Title 40 CFR Part 191
Compliance Certification
Application
for the
Waste Isolation Pilot Plant

MASS Attachment 16-3

THIS PAGE INTENTIONALLY LEFT BLANK

INADVERTENT INTRUSION BOREHOLE PERMEABILITY

July 8, 1996

T.W. Thompson
W.E. Coons
J. L. Krumhansl
F.D. Hansen

CONTENTS

1.0 INTRODUCTION

The inadvertent human intrusion scenario envisions that boreholes may penetrate the Waste Isolation Pilot Plant (WIPP) repository and extend through a pressurized brine reservoir in the Castile Formation. These boreholes represent a potential pathway between the brine reservoirs and the repository, and between the repository and the overlying aquifers of the Rustler Formation or the surface. Estimates of borehole permeability are important inputs to the WIPP Performance Assessments (PA). The boreholes will be plugged on abandonment, and prediction of the time variation of this permeability as the plugs degrade and the boreholes close is also important information for PA. As noted in Appendix A, the borehole permeability model presented here should also be applied when analyzing intrusion into a contaminant plume, as well as when considering whether a borehole that does not penetrate any contaminated zone can affect performance of the disposal system.

A methodology has been developed for predicting this borehole permeability, based upon reviews of current plugging and abandonment practices, technical data and predictive methodologies in the published literature, and data from WIPP-specific tests. Part 194 of Title 40 of the Code of Federal Regulations (40CFR194) requires that the frequency with which holes are plugged, the depths of plugged intervals, and the dimensions and materials used to fabricate the plugs be based on current practice. In this area the authors have relied on a study by the Westinghouse Waste Isolation Division (WID) that defines these current practices (WID, 1996). The methodology and materials properties used to assess the behavior of the boreholes and the plugging materials over time, and thus to make long-term predictions of performance, have been taken principally from the professional literature, or from standard engineering and scientific practices. Borehole plugging field test results and experience reported by oil and gas exploration companies have been used to test the credibility of assumptions and predictions.

This report presents the results of the investigations. The principal results are included in the main body of the report, with supporting calculations and detailed information included in the Appendices. Section 2.0 discusses the current plugging practices in the Delaware Basin, as a means of identifying the classes of plugged wells to be considered. Related regulatory issues are discussed in Appendix A which was prepared by Sharla Bertram of Sandia National Laboratories. Conceptual models for the plugged holes, and for casing corrosion and cement degradation are described in Section 3.0, with more details being given in Appendices B and C, while Section 4.0 and Appendix D discuss the creep closure of the boreholes and its effect on permeability. Section 5.0 summarizes the predicted behavior of the three classes of well considered, while Section 6.0 includes the overall conclusions of the study.

2.0 CURRENT BOREHOLE PLUGGING PRACTICES

2.1 Available Information

Current borehole plugging practice in the Delaware Basin is specified in well abandonment regulations promulgated by the New Mexico Oil Conservation Division (OCD) and/or the federal Bureau of Land Management (BLM) (See Appendix A for analysis and discussion). The regulations are universally observed, as borne out by a detailed review of actual field practices (WID, 1996). Current regulations and field practices in the Delaware Basin, and specifically in the vicinity of the WIPP, entail plugging boreholes with portland cement based materials (hereafter, "concrete"). The WIPP lies within a portion of the Delaware Basin that contains potash resources, which are protected by both State and Federal regulations. At the Federal level, an area known as the "Secretary's Area" was designated by the Secretary of the Interior in October 1986 as an area within which the BLM should protect potash resources when considering Applications for Permits to Drill (APD's) for oil or gas wells. At the State level similar considerations apply as specified by the NMOCD in July 1985. Within this area, known variously as the Known Potash Leasing Area (KPLA) or the (almost) equivalent R-111-P area, certain regulations apply relative to drilling, completion and plugging of boreholes. In particular, within this area permission to drill may be denied to protect potash, or because of the presence of the WIPP, and between August 1993 and April 1996 this permission was denied by BLM for 63 wells. Where drilling is allowed BLM is required to take account of the State regulations that stipulate special drilling and plugging practices.

These special State regulations came into force in 1988, so any review of current practice must be restricted to wells plugged since that time. The WID survey identified only one well plugged since 1988 in the potash enclave, apparently because drilling is not generally allowed here. For this reason the survey was extended to cover all boreholes in the Delaware Basin which were subject to plugging since 1988 under BLM regulations, a total of 115 wells, and since the practice in federal and state lands were essentially the same, State wells were added to the survey raising the total sample population 188 wells (see Table C-2 in Appendix C).

Based on this population, the number and distribution of concrete plugs in a given plugged and abandoned borehole are variable and somewhat dependent on the practice of individual operators. However, for the purposes of predicting long-term performance, review of the records indicates that current practice on federal lands may be adequately represented using three scenarios: one with two deep plugs, one with at least three deep plugs, and one in which multiple plugs may approximate the OCD requirement for a continuous plug that extends all the way through the host salt formation. Further discussion is given in the following section.

2.2 Borehole Plugging Configurations

The dimensions and locations of the concrete members (plugs) largely determine their predicted performance lives, and can exert significant performance effects on releases from the overall system under human intrusion scenarios. A number of configurations have been used in the Delaware Basin, including:

- a single continuous plug through the evaporite sequence;
- a two plug configuration that contains one plug in the Bell Canyon Formation (below the depth of potential brine reservoirs) plus one plug in the Rustler Formation (between the Culebra aquifer and the repository); and

- a three (or multi-) plug configuration that contains the two plugs described for the two plug configuration, plus an additional plug in the Salado Salt Formation (see Table C-4 in Appendix C).

In addition to the plugs located at depth, all boreholes have surface plugs that extend ~15 m (50') down from the land surface. These shallow plugs are located in surface casings and are primarily intended to prevent debris or biota from entering the hole. For physical support, the concrete elements of the surface plug are keyed into the near-surface geologic media.

All of these configurations have been modeled in this study for completeness, and are discussed in more detail below.

Under OCD regulations for the R-111-P (KPLA) area a continuous plug of salt-saturated cement is required to extend from the top of the Bell Canyon Formation to the top of the Salado Formation (See Figure 1). This long plug is emplaced to ensure that water inflow cannot effect potash reserves. A deeper plug (typically 15 m of concrete on top of a cast iron bridge plug) is assumed to exist no deeper than 2438m (8000 feet), although this deep plug has no effect on borehole performance for this scenario.

Under BLM regulations outside of the KPLA, or where OCD regulations are not adhered to, plugs are required to isolate the top and bottom of the evaporite sequence from waters not saturated with indigenous salts. For practical reasons, plugged intervals tend to be tied to changes in casing diameter, which tend to be related to drilling and production considerations. One change in casing size typically occurs at the top of the Salado, where the large diameter surface casing is changed to a smaller diameter intermediate casing. In boreholes proximate to the WIPP Site, this step-down in casing diameter occurs below water producing zones in the Rustler. In deep holes associated with hydrocarbon production, an additional step-down occurs at the base of the evaporite sequence, defined typically as from the top of the Salado Formation to the bottom of the Castile (Figure 2). At this location the intermediate casing changes into the smaller diameter production string. During production, this production casing string typically extends to the surface, but is only cemented to above the potential production zones: on abandonment this casing is sometimes cut above the cemented zone and is reclaimed. Typically, the first of these changes (from the surface to the intermediate casing) occurs at or above 245m (800') depth and the second at about 1220m (4000') depth (WID, 1996).

At abandonment, concrete is poured to create plugs which overlap the casing transitions. The plugs are intended primarily to prevent the flow of aqueous media within and around the borehole casing, and are typically about 40m long, centered at the depth where the change in casing diameter occurs. The net effect of this process is that at the WIPP, the minimum plugging arrangement (hereafter, the "two plug configuration") results in upper and lower plugs which isolate the evaporite sequence (Figure 2), with about one-third of the wells being plugged in this way (WID, 1996).

In approximately two-thirds of the sampled wells, one or more intermediate plugs are placed between the Bell Canyon and the Rustler (hereafter, the "three plug configuration"; Figure 3) in addition to the plugs at the base of the Rustler and top of the Bell Canyon. This three plug configuration is associated with holes where hydrocarbon production has occurred, and where a production casing is installed within the intermediate casing. When the production casing is salvaged it is cut and stubbed, and a 40 m thickness of concrete, centered on the stub location, is typically poured to seal off the abandoned production casing that remains in the hole. Near the WIPP, stubbing occurs at a depth averaging ~ 790m (2600'; Westinghouse, 1996) which is above the horizon of the Castile brine reservoirs, but below the repository level. However in some cases, the intermediate plug may lie in the Salado above the repository horizon. For simplicity, this minor occurrence is grouped with the three plug layout.

3.0 CONCEPTUAL MODELS

3.1 General Configuration

Plugged sections of boreholes are assumed to have circular axial cross-sections with alternating layers of concrete plug and steel casing (See Figure 4). In parts of the boreholes which are not plugged, concrete only exists between the casing and the rock, and volumes within the casing are filled with a suspension that contains less than 5% solids in brine. In the borehole plug degradation model, it is assumed that the plugs will fail from a combination of steel casing corrosion and chemical deterioration of the concrete's matrix. The expected performance lives of the different plugs vary because different plugs are located within different hydrologic and chemical environments.

3.2 Conceptual Model for Casing Corrosion

Corrosion of iron-based materials, such as steel, is a complex subject because steel varies in composition, and because the corrosion of steel is highly dependent upon the corrosion environment. For example, the corrosion of different steels under the same conditions can vary by as much as an order of magnitude (e.g., see data in Manfredi 1989). Similarly, the corrosion rate and mechanisms for a given steel will be dependent upon the composition of the corroding medium, including, for example, any volatiles present. Corrosion of steel under oxic conditions is generally much faster than when oxygen is absent (e.g., Escalante et al. , 1990). Corrosion in the presence of hydrogen disulfide gas is aggressive at partial pressures lower than a few atmospheres (Videm and Kvarekval, 1994) and passivated at higher partial pressures (Westerman and Brush, 1996).

Corrosion of borehole casings at WIPP will occur under a number of different environments. Air saturated brine will corrode the casing from the inside-out. De-aired, and in some cases anoxic, formation brines will corrode the casing from the outside-in. None of these borehole environments is similar to the repository, and borehole casing will not show the slow corrosion rates expected to be experienced by steel drums in the repository (see Brush and Westerman, 1996).

Prediction of the corrosion rates and mechanisms for the steel borehole casing has required a number of simplifications. For example:

- It has been assumed that corrosion data for low carbon steel are generally applicable here. Corrosion rates have been bounded by using corrosion data from experiments conducted in brine under low oxygen conditions with carbon dioxide and hydrogen disulfide present, in de-aired conditions with carbon dioxide (only) present, and under air-saturated conditions.

- Complex gas-steel interactions have been ignored in developing generally applicable conceptual models for casing corrosion, and calculations have only considered the reaction of iron and oxygen.

In the simplified iron-water system, corrosion of the casing occurs as available waters react with the steel to form hydrous solids. While other alteration products are possible, corrosion of iron-based materials is generally assumed to produce goethite (FeOOH) or ferrous hydroxide, $Fe(OH)_2$, and generate hydrogen as a byproduct. The extent of corrosion that may occur is theoretically limited both by the amount of reactants and the partial pressure of hydrogen that is generated. When hydrogen partial pressures build up to ~45 atm at 25 ^{o}C, thermodynamic calculations indicate that iron will no longer react to form goethite (Appendix B), and within the compositional limits of the brine-steel system considered, the corrosion of iron theoretically ceases.

From this analysis, it follows directly that the extent of casing corrosion in a borehole will be affected by the "tightness" of the system. If hydrogen can escape, hydrogen partial pressures will not build up and corrosion will proceed until the supply of either steel or water is exhausted. If the system is gas-tight, then corrosion will be limited. Hydrogen is effectively contained in the system if the diffusion of hydrogen through the steel and surrounding rock is sufficiently slow that constant composition is effectively maintained. As a gas, hydrogen is notorious for its ability to diffuse rapidly. Escape of hydrogen from the system is virtually assured if hydrogen exists as a gas and perforations in the casing lie adjacent to conductive formations.

Casings are most likely to corrode and perforate adjacent to strata with appreciable conductivity, where brine can be produced (Warner and McConnell, 1990). Thus, when hydrogen is present as a gas and the casing fails from contact with formation brines, the casing is expected to continue corroding until it disintegrates. In contrast, if hydrogen is not present as a gas, or if localized failure of the casing does not coincide stratigraphically with conductive formations, then corrosion is expected to be restrained. In such cases, the casing may perforate locally, but total disintegration and loss of physical integrity is not expected.

3.3 Conceptual Model for Concrete Alteration

After hardening, concrete materials consist of coarse and fine-grained elements. In a simplified sense, aggregate comprises the coarse material while the fine material is generated by the reactions between the cement and the mix water. The permeability of concrete is determined by the connected porosity that exists through the fine-grained matrix. This porosity includes microcracks, intergranular pores, and small voids that contained bleed water or gas prior to curing. The hardened concrete's initial permeability may be related to the ratio of water to cement used when mixing the concrete (e.g. Neville, 1983; See Figure 5). This general relationship holds because excess water leads to increased connected porosity.

The solid phases that form in concrete are primarily a function of the cement composition, the amount and identity of additives and the composition of the mix water. For the purposes of performance calculations, we have assumed that all cementitious materials are based on ordinary portland cement (OPC) with halite saturated mix waters. The crystalline phases that commonly occur in OPC include portlandite, calcium silicate hydrate (CSH) and often ettringite; however, the bulk of the solid is comprised of cryptocrystalline, or amorphous, CSH and silica. The simplified system may be considered to be portlandite dispersed in a CSH matrix. The solids which make up the concrete will react upon exposure to water. The phases which dissolve and react most readily are alkali salts and portlandite. Dissolution and reaction of portlandite is followed by ettringite (primary and secondary) and then CSH. The alteration phases that are produced include gypsum, calcite, brucite and ultimately clays and perhaps zeolites (Onofrei et al., 1992; Coons and Alcorn, 1989).

Alteration of the solid results in a change of the concrete's permeability. This change can be related mathematically to changes in the concrete's porosity (Coons and Alcorn, 1989). In an unconfined system, the porosity of the concrete increases as the volume of water that flows through the concrete increases. There are two reasons for this change. Firstly, the alteration phases occupy more volume than the original concrete phases (e.g. Robie and Waldbaum, 1978), and alteration causes unconfined concrete to crack, thereby increasing porosity and permeability of the mass. Secondly, in an open system, if flow rates are sufficiently high, then dissolution and removal of highly soluble portlandite can outpace deposition of new solids. This process removes mass from the concrete and causes the porosity and permeability of the mass to increase.

In contrast, in a confined system, alteration of the concrete causes the permeability of the mass to decrease. The solid products produced by alteration of concrete occupy more space than the original solid. If the volume of the mass is not allowed to increase (or if the chemical changes occur very gradually), then as new phases are formed, they clog the internal porosity of the mass. This phenomenon has been observed to produce a decrease in average pore size and total porosity which results in decreased permeability (See Figures 6 and 7; Onofrei et al., 1992). The result is an altered concrete mass with a permeability that is lower than the original, unaltered, value (Alcorn et al., 1992). Models for predicting changes in concrete plug permeability require the use of both the confined and open system results. Long plugs will be self-confining and will approximate the closed or constrained system. Short plugs cannot be safely assumed to be self-confining and must be treated more as an open system.

The conceptual model for changes in short plug performance is a step function, with decreases in plug performance occurring as sudden changes that coincide with plug failure. Failure is conservatively taken to occur when a sufficient volume of water has passed through the concrete mass that the CSH matrix undergoes measurable alteration. At this point, it is assumed that the matrix has degraded significantly, and the plug is subject to unconstrained microfracturing and physical failure. The 'critical volume' of water for causing plug failure has been taken as the volume required before breakdown of the CSH matrix is expected to begin. Based on data in Berner (1990), the critical volume has been conservatively assumed to be equal to 100 pore volumes. The time required for this volume to pass through the concrete mass can be calculated from Darcy's Law using site-specific conditions (See Appendix C). For long plugs, decreases in permeability from the initial, as-emplaced concrete values, have not been considered because it is believed that they will result in no effective difference in system performance predictions.

4.0 CREEP-DRIVEN DENSIFICATION OF BOREHOLE DEBRIS

Rocksalt is a medium which flows viscoelastically under applied deviatoric, or shear, stress, with the rate of flow, or creep, increasing as the stresses increase. This flow may be expected to cause increased closure of the boreholes over time.

