July 3, 1996

Dr. W. A. Gray
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Pacific Northwest National Laboratory
PO Box 999
Richland, WA 99352

Dear Dr. Gray:

Enclosed is the abstract and the summary of a paper entitled "Dry Oxidation of Waste Package Materials." This abstract is being resubmitted to the Materials Research Society Symposium: Scientific Basis for Nuclear Waste Management XX, December 1-5, 1996, Boston, MA. Please replace previous copies dated July 1, 1996, with this transmittal letter, the abstract, and the summary.

Sincerely,

Tae M. Ahn
Engineering and Material Section
Engineering and Geosciences Branch
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

Enclosure: As stated

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Enclosure

# DRY OXIDATION OF WASTE PACKAGE MATERIALS*

This paper evaluates dry oxidation of the candidate outer container for high-level waste management at the Yucca Mountain repository site. Although uniform dry oxidation may not be significant for dry periods, there is potential of localized attack by dry oxidation. The localized dry oxidation may not guarantee the container integrity for extended periods. Example data on unprotective external oxidation, internal oxidation, and intergranular oxidation are presented from high temperature data of iron-based alloys. The data are extrapolated to repository conditions for candidate alloys. Additionally, the diffusional penetration of oxygen is also calculated to clarify the extrapolation. This analysis suggests that oxygen may penetrate through the outer container under extreme conditions. Various uncertainties associated with the analysis are discussed. For the assessment of container life, consequences of this oxygen penetration are addressed. For more quantitative judgments, future necessary work is also proposed.

* *DISCLAIMER*: The information contained in this report does not necessarily reflect the official position of the U.S. nuclear Regulatory Commission.

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SUMMARY (DRY OXIDATION OF WASTE PACKAGE MATERIALS)

This paper evaluates dry oxidation of the candidate outer container for the mined geological disposal system planned at the Yucca Mountain (YM) repository site. At the YM repository site, the oxidation of the candidate outer container with air has been assessed to be negligible under dry conditions of relative humidity less than 70% [1]. The oxide formed is considered to protect the container against further oxidation. However, there is potential that the oxide will grow continuously at a constant rate and the oxidation will be highly localized. The unprotective or the localized dry oxidation may not guarantee the long-term container integrity in dry environments.

The oxide may become unprotective (porous, amorphous, defected, or new crystalline) as the oxide grows. Thermodynamic driving force for the oxidation makes the thicker oxide be transformed structurally. This transformation will allow easy mass transport in the oxide for the continuous oxide growth. The localized dry oxidation includes internal oxidation and intergranular oxidation. In the internal oxidation, the oxide forms as islands below the uniform oxide layer. In the intergranular oxidation, the oxide forms preferentially along grain boundaries. The localized dry oxidation takes place by mass transport through short-circuit diffusion paths, such as interfaces between metal and oxide or grain boundaries. Therefore, the localized dry oxidation can be much deeper than the uniform dry oxidation.

Literature data are presented showing the unprotective oxide, the internal oxidation, and the intergranular oxidation, for iron-based engineering alloys. These data were mostly obtained from tests above 600 C for less than a year. Based on these data, the dry oxidation of candidate carbon steels (A516 Grade 55 and A387 Grade 22) is evaluated at 100 to 200 C for up to 10,000 years. Effects of alloying elements are also evaluated. The quoted engineering alloys have higher concentrations of alloying elements than candidate alloys.

The stress associated with volume expansion by oxides is calculated using linear elastic formula. The calculated stresses exceed fracture stresses of alloys and oxides. At lower temperatures, this tendency is more likely because of less stress recovery. The original and modified Wagner criteria [2] suggest easier internal oxidation at lower temperatures or with less amounts of alloying elements. Shida and Moroish criteria [3] suggest that the tendency of intergranular oxidation would be insensitive to temperatures. However, less Cr in candidate alloys would facilitate the intergranular oxidation. Less Cr will deplete Cr along grain boundaries faster, which, in turn, allows faster oxygen transport.

For quantitative predictions of internal oxidation and intergranular oxidation, kinetic data for Fe-1Mn, Fe-1Mn-1C, Fe-10Cr-32Ni, and stainless steels above 600 C are extrapolated to 150 and 200 C for up to 10,000 years. The extrapolation uses the parabolic law from the Wagner theory. The calculation chooses the activation energy of 20.2 kcal/mol-K for the grain boundary diffusion of oxygen as a lower bound [4]. The results show thin penetrations, a maximum of 188 $\mu$m.

However, the data quoted were obtained above 600 C at which mobile species include not only interstitial oxygen ions but also substitutional metal ions. At lower temperatures, substitutional metal ions are expected to be frozen. If only interstitial oxygen ions are allowed to move, the actual penetration would be deeper than the case of simultaneous diffusion of oxygen ions and metal ions.

To bound this fast penetration, the diffusional penetration of oxygen in grain boundaries is calculated at 150 and 200 C for up to 10,000 years. For the calculation, an existing mathematical model by

Oishi and Ichimura [5] is used. This model calculates simultaneous oxygen diffusion in the matrix and the grain boundary. Diffusion distance, (diffusivity times time)$^{1/2}$, is also calculated to bound the uncertainties associated with the oxide formation during the oxygen diffusion. Table shows calculated results using the Oishi and Ichimura model. Oxygen may penetrate through the outer container under extreme conditions. Using the same parameters, the diffusion distances are much longer ranging from 0.17 to 190 cm. Extreme conditions mean that parameters chosen may be lower bound values. For instance, if the activation energy of 32.3 kcal/mol-K instead of 20.2 kcal/mol-K is used, the diffusion distance will be decreased by more than a factor of 100.

Table. Calculated Penetration Distance (cm) for 10,000 Years Using Oishi and Ichimura Model [5]*

| $D_{go}$** | $2x10^{-3}$ | $2x10^{-2}$ | $2x10^{-1}$ | 2 | 2x10 | $2x10^{2}$ |
|---|---|---|---|---|---|---|
| 200 C | . $4.3x10^{-2}$ | 0.14 | 0.43 | 1.4 | 4.3 | 14 |
| 150 C | $5.8x10^{-3}$ | $1.8x10^{-2}$ | $5.8x10^{-2}$ | 0.18 | 0.58 | 1.8 |

* : Activation Energy of Grain Boundary Diffusivity is 20.2 kcal/mol-K. At 250 C, the penetration exceeded 10 cm for all cases.

**: Pre-exponential Term in Grain Boundary Diffusivity of Oxygen (cm/sec$^2$)

Finally, the consequences of unprotective oxidation, internal oxidation and intergranular oxidation are discussed. The consequences include direct container breach, degradation of mechanical properties, oxygen embrittlement, and easy initiation of localized aqueous corrosion. For more quantitative judgments, future necessary work is also proposed.

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[1] Stahl, D., 1993, Waste Package Corrosion Inputs, CRWMS M&O Interoffice Correspondence, TRW Environmental Safety Systems, Inc., Las Vegas, NV.

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MRS MATERIALS RESEARCH SOCIETY

# MRS 1996 FALL MEETING
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Submitted to Symposium (Letter) W. Gray

Symposium Title: Scientific Basis for Nuclear Waste Management, XX

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