DRY OXIDATION OF WASTE PACKAGE MATERIALS

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ABSTRACT

This report preliminarily 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 a potential for localized attack by dry oxidation. Localized dry
oxidation may prevent guaranteeing the container integrity for extended
periods. Examples of data on unprotective external oxidation, internal
oxidation, and intergranular oxidation are presented, derived from
high-temperature data for 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. Possible consequences of this potential oxygen penetration are
addressed on container life. Future work essential for the derivation of more
quantitative judgments is also proposed.

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1. INTRODUCTION

The implementation of the Nuclear Regulatory Commission's Key Technical Issue (KTI) for the Container Life and Source Term evaluates and conducts sensitivity analyses on the performance of the U. S. Department of Energy's (DOE's) Engineered Barrier System (EBS) for the mined geological disposal system (MGDS) planned at the Yucca Mountain (YM) repository site. A technical assessment requirement of this KTI is to evaluate the interaction of the waste container with gaseous oxygen, in potential dry environments. The container is the primary EBS component.

The container performance for the initial several thousand years is extremely important in the current DOE strategy for waste containment and isolation for the proposed YM repository [TRW Environmental safety Systems, 1995a]. There are several hypotheses that could demonstrate that radioactive waste can be isolated for long periods of time. One of them is that environments near the container could be dry, to prevent aqueous corrosion of the container. The heat from the radioactivity decay will cause low relative humidity (RH) and thus prevent an aqueous film from forming on container surfaces. Currently, an RH of ~70 percent is considered necessary for the onset of aqueous corrosion [TRW Environmental safety Systems, 1995b]. Modeling of the relative humidity near the container for the MGDS planned at the YM repository site, predicts an RH of less than ~70 percent, for several hundred years, to over 10,000 years, depending on the areal mass loading [TRW Environmental safety Systems, 1995b].

The current DOE repository concept proposes two concentric containers (overpacks) surrounding the multi-purpose canister or the uncanistered spent fuel [TRW Environmental safety Systems, 1994]. The primary candidate material for the inner container is alloy 825, which is a Ni-based and highly corrosion-resistant alloy. The outer container will be made from a corrosion-allowance material. Corrosion-allowance materials are thick-walled, and are expected to corrode slowly and predictably over time in aqueous environments. DOE selected three candidate materials for the outer container: (i) a wrought C-Mn steel, A516 Grade 55; (ii) a centrifugally cast C steel, similar in chemical composition to A516 Grade 55 steel; and (iii) a low-alloy steel, A387 Grade 22. The nominal chemical compositions of these steels are listed in Table (1).

Under dry conditions of an RH of less than 70 percent, one degradation mode of the outer container is dry oxidation caused by the interaction with gaseous oxygen in air. The YM repository site is considered buffered with air, mainly by fractured hostrocks. Currently, DOE postulates that dry oxidation of the outer container would be negligible for the MGDS planned at the YM repository site: at 200 C, 0.40, 0.86, and 1.84 μm, after 100, 1000, and 10,000 years, respectively [Stahl, 1993]. However, this assessment is based on uniform oxidation of carbon steels, observed at moderately elevated temperatures of 454 and 538 C. At temperatures above 600 C, iron-based alloys often show localized dry oxidation [Newcomb and Stobbs, 1991]. This localized oxidation is normally much deeper than the uniform oxidation. Therefore, if localized oxidation takes place under repository conditions, dry environments would not guarantee container integrity for extended periods.

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Table (1). Chemical Composition of A516 Grade 55 and A387 Grade 22 Steels [Cragnolino and others, 1996]

Steel	Element (wt.%)						
	C	Mn	Si	Cr	Mo	S	P
A516 Grade 55	<0.24[a]	0.55-1.30[b]	0.13-0.45	-	-	0.035 max	0.035 max
A387 Grade 22	<0.17[a]	0.25-0.66[b]	0.50 max	1.88-2.62[b]	0.85-1.15[b]	0.035 max	0.035 max

[a]: 100 to 200-mm-thick plate.   [b]: Product analysis.

This report conducts a preliminary evaluation of the dry oxidation of the outer container. The evaluation is based on the available literature related to the candidate materials for the outer container for the MGDS planned at the YM repository site. The results of this evaluation will be used in Engineered Barrier System Performance Assessment Codes (EBSPAC) as the bases for the review of DOE assessments of container life.

2. ISSUES INVOLVED IN DRY OXIDATION

Dry oxidation in alloys has been studied mostly at high temperatures above 600 C over laboratory time scales. At these temperatures and times, a major issue in dry oxidation has been whether the formed oxide scale protects against further oxidation. When the oxide forms uniformly, the oxide can protect the metal matrix underneath the uniform oxide against further oxidation. The oxide can prevent or slow diffusion of mobile species such as oxygen or metallic ions necessary for the oxide growth. The diffusion of these mobile species in oxides is normally slower than that in metals.

Unfortunately, the oxide formed is not always protective. A large-volume expansion can accompany the oxidation. This volume expansion, in turn, can create stresses, possibly leading to mechanical failure of the oxide. Even without mechanical failure, the oxide may grow continuously by the formation of unprotective (porous, amorphous, defective, or other crystalline) oxide on top of protective oxide (or of metal). Diffusion of mobile species will not be retarded effectively through unprotective oxide. Once this complex structure is formed, metal could be oxidized at a constant rate.

A more detrimental mode of oxidation is localized oxidation. The oxide forms as islands below the uniform oxide (a schematic and an example are shown in Figure (1)). This island formation is called internal oxidation, whereas the uniform oxidation on the surface is called external oxidation. In the internal oxidation, much deeper overall penetration (or affected thickness of metal) is expected than in the external oxidation. Another type of localized oxidation is the preferential oxidation along grain boundaries. This mode is called intergranular oxidation (a schematic and an example are shown in Figure

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(1)). The intergranular oxidation can be deeper than the internal oxidation because the intergranular oxidation is more localized. The mechanistic basis for internal oxidation is better established than that for intergranular oxidation.