The salt around a borehole will be subject to stress difference brought about by the presence of the borehole. At some distance from the borehole the salt will be under a uniform lithostatic load, but at the borehole surface the salt will be confined only by any hydraulic gradient from fluids in the borehole or back pressure from plugs. Away from the plugs the salt will creep into the hole at a rate dictated by the depth (and thus the magnitude of the far-field stress) and the back pressure caused by any borehole fill material. Salt is a highly non-linear material, with the creep rate depending on the applied stress to a power of 4.9 (SNL, 1992), so the rate of closure of the borehole is highly dependent on both depth and backpressure. The far-field stress and any fluid backpressure in the hole work against each other, with the far-field stress trying to close the borehole and the fluid pressure tending to open it. Both of these pressures increase with depth, although the far-field lithostatic stress increases more rapidly. Deeper holes therefore tend to close faster, and holes with an internal fluid pressure will close more slowly than empty holes. One result of this is that only the deepest parts of the borehole, that is those below the repository, will show meaningful closure in the 10,000 year regulatory time period (Appendix D).

In addition to the effects of depth and fluid back-pressure, the closure of the hole is controlled by its geometry. A circular borehole in a uniform stress field is a highly stable configuration, and any additional closure is resisted by the constraint imposed by the shape of the hole. For this reason even the deepest boreholes will not close completely over the 10,000 year regulatory time frame, and permeability effects will only be seen where the holes are filled with a compressible granular material. Thus, at depths below the repository any debris in the borehole will experience compression as the salt creeps inward, leading to a decrease of both the porosity and the permeability of the sediment pile. The amount of permeability decrease will be related directly to the volume of creep closure experienced by the borehole.

Creep closure has been calculated using a "pineapple slice" plane strain model in the Spectrom 32 code, with the MDCF model and WIPP salt parameters (See Appendix D). Only steady state creep was included. Far-field horizontal stresses were estimated at 1 psi/ft depth, with a back-pressure due to a column of brine (density 1.2) to the surface. No back pressure due to consolidating borehole fill was assumed. It has also been assumed that all change in volume is due to loss of pore volume, i.e. the solids are infinitely stiff relative to the borehole fill, and that the Kozeny-Carman relationship for porosity and permeability holds (Bear, 1972; Lambe and Whitman, 1969; Koltermann and Gorelick, 1995).

Given these assumptions changes in the porosity have been calculated that will give rise to an order of magnitude decrease in permeability of the silty sand borehole debris. Calculations have been performed at several depths and times to provide guidance on the rate and locations where permeability changes might be expected (See Figure 8). The calculations indicate that an order of magnitude decrease in permeability will occur if the porosity of the borehole is decreased by between 14 to 23 percent (the range results from the effect of different assumptions for the initial porosity of the debris). At the base of the Salado (850 m depth) 14 percent creep closure will occur in slightly less than 500 years and 23 percent in about 850 years (See Figure 9). Similarly, at the repository level 14 percent closure will take about 1800 years, and 23 percent over 3500 years.

For the purposes of estimating the performance of a plugged borehole at WIPP, the median of the range of properties is useful. Figure 8 indicates that the median (18%) closure will be realized for a column of about 100 meters in 1000 years. As a result, a creep-induced decrease in the permeability of the silty sand fill below the repository of one order of magnitude is predicted to occur after about 1000 years. Above the repository horizon, pressure gradients are low enough that, given the strong non-linearity of creep rates with applied stress, creep induces no significant change to the fill properties within the period of performance.

5.0 PREDICTED PERFORMANCE

5.1 Continuous Plug Configuration

In this scenario, OCD requires that a continuous concrete plug shall extend through the entire evaporite sequence (Castile plus Salado Formations; See Figure 1). Within the WIPP Site, such a plug would have a length of over 900m (3000 feet) and a volume of more than 20 cubic meters (i.e., more than 50 tons of concrete). The length of the plugged interval and its location in media which will creep tightly around the radius of the plug produce a physically confined system.

In a physically confined system, concrete will maintain very low permeabilities for time periods well in excess of the period of performance (see: Atkinson, 1985, 1986; Alcorn et al., 1992; Berner, 1990; Lagerblad and Tragardh, 1995) The mechanisms that lead to predicted long term performance include the very low initial permeability of the concrete and the fact that alteration of the concrete will lead to filling of the internal porosity that permits flow to occur. The predicted permeability of a steel-cased borehole plugged continuously with concrete through the entire evaporite sequence therefore will be equal to or less than the initial permeability of the hardened concrete (which is taken to be 5 x 10^{-17} m^2, as discussed in the following paragraph). It is predicted that this permeability will not experience an effective increase during the 10,000 year period of performance.

These predictions, and the key assumptions concerning the performance of materials that they are based on, are consistent with field and laboratory observations. The initial permeability estimate of hardened concrete is based on field measurements made on test plugs emplaced in the Bell Canyon formation (Christensen and Hunter, 1980; Petersen and Christensen, 1980), and supported by laboratory measurements made on ordinary portland cement grouts (Figure 5; Neville, 1983). Continuous concrete plugs placed through the evaporite sections by potash mining concerns have remained hydraulically tight for decades and show a general lack of concrete alteration (Bonen, 1996). From these findings, and the permeabilities predicted for concrete altered in a confined system, it is concluded that a continuously plugged borehole approximates the isolation capability of the undisturbed geology.

The plug system includes both the grouted steel casing and the internal concrete plug. While the concrete elements are predicted to maintain low permeabilities, it might be argued that corrosion of the steel casing at the rock-steel interface could form a preferred pathway for flow. However, formation of even an incipient annulus is not expected. The most aggressive relevant corrosion rates for carbon steel approach 3mm/yr (Andrade et al., 1990; Manfredi et al., 1989; Videm and Kvarekval, 1994: See Appendix B). The expected length of the continuous plug (900,000 mm), combined with the corrosion rate, the low solubility of iron in brine reservoir fluids (Appendix B), the finite volume of brine assumed (1,000,000,000 liters; Popielak, 1983; Sandia National Laboratories, 1992), and the ability of salt creep to close any small gaps, result in the prediction that corrosion will not create an annular pathway from the Castile, through the repository to the Culebra (See Appendix B).

5.2 Two Plug Configuration

In the two plug configuration, a plug does not separate the hypothesized Castile brine reservoir from the repository (See Figure 2). There is a plug in the Rustler Formation, above the repository, and in the Bell Canyon Formation, below the brine reservoir.

In this scenario connection from the brine pocket to the repository is expected to be essentially instantaneous, since in the first several tens of years the steel casing is projected to perforate locally. The system will not be gas or water tight from this time onward, and interbed permeabilities will control the local release of fluids. Because the transmissivities of local breaches in the casing are expected to be small for 200 years or so, the permeability of the borehole plugs in the Rustler (above the repository) and the Bell Canyon (below the Castile brine reservoir) are expected to be about 5×10^{-17} m^2 for this period. After 200 years the upper casing and the Rustler plug will decay and fail due to aggressive corrosion. Debris from this casing and plug will fill the borehole from the top of the Bell Canyon Plug up to a point above the Rustler with a material equivalent to silty sand (Appendix B), so that the permeability from the brine pocket in the Castile to the Culebra will be in the range 10^{-11} to 10^{-14} m^2, while the permeability of the brine pocket-Bell Canyon flow path remains about 5×10^{-17} m^2. After an additional 1000 years, creep closure causes compaction of the debris and decreases the permeability of the borehole fill below the repository to a range of 10^{-12} to 10^{-15} m^2, while the pathway from the repository to the Culebra remains unchanged at 10^{-11} to 10^{-14} m^2 (Appendix D). After a median time of about 5000 years (See Appendix B for details on the full range), the Bell Canyon plug fails, and the debris pile falls to the bridge plug at 8000 feet, but still extends above the Culebra. From this time onward, the permeability of the entire borehole approximates silty sand, with that below the repository being one order of magnitude less permeable due to creep closure. The bases for this prediction are elaborated upon below, and in Appendices B, C and D.

In the upper reaches of the borehole, (depths less than ~300 m) corrosion of the steel casing will speed the failure of the Rustler Plug. At these shallow depths, total corrosion damage to the steel is expected to be generalized, and much greater than the localized damage expected at greater depths. This prediction is a result of the lower hydrostatic pressures at shallower depths, which will be insufficient to keep corrosion-generated hydrogen from nucleating as a gas and escaping into the surrounding formations. Loss of this gas substantially removes chemical controls on corrosion, and allows the reaction to proceed until the supply of steel is exhausted, and the upper portions of the casing disintegrate. Laboratory-derived linear corrosion rates (See Figures 10 and 11; Videm and Kvarekval, 1994; Andrade et al., 1990) suggest that localized breaches of the casing may be expected in periods as short as several months to tens of years, which is consistent with oil field experience in the Delaware Basin (Bailey, 1990), so that within decades the borehole casings will not be "gas-tight". Scaling up from these same experiments, extensive corrosion and total disintegration of the casing are expected within less than 200 years.

Loss of the casing will remove physical support for the concrete plug and will expose new concrete surfaces to alteration. Experiments conducted by Waterways Experiment Station indicate that diffusion driven processes result in a spall rate of 0.05 cm/yr from concrete surfaces (Atkinson and Hearne, 1990). In 200 years, radial diffusion would be capable of reducing the diameter of the plug by over 90 percent. As a result, in a practical sense the Rustler Plug is predicted to lose its functionality within about 200 years.

The corrosion products from the casing will be fine-grained materials. Degraded concrete and sloughed rock will also fall into the hole and will likely be coarser material. The debris will comprise a granular fill for the borehole above the Rustler plug. Because of the telescoping geometry of the borehole, the debris pile will extend above the Culebra Dolomite. The permeability of this fill is expected initially to approximate silty sand (10^{-11} to 10^{-14} m^2), and subsequent consolidation by salt creep in lower sections of the borehole will ultimately reduce this conductivity range by an order of magnitude below the repository (See Section 4.0, and Appendix D).

The deeper Bell Canyon plug will degrade more slowly than the Rustler plug. At the depth of the Bell Canyon (~4000 feet), the hydrostatic pressure greatly exceeds the equilibrium hydrogen pressure created by steel corrosion, and hydrogen gas is not expected to nucleate and escape.

The consequence is that corrosion of the casing will be limited to local perforation (pitting failures), and while this corrosion will result in isolated holes in the casing, total disintegration of the casing is not expected to occur within the 10,000 year performance period.

The process that will cause degradation of the Bell Canyon plug will be chemical alteration, due to reaction with water that flows axially through the plug's porosity. As noted above, approximately 100 pore volumes are conservatively taken to be required before chemical reactions significantly attack the concrete's calcium-silicate-hydrate matrix (See Figure 12; Berner, 1990). The comparatively short length of the plug (40 m), and the high hydraulic gradients produced by the pressurized brines, will allow significant volumes of water to pass through and chemically alter the concrete mass of the plugs during time frames of interest. In contrast to the continuous plug configuration discussed above, it may not be reliably assumed that this plug is physically confined. The performance life of the concrete is controlled by water access (See Clifton and Knab, 1989), and chemical degradation of the matrix will allow the concrete mass to fracture and cause the plug to fail. Under the site-specific conditions assumed, the expected performance life of the Bell Canyon plug has a median of 5000 years and a range of from 500 to 50,000 years (See Appendix C). At that time, the permeability of the plug will decrease to that of the consolidated debris.

5.3 Three Plugs

The three plug configuration includes a plug between the brine pocket and the repository. The plugs between a) the brine pocket and the repository (the Salado plug), and b) the repository and the Culebra (the Rustler plug), are expected initially to have permeabilities of 5 x 10^{-17} m^2 (as is the pathway through the Bell Canyon). Failure of the casing and Rustler Plug are not driven by processes that require connection to the Castile Brine Reservoir, and, as in the two plug configuration, the upper casing and the Rustler plug will fail at around 200 years. In most cases this will cause the predicted permeability from the repository to the Culebra to be that of silty sand. Such a condition will prevail except in those instances when an additional plug is located in the Salado above the repository horizon. When such off-normal plugging occurs, the permeability above the extra plug will approximate silty sand (10^{-11} to 10^{-14} m^2), but the permeability from the repository to the plug will remain 5×10^{-17} m^2.

At depths below about 1100 feet, the hydrostatic pressure will be high enough to prevent hydrogen gas nucleation. Casing corrosion will be constrained and the plugs will remain physically supported. Nevertheless, pressurized brines may be expected to reach the inside volumes of the unplugged casing beneath the plug in times as short as months to tens of years after abandonment. Predictions of localized perforation are based on linear corrosion by brines with compositions similar to the Castile Brines analyzed by Popielak et al., 1983 (but with reduced partial pressures of hydrogen disulfide, assumed due to atmospheric venting that occurred at the time of drilling). While a concrete cladding *may* slow corrosion, the presence of concrete around the steel *cannot be relied upon* to decrease linear corrosion rates significantly (compare Figure 10 and Figure 11 and see Appendix C). Once the pressurized brines from the Castile gain access to the inside of the casing, a steep hydraulic gradient will be established across the Salado and Bell Canyon plugs, and even with the low initial permeability of the concrete (5×10^{-17} m^2), the gradient is sufficient to drive brine through the plug in appreciable volumes within the 10,000 year period of performance.

The chemical alteration of these concrete plugs, which lack axial confinement, is expected to lead to failure of the plugs and a consequent increase in borehole conductivity. The driving force behind plug failure is that chemical alteration products occupy more volume than the original concrete material. In the continuous plug configuration, this expansion clogged available pores and decreased permeability because the system was physically confined. In the two and three plug configurations, formation of the same alteration phases leads to increased pore pressures and results in fracturing and loss of the physical integrity of the Salado plug.

The Salado plug's initial permeability is estimated to continue for a median time of about 5000 years (with a range of 500 to 50,000 years), when both the Salado and the Bell Canyon plugs are predicted to fail. As noted above, the Rustler plug is expected to have failed at about 200 years, and the portion of the borehole above the intermediate plug will have filled with corrosion and other debris approximating a silty sand like material. Prior to failure of the intermediate plug, creep will have densified the lower portions of the sediment pile, below the repository. As a result, upon failure of the intermediate plug at 5000 years, the permeability of the brine pocket-repository pathway will be 10^{-12} to 10^{-15} m^2, while the pathways above the repository will approximate silty sand (10^{-11} to 10^{-14} m^2).

5.4 Surface Plugs

Surface plugs will exist in all boreholes and their expected degradation applies equally well to all plugging scenarios. Surface plugs will be located in and around the casing that extends 50 ft downward from the surface. The top 4 to 6 feet of these plugs is keyed into the geologic media, providing a physical support.

The entire mass of the surface plug and associated casing lies above the water table at the site. The casing between the surface plug and the Rustler runs through both saturated and unsaturated media. The casing will corrode quickly in the saturated environments and more slowly in unsaturated zones. Failure of the casing is not expected to cause the surface plug to fail by loss of physical support because of the construction geometry.

The concrete elements of the surface plug will degrade very slowly. No long lasting hydraulic head will drive water to flow through and chemically alter the plug. Degradation beyond surface phenomena (such as freeze-thaw) is expected to be driven by diffusion and evaporation mechanisms. These processes are not expected to alter plug performance to a significant degree during the 10,000 year period of performance.

In summary the section of the borehole above the Rustler plug is expected to have hydraulic properties controlled by the surrounding formations. The control will begin within decades after abandonment due to local perforation of the steel casing; however, limited transmissivity may restrict water flows to small amounts. Total hydraulic control by the host geology is expected within 200 years, by which time the saturated portion of the casing is expected to disintegrate. Prior to that time the surface plug is taken to have a permeability of 5×10^{-17} m^2.

6.0 SUMMARY AND CONCLUSIONS

Permeabilities have been predicted for borehole plugs as they are likely to exist at the WIPP over long time periods. Borehole plug configurations, dimensions and materials have been estimated from a review of current regulations and practices. Expected changes in performance have been estimated using models and data for steel corrosion and concrete alteration taken from the published literature. Predictions have been calibrated, where possible, by comparing predicted behavior with field observations and measurements.

Plugs are initially expected to have a permeability of 5×10^{-17} m^2. In the continuous plug configurations, this performance remains permanently undiminished. Under alternative plugging configurations, permeabilities associated with different sections of the borehole vary with time. Casing above the Rustler Formation is estimated to completely degrade in about 200 years, and the plug in the Rustler Formatio will fail at this time. This corroded casing and degraded plug will fill the hole with material with a permeability approximating that of silty sand (10^{-11} to 10^{-14} m^2), and over time any of this material below the repository will compress through creep` closure of the borehole to a permeability about one order of magnitude lower. Deeper casing will not corrode so extensively, and the deeper plugs will not fail for an estimated median time of 5,000 years. The predicted changes in borehole performance for the different potential configurations are shown in Figures 13 and 14 and in Tables 1 and 2, and summarized below:

- Continuous Plug: The permeability of the plug remains at 5×10^{-17} m^2 for the whole regulatory period.

