uptake (oxygen/cm<sup>2</sup>/sec) then reaction behavior may be characterized by Eq. (1)

$$-\left(\frac{\partial \log V}{\partial \log N}\right)_{T,P} = \epsilon \quad (1)$$

The term,  $\epsilon$ , which may be plotted against the extent of oxidation,  $N$ , indicates the type of reaction occurring. If  $\epsilon = 0$ , the oxidation reaction is occurring without benefit of a protective oxide scale. The condition,  $\epsilon = 1$ , corresponds to a parabolic oxidation rate;  $\epsilon = 2$  corresponds to a cubic law, etc.  $\epsilon$  may be a continuously varying function showing a particular singularity after a given extent of scale buildup. Systematic variations in temperature and pressure can give further insight into the mechanism.

## EXPERIENCE IN THE LITERATURE

Among the multitude of research papers on oxidation, there is little reference to interrupted oxidation as a tool for understanding mechanisms. In recent years there have been tremendous advances in physically viewing oxide scales through electronic instrumentation and the highly sensitive gas reaction kinetic methods are less used. Rosenberg<sup>1,2</sup> used this technique in a series of articles on oxidation of compound semiconductors InSb and GaAs. The full value of this technique was revealed in the interpretation of the  $\epsilon$  term on the oxide layer on InSb. The evolution of a pure In<sub>2</sub>O<sub>3</sub> film was followed as it changed character from a field driven oxidation process to a diffusion driven process. The volatilization of antimony oxide and its influence on the oxidation process was also demonstrated.

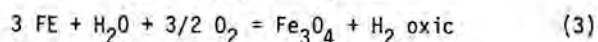
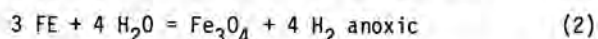
The methodology and procedure for performing an interrupted oxidation experiment is described in Ref. 3. Although this reference applies the method to krypton adsorption for surface area measurements of powder, the principles apply to any oxidation process that consumes a gaseous constituent containing oxygen.

The author<sup>4</sup> used this technique for interpreting oxidation mechanisms of highly defected solid solutions of uranium oxide. Here it was shown that paired anion vacancy transport was responsible for orders of magnitude increase in the oxidation rate compared to single vacancy transport.

The high sensitivity for measuring the gaseous uptake is achieved by use of a thermistor in a controlled chamber such that slight changes in the thermal conductivity of the gas registers a change in thermistor resistance. Using Wheatstone bridge methods very small changes in resistance are noted. The thermal conductivity of the gas phase is a direct function of the pressure in the region of 0.001 atmospheres. At higher pressures, the conductivity becomes influenced by convection and the sensitivity diminishes. The thermal conductivity is also influenced by the gaseous constituents, lighter molecules such as hydrogen and helium are more sensitive than heavier molecules.

### APPLICATION TO OVERPACK MATERIALS

Studies<sup>(5)</sup> on corrosion of overpacks result in two types of reactions shown in Eqs. (2) and (3)



The anoxic reaction operates when the environment is starved of oxygen or is reducing by virtue of the geological constituents. The oxic reaction operates when the repository environment has a surplus of oxygen. Early in the repository period the oxic reaction may predominate but later may give way to anoxic reaction after the sealing action of the system isolates sources of oxygen caused by human activities during burial.

Both reactions consume water, and produce hydrogen and form the Fe<sub>3</sub>O<sub>4</sub> oxide. Other alloy constituents would form oxide compounds in a similar manner if they are stable. Only the oxide reaction consumes oxygen.

The interrupted oxidation methodology as used in the literature measures the oxygen uptake via minor changes in the system pressure. The sensors used depend on thermal conductivity of the gas in the system and on the constituents. Modern gas chromatography tests could be used too as an added feature to register the composition.

The gaseous constituents in Eqs. (2) and (3) are hydrogen, oxygen and possibly water. The major attack process is viewed to occur when water or salt solutions are in contact with the metal in the condensed liquid state. In the dry state the aqueous form of corrosion cannot occur. Initially the overpack temperatures are high from decay heat. Water is not expected to be present in sufficient quantities to condense on the surface so that the initial oxidation is in the dry state. This condition can be readily characterized by the interrupted oxidation method.

When condensation occurs, electrochemical kinetic processes may predominate building an oxide scale represented by Eqs. (2) and (3). The net change in pressure is the sum of oxygen and/or hydrogen.

The vapor pressure of water would also influence the sensor. At constant temperature, the water vapor pressure should be constant if there is an excess of water condensed on the metal surface. Because of changes in hydrogen/oxygen pressure, the reaction rate could be established by stoichiometric balance of Eqs. (2) or (3). For the anoxic case the principal reaction rate would be registered by the evolution of hydrogen. For the oxic case the reaction rate would be a combination of a declining oxygen partial pressure and an increasing hydrogen pressure with the sensor biased to the hydrogen. If the system temperature precludes coexistence of hydrogen and oxygen in the gas phase then the oxygen consumption would be the principal gas influencing the sensor.

Management of the water vapor is particularly troublesome in glass systems. If the required corrosion temperatures are not too high, controlled temperature gradients could limit the water to regions where the corrosion sample is located and use of non-absorbing materials such as inert metals for containment would prevent spurious or drifting results.

### REFERENCES

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