Figure (1). A Schematic Illustration of Various Modes of Oxidation and An Example for Fe-21Cr-32Ni (Cross-section after oxidation at 900 C for 3000 hours) [Shida and Moroishi, 1992]
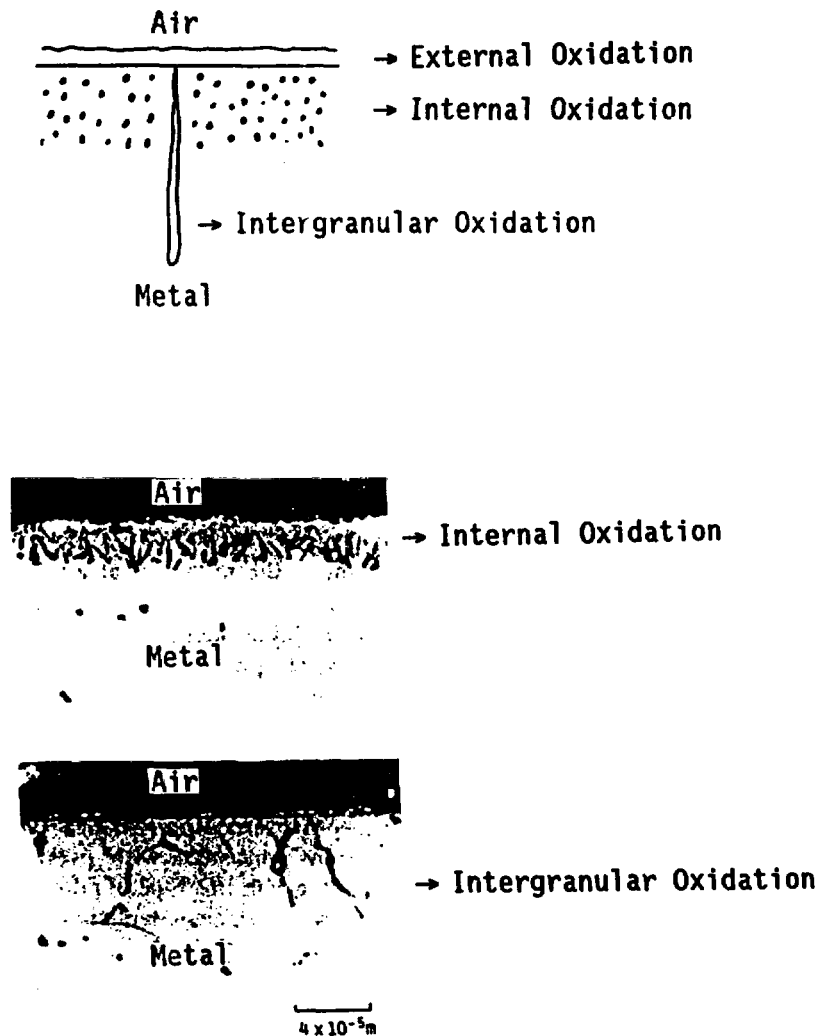
Wagner originally proposed theoretical criteria for the transition from internal oxidation to external oxidation in the binary alloy system [Wagner,1959]. The Wagner criteria have been further modified in more realistic situations such as the ternary alloy system [Nesbitt, 1989]. The Wagner criteria are:

(a) Diffusion of alloying element (cation) and diffusion of oxygen should be balanced for external oxidation. If oxygen diffusion is faster than cation diffusion, internal oxidation is expected;

(b) Oxide should form in a significant amount for a continuous blanket formation of oxide layer. Otherwise, oxygen will penetrate locally, resulting in internal oxidation; and

(c) Oxygen solubility should be minimal so that all available oxygen can be consumed in the growth of the external oxide. From this oxygen consumption, oxygen penetration beyond the external oxide should be prevented.

The general theories of solid state transformation identify the physical parameters involved in evaluating the above Wagner criteria. The parameters are: (i) mobile species: identity, solubility and availability, reactivity, and diffusivity; and (ii) thermodynamic stability of oxides and protectiveness of external oxides.

Whereas internal oxidation is often interpreted by Wagner theory, intergranular oxidation is not well-understood. Only one criterion proposed by Shida and Moroishi is available [Shida and Moroishi, 1992a]. They postulate that intergranular oxidation takes place by vacancy condensation along grain boundaries during selective removal of alloying elements. Condensed vacancy can compensate for the extra volume associated with the oxidation.

Given the presumption of (a) unprotective external oxide, (b) internal oxidation; and (c) intergranular oxidation, the consequences of these oxidation modes in container life need to be assessed. Oxidation penetration may itself breach the container. Even if not breached, internal embrittlement or stress concentration by the oxidation may lead to easier mechanical failure at lower stress levels than the normal case of no oxidation. Also, a partial container penetration by oxidation could lead to an early onset of various kinds of aqueous corrosion, when aqueous environments form, subsequently. Partial container penetration can initiate pitting corrosion, stress corrosion, and hydrogen embrittlement, readily.

Regarding the consequences other than the direct breach of the container, aqueous corrosion has been assessed extensively for candidate container materials [Sridhar and others, 1994]. On the other hand, there have been very few discussions about the degradation of mechanical properties by oxidation. With internal oxidation, alloy can be strengthened or weakened. If the volume fraction of oxides is appropriately small and oxides are distributed uniformly, alloys could be strengthened (i.e., dispersion strengthening). On the other hand, if the volume fraction of oxides is large and the associated

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stress is high, the alloys could be embrittled. Similarly, intergranular oxidation can breach or embrittle the container by oxide formation along grain boundaries. Besides the direct breach or the embrittlement, any localized attack may lead to stress concentration, causing easy mechanical failure.