- Two Plugs: The permeability between the repository and the surface is 5×10^{-17} m^2 for 200 years and 10^{-11} m^2 to 10^{-14} m^2 after that. Between the Castile and the repository has a very high permeability for 200 years, values of 10^{-11} to 10^{-14} m^2 up to 1,200 years, and 10^{-12} to 10^{-15} m^2 after that.

- Three Plugs: The permeability between the intermediate plug and the surface is 5×10^{-17} m^2 for 200 years and 10^{-11} m^2 to 10^{-14} m^2 after that. The intermediate plug has a permeability of 5×10^{-17} m^2 for a median time of 5,000 years, and the borehole between the Castile and the repository has values of 10^{-11} to 10^{-14} m^2 for 1,000 more years , and 10^{-12} to 10^{-15} m^2 after that.

Under all scenarios considered, the permeability of the borehole plug system never exceeds that of silty sand (10^{-11} to 10^{-14} m^2).

7.0 REFERENCES CITED

Alcorn, S.R., Coons, W.E., Christian-Frear, T.L., and M.G. Wallace, 1992, "Theoretical Investigations of Grout Seal Longevity," Final Report, Stripa Project TR 92-23, SKB, Stockholm, Sweden.

Aguilar, A., Sagues, A.A., and Powers, R.G. (1990) Corrosion of reinforcing steel in partially submerged concrete slabs: in Corrosion Rate of Steel in Concrete: ASTM, Philadelphia, PA, pp66-85.

Andrade, C., Alonso, M.C. and Gonzalez, J.A. (1990) An initial effort to use the corrosion rate measurements for estimating rebar durability: in Corrosion Rate of Steel in Concrete: ASTM, Philadelphia, PA, pp29-37

Atkinson, A., Goult, D.J., and Hearne, J.A., 1985, "An Assessment of the Long-Term Durability of Concrete in Radioactive Waste Management." Materials Research Society Symposium Proceedings: Scientific Basis for Nuclear Waste Management IX, v. 50,pp 239-246.

Atkinson, A., 1986, "The Time Dependence of pH Within a Repository for Radioactive Waste Disposal.: Report AERE-R 1177, Materials Development Division, Harwell Laboratory, Oxfordshire, England.

Bailey, J., 1990. "Water Level Rises in Culebra Dolomite Monitor Wells," NM State Land Office, Technical Letter Memorandum, August 13, 1990.

Bear, J., 1972, Dynamics of Fluids in Porous Media, Elsevier, New York.

Berner, U., 1990, "A Thermodynamic Description of the Evolution of Pore Water Chemistry and Uranium Speciation During the Degradation of Cement," Technical Report 90-12, Paul Scherrer, Villigen, Switzerland.

Bonen, D., 1996, "Petrographic Analyses of Concrete and Grout Recovered from the WIPP," The Technological Institute, Northwestern University, Interim Report, January 15, 1996, 9pp.

Buiil, M., Revertagat, E., and Oliver, J., 1992, "A model of the attack of pure water or undersaturated lime solutions on cement. in Stabilization and Solidification of Hazardous Radioactive and Mixed Wastes," Special Publication 1123, ASTM, Philadelphia, PA, pp 227-241

Burski, J.L., 1994, "Yates Petroleum et al.v. New Mexico State Office, Bureau of Land Management:" IBLA 92-612 decided November 18,1994.

Christensen, C.L. and Hunter, T.O., (1980) "The Bell Canyon Test Results" SAND80-2414C. Sandia National Laboratory, Albuquerque NM

Clifton, J.R. and Knab, L.I., 1989,"Service Life of Concrete." NUREG/CR-5466 and NISTIR 89-4086; National Institutes of Standards and Technology, Gaithersburg, Maryland.

Coons, W.E. and S.R. Alcorn, 1989, "Estimated Longevity of Performance of Portland Cement Grout Seals," in Sealing of Radioactive Waste Repositories, Conference Proceedings, Braunschweig, Germany, May 22-25, 1989.

Dale, T., and L. D. Hurtado, 1996, "WIPP Air Intake Shaft Disturbed Rock Zone Study," to be presented at 4th. International Symposium on Salt, Montreal, June, 1996.

Escalante, E. and Ito, S. (1990) Measuring the corrosion rate of steel in concrete: in Corrosion Rate of Steel in Concrete: ASTM, Philadelphia, PA, pp86-102.

Freeze, R.A., and J.A. Cherry, 1979, Groundwater, Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Garrels, R.M. and Christ, C.L., 1965, Solutions, Minerals, and Equilibria, Jones and Bartlett, 450p

John Hart and Associates. P.A., 1995, "Review and Comparison of Regulatory Requirements Governing Plugging and Abandonment of Oil and Gas Wells in New Mexico, Texas, Oklahoma, Colorado and Nevada," Report to Westinghouse Waste Isolation Division, March 1995

Kelley, V., Jones, T., and J. Ogintz, 1996, "WIPP Seal System Parameters for PA BRAGFLO Compliance Calculations", Memorandum from Intera to Diane Hurtado, January 15 1996

Knowles, M. K. and C. L. Howard, 1996, "Field and Laboratory Testing of Seal Materials Proposed for the Waste Isolation Pilot Plant," to be presented at the Waste Management Conference, February 1996.

Koltermann, , and Gorelick, 1995, "Conductivity in Sediment Mixtures"

Krumhansl. J. L., 1993, "The accelerated testing of cements in brines," Proc. Am. Ceramic Soc, "Cement-based Materials," April 19-22, 1993, Cincinnati, Ohio, p. 153-164.

Lagerblad, B., and J. Tragardh, 1995, "Conceptual Model for Concrete Long Time Degradation in a Deep Nuclear Waste repository," Swedish Cement and Concrete Institute, TR 95-21, SKB, Stockholm, Sweden, 103pp.

Lambe, T.W., and R.V. Whitman, 1969, Soil Mechanics, Wiley, New York.

Lambert, S.J., and R.L. Robinson, 1984, "Field Geochemical Studies of Groundwaters in Nash Draw, Southeastern New Mexico," SAND83-1122, Sandia National Laboratories, Albuquerque, 1984.

LaVenue, M., 1991, "Anomalous Culebra Water-Level Rises near the WIPP Site," INTERA: Technical Letter Memorandum, January 28, 1991.

Manfredi, C., Mozhi,T.A., and Wilde, B.E., 1989, Corrosion of carbon steel in saturated brine at 150oC- the effects of pH. Corrosion, v. 45 no.2, pp 172-177

Munson, D.E., deVries, K.L., Schiermeister, D.M., deYonge, W.F., and R. L. Jones, 1992, "Measured and Calculated Closures of Open and Brine filled Shafts and Deep Vertical Boreholes in Salt," SAND91-1869, Sandia National Laboratories, Albuquerque, January 1992.

Myers, J., Drez, P, and P. James, 1991, "The Redox State and the Occurrence and Influence of Organics in the Culebra," in Hydrogeochemical Studies of the Rustler Formation and Related Rocks in the Waste isolation Pilot Plant Area, Southeatern New Mexico, Siegel, Lambert and Robinson (eds), SAND88-0196, Sandia National Laboratories, Albuquerque.

Neville, A., 1981, Properties of Concrete, John Wiley and Sons, London.

Onofrei, M., Gray, M., Coons, W.E.., and S.R. Alcorn, 1992, "High Performance Cement Based Grout for Use in a Nuclear Waste Disposal Facility, " Waste Management, v.12, pp. 133-154.

Petersen, E.W., and Christensen, C.L. (1980) "Analysis of Bell Canyon Test Results" SAND80-7044C. Sandia National Laboratories, Albuquerque NM

Popielak, R.S., Beauheim, R.L., Black, S.R., Coons, W.E., Ellinson, C.T., and R.L. Olsen, 1983, "Brine Reservoirs in the Castile Formation, Waste Isolation Pilot Plant (WIPP) Project, Southeastern New Mexico," Report TME 3153, U.S. Department of Energy, Albuquerque, NM.

Robie,J and Waldbaum, D.J., 1978, "The Thermodynamic Properties of Minerals" American Mineralogic Society. Washington, D.C.

S. M. Stoller Corporation, "Investigation of Borehole Brine Migration in Potash Mines - Phase I and Phase II," Report to Westinghouse Waste Isolation Division, Undated.

Sandia National Laboratories, 1992, "Preliminary Performance Assessment for the WIPP, December 1992, Volume 3: Model Parameters," SAND92-0700/3, Sandia National Laboratories, Albuquerque, NM.

Sandia National Laboratories, 1995, "Status Meeting for the Delivery of Shaft Seal System Parameter Distributions for BRAGFLO (Draft)", December 15, 1995

Sienko, M.J. and Plane, R. A., 1966, Chemistry: Principles and Properties. McGraw-Hill, NY, New York

State of New Mexico, 1988, Minerals and Natural Resources Department, Oil Conservation Division, Order No. R-111-P (April 1988).

U.S. Department of the Interior, 1989, "Inspection and Enforcement Program and Selected Related Management Activities Bureau of Land Management," Office of Inspector General Audit Report, Report No. 90-18, November 1989.

US Department of Energy, 1995, "Waste Isolation Pilot Plant Sealing System Design Report," DOE/WIPP - 3117, October 1995.

Videm, K, Loren, A.M., and J. Kvarekval, 1992, "Passivity, Pitting and Uniform Corrosion of Carbon Steels in Aqueous Sodium Bicarbonate Solutions and in Simulated Oil Well Water Phases," Proc. 12th Scandinavian Corrosion Congress and Eurocorr '92, V1, Corrosion Soc. of Finland, Espoo Finland, pp. 327-336.

Videm, K, and J. Kvarekval, 1995, "Corrosion of Carbon Steel in Carbon Dioxide-Saturated Solutions Containing Small Amounts of Hydrogen Sulfide," Corrosion, V51(4), pp. 260-269.

Wakeley, L. D., Harrington, P. T., and C. A. Weiss, Jr., 1993, "Properties of Salt Saturated Concrete and Grout after 6 Years In-Situ at the WIPP, " SAND93-7019, Sandia National Laboratories, Albuquerque, NM.

Wakeley, L.D., Poole, T.S., and Burkes, J.P., 1994, "Durability of concrete materials in high-magnesium brines," SAND 93-7073

Walton, J.C., Plansky, L.E., and Smith, R.W., 1990, "Models for estimation of service life of concrete barriers in low-level waste repositories," NUREG/CR-5542

Warner, D.L. and McConnell, C.L. (1990) Abandoned oil and gas industry wells-a quantitative assessment of their environmental implications wih emphasis upon the lower Tuscaloosa Sand oil-producing trend of Mississippi and Louisiana. Report to American Petroleum Institute, Health and Environmental Sciences Department and Production Department. Washington, D.C.

Westinghouse Electric Corporation, and John Hart and Associates, 1996, Drilling Requirements and Practices in the Delaware Basin of New Mexico and Texas as Related to Inadvertent Human Intrusion into the Waste Isolation Pilot Plant (WIPP). March 1996 Draft.

Xia, Z., Chou, K.-C., and Szklarska-Smialowska, 1989, Pitting corrosion of carbon steel in CO2-containing NaCl brine. Corrosion; v.45 no. 8 pp 636-642.