Intergranular oxidation can be more generalized. Besides grain boundary oxidation, other embrittlement mechanisms in grain boundaries have been reported [Woodford and Bricknell, 1983]. In this case, oxygen penetrates intergranularly. This penetration leads to: (a) oxygen sorption in grain boundaries; (b) formation of cavities such as CO gas or void; and (c) release of other embrittling elements by oxidation of compounds such as sulfides [Bricknell and Woodford, 1980]. This intergranular embrittlement of (a), (b), and (c), and embrittlement by intergranular oxidation, are called, specifically, oxygen embrittlement. (There is another potential embrittlement caused by gases in dry environments. The responsible gas for this embrittlement can be hydrogen from moisture [Stoloff and Liu, 1994]. This topic, however, is beyond the scope of the subject of dry oxidation.)

The aforementioned bases for external oxidation, internal oxidation, and intergranular oxidation, have been obtained from observations in laboratory time scales at higher temperatures than repository temperatures. Similarly, these bases have been obtained from non-candidate alloys having different alloying elements from those of candidate alloys. Al and Cr are generally most effective to prevent deeper penetration by oxidation. The next most effective group includes Ni, Mo, and Mn. In most cases, the candidate alloys have much lower concentrations of these alloying elements than the non-candidate alloys studied extensively for high-temperature oxidation.

Therefore, it is necessary to reassess these bases for candidate alloys under repository conditions. In Section 3.1, examples of data for non-candidate alloys, extensively studied at higher temperatures, will be presented. Based on this presentation, examples of assessments will be made qualitatively for candidate alloys under repository conditions.

3. EXAMPLES OF EXPERIMENTAL DATA AND SAMPLE EVALUATIONS

3.1. Examples of Experimental Data

3.1.1. External Oxidation

In one study, high-purity iron is protected (or passivated) by air oxidation at room temperature. Over 20 years, oxide film grew to a thickness of no more than (5-6) nm [Frankental and others, 1985]. Stahl estimated a uniform attack of 14 and 38 μm for about 1 year at 454 and 538 C from one set of data in the ASM Handbook for carbon steels [Stahl, 1993]. All the high-temperature data below were obtained in a laboratory time scale of less than 1 year and were of the type of diffusion-limited kinetics. At (800-1000) C and an oxygen pressure of (4×10^{-4}-1) atm, a duplex scale of wüstite and magnetite grew in iron [Goursat and Smeltzer, 1973]. Growth of whiskers and platelets of Hematite followed the duplex scale formation. Fe-25Al developed protective alpha-Al_2O_3 scale at 1100 C and an oxygen pressure of ~7×10^{-6} atm [Prescott and

others, 1992]. Fe-15Cr-160(ppm)S showed cracked and spalled scale with cavities after heating at 900 C in 10^{-5} atm O_2 and subsequent cooling [Grabke and others, 1991]. Sulphur was segregated in this test. Fe-23Cr-5Al-0.2Zr at 1200 C in oxygen also showed cracks in oxide [Jedlinski, 1991]. Shida and Moroishi observed scale spallation for Fe-21Cr-32Ni during oxidation in an impure helium environment at (700-900) C [Shida and Moroishi, 1992a]. Newcomb and Stobbs observed that the scales formed on Fe-10Cr-34Ni at 600 C were mainly magnetite and hematite, and were not protective [Newcomb and Stobbs, 1991].

The oxidation of iron-nickel-based alloys -- Incoloy DS (Fe-33.1Ni-18.7Cr); Incoloy 800H (Fe-30.5Ni-21.8Cr); and Incoloy 825 (Fe-36.5Ni-21.3Cr) -- in oxygen at 800 C and 1000 C, resulted in a significant scale spallation [Wei and Stott, 1989]. The oxide for alloys of alloying elements in iron-based alloys is not always protective either. For instance, nickel-based alloys at 1000 C in oxygen showed separation of oxide from metal and large strain [Hou and Stringer, 1991]. In the experiments quoted above, the mechanical failure of oxide is sometimes assisted by contaminants such as sulphur. Besides mechanical failure, other mechanisms of the unprotective characteristics of oxide have been also identified. For instance, short-circuit diffusions along grain boundaries and amorphous structures were observed [Frankental and others; 1985, Goursat and Smeltzer, 1973].

3.1.2. Internal Oxidation

Mayer and Smeltzer observed internal oxidation for Fe-1Mn and Fe-1Mn-1C in $CO-CO_2$ atmosphere at 1000 C [Mayer and Smeltzer, 1973]. A model based on oxygen diffusion within the internal oxidation zone accounted for the observed kinetics of internal oxidation. Shida and Moroishi observed internal oxidation for Fe-21Cr-32Ni in an impure helium environment at (700-900) C [Shida and Moroishi, 1992a]. Newcomb and Stobbs observed internal oxidation at and around a grain boundary for Fe-10Cr-34Ni in air at 600 C [Newcomb and Stobbs, 1991]. It was believed that easy ingress of oxidant around a grain boundary was the cause of this. Stainless steels of Fe-20Cr-19Ni-4Al and type 314 (Fe-25Cr-19Ni) also showed internal oxidation in air at 1100 C [Tasovac and others, 1989]. Iron-nickel-based alloys, Incoloy DS, Incoloy 800H, and Incoloy 825 in oxygen at 800 and 1000 C showed internal oxide precipitates [Wei and Stott, 1989]. Non-iron-based alloy (of alloying elements in iron-based alloys) also showed internal oxidation: (a) Ni-15.1Cr-1.1Al and Ni-28.8Cr-1.0Al in oxygen at 1000 and 1200 C [Stott and others, 1981]; (b) Ni-Al and Ni-Cr alloys in oxygen at (800-1100) C [Whittle and others, 1982]. A model was developed to incorporate enhanced diffusion of oxygen along the incoherent interface between the internal oxide and the alloy; and (c) reviewed of data on the effects of alloying elements for non-iron based alloys [Stott, 1992].

3.1.3. Intergranular Oxidation

Shida and Moroishi observed intergranular oxidation for Fe-21Cr-32Ni in an impure helium environment at (700-900) C [Shida and Moroishi, 1992a]. Vacancy condensation along grain boundaries was proposed to be responsible for the intergranular oxidation. Newcomb and Stobbs observed intergranular oxidation

in Fe-10Cr-34Ni in air at 600 C [Newcomb and Stobbs, 1991]. Easy ingress of oxidant around a grain boundary was believed responsible for the observation. Iron-nickel-based alloys -- Incoloy DS, Incoloy 800H, and Incoloy 825 -- in oxygen at 800 and 1000 C, showed intergranular oxidation [Wei and Stott, 1989]. This study suggested that intergranular oxidation is correlated with the depth of chromium depletion near grain boundaries. Stainless steels of Fe-20Cr-19Ni-4Al and type 314 showed intergranular oxidation [Otsuka and Fujikawa, 1991, Tasovac and others, 1989]. Non-iron based alloys also showed intergranular oxidation: (a) Ni-15.1Cr-1.1Al and Ni-28.8Cr-1.0Al in oxygen at 1000 and 1200 C [Stott and others, 1981]; (b) Ni-Al and Ni-Cr alloys in oxygen at (800-1100) C [Whittle and others, 1982]; and (c) alloy 800 (Fe-32.4Ni-21.1Cr) in impure helium at (700-900) C [Shida and Moroishi, 1992a].

3.1.4. Mechanical Properties and Oxygen Embrittlement

Stainless steels of Fe-20Cr-19Ni-4Al and type 314 showed a significant gdegradation of mechanical properties, when subjected to 1100 C in air [Tasovac and others, 1989]. More than 50 percent decrease in elongation, reduction of area and Charpy impact value were observed after five cycles of 120 hours each, with intermittent cooling to room temperature. This degradation of mechanical properties was caused by uniform and intergranular oxidation as well as by structural transformation. In the intermetallic phases, a severe intergranular disintegration called "pest" is well-known [Grabke and others, 1991]

Woodford and Bricknell reviewed oxygen embrittlement of iron-based alloys [Woodford and Bricknell, 1983]: Fe-19Cr-25.2Ni-0.92Si-1.55Ti steel showed an appreciable loss of ductility after exposure at 900 C for 6000 hours and subsequent burst tests at 750 to 850; and Fe-Ni-Co alloys also showed a substantial reduction in ductility after air exposure at 1000 C for 100 hours.

More extensive studies were made for Ni-based alloys Ni270 (99.98Ni). This alloy displayed embrittlement and intergranular fracture after exposure at 1000 C in air [Bricknell and Woodford, 1980]. This embrittlement manifests itself on a severe loss of tensile ductility, around 800 C, but with no loss in strength. Embrittlement also occurred in the other grades of Ni and superalloys. Exposure of IN738 (Ni-15.8Cr) in air at (900-1100) C produced a major loss in stress rupture life and ductility. Sensitivity to this environmental damage increases with decreasing test temperatures of (700-1000) C [Woodford, 1981].

3.2. Sample Evaluations

In this section, sample evaluations of external oxidation, internal oxidation, and intergranular oxidation are made. Diffusional oxidation is emphasized on a conservative basis because data for other mechanisms are scarce, especially for internal oxidation and intergranular oxidation. Non-diffusional oxidation may result in less oxidation penetration. In long-term periods, however, the non-diffusional oxidation is likely to shift to the diffusional oxidation.

3.2.1. External Oxidation

Calculations by Fromhold [Fromhold, 1976] suggested that electron tunneling currents across the protective oxide layer cease in iron as the layer grows. The oxide stopped growing at 2 to 3 nm of thickness. The voltage drop across the protective layer increases as the oxide grows. However, the growing protective oxide cannot hold a large voltage as the oxide layer becomes thicker. The large voltage developed will, in turn, limit the continuous growth of the protective oxide. Also, diffusion of mobile species (oxygen or metal ions) across the protective oxide slows down, as the oxide grows. The slow diffusion will, in turn, slow the growth of the protective oxide. Contrary to this trend, there is a thermodynamic driving force for continuous oxidation, because the oxide is more stable than metal.

To satisfy these opposite requirements, unprotective (porous, amorphous, defective, or other crystalline) oxide can grow on top of the protective oxide (or metal). Initially, other oxides may be of lower diffusion in a crystallographic scale (for example, hematite formation at low temperatures). Nevertheless, the oxide may become unprotective later, assisted by stress buildup, impurity segregation, or outward diffusion of metallic ions. In this way, a thin layer of the protective oxide can carry the voltage, and mobile species can diffuse continuously, resulting in a continuous oxide growth. This type of complex structure has been observed in atmospheric (aqueous) corrosion. Atmospheric corrosion and (dry) oxidation have many similarities. For instance, atmospheric corrosion and (dry) oxidation could both be electrochemical, facilitating the formation of complex structures by separating anodic and cathodic processes. Therefore, it is possible that complex oxide grows continuously at a constant rate.