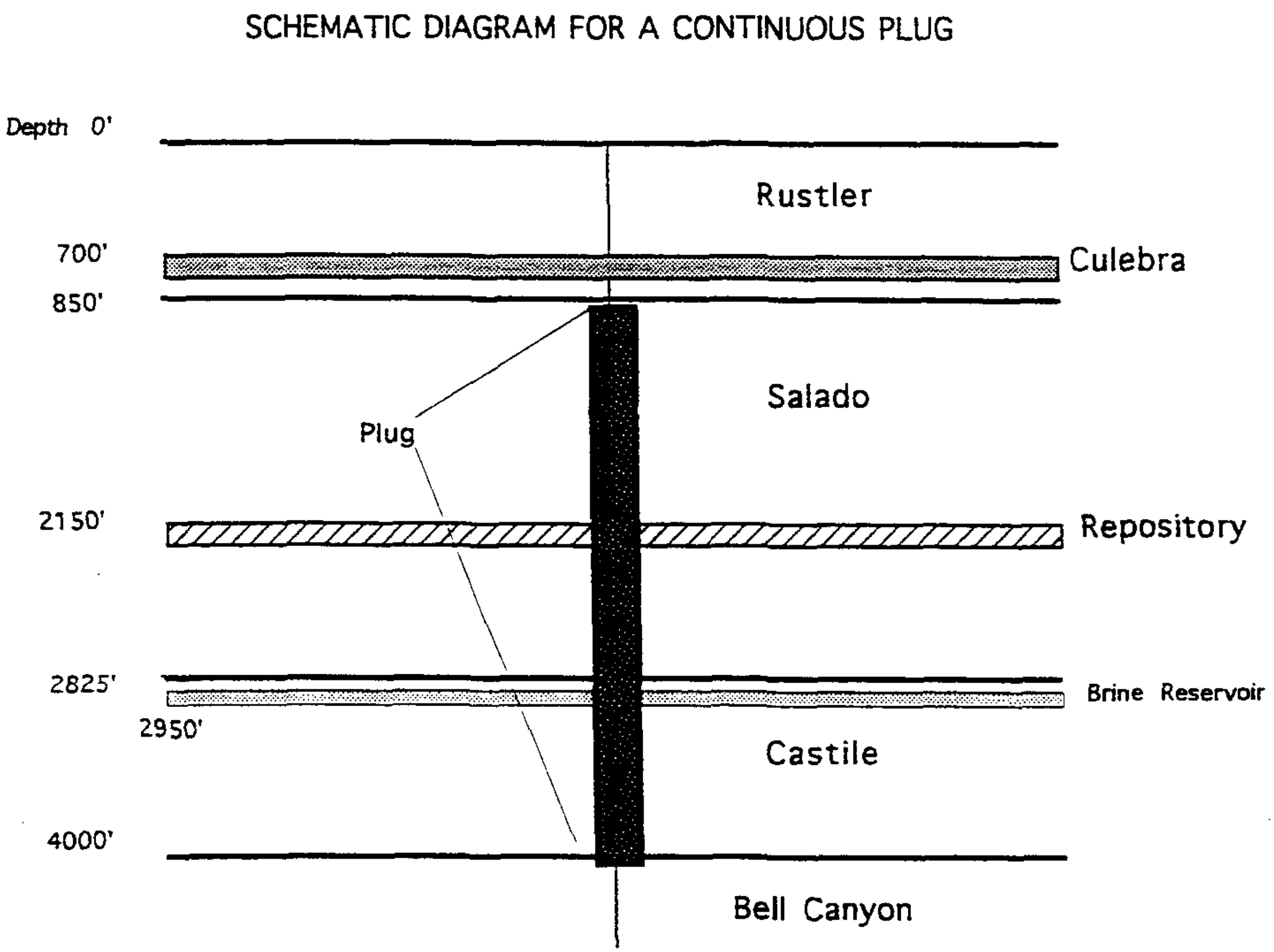

SCHEMATIC DIAGRAM FOR A CONTINUOUS PLUG

Figure 1

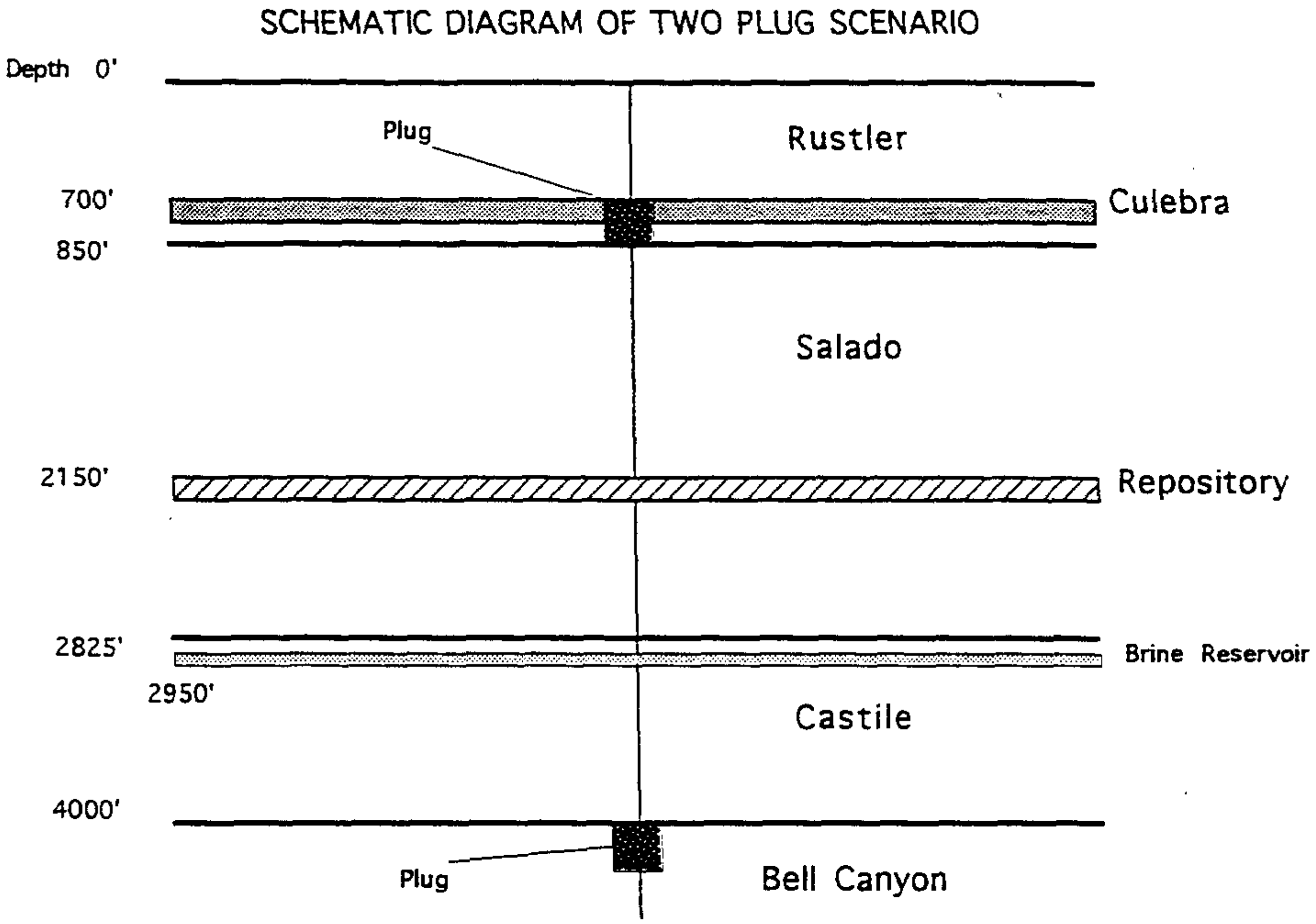

SCHEMATIC DIAGRAM OF TWO PLUG SCENARIO
Depth 0'
Plug
Rustler
700'
Culebra
850'
Salado
2150'
Repository
2825'
Brine Reservoir
2950'
Castile
4000'
Plug
Bell Canyon

Figure 2

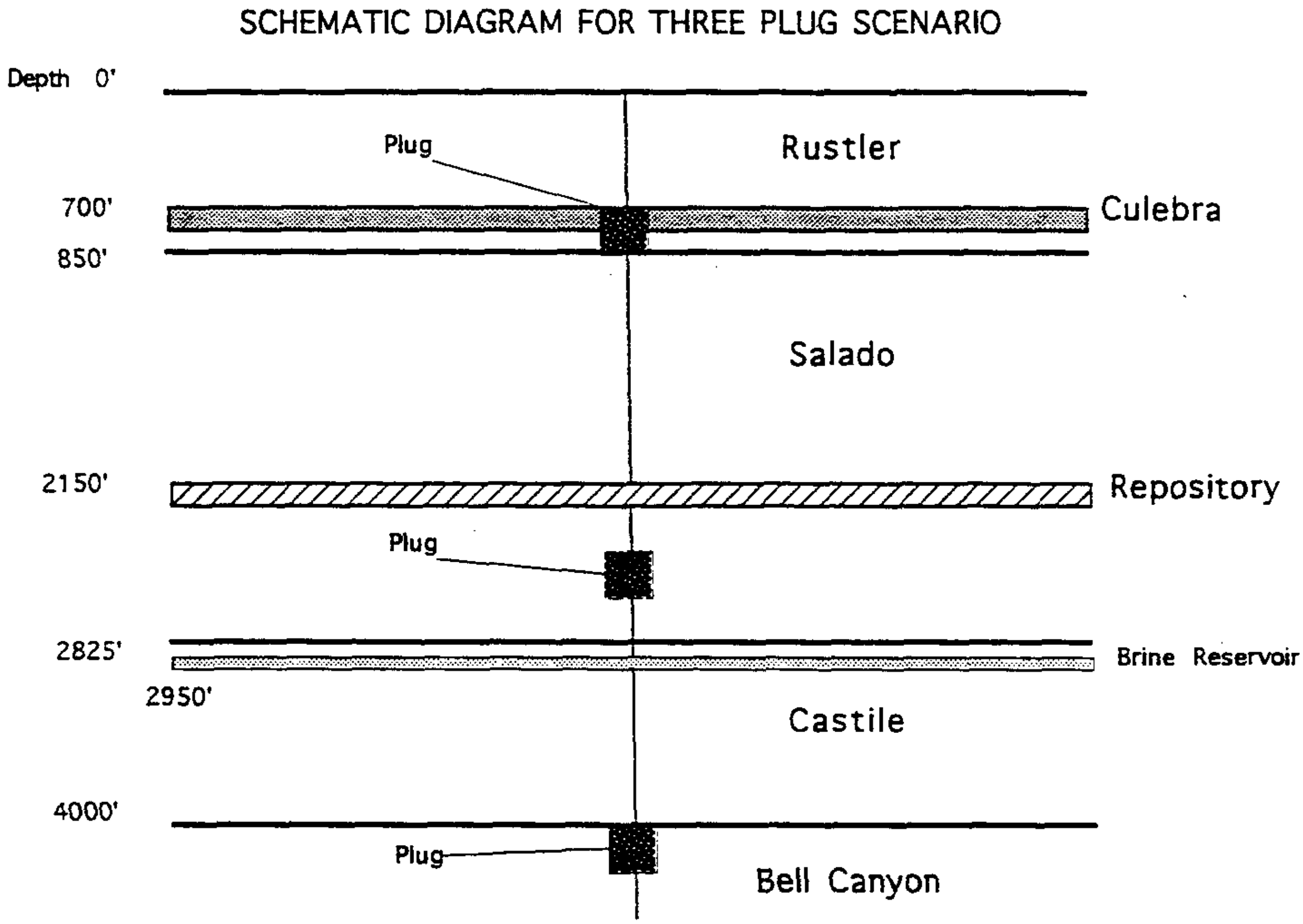

SCHEMATIC DIAGRAM FOR THREE PLUG SCENARIO
Depth 0'
Plug
Rustler
700'
Culebra
850'
Salado
2150'
Repository
Plug
2825'
Brine Reservoir
2950'
Castile
4000'
Plug
Bell Canyon

Figure 3

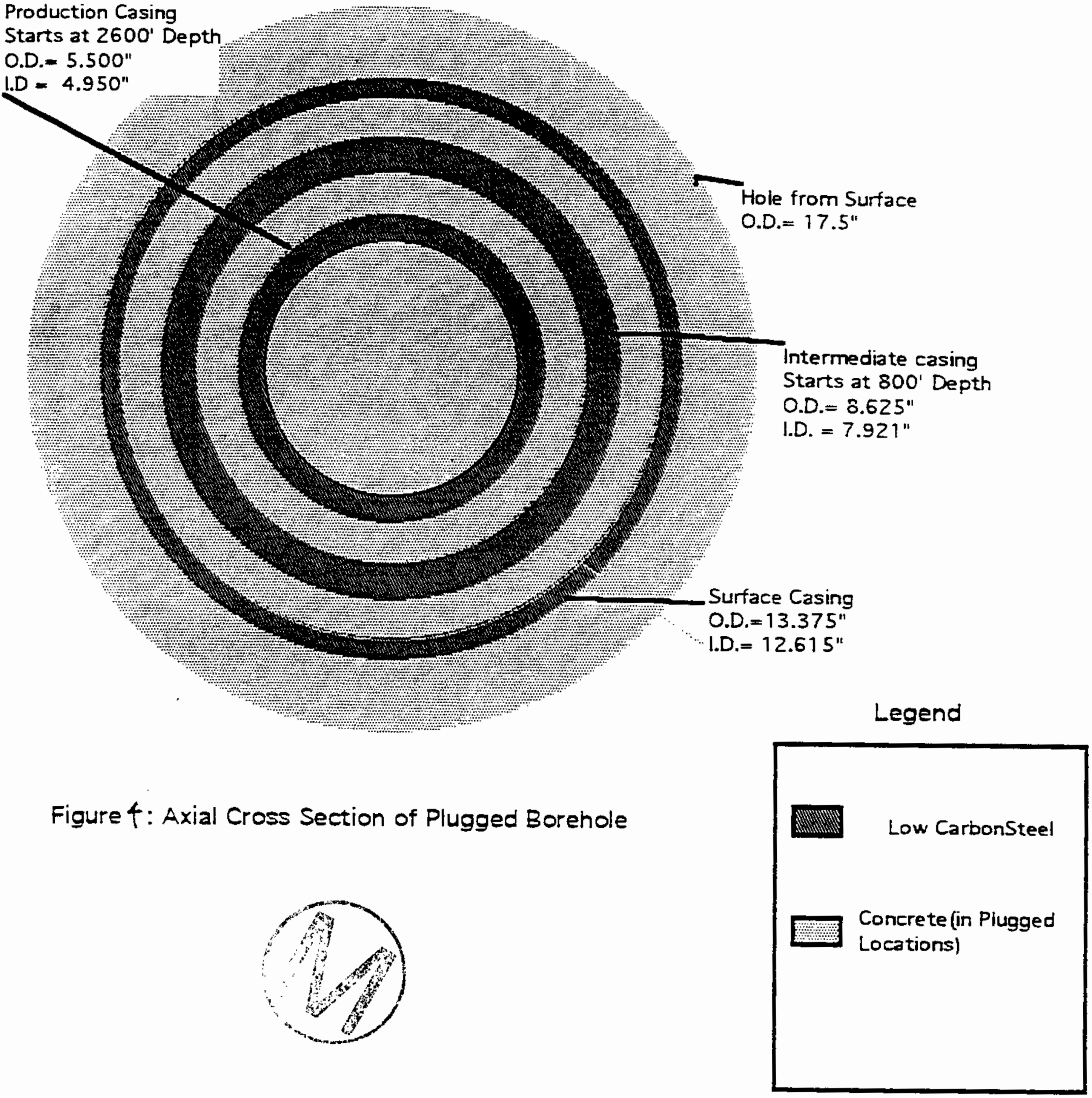
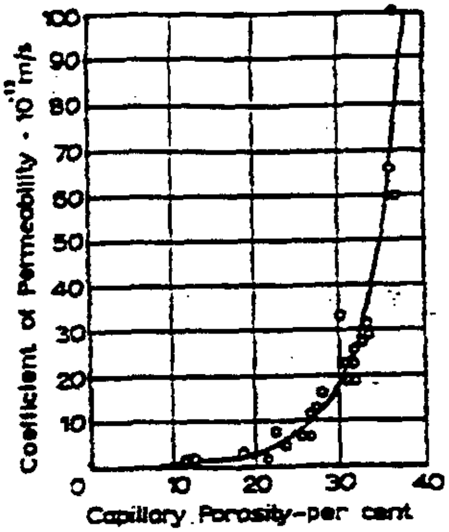
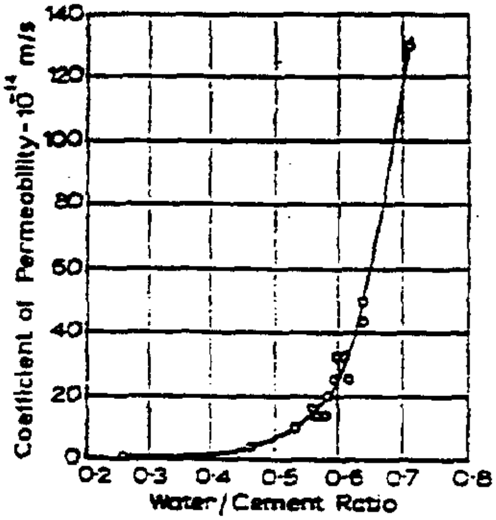


Figure 4: Axial Cross Section of Plugged Borehole

Figure 4



Relation between permeability and capillary porosity of cement pastes (Neville, 1981).



Permeability as a function of water - cement ratio for mature cement pastes (93% of cement hydrated). From Neville, 1981.

Figure 5

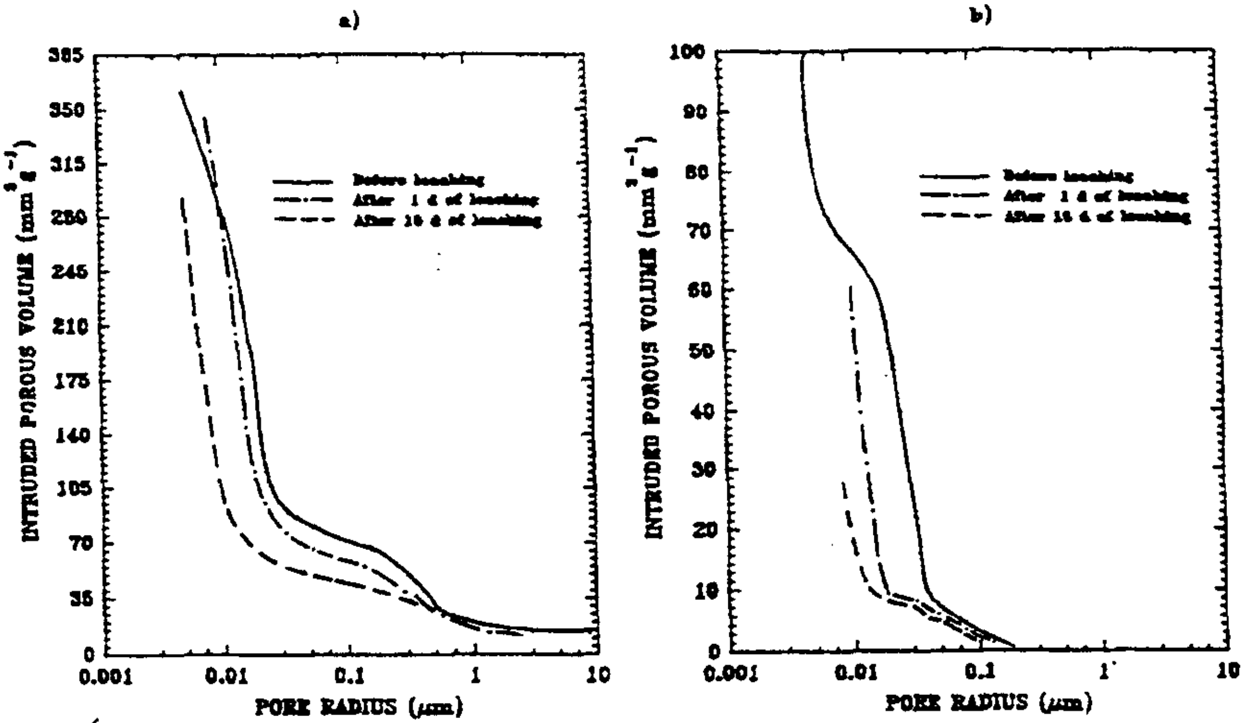


FIG 6 The effect of leaching time on cumulative pore size distribution measured by mercury intrusion porosimetry for: (a) ALOFX -MC grout (MC-500, 0.7/1/10), and (b) reference grout (Type-50, 0.4/1/10).

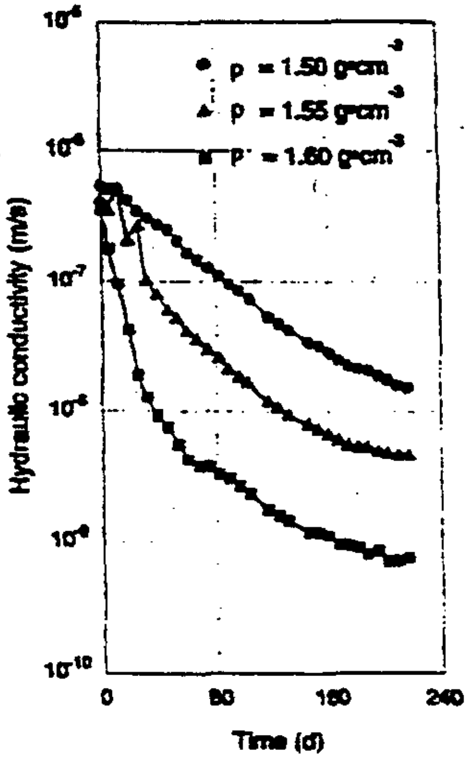


FIG-7 Decreases in hydraulic conductivity measured in crushed, reconsolidated grout as a function of time of exposure to flowing ground water (from Gray, 1992; after Onofrei et al., 1992).