The stress buildup may disintegrate the oxide. Large-volume changes accompany the oxidation of iron and alloying elements. The volume change would be nearly 30 percent for Fe, Cr, Mo, and Mn [CRC Press, 1975a]. The stress associated with this volume change may be estimated by the linear elastic formula [McClintock and Argon, 1966]

$$\sigma = \frac{E}{(1 - 2 v_s)} \frac{\Delta V}{3 V} \tag{1}$$

"$\Delta V/V$" represents volume expansion, "E" is Young's modulus, and "v_s" is Poisson's ratio. For most ceramics, the "E" value is (10^4 - 10^5) MPa; the "v_s" value is (0.2 - 0.3); and tensile strength is ~ 10^2 MPa [CRC Press, 1975b; CRC Press, 1992]. Therefore, for a 30 percent of volume expansion, the stress will be about 20 percent of the "E" value from this equation. Therefore, the oxide becomes unstable mechanically. This stress also exceeds the tensile stress of candidate alloys ((380-690) MPa) [Cragnolino and others, 1996].

This assessment may be over-simplified. For instance, stress buildup can be recovered, partly, at elevated temperatures. Nevertheless, the calculated results agree with experimental data, qualitatively. As presented previously, in Section 3.1.1, such mechanical failures were observed during oxidation. At lower repository temperatures, there will be less stress recovery.

Consequently, the oxide formed will become more unstable, mechanically.

Despite the aforementioned concerns regarding unprotective nature of oxide, currently available data shows very thin penetration by uniform dry oxidation in carbon steels. Stahl extrapolated data for carbon steels in a steam atmosphere at 454 and 538 C, to 200 C. After 10,000 years, penetration by oxidation was only 1.84 μm [Stahl, 1993]. However, it is noted that the experimental data were obtained at higher temperatures than repository temperatures. This could have resulted in underestimates of the actual penetration, for extended periods, at repository temperatures. Therefore, the following two sections assume that the external scale is not protective, in evaluating internal oxidation and intergranular oxidation. This is a conservative approach because iron oxides (for example, hematite) themselves may become protective at lower temperatures.

3.2.2. Internal Oxidation

Wagner developed the first criterion for the bulk solute concentration, "$N^o_{B(min)}$," necessary for sustaining the growth of an external solute oxide under an idealized condition [interpretation by Nesbitt, 1989]:

$$N^o_{B(min)} \rangle (\pi \, k_c / 2 \, D_{AB})^{1/2} \tag{2}$$

"k_c" is the parabolic rate constant in oxide growth kinetics and "D_{AB}" is the interdiffusion coefficient in the A-B binary alloy. Both "k_c" and "D_{AB}" have Arrhenius relations of the same dimension. Wagner also developed an additional model for the case where a protective oxide scale is not formed, resulting in internal oxidation of solute. The bulk concentration of solute for the oxide protection, N^o_B, is

$$N^o_B = [VF] \; (V_{AB}/V_{OX}) \; \gamma \; (\pi \, \phi)^{1/2} \exp(\gamma^2 \, \phi) \; erfc(\gamma \, \phi^{1/2}) \tag{3}$$

where "[VF]" the volume fraction of solute precipitates; "V_{AB}" is the molar volume of the alloy; "V_{OX}" is the molar volume of the oxide; "ϕ" is the ratio of the diffusivity of oxygen in the alloy to the interdiffusion coefficient in the alloy (i.e., "D_o/D_{AB}"); and the parameter "γ" is defined by the equation

$$\frac{N_o^s}{v \, N^o_B} = \frac{\exp(\gamma^2) \; erf(\gamma)}{\phi^{1/2} \exp(\gamma^2 \, \phi) \; erfc(\gamma \, \phi^{1/2})} \tag{4}$$

where "N_o^s" is the mole fraction of oxygen in the alloy at the external alloy surface and "v" is the ratio of oxygen atoms to solute atoms in the oxide. The width of the internally oxidized zone, or subscale region, "ξ," is defined as

$$\xi = 2 \, \gamma \; (D_o \, t)^{1/2} \tag{5}$$

In the first criterion of Eq.(2), the "$N^o_{B(min)}$" value is likely to increase as

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temperature decreases, because the activation energy for "k_c" is likely to be smaller than that for "D_{AB}." For instance, in Stahl's correlation of oxide growth in carbon steels, the activation energy was 14 kcal/mol-K [Stahl, 1993]. This value is much lower than activation energies for metals as shown in Table (2). Oxygen is the interstitial mobile species that is likely to be responsible for "k_c." On the other hand, metal ions are substitutional diffusion species that are responsible for "D_{AB}." Normally, interstitial diffusion is faster than substitutional diffusion. Table (2) tabulates pertinent data on the activation energy of diffusivity, showing this trend. In addition, the oxide layer is often of an amorpphous structure and cracked, resulting in low activation energies for the oxide growth. The increase of the "$N^o_{B(min)}$" value means easier internal oxidation. Regarding the effect of alloying elements, the candidate alloys have lower concentrations of alloying elements than do the non-candidate alloys studied, in most cases. This means that candidate alloys are more susceptible to internal oxidation because Eq.(2) requires a certain amount of alloying elements, to avoid internal oxidation.

Table (2). Activation Energies (kcal/mol-K) of Various Diffusivities

Matrix	Diffusion of Metal	Diffusion of Oxygen
FeO Fe_3O_4 Fe_2O_3 Stainless Steel Iron	Fe: 30 (800 - 1100 C) 55 (750 - 1000 C) 100 (950 - 1050 C) 67 (800 - 1200 C) 68	17 (300 - 550 C) 78,146 (900 - 1250C) 40 27 (bcc)(950 -1150C)
Cr_2O_3 Iron Stainless Steel Fe-25Cr-5Ni	Cr: 100 (1150 - 1500 C) 70 ~60 51 (600 - 1000 C)	101 (1200 - 1500 C)
MnO_2 Stainless Steel Fe-17Cr-12Ni-2.5Mo	Mn: 30-35 (900 - 1100 C) 62 62 (750 - 1200 C)	
Stainless Steel Mo	Mo: 34 (930 - 1200 C)	31

References [Kedves and Beke, 1983; Wöhlbier, 1981-1975; Kofstad, 1972]

The second criterion of Eq.(3) implies that the change of the "N^o_B" value depends on the magnitude of "γ" and "Φ" values. If the solubility change (equivalent to "γ" change from N_o^s change in Eq.(4)) is less sensitive to diffusivity change "Φ", as temperature decreases, more alloying elements are needed for external oxidation. Normally activation energies for solubility are less than those for diffusivity. Also, the "γ" value varies very little compared with "Φ," functionally in Eq.(4). Therefore, alloys are more

susceptible to internal oxidation, as temperature decreases. Regarding the effect of alloying elements, candidate alloys are more susceptible to internal oxidation than non-candidate alloys because Eq.(3) requires a certain amount of alloying element to avoid internal oxidation.

Although this qualitative analysis suggests more likelihood of internal oxidation at lower temperatures, the extrapolated values of high-temperature data show thin penetration under repository conditions. Table (3) tabulates pertinent high-temperature data of internal oxidation for non-candidate alloys and their extrapolated values at 150 and 200 C for 10,000 years. For the extrapolation, Eq.(5) with constant "γ" was used. The activation energy used was 20.2 kcal/mol-K for the grain boundary diffusion of oxygen (more details are in Section 3.2.3). In this table, results of Fe-1Mn and Fe-1Mn-1C show that lowering the concentration of alloying elements increases the tendency of internal oxidation.

The detailed evaluation of Eq.(5) is more complicated. Usually, Eq.(5) is used in one of two limiting forms [Whittle and others, 1982]: (a) $\gamma \propto (N_o^s/N_B^o)^{1/2}$ and (b) $\gamma \propto \phi^{1/2} (N_o^s/N_B^o)$. The oxygen solubility, N_o^s, is not known at various temperatures. Especially when other oxides such as Cr_2O_3 form in iron, the solubility value decreases significantly. For this reason, oxygen solubility often shows negative activation energies (i.e., solubility increases as temperature decreases.) Therefore, possibly both limiting cases of (a) and (b) are present. In both cases, if the "γ" value decreases at lower temperatures, the calculation in Table (3) would be an upper bound. On the other hand, if the "γ" value increases at lower temperatures, a thicker oxide layer would be projected. In addition, there would be a limited retardation of oxygen diffusion by the external oxide. The maximum penetration, however, would be no more than the diffusion distance of oxygen. The diffusion distance of oxygen is discussed in Section 3.2.3.

There are further questions regarding whether calculated values in Table (3) for higher-temperature data represent oxidation kinetics at repository temperatures. Data on high-temperature oxidation result from diffusion of both metal and oxygen. On the other hand, only oxygen is expected to move at repository temperatures. Therefore, if only oxygen moves at high temperatures, the penetration in Table (3) could be much deeper. For instance, there could be deeper oxygen diffusion along grain boundaries in iron (there will be more details on this in Section 3.2.3).

The Wagner theory has been modified by many authors to improve various assumptions he made. Nesbitt extended the theory to the ternary alloy system with external scale growth [Nesbitt, 1989]. Wang and his coworkers considered thermodynamics and kinetics involving receding of the alloy/scale interface [Wang and others, 1991]. Whittle and his coworkers modified the diffusion paths of mobile species, including fast diffusion paths of the interface between metal and precipitate [Whittle and others, 1982]. Smeltzer and his coworkers presented the criteria with more realistic diffusivity and solubility values [Guan and Smeltzer, 1994; Smeltzer and Whittle, 1978].

This report has exercised those modified criteria to judge whether internal oxidation would be more likely at lower temperatures and alloying elements.

This exercise has not altered the aforementioned judgment made with Wager's original criteria. Therefore, Wagner's original criteria has been presented in this report for simplicity. Finally, it is mentioned that Wagner's criteria does not assume any range of alloying-element concentration or of temperature. In low-alloy steels, protective scales can form by sufficient amounts of alloying elements diffused outward for a geological period at low temperatures. As long as the physical processes for oxidation do not change, the criteria can be used.

Table (3). Data on Internal and Intergranular Oxidation and Their Extrapolated Values under Repository Conditions

		Stainless Steels	Fe-1Mn and Fe-1Mn-1C	Fe-10Cr-34Ni	Fe-21Cr-32Ni (varying Al addition)	Stainless steels of Fe-20Cr-19Ni-4Al and type 314
Mode		Internal	Internal	Inter-granular	Internal (a) Inter-granular (b)	internal
Temperature (C)		700	1000	600	900	1100
Time (hour)		1000	30	1000	3000	360
Penetration (μm)		100	90	40	20 (a) 90 (b)	30.
Reference		Otsuka and Fujikawa, 1991	Mayer and Smeltzer, 1973	Newcomb and Stobbs, 1991	Shida and Moroishi, 1992	Tasovac, 1989
P^* (μm)	200 C	123	188	89	7 (a) 32 (b)	14
	150 C	35	53	25	2 (a) 9 (b)	4

*: Extrapolated penetration for 10,000 years.

3.2.3. Intergranular Oxidation

Theories for intergranular oxidation have not been fully developed. However, the general principles of internal oxidation could be used for the evaluation of intergranular oxidation. An additional factor in intergranular oxidation may be the fast diffusion of mobile species along existing grain boundaries.