RE/SPEC Inc. **CALCULATION SHEET** Page 8 of 8

Title Creep Closure of a Brine-Filled Open Borehole in Salt

Calculation No. 325/3.9/01 Engineer MCL Date 3/20/96 Checker ________ Date ________

RSI-325-96-121

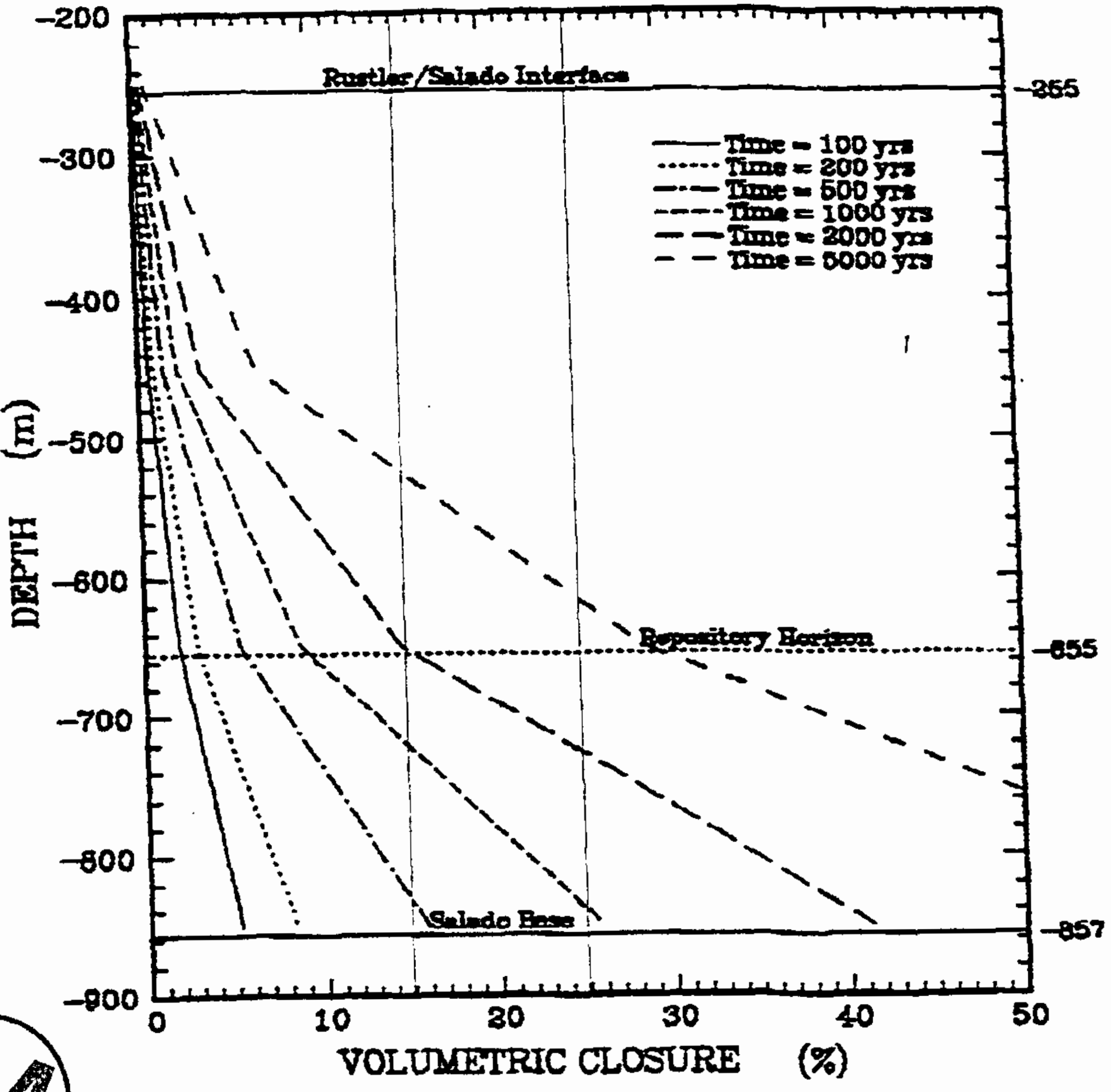


Figure ~~5~~ 11. Volumetric Closure as a Function of Depth at Six Representative Times.

— PRELIMINARY —

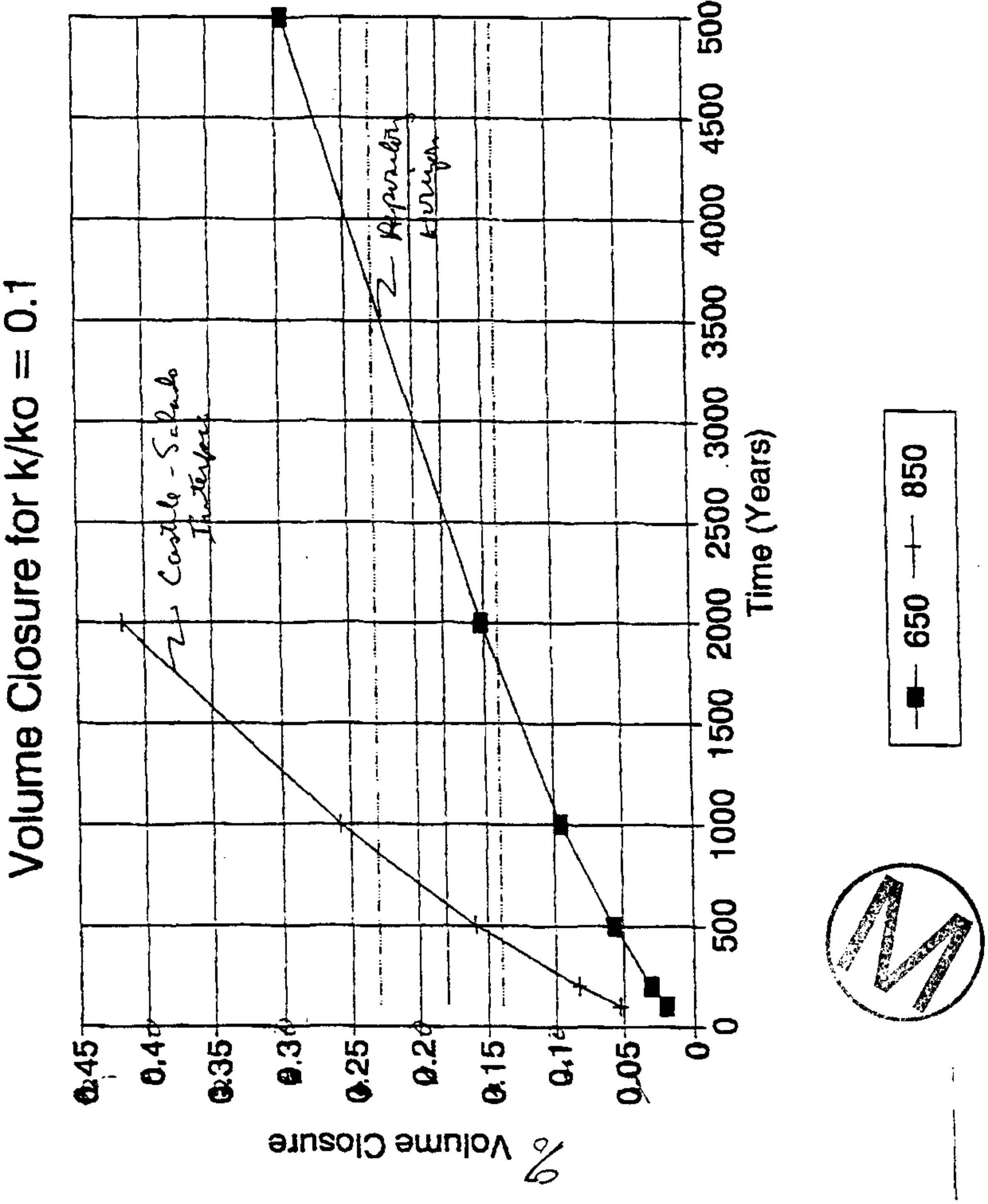
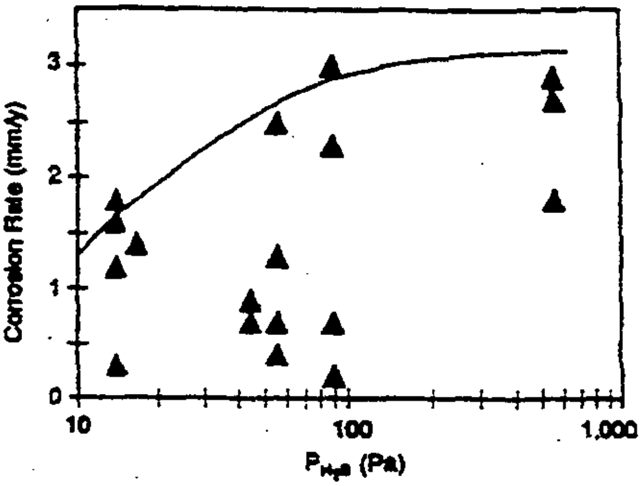
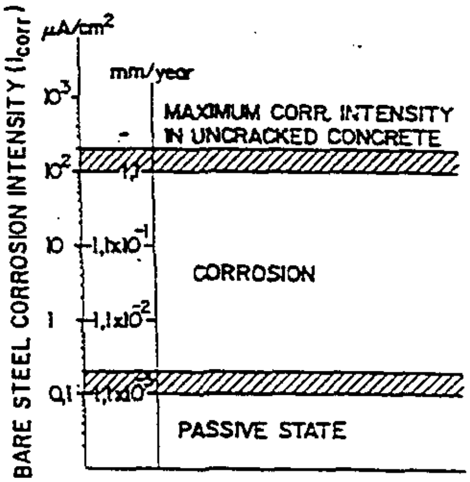

Volume Closure for k/ko = 0.1
% Volume Closure
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Time (Years)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
Castile - Salado Interface
Repository Horizon
650
850

Figure 9

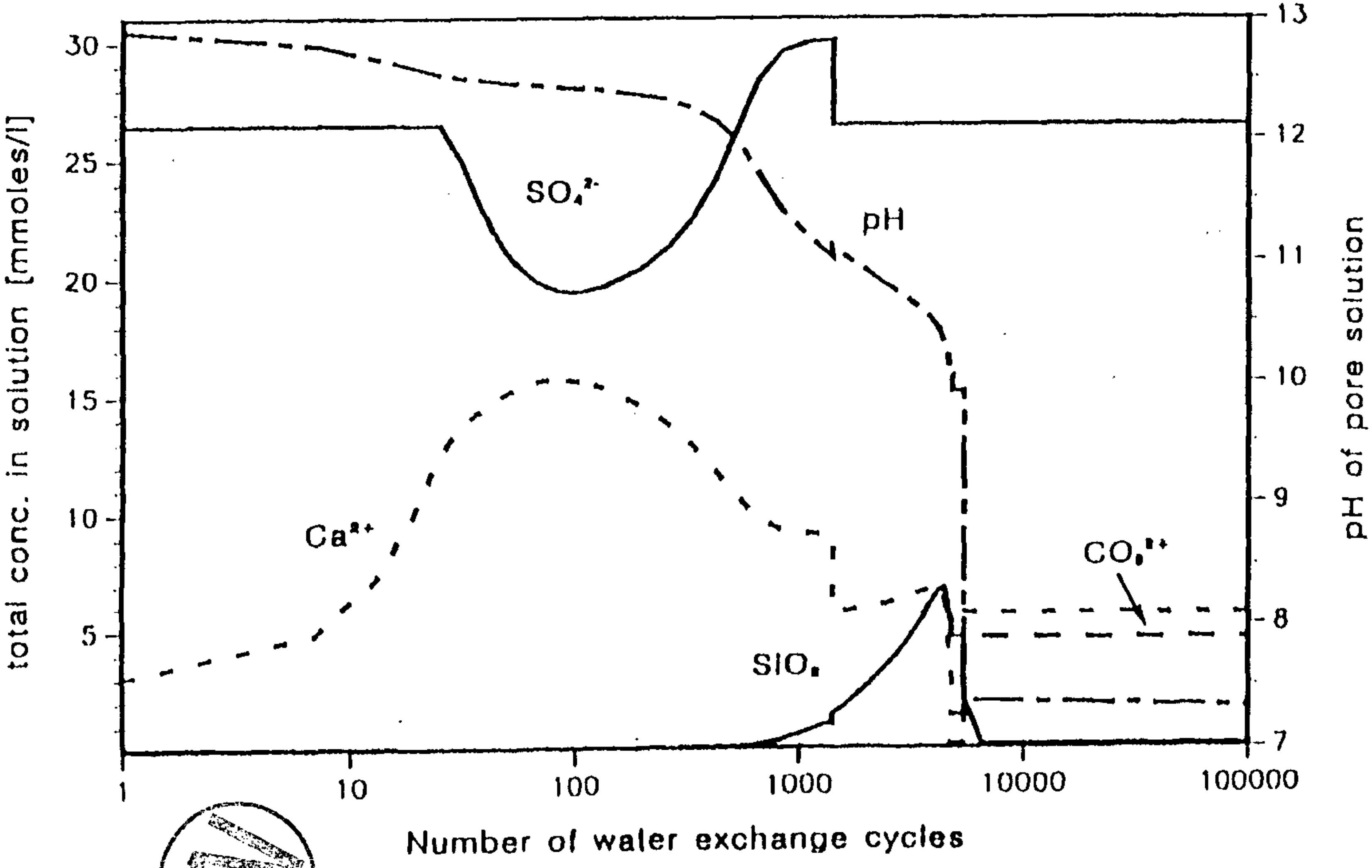


Corrosion rate of low carbon steel in carbon dioxide saturated solutions as a function of the partial pressure of hydrogen disulfide (from Videm and Kvarekval, 1995)

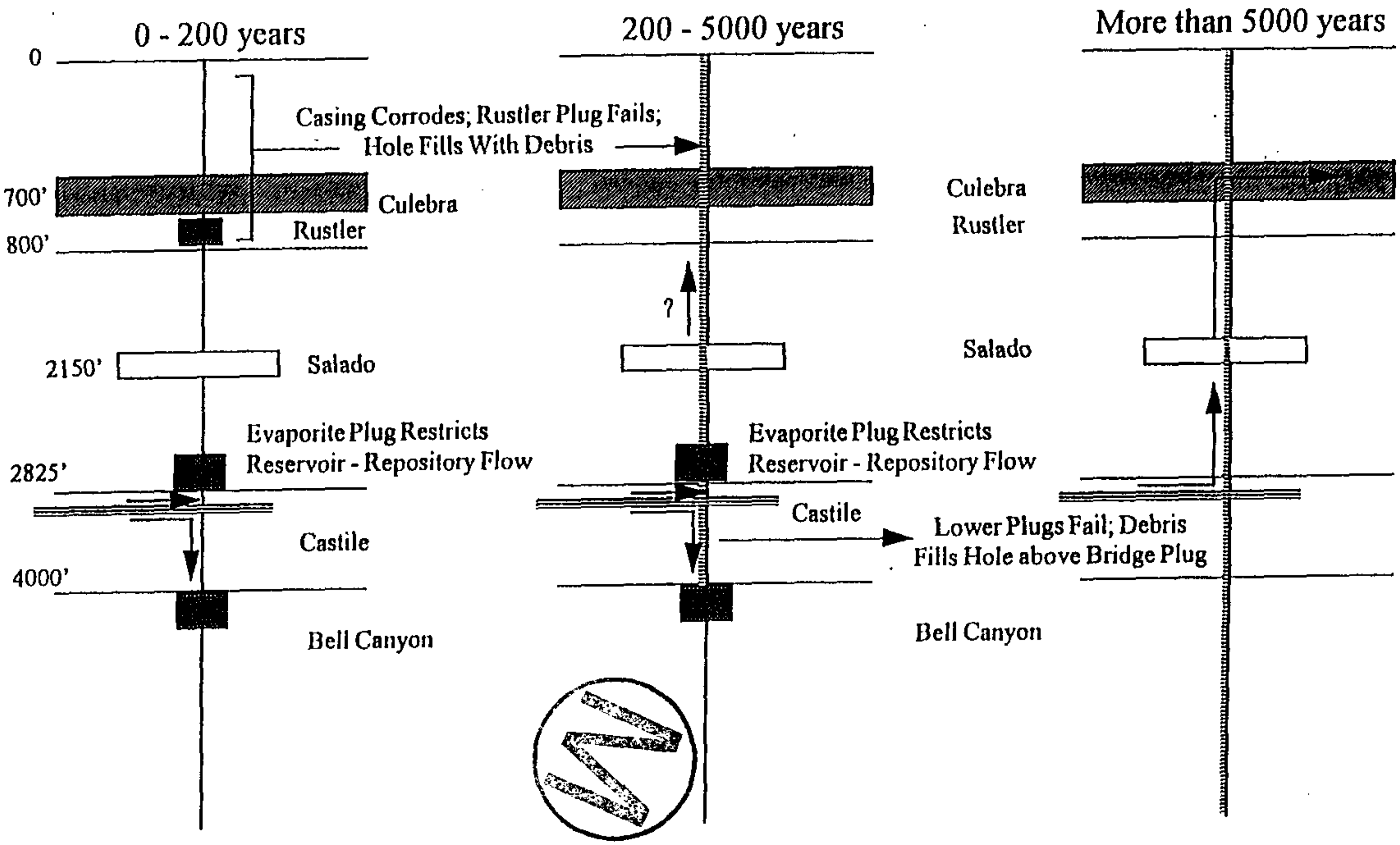


—Values of corrosion intensity in μA/cm² and in mm/year which may be measured in concrete. Below the range 0.1 to 0.2 μA/cm² the amount of corrosion is negligible. Between this range and until 100 to 200 μA/cm², corrosion is active and brown oxides develop. Values above 100 to 200 μA/cm² were never recorded in uncracked concrete.

Figure 10 Degradation of "HTS" in standard marl grundwater "MAR". After 6650 cycles calcite is the only solid phase present (T = 25 °C).



Permeability Changes in a 3 Plug Scenario



0 - 200 years

200 - 5000 years

More than 5000 years

0

700'

800'

2150'

2825'

4000'

Casing Corrodes; Rustler Plug Fails; Hole Fills With Debris

Culebra

Rustler

Salado

Evaporite Plug Restricts Reservoir - Repository Flow

Castile

Bell Canyon

?

Evaporite Plug Restricts Reservoir - Repository Flow

Castile

Lower Plugs Fail; Debris Fills Hole above Bridge Plug

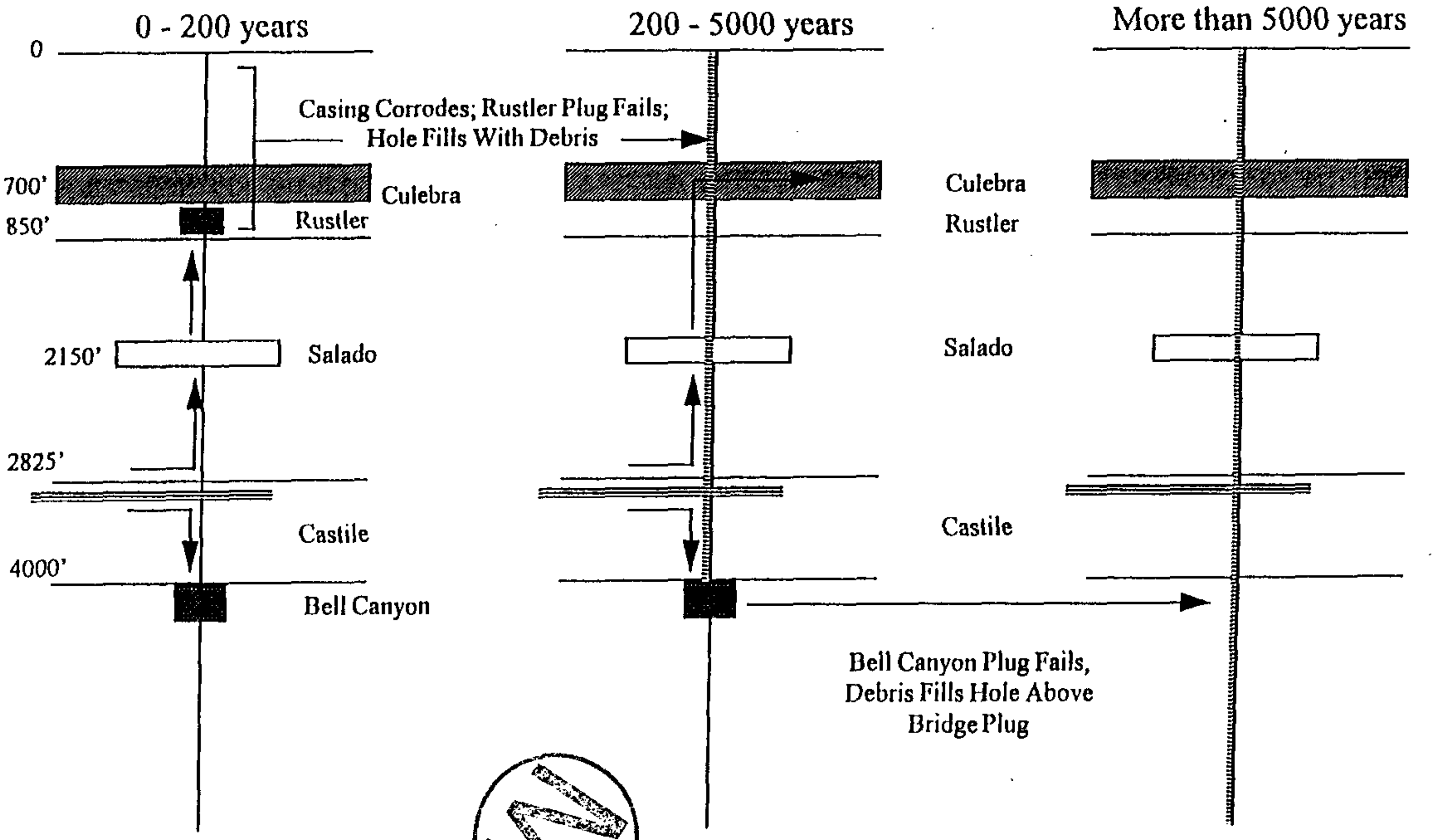
Culebra

Rustler

Salado

Bell Canyon

Permeability Changes in a 2 Plug Scenario



0 - 200 years

200 - 5000 years

More than 5000 years

Casing Corrodes; Rustler Plug Fails;
Hole Fills With Debris

Bell Canyon Plug Fails,
Debris Fills Hole Above
Bridge Plug

Table 1: Hydraulic Properties of Borehole Plugs as a Function of Time: 2 Plug Scenario

Location of Plugs: Top of Bell Canyon; Bottom of Rustler (Below Culebra)
Length of Plugs: 40 m.

Years After Abandonment	Castile - WIPP Repository	WIPP - Culebra (Rustler Plug)	Culebra - Surface (Surface Plug)	Castile - Bell Canyon (Bell Canyon Plug)
0 - 200	unrestricted	5×10^{-17} m^2	5×10^{-17} m^2	5×10^{-17} m^2
200 - 1200	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	5×10^{-17} m^2
1200 - 5000	10^{-12} to 10^{-15} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	5×10^{-17} m^2
> 5000	10^{-12} to 10^{-15} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	10^{-12} to 10^{-15} m^2

Note: Permanent Bridge Plug Assumed at 8,000 feet.

Table 2: Hydraulic Properties of Borehole Plugs as a Function of Time: 3 Plug Scenario

Location of Plugs: Top of Bell Canyon; Between Brine Pocket and Repository; Bottom of Rustler (Below Culebra)
Length of Plugs: 40 m.

Years After Abandonment	Castile - Lower Salado (Salado Plug)	Lower Salado - Repository	Repository - Culebra (Rustler Plug)	Culebra - Surface (Surface Plug)	Castile - Bell Canyon (Bell Canyon Plug)
0 - 200	5×10^{-17} m^2	unrestricted	5×10^{-17} m^2	5×10^{-17} m^2	5×10^{-17} m^2
200 - 1200	5×10^{-17} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	5×10^{-17} m^2
1200 - 5000	5×10^{-17} m^2	10^{-12} to 10^{-15} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	5×10^{-17} m^2
> 5000	10^{-12} to 10^{-15} m^2	10^{-12} to 10^{-15} m^2	10^{-11} to 10^{-14} m^2	10^{-11} to 10^{-14} m^2	10^{-12} to 10^{-15} m^2

Note: Permanent Bridge Plug Assumed at 8,000 feet.

APPENDIX A:
REGULATORY BASIS FOR CONSEQUENCE ANALYSIS OF BOREHOLES

Sharla G. Bertram
Sandia National Laboratories

This Appendix describes the regulatory framework, then discusses the pertinent requirements from 40 CFR Part 194 for consideration of boreholes. Although the main report focuses on a deep borehole that penetrates the underground repository, the context for borehole analyses is much broader.

A.1 REGULATORY FRAMEWORK

On February 9, 1996, the EPA published "Criteria for the Certification and Re-Certification of the Waste Isolation Pilot Plant's Compliance With the 40 CFR Part 191 Disposal Regulations" (40 CFR Part 194, 61 FR 5224-5242). An implicit hierarchy of authority consisting of legislative mandates, regulatory language, and supporting documentation must be considered when applying the rule. The Nuclear Waste Policy Act of 1982, as amended (42 U.S.C. 10101–10270) and the Waste Isolation Pilot Plant Land Withdrawal Act (P.L. 102-579) provide the foundation upon which the implementing regulations, 40 CFR Parts 191 and 194, are based[1]. Supporting documents for 40 CFR Part 194 include:

- the Supplementary Information (SI) published with the final 40 CFR Part 194 (EPA, 1996a),
- the Background Information Document (BID) for 40 CFR Part 194 (EPA, 1996b),
- the Response to Comments Document (RCD) for 40 CFR Part 194 (EPA, 1996c),
- the SI published with the proposed 40 CFR Part 194 (EPA, 1995), and
- the Compliance Application Guide (CAG) (EPA, 1996d).

With respect to the regulations and their supporting documents, the following hierarchy exists:

1. The language found in the regulations (40 CFR Parts 191 and 194) is controlling in all cases, since the regulations bear the "force of law." Where inconsistencies occur between the wording in the regulations and related discussions in the SI, BID, RCD, or the CAG, the regulations always take precedence.

---

[1] Interpretation of 40 CFR Part 194 requires consideration of 40 CFR Part 191, its technical bases, and the Supplemental Information (SI) published with Part 191 in 1985 (50 FR 38066) and in 1993 (58 FR 66398). The SI's for Part 191 continue to apply except where Part 194 modifies them.

2. The SI ("supporting rationale" or "preamble") published in the *Federal Register* with both the proposed and final rules is, after the regulatory language itself, the most authoritative source for interpreting the rules. In addition, an implicit hierarchy exists between the SI for a proposed rule and the resulting final regulation. In cases where there is no significant change between a proposed requirement and the final requirement, the SI for the proposed rule continues to be applicable. In cases where the proposed rule is changed, the SI for the final rule becomes controlling. This interpretation is supported by the statement in the SI for the final Part 194 which states that "[T]hose sections of the final rule which have remained unchanged since the rule's proposal are also further explained in the notice of proposed rule (60 FR 5766–5791)" (61 FR 5225). The SI for the final Part 194 states at 61 FR 5225 that "[T]he supporting rationale for today's action, found in the following summary and discussion of principal changes, **is further explained** in the Background Information Document and the Response to Comments which accompany today's action" (emphasis added).

3. The EPA publishes, coincidentally with both proposed and final regulations, a BID that is intended to further explain the Agency's considerations in developing the rule. Again, the BID for the final rule takes precedence over the BID for the proposed rule, except where no changes have been made. The BID for the final rule states in its Introduction (EPA, 1996b) that: "[T]he final preamble and regulation to 40 CFR part 194, as they appear in the Federal Register, take precedence over any descriptions or interpretations of the final rule that appear in this document."

4. Upon publication of a final rule, the EPA publishes an RCD, in which the Agency responds to public comments submitted to the Docket regarding the proposed rule. In terms of the hierarchy for Part 194, the RCD (EPA, 1996c) is assumed to take precedence over the BID because the RCD contains no disclaimer regarding status vis-à-vis either the BID or the final rule and preamble. This interpretation is supported by the reference to the RCD and the BID in the SI for Part 194, quoted above.

5. The CAG (EPA, 1996d), published as a companion to the final 40 CFR Part 194, is subsidiary to the rule as well as to all of the other supporting documents. The CAG was issued by EPA as simply a guidance document. The EPA states in a Disclaimer to the CAG that "[T]he CAG is intended solely as guidance. The CAG does not establish compliance criteria or any other binding rights and duties...Any inconsistencies between the CAG and the...final rule are wholly inadvertent and, in all circumstances, the final rule is dispositive of any inconsistencies."

A.2 CONSIDERATION OF BOREHOLES IN 40 CFR PART 194 AND SUPPORTING DOCUMENTS

The final rule requires that boreholes drilled within the controlled area and its vicinity be evaluated in performance and compliance assessments. The rule establishes requirements for consideration of borehole drilling, use, and abandonment in sections 194.32, 194.33, and 194.54. The rule also establishes requirements for consideration of future technological capabilities and practices of humankind in section 194.25 and these requirements must be considered in conjunction with sections 194.32, 194.33, and 194.54. Definitions pertinent to borehole modeling are found in section 194.2 of the rule. This appendix discusses the regulatory basis established by the rule for consequence analysis of boreholes. The likelihood of drilling is not considered here.

A.2.1 Future States Assumptions Applicable to Modeling of Boreholes

Because the rule applies today's conditions to the future, we must first consider the "future states" requirements. The rule states that:

> *§ 194.25 Future state assumptions.*
> *(a). Unless otherwise specified in this part or in the disposal regulations, performance assessments and compliance assessments conducted pursuant the provisions of this part to demonstrate compliance with §191.13, §191.15 and part 191, subpart C shall assume that characteristics of the future remain what they are at the time the compliance application is prepared, provided that such characteristics are not related to hydrogeologic, geologic or climatic conditions.*

This requirement is interpreted to mean that, for the purposes of performance assessments and compliance assessments, that only naturally occurring processes and events will change during the period of regulatory concern. Societal, technological, and economic factors of today can be assumed to be in effect for the entire time period of regulatory concern. Indirect anthropogenic effects on repository performance need not be considered.

The SI (EPA, 1996a) published with the rule states that:

> The Agency recognizes the inherently conjectural nature of specifications on future states and wishes to minimize such speculation in compliance applications. The Agency has found no acceptable methodology that could make reliable predictions of the future state of society, science, languages or other characteristics of future mankind. DOE shall assume that [these] present day conditions will exist in their present state for the entire 10,000-year regulatory time frame.

This means that the economic or societal conditions that would motivate human activities, the technological approaches taken in human activities, and the legal requirements that bound human activities must all be assumed to remain the same as prevail on the day that the compliance application is submitted to the EPA (considered to be "today"). Considerations of resource exploration and exploitation between today and sealing of the repository shafts should be limited to those activities that are currently occurring in the vicinity of the WIPP and can be expected to continue to occur given today's economic conditions. Laws and regulations of the State of New Mexico and of the U.S. Department of the Interior should be assumed to govern the practices associated with resource exploration and recovery within the New Mexico portion of the Delaware Basin.

A.2.2 Scope of Analysis of Borehole Drilling for Performance Assessment

Conditions for "undisturbed performance" and for "disturbed performance" are established by the rule.

> *§ 194.32 Scope of performance assessments.*
> *(a) Performance assessments shall consider natural processes and events, mining, deep drilling, and shallow drilling that may affect the disposal system during the regulatory time frame.*
> *(c) Performance assessments shall include an analysis of the effects on the disposal system of any activities that occur in the vicinity of the disposal system prior to disposal and are expected to occur in the vicinity of the disposal system soon after disposal. Such activities shall include, but shall not be limited to, existing boreholes and the development of any existing leases that can be reasonably expected to be developed in the near future, including boreholes and leases that may be used for fluid injection activities.*

The requirement 194.32(c) is interpreted to mean that, for the purposes of performance assessment, activities outside of the Land Withdrawal Area (controlled area) that occur prior to or are initiated before disposal must be evaluated for their possible effects on performance of the disposal system. The effects of any activities, including borehole drilling, completion, and plugging, and all types of resource extraction activities that have occurred or may be initiated prior to shaft sealing, and that can significantly affect radionuclide transport, must be included. These activities are considered to be part of the "undisturbed performance" of the disposal system. Effects of abandoned boreholes must be evaluated over 10,000 years. "Vicinity" means the area adjacent to but outside of the controlled area and extends far enough to include any activities that can affect the disposal system within the 10,000 years of regulatory concern.

The SI (EPA, 1996a) states that:

> In today's final rule, the Agency requires that performance assessments and compliance assessments must include -- among other processes and events -- the effects on the

> disposal system of drilling and all types of resource extraction activities, including inter alia solution mining and fluid injection, that will have occurred prior to the time at which the compliance application is prepared or that may be expected to occur soon afterward based on existing plans and leases for drilling.

This means that analyses of postclosure (after sealing of the repository shaft system) disturbed performance need consider only natural processes and events, mining, deep drilling, and shallow drilling. Preclosure activities are not limited to those required to be considered for postclosure disturbances. Undisturbed conditions that form the base case for the performance assessment must consider the effects on the disposal system over the long term of any human activities that are occurring in the vicinity of the disposal system today. Continued occurrence or initiation of new occurrences of the same activities in the near future must also be considered, if reasonably expected under today's conditions. Activities expected to be under way at the time of shaft sealing should be assumed to continue to their planned completion. The SI (EPA, 1996a) for the final rule recognizes three categories of drilling that have a time component.

> Sections 194.32 and 194.33 of the final rule require that performance assessments include the effects of both deep drilling and shallow drilling, whether such drilling has occurred prior to the time at which the compliance application is prepared, can be reasonably expected to occur in the near future based on existing leases, or can be expected to occur in the future during the 10,000-year regulatory time frame.

Because human activities initiated after shaft sealing will begin more than 30 years from today and the history of such activities covers only 100 years, attempting to project new activities is not reasonable. For this reason, no activities initiated after shaft sealing should be considered for undisturbed performance. "Near future" thus would be defined as the period between today and the time of shaft sealing, but would include completion of ongoing activities (e.g., for the typical "lifetime" of an oil or gas well today).

Projections of human activities for the "near future" need consider only existing leases and plans. Because proprietary plans are not likely to be available, only publicly available information should be considered as plans. Because existence of a lease does not guarantee that resource exploration and exploitation will occur, economic considerations should take precedence over leases and plans in projecting activities.

Both shallow drilling and deep drilling activities must be considered to continue to occur as they are today. Section 194.2 of the rule defines both drilling events. "Deep drilling" denotes those drilling events that reach or exceed a depth 2150 feet below the surface where such drilling occurred. "Shallow drilling" denotes those drilling events that do not reach to a depth 2150 feet below the surface where such drilling occurred.

The requirement in section 194.32(c) defines undisturbed performance, because similar language in 194.54 requires the same considerations, and 194.54 applies to undisturbed performance only.

The RCD (EPA, 1996c) corroborates this interpretation (see Issue 7.D.10): "It is reasonable to assess the undisturbed performance of WIPP to fully consider the realities of the site-specific conditions."

Examining the interaction of boreholes is supported by the language of the SI (EPA, 1996a), which states that "When analyzing the effects of all later boreholes, performance assessments must account for the effect that these existing boreholes will have had on the hydrogeologic properties of the disposal system and on the creation of new pathways for releases."

The SI (EPA, 1996a) indicates three time frames when considering activities that may affect the disposal system: first, occurred prior to the submittal of the Compliance Certification Application (CCA) (i.e., "historical" time); second, expected to occur prior to disposal or soon after disposal i.e., ("near future" time); and third, assumed to occur after disposal (i.e., "future" time). Activities during the first and second time frames are defined by 194.32(a) and 194.32(c) to occur in the **vicinity** of the disposal system (i.e., in the vicinity of the controlled area by DOE's definition of disposal system), and are prevented from occurring within the controlled area during the period of DOE control. It is important to note that only those activities currently taking place in the vicinity of the disposal system need be considered for projection into the near future. Historical activities (e.g., nuclear testing) need not be projected into the near future. It will be necessary for the DOE to determine what human activities will be initiated prior to repository closure, but will end after repository closure (after being carried to the reasonable completion of the activity), and to assess the duration and long-term impacts of those activities. For example, if a permit application for an injection well at a given location is predicted to be submitted to the appropriate regulatory authority by the lessee of the resource prior to repository closure, then the associated fluid injection activity would be projected to its completion for the borehole in question.

Consideration of drilling activities during the third time frame is limited by 194.33 to locations where drilling may affect the disposal system, by 194.33(d) to the act of drilling and the effects of the abandoned borehole (excluding any resource recovery subsequent to drilling), and by the institutional controls (194.41 and 194.43) to some future century when passive institutional controls (PICs) are ineffective. Future human activities are part of disturbed performance and are to be considered in evaluating compliance with the Containment Requirements of 40 CFR Part 191. All "near future" and "future" activities are limited by the Future States requirements (194.25) as discussed in Section A.2.1 above.

The distinction between "near future" and "future" is vague in both the SI and the rule. The rule says consider "near future" activities occurring after disposal. The logical way to define "near future" is to consider the continuation of any activity that is initiated prior to shaft sealing (preclosure) by predicting the end of that activity at some reasonable date after shaft sealing (postclosure). The demarcation between "near future" and "future" is assumed to be the date of shaft sealing (closure). The CAG (EPA, 1996d, Section 194.32) states that:

> The EPA recommends that the terms 'near future' and 'soon after disposal' for oil and gas drilling be considered to consist of the expected lives of the oil and gas fields in existing leases that can reasonably be expected to be developed in the vicinity of the WIPP.

Considerations of resource exploration and exploitation between today and sealing of the repository shafts should be limited to those activities that are currently occurring in the vicinity of the WIPP and can be expected to continue to occur given today's economic conditions, existing leases, and plans. Laws and regulations of the State of New Mexico and of the U.S. Department of the Interior should be assumed to govern the practices associated with resource exploration and recovery. Furthermore, the Future States requirement (194.25(a)) limits consideration of the "near future" to activities that could be undertaken given today's economic conditions, technology, and regulations. For example, the Future States requirement limits this CAG guidance to today's economics regarding the continued exploitation of the target oil or gas "field" for a given lease. If secondary or tertiary recovery are not economic today, they need not be considered.

Hence, drilling activities that are **initiated** subsequent to repository closure should be considered to be future activities and, as such, performance assessments need only consider the impacts of the process of drilling the borehole and the condition of the borehole after abandonment. The impacts of the use of a future borehole are specifically excluded from performance assessments. This concept is supported by the RCD (EPA 1996a, Issue 19.R):

> Section 194.54 limits the scope of compliance assessments to undisturbed scenarios; only existing boreholes and other activities which **occur before disposal** must [be] accounted for in compliance assessments (since such current human activities constitute part of the baseline site characterization) (emphasis added).

The RCD takes precedence over the CAG, as discussed in Section A.1 above.

In the RCD (Issue 12.J.4), EPA states:

> The boreholes resulting from such activities shall be analyzed for their effects on the properties of the disposal system for this entire 10,000-year regulatory time frame. Predictions about the effects of such existing boreholes should be based on the actual characteristics of the boreholes, as far as it is practicable to determine them. Such characteristics would include drilling, completion, and plugging procedures.

A.2.2.1 Constraints on Conditions of the Borehole

The manner in which the DOE must assess the impacts from drilling are specifically addressed in Part 194. Beyond the requirements presented in §194.32, as discussed above, the EPA addresses the consideration of drilling in performance assessments in §194.33.

§ 194.33 Consideration of drilling events in performance assessments.

(a) Performance assessments shall examine deep drilling and shallow drilling that may potentially affect the disposal system during the regulatory time frame.

(b) The following assumptions and process shall be used in assessing the likelihood and consequences of drilling events, and the results of such process shall be documented in any compliance application:

(1) Inadvertent and intermittent drilling for resources (other than those resources provided by the waste in the disposal system or engineered barriers designed to isolate such waste) is the most severe human intrusion scenario.

(c) Performance assessments shall document that in analyzing the consequences of drilling events, the Department assumed that:

(1) Future drilling practices and technology will remain consistent with practices in the Delaware Basin at the time a compliance application is prepared. Such future drilling practices shall include, but shall not be limited to: the types and amounts of drilling fluids; borehole depths, diameters, and seals; and the fraction of such boreholes that are sealed by humans; and

(2) Natural processes will degrade or otherwise affect the capability of boreholes to transmit fluids over the regulatory time frame.

(d) With respect to future drilling events, performance assessments need not analyze the effects of techniques used for resource recovery subsequent to the drilling of the borehole.

This requirement is interpreted to mean that, for the purpose of performance assessment:

(a) All possible locations in the Delaware Basin, both within and outside of the boundary of the Land Withdrawal Area (LWA), must be examined to determine whether either shallow or deep boreholes at particular locations, either alone or in combination with other shallow or deep boreholes, could potentially affect the disposal system, e.g., by modifying ground-water flow and associated phenomena within the disposal system. The vicinity for this analysis is the area within which such drilling can affect the performance of the disposal system during the 10,000 years of regulatory concern.

(b) When considering human actions that directly penetrate the waste, the most severe action that must be analyzed is drilling for natural resources by drill crews who are unaware of the presence and contents of the repository. Both exploratory and developmental drilling must be considered.

(c)(1) Performance assessments should be based on a defensible analysis of current drilling technology and borehole drilling and sealing practices, considering applicable regulations in effect in the Delaware Basin at the time the certification application is prepared. The assessment should be adjusted to realistically reflect the extent to which applicable requirements are actually satisfied. The rate at which boreholes are sealed can be based on the sealing rate since the effective date of pertinent regulations for boreholes (hydrocarbons,

> potash, and water each considered separately) within the portion of the Delaware Basin containing similar resources to those in the vicinity of the WIPP. The sealing practice can be based on the practice for boreholes in the vicinity of the WIPP. "Vicinity" can be defined by the extent of the Salado Formation on Federal lands within the Delaware Basin in the State of New Mexico, for the purposes of establishing the sealing-practice data base. A deep borehole can be assumed to remain uncased at the repository horizon for three days during drilling.
>
> (c)(2) The hydraulic conductivity of boreholes can be assumed to change after the hole is abandoned. This property may increase or decrease depending on the drilling practice (presence of casing and sequence of casing and grout), sealing practice (on abandonment) for a particular borehole, and the chemical and mechanical processes affecting the casing, grout, seals, and host rock after the hole is abandoned.
>
> (d) In analyzing **future** boreholes under the Containment Requirements of 40 CFR Part 191, the only effects that need to be considered are the drilling of the borehole and the potential for the subsequently abandoned borehole to act as a pathway for ground-water flow. Any effects on the disposal system resulting from the use of boreholes for any post-drilling activities can be excluded from the analyses.

The effectiveness of borehole seals[2] is required to be assumed to change over time, either degrading or improving, depending on the processes acting on the seals.

Taken together, §§194.25, 194.32, 194.33 and 194.54 require that the DOE assess the impacts of boreholes in three distinct phases. The first phase includes those boreholes abandoned prior to the current regulations (about 1988) requiring specific sealing practices. The types and uses of boreholes that must be considered are those that occurred historically in the Delaware Basin, including the controlled area, and that could affect the long-term performance of the disposal system. Performance assessments and compliance assessments must include the long-term impacts from both plugged and unplugged boreholes in assessing the undisturbed performance of the disposal system. The number of plugged and unplugged boreholes and their uses should be based upon currently available data. In the RCD (EPA 1996c, Issue 12.J.4), EPA states:

> The boreholes resulting from such activities shall be analyzed for their effects on the properties of the disposal system for this entire 10,000-year regulatory time frame. Predictions about the effects of such existing boreholes should be based on the actual characteristics of the boreholes, as far as it is practicable to determine them. Such characteristics would include drilling, completion, and plugging procedures.

The second phase that must be considered in performance assessment and compliance assessment includes boreholes abandoned after 1988 but initiated prior to sealing of the repository shafts.

---

[2] Sealing includes grouting between the casing and the host rock and grouting inside the casing.

The types and uses of boreholes that must be considered are those that are occurring today in the vicinity of the WIPP. Current field practices are to be assumed for these boreholes (194.33(c)). While both performance assessments and compliance assessments must consider these boreholes in assessing undisturbed performance, they can do so assuming that the holes have been sealed in accordance with the appropriate regulatory guidelines (194.25(a)). The primary distinction between these boreholes and those in the previous phase is that the State of New Mexico Oil Conservation Division (OCD) regulatory requirements (Order R-111-J) on borehole sealing apply to those drilled on State or private lands after 1988. The OCD implementing regulation (Rule 202) states that "before any well is abandoned, it shall be plugged in a manner which will permanently confine all oil, gas, and water in the separate strata originally containing them." Regulations of the U.S. Dept. of the Interior are implemented by the Bureau of Land Management (BLM). Those regulations also stipulate plugging practices, and the BLM strives for consistency with the NM OCD. The BLM regulations have been consistently enforced since about 1990. While these requirements apply to drilling of oil and gas wells, other requirements relating to potash exploration and groundwater protection would also apply to boreholes where appropriate.

The third phase includes those boreholes initiated after the repository has been sealed. These boreholes are assumed to be drilled, completed, and abandoned exactly as those in the second phase, but the EPA considers these "future" boreholes to be disturbed performance and excludes them from compliance assessments (194.54(a)). Part 194 requires that performance assessments must consider future boreholes, but limits the impacts to the effects of drilling and the subsequent condition of the abandoned borehole with respect to the transmission of fluids. Any use of the borehole is excluded from consideration, but the effects on the hydrogeologic state of and possible spread of contaminants through the disposal system resulting from natural or waste- and repository-induced flow into near-miss boreholes and flow through boreholes to units above or below the Salado must be considered in performance assessments.

Once a borehole is drilled and sealed, the borehole will affect the disposal system indefinitely into the future. The specific concerns stated in the SI (EPA, 1996a) are affects on the hydrogeology and the creation of new pathways for radionuclide releases.

> Further, boreholes drilled after closure of the repository shall be assumed to affect the properties of the disposal system for the remainder of the 10,000-year regulatory time frame. When analyzing the effects of all later boreholes, performance assessments must account for the effect that these existing boreholes will have had on the hydrogeologic properties of the disposal system and on the creation of new pathways for releases.

The SI (EPA, 1996a) repeated essentially the same language as section 194.33 with regard to future drilling practices and sealing rates. The proximity of this language on seals to the discussion of future sealing rates indicates that EPA is discussing the future and not the past.

> Section 194.33 requires performance assessments to make several specific assumptions about future deep drilling and shallow drilling. These assumptions include that drilling will

> occur randomly in space and time and may occur at different rates for each resource, and that drilling practices will remain as those of today and may vary depending on the resource. Performance assessments should assume that the permeability of sealed boreholes will be affected by natural processes, and should assume that the fraction of boreholes that will be sealed by man equals the fraction of boreholes which are currently sealed in the Delaware Basin.

Considering the future states requirements, "fraction currently sealed" can be interpreted to mean the fraction of future boreholes sealed under today's State and Federal laws, regulations, and enforcement practices. The SI (EPA, 1996a) further instructs that the analyses must consider affects of drilling for each resource separately. The resources associated with borehole drilling today are water (shallow drilling), potash (shallow exploration drilling), and hydrocarbons (deep drilling).

> The Agency recognizes that drill operators currently employ different techniques in the exploration and development of each resource. Hence, performance assessments shall conduct a separate analysis of the effects that future drilling for each different resource -- the act creating a borehole -- will have on the disposal system. Each separate analysis should set the future rate of drilling for the particular resource equal to the historical rate at which that resource has been drilled for in the Delaware Basin during the past 100 years. The analyses of the consequences of each type of drilling might remain conceptually similar, but vary with regard to assumptions made on size and depth of boreholes, quantity of drilling fluid used, or any other characteristic specific to that type of resource. Analyses of the consequences of future drilling events may be confined only to the drilling activity and the subsequent effect of the borehole's presence and need not include an analysis of extraction and recovery activities which would occur subsequently.

Analyses of consequences of borehole drilling cannot assume that drillers will recognize the hazards associated with drilling into the disposal system, nor can one intrusion be assumed to deter another.

The vicinity within which either shallow or deep drilling must be analyzed can be defined as the area in which the drilling or the abandoned borehole can affect the disposal system within the 10,000 years of regulatory concern. The vicinity for deep drilling is not necessarily the same as the vicinity for shallow drilling. In the RCD (EPA, 1996c, Comment 12.B.1), the EPA states

> In performance assessments, scenarios involving human intrusion anywhere in the Delaware Basin must be analyzed if they could have an effect on the repository, per §194.32(a). Section 194.32 establishes the scope of processes and events that need be considered in performance assessments (PA). The final rule logically limits the scope of PA to those events that may affect the disposal system during the regulatory time frame [§194.32(a)].

The EPA clearly considers penetration of the lithosphere anywhere in the Delaware Basin to be human intrusion. Furthermore, mining is considered to be intrusion, even though the mining being considered does not intersect the repository. The response to comments 12.B.2-12 in the RCD (EPA, 1996c) contains this logic:

> In §194.32 and §194.33 of the final rule, the Agency has provided further clarification on which activities fall within the scope of human intrusion, and, in response to public comments, has modified the terms used to avoid confusion. Section 194.33 of the final rule requires that two types of activities be analyzed—deep drilling and shallow drilling. Deep drilling (referred to as "human intrusion" in the proposed rule) is defined as drilling events in the Delaware Basin that reach or exceed a depth of 2150 feet below the surface (the level of the waste in the disposal system). Shallow drilling (referred to as "human activity" in the proposed rule) is defined as those drilling events in the Delaware Basin that do not reach a depth of 2,150 feel below the surface relative to where such drilling occurred.
>
> Consistent with the changes in defined terms, §194.33 in the final rule is titled *Consideration of drilling events in performance assessments*.... **This clarifies the Agency's intent that neither deep drilling nor shallow drilling events shall be considered in analyses of undisturbed performance of the disposal system (emphasis added).** The term human intrusion should not be interpreted as being confined to drilling only. The preamble accompanying the final rule explains the various types of drilling activities encompassed by the terms deep and shallow drilling. Further, as discussed in §194.33(c)(1), those ancillary activities which are associated with drilling, such as borehole sealing, are within the scope of this term. In response to public comments, EPA has also required consideration of excavation mining events as described in §194.32(b). The consideration of human intrusion is limited to those events which are made without knowledge of the repository's presence. This type of event would constitute an 'inadvertent intrusion.'

The key to interpreting the requirement in 194.33(b)(1) is the word "severe." No definition for this term is provided in the rule or the SI. "Severe" could mean either enhancing transport of radionuclides out of the engineered facility (repository) or disrupting the geohydrologic conditions within the disposal system. Because 194.32 requires that the performance assessment include effects of mining, which has a much greater impact on the geohydrology of the disposal system than does a borehole, "severe" must refer to enhancing transport of radionuclides from the engineered facility. Based on this rationale, drilling penetrations of the disposal rooms are the most severe human intrusion into the repository that must be included in performance assessment. This does not preclude consideration of a borehole penetrating a plume of radionuclides elsewhere in the disposal system. This conclusion is supported by the EPA's statement in the BID (EPA, 1996b, Section 9.1) that

> These criteria are based on the assumption that inadvertent and intermittent drilling for resources is the most severe scenario to be considered when addressing human intrusion for performance assessment calculations because it provides a direct intersection with the waste and a pathway to the surface. Mining of resources is a very important, though less direct form of a human-initiated process or event.

Subsequent discussions in the BID (sections 9.1 and 9.3.2-4) on shallow drilling corroborate that the analyses must also consider drilling that encounters strata "contaminated with radioactivity from the repository. Therefore, the borehole permeability model should also be applied when analyzing intrusion into a contaminant plume, as well as when considering whether a borehole that does not penetrate any contaminated zone can affect performance of the disposal system

The CAG (EPA, 1996d) states that the compliance application is expected to:

> demonstrate that exploratory and development wells were included in the analysis of inadvertent and intermittent intrusion by drilling for resources and the manner in which they were evaluated.

A.2.2.2 Drilling Practices

The EPA has stated that drilling practices used in the Delaware Basin at the time the application is prepared can be assumed to be the drilling practices for the entire time of regulatory concern. This is consistent with the future states requirements (194.25). The requirement deals with documenting assumptions about drilling activities. The CAG (EPA, 1996d) states that the compliance application is expected to identify:

> current drilling practices in the Delaware Basin; the current drilling practices that affect performance assessments; types and amounts of drilling fluids; borehole depths typically used; borehole diameters typically used; seals typically used; the fraction of boreholes sealed by humans today; and the source(s) of the above information.

Review of the SI, BID, and the RCD for 40 CFR Part 194 leads to the conclusion that the EPA intends that performance assessments realistically address today's practices and conditions in the Delaware Basin.

The SI (EPA, 1996a, p. 5230, Col. 2) states

> Section 194.33 requires performance assessments to make several specific assumptions about future deep drilling and shallow drilling. These assumptions include...that drilling practices will remain as those of today and may vary depending on the resource. Performance assessments...should assume that the fraction of boreholes that will be sealed by man equals the fraction of boreholes that are currently sealed in the Delaware Basin....

In its first set of comments on proposed Part 194 (EPA Air Docket IV-D-10, April 27, 1995), SNL observed that the proposed rule was internally inconsistent in that one section stated that boreholes should be considered to be sealed at a rate representative of the sealing practices for the last 50 years, while another section refers to "current " practices. To resolve the inconsistency, SNL suggested that 194.33 be revised to state that "Boreholes will be sealed **consistent with current drilling practices** in the Delaware Basin." EPA, in its RCD, responded (EPA, 1996c, Issue 12.E) that

> [T]reatment of sealing of boreholes must assume, per section 194.33(c) of the final rule, that borehole depths, diameters, and seals will remain consistent with current practice in the Delaware Basin. In addition, an examination of current practice must be used to determine the fraction of boreholes which are sealed by humans...."

In its supplementary comments on proposed Part 194 (EPA Air Docket No. A-92-56, September 13, 1995), SNL re-iterated the earlier comment, and expanded it further by stating that "[S]ealing practices have improved considerably over the past 50 years, and credit should be allowed for this improvement." "In the context of borehole seals, *current practice* (194.33) and *today* (194.25) should refer to those rules and regulations issued by the State of New Mexico and in effect at the time of the final PA analyses regarding the abandonment and plugging of wells." In response to this comment, EPA in the RCD (EPA, 1996c, Issue 12.J.3) simply re-iterates the content of 194.33(c)(1), but then goes on to state that

> [T]he analyses of current practice must be substantiated in any compliance application, showing references and the factual basis used to establish 'current practice'. The Agency believes that the criteria in the final rule provide adequate direction to DOE.

The EPA in its response does not refer to any specific borehole sealing regulations and requirements. The response noted above does appear, however, to implicitly recognize that such an approach on the part of DOE would be acceptable, if justified.

Section 9 of the BID (EPA, 1996b), "Consideration of Human Intrusion" contains an extensive discussion of drilling and borehole sealing in the Delaware Basin, including State and Federal (BLM) permitting and drilling and casing practices (Sections 9.3.1,1 and 9.3.1.2

respectively). Specifically, Section 9.3.1.4 (Borehole Plugging and Abandonment) relates plugging techniques to BLM and State requirements but observes that:

> [T]he number of unplugged boreholes drilled **prior to the more stringent institutional controls now employed** is unknown, but has been characterizes as 'many' by OCD field personnel...The issue of unsealed or improperly sealed boreholes must also be factored into analysis of repository integrity.

An evaluation, in context, of the contents of Section 9.3.1.4 leads to a reasonable conclusion that, while EPA may be somewhat skeptical about the degree to which boreholes are sealed, the Agency has no fundamental objection to the Department's reliance on the current regulatory constraints imposed on drillers. The application of *current* institutional (i.e., regulatory) controls as input assumptions for PA must, however, be tempered by a realistic assessment of the existing level of compliance in the Basin, i.e., neither 100% effectiveness nor zero compliance with the applicable regulations is realistic.

Section 9.3.1.5 (Human Intrusion Scenarios) of the BID (EPA, 1996b) supports using realistic borehole-sealing assumptions. The first paragraph of the section (quoted in its entirety) follows:

> In addition to the radioactivity release scenarios involving direct transfer of waste to the surface by a borehole which penetrates the repository, several other scenarios involving human intrusion can be theorized. For example, SNL developed a family of scenarios involving boreholes which penetrate the waste and are then plugged above the overlying transmissive Culebra Member of the Rustler Formation. Solubilized waste then moves up the borehole by brines found in the underlying formations and then, **due to the borehole seal**, laterally through the relatively transmissive Culebra towards the WIPP site boundary (SAN92). **The assumption of borehole sealing depth is consistent with the sealing practices in the area and the regulatory requirements.** The assumption is also reasonably analogous to the other geologic systems that were analyzed **so that DOE should be able to defend** the above scenario" (emphasis added).

Thus, the EPA believes that the presence of a surface plug is consistent with their concept for evaluating borehole seals. Furthermore, the reference to "regulatory requirements" indicates that the Agency is prepared to accept a defensible argument that current practice is indeed constrained by the need to comply with applicable sealing requirements.

The EPA states in the SI (61 FR 5230)

> The analyses of the consequences of each type of drilling might remain conceptually similar, but vary with regard to assumptions made on size and depth

> of boreholes, quantity of drilling fluid used, or any other characteristic specific to that type of resource.

Characteristics of deep drilling vary depending on the stratigraphy, particularly on the presence (or absence) of salt and the thickness of the strata overlying the target horizon. For example, sealing practices are dependent on whether the salt section is present. Therefore, basing sealing practices on boreholes where the stratigraphy is similar to the stratigraphy of the Controlled Area is realistic.

The EPA states in the BID (EPA, 1996b, Section 9.3.1.2):

> If the WIPP site were to be penetrated by inadvertent human intrusion, such an event would occur during drilling through the salt section before the intermediate casing is set. Once the intermediate casing is set in place and the annulus between the casing and the borehole wall is sealed with cement, then the possibility of radionuclide contamination reaching the surface will be prevented as long as the casing remains intact. Typically, casing integrity is demonstrated by pressure testing and ultrasonic logging of the cemented section for bonding between the casing and the cement and between the cement and the formation. It is estimated that this critical section of a borehole would remain uncased for no more than three days during drilling.

A.2.2.3 Conditions in the Abandoned Borehole

The language in 194.33(c)(2) establishes two opposite results. Degradation would result in higher hydraulic conductivity than the borehole had when originally abandoned. The phrase, "Or otherwise affect," allows an alternative result that can lower the hydraulic conductivity. Application of 194.33(c)(1) requires consideration of drilling practice and sealing practice to determine the materials in the borehole and whether the hydraulic conductivity of the materials decreases or increases.

The CAG (EPA, 1996d) states that the compliance application is expected to:

> identify the processes that are expected to affect boreholes over time [and] discuss the portions of the borehole over which particular processes are expected to act. For example, creeping of the salt is one process that could affect a borehole in the salt section, while other processes may affect other portions of a borehole[.]" The application is expected to "discuss the effects that natural degradation are expected to have on the capability of boreholes to transmit fluids; and identify the models in which borehole degradation is addressed.

A.2.3 Scope of Analysis of Borehole Drilling for Compliance Assessment

§ 194.54 Scope of compliance assessments.
(b) Compliance assessments of undisturbed performance shall include the effects on the disposal system of:

> *(1) Existing boreholes in the vicinity of the disposal system, with attention to the pathways they provide for migration of radionuclides from the site; and*
> *(2) Any activities that occur in the vicinity of the disposal system prior to or soon after disposal. Such activities shall include, but shall not be limited to: existing boreholes and the development of any existing leases that can be reasonably expected to be developed in the near future, including boreholes and leases that may be used for fluid injection activities.*

The SI (EPA, 1996a) states that:

> Section 194.54 defines the scope of compliance assessments. Compliance assessments should be conducted of the undisturbed performance of the disposal system, which, by the definition in section 12 of 40 CFR Part 191, denotes that the disposal system is not disrupted by human intrusion or the occurrence of unlikely natural events.
>
> The Agency recognizes, however, that resource extraction and fluid injection activities which are currently performed in the Delaware Basin can alter the hydrogeologic properties of the initial state of the disposal system. The final rule requires that performance assessments and compliance assessments analyze the effects of all types of fluid-injection and all boreholes which can have an effect on the disposal system and which have been or will have been drilled prior to or soon after disposal. These boreholes shall be assumed to affect the properties of the disposal system for the entire 10,000-year regulatory time frame. Predictions about such future activities shall be strictly limited to the expected use of existing leases.

Compliance assessments of undisturbed conditions for 40 CFR Part 191 section 15 and Subpart C must consider the effects on the disposal system over the long term of any borehole drilling activities that are occurring in the vicinity of the disposal system today. Continued occurrence or initiation of new occurrences of the same activities must also be considered, if expected to occur on existing leases given today's conditions, up until the time of shaft sealing. Activities under way at the time of shaft sealing should be assumed to continue to their planned completion. For the reasons previously given, activities initiated after shaft sealing should not be considered in analyses of as undisturbed conditions. Preclosure borehole drilling-related activities are the same as those required to be considered as the base case for the performance assessment.

References

U.S. EPA, 1995, Proposed Rule 40 CFR Part 194, Criteria for the Certification and re-Certification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR Part 191 Disposal Regulations, in *Federal Register* Vol. 60, pp. 5776-5791, January, 1995.

U.S. EPA, 1996a, 40 CFR Part 194, Criteria for the Certification and re-Certification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR Part 191 Disposal Regulations, in *Federal Register* Vol. 61, pp. 5224-5245, February 1996.

U.S. EPA, 1996b, Criteria for the Certification and re-Certification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR Part 191 Disposal Regulations, Background Information Document for 40 CFR Part 194, EPA 402-R-96-002, January 1996.

U.S. EPA, 1996c, Criteria for the Certification and re-Certification of the Waste Isolation Pilot Plant's Compliance with the 40 CFR Part 191 Disposal Regulations, Response to Comments Document for 40 CFR Part 194, EPA 402-R-96-001, January 1996.

U.S. EPA, 1996d, Compliance Application Guidance for 40 CFR Part 194, EPA 402-R-95-014, March 1996.

APPENDIX B: CORROSION OF STEEL

B.1 INTRODUCTION

Corrosion of steel is an important process in the performance of boreholes because the holes will be steel cased, and these casings will physically support the concrete plugs used on abandonment. When the steel casing breaches, formation waters can enter and flow within the borehole, except where this flow is inhibited by an effective plug. If the formation waters are pressurized, as they may be for example in the Castile brine pockets, connection with the inside of the borehole will lead to steep hydraulic gradients across plugs, enhanced flow through the concrete, and accelerated concrete degradation. If the casing corrodes to the point where it ceases to provide physical support for the concrete plug, then the plug will be by-passed, and will eventually fail. Flow around the plug will expose an increased surface area for chemical attack which, combined with the plug's loss of physical confinement, will result in rapid disintegration of the concrete element. Deterioration of the steel casing, which is considered in this Appendix is therefore an important element of plug performance, as are the rate and failure associated with concrete degradation which are discussed in Appendix C.

Corrosion is a process which alters metal materials and causes them to lose both density and strength. The mechanisms and rates with which metals corrode vary with the composition and fine structure of the metal, as well as with variations in the corroding environment. Borehole casing material is "steel", which is a term applied to a wide variety of metal alloys that contain iron as a principal ingredient. As a result, there is no unique corrosion rate or mechanism for "steel". Similarly, there is no unique corrosion environment at WIPP. Rather, there are a number of brine environments in which corrosion is expected. Because of these variabilities, the technical approach taken in this document is to make reasonable simplifications to the composition of the reactants (water and steel), and to attempt to set reasonable limits or brackets on those variables that cannot be simplified or defined.

Estimations of steel corrosion have been derived from both calculations and empirical data. Calculations have relied on traditional concepts embodied in equilibrium thermodynamics, while empirical data have been taken from experiments described in the open literature. Both of these methods have their shortcomings, since the thermodynamic calculations assume equilibrium in chemically simplified systems, and the empirical results assume that generic data apply reasonably well to site-specific WIPP conditions. Clearly, neither method alone will result in a highly accurate estimate of borehole casing corrosion at the WIPP. However, the use of both methods, and the comparison of predictions with the experience of oil and gas field developers near the WIPP, and similar practical comparisons, adds confidence that the results described in later sections are reasonable and are expected to be correct within an order of magnitude.

B.2. ORGANIZATION

The sections below contain descriptions of the theoretical calculations (Section B.3) and empirical analyses (Section B.4) performed to evaluate casing corrosion at the WIPP. Each of these section contains several subsections which contain discussions of the details of the method, assumptions employed, deduced results and limitations or cautionary notes that apply to the results. The subsections of Section B.4 include reviews of corrosion experiments conducted under oxic and anoxic conditions. Section B.5 contains a discussion of the findings, including observations that support the reasonableness