Although internal oxidation does not include grain boundary diffusion specifically, it is often explained by another equivalent fast diffusivity. This another fast diffusivity is the interface diffusivity between oxide and metal. Diffusion along grain boundaries or interfaces is fast because regular crystalline structures are not present. Interface diffusion can be even faster than grain boundary diffusion.

Experimental results of intergranular oxidation (quoted in Section 3.1.3) discussed fast oxygen diffusion along grain boundaries or along interfaces between the grain boundary oxide and the metal matrix. Whereas substitutional metallic species are expected to be frozen at lower temperatures, fast oxygen diffusion along grain boundaries would remain even at lower temperatures. Therefore, a calculation will be made below, regarding this mechanism of oxygen diffusion along grain boundaries.

The first calculation was a simple extrapolation of the data, in Table (3), for intergranular oxidation. This extrapolation uses the diffusion distance relation as in the internal oxidation. The activation energy used was 20.2 kcal/mol-K for the grain boundary diffusion of oxygen, as approximated below. The results show thin penetration at 150 and 200 C for 10,000 years. The second calculation was to determine the distance of oxygen penetration or the oxygen diffusion distance along grain boundaries in metal. This case is not based on the data in Table (3) and oxygen is considered the only mobile species from the beginning of oxidation.

For mathematical simplicity, the calculation of the distance of oxygen penetration adopted an existing formula for the simultaneous diffusion of oxygen along grain boundaries and within grain matrices in an infinite one-dimensional body [Oishi and Ichimura, 1979]. Primary assumptions involved in this formula are: (a) the effects of external oxide are negligible; (b) oxygen diffuses in its metallic phase near the interface between grain boundary oxide and metal; and (c) oxygen also diffuses into metallic matrices from grain boundaries. This formula gives the distance of oxygen penetration in metal thickness as:

$$Y_p = [\frac{4\ D_l}{r_g\ \delta\ D_g}\sum_{n=1}^{\infty}\exp(-\frac{D_l\ n^2\ \pi^2\ t}{r_g^2})]^{-1/2} \tag{6}$$

where "D_l" is matrix diffusivity; "D_g" is grain boundary diffusivity; "δ" is the thickness of grain boundary; and "r_g" is grain radius.

Table (4) shows the calculated distance of oxygen penetration using Eq.(6). The calculation used "δ" ~0.7 nm [assuming the value from Lobnig and others, 1992] and "r_g"~ 10 μm for cast steel [Ahn and Soo, 1983, 1984], and "D_l = 5.75x10$^{-40,400g(kcal/mol-K)/RT}$" was from measurements for oxygen interstitials in gamma iron [Kedves and Beke, 1983]. "D_g" values were varied. The activation energy of "D_g" varied from 0.5 to 0.8 of that of "D_l" from data on various metals [assumed from Shida and Moroish, 1992b; Whittle and others, 1982; Shewmon, 1963]. Because oxygen is interstitial, "D_g" and "D_l" are less distinctive compared with substitutionals. Nevertheless, the lower-bound value of 0.5 was included because grain boundaries could open up because of

stress buildup.

The pre-exponential term of "D_g" was determined assuming that the "D_g" value and the "D_l" value have a certain ratio at high temperatures. The (D_g/D_l) varied from 1 to 10^5 [Lobnig and others, 1992; Whittle and others, 1982] at 1000 C. This variation determines the pre-exponential term in grain boundary diffusivity of oxygen (cm/sec^2), "D_{go}." Varying (D_g/D_l) ratio and their activation energies results in various values of pre-exponential terms. This variation of pre-exponential terms comes strictly from data uncertainties rather than from uncertainties associated with diffusion processes.

Table (4) shows an extreme case of calculated results at 150 and 200 C, suggesting the possibility of significant oxygen penetration through the container. If the activation energy of "D_g" is chosen to be 32.3 kcal/mol-K, the equivalent penetration will be much shorter in a couple of orders of magnitude. At 250 C, however, the penetration was infinite for both activation energies for grain boundary diffusion. If the activation energy of "D_l" is increased to 55.0 kcal/mol-K, the penetration becomes less in general. However, in certain cases, the penetration could be significant at the even lower temperature of 100 C. This is probably because the matrix diffusion of oxygen is almost frozen, allowing only grain boundary diffusion.

Table (4). Calculated Penetration Distance (cm) for 10,000 Years Using Eq.(6)*

D_{go}**	2×10^{-3}	2×10^{-2}	2×10^{-1}	2	2×10	2×10^2
200 C	4.3×10^{-2}	0.14	0.43	1.4	4.3	14
150 C	5.8×10^{-3}	1.8×10^{-2}	5.8×10^{-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.
** : cm^2/sec.

In this formula of Eq.(6), oxide formation was not considered for two reasons. The first is that oxide may never form. The oxyge diffusion may simply cause oxygen embrittlement in a dissolved state. The second is that analytical solution is unlikely to exist with oxide formation along grain boundaries and within matrices. In addition, the oxide formation kinetics are not known at lower temperatures. The kinetics can be non-diffusional. Certainly, numerical thought experiments can be done for further clarification. Slow diffusion in oxide could localize the penetration more along grain boundaries. On the other hand, oxygen consumption in oxide could localize the penetration less. Also, there would be a limited retardation of oxygen diffusion by the external oxide. To bound these uncertainties, an extremely simple diffusion distance (square-root of diffusivity x time) is also provided. The calculated results of the diffusion distance in Tables (5) and (6) suggest a significant penetration of oxygen at 150 and 200 C. The calculation used the activation energies for grain boundary diffusion of 20.2 and 32.3 kcal/mol-K.

Grain boundary oxidation would be facilitated when vacancies injected by Kirkendall effects could accommodate the stress built up on oxidation [Shida

and Moroishi, 1992a; Stott and others, 1982]. Shida and Moroishi established a quantitative criterion for this mechanism. They used oxygen taken up by internal oxides and the external oxide, as the criterion. Then, the criterion was applied for Fe-21Cr-32Ni, varying aluminum concentration. Their criterion is expected to be insensitive to temperature because the oxide stoichiometry will not change. Therefore, the tendency of intergranular oxidation at high temperatures would remain at lower temperatures.

Another criterion presented in literature was that Cr could be depleted near grain boundaries for easy grain boundary oxidation. Candidate alloys have less Cr than non-candidate alloys studied at high temperatures. Lower Cr concentration would facilitate the grain boundary attack in candidate alloys. On the other hand, Cr depletion along grain boundaries would be slower at lower temperatures. If Cr diffusivity, $D_{Cr} = 6 \times 10^{-2} x e^{-50.9 \text{ kcal-mol-K/RT}}$ cm^2/sec (for Fe-25Cr-5Ni steel from [Wöhlbier, 1981 - 1975]), the diffusion distance for time t = 10,000 years, $(D_{Cr} \, t)^{1/2}$, would be ~ 3×10^{-7} cm at 200 C and 1×10^{-8} cm at 150 C. These values are very small but still can affect the chemistry of grain boundaries. Regarding the effects of other alloying elements, the principle of internal oxidation could be applied. According to this principle, less alloying elements generally would result in more grain boundary penetration.

Table (5). Calculated Penetration Distance (cm) for 10,000 Years[*] Using Square-Root of Diffusivity x Time (Activation Energy of Grain Boundary Diffusivity: 20.2 kcal/mol-K)

D_{go}[**]	2×10^{-3}	2×10^{-2}	2×10^{-1}	2	2×10	2×10^2
200 C	0.59	1.9	5.9	19	59	190
150 C	0.17	0.54	1.7	5.4	17	54

[*] : For 1000 years, the penetration will be decreased by a factor of $10^{0.5} = 3.2$.
[**]: cm/sec^2.

Table (6). Calculated Penetration Distance (cm) for 10,000 Years[*] Using Square-Root of Diffusivity times Time (Activation Energy of Grain Boundary Diffusivity: 32.3 kcal/mol-K)

D_{go}[**]	0.24	2.4	24	240	2,400	24,000
200 C	1.0×10^{-2}	3.2×10^{-2}	1.0×10^{-1}	3.2×10^{-2}	1.0	3.2
150 C	1.4×10^{-3}	4.4×10^{-3}	1.4×10^{-2}	4.4×10^{-2}	1.4×10^{-1}	4.4×10^{-1}

[*] : For 1000 years, the penetration will be decreased by a factor of $10^{0.5} = 3.2$.
[**]: cm/sec^2.

3.2.4. Mechanical Properties and Oxygen Embrittlement

If lower temperatures and lower alloying elements lead to easier internal or

intergranular oxidation, the degradation of mechanical properties would be more pronounced. At lower temperatures, fracture or impact properties are normally influenced by oxides more than at higher temperatures. This is because stress/strain recovery could be easier at higher temperatures.

The aforementioned mechanisms for oxygen embrittlement (other than oxide formation) have been identified for Ni-based alloys. Assuming that these mechanisms also govern oxygen embrittlement of iron-based alloys, the embrittlement behavior under repository conditions is considered. These mechanisms are oxygen sorption, void/gas formation, and release of other embrittling elements. Normally sorption isotherm implies that more oxygen will be sorbed at lower temperatures. For the case of void formation, prior oxide formation may be required. Once oxides form at lower temperatures, voids are likely to form. On the other hand, it is difficult to predict gas formation and release of embrittling elements because kinetics are slow, but time is long under repository conditions. The relative magnitudes of these opposite behavior are not assessed here.

4. CONCLUSIONS AND RECOMMENDATIONS

This report preliminarily evaluates dry oxidation of the candidate outer container for the MGDS planned at the YM repository site. Although uniform dry oxidation may not be significant under repository conditions, there is a potential for localized penetration by dry oxidation. This localized dry oxidation may prevent guaranteeing the container integrity for extended periods. The localized dry oxidation includes internal oxidation and intergranular oxidation. Examples of data on iron-based alloys above 600 C are presented and the data were extrapolated to the repository conditions by lowering temperatures and increasing times. The extrapolated values suggest very thin (at most 100 μm at 200 C) penetration by localized dry oxidation.

However, simple extrapolations may underestimate the real penetration. The dry oxidation can be more localized than that observed above 600 C for non-candidate alloys. Lower concentration of alloying elements and lower performance temperature, in candidate alloys, can be the main cause for this further localization. Additionally, if all metal ions are essentially frozen under repository conditions, the oxygen penetration can be deeper. Extreme diffusion calculations show that oxygen can penetrate through-10 cm container over 10,000 years, at 150 and 200 C. The consequences of this penetration were discussed, including container breach, easy mechanical failure, and oxygen embrittlement.

This report is a preliminary and scoping evaluation, therefore, a follow-up study is recommended. In the follow-up evaluation, all relevant data and theories, especially at low temperatures, should be interpreted more quantitatively, so that the models presented here (for instance, Eq.(6) for oxygen penetration) can be refined more realistically. For proper analytical assessments, experiments should be conducted to understand the mechanisms for low-temperature oxidation. Also, future work may need to focus on oxygen embrittlement (or hydrogen gas embrittlement) more quantitatively. There was very little quantitative evaluation, on this topic, in this report. If oxides

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do not form under repository conditions, the embrittlement may be a dominant failure mechanism in the dry performance of the outer container.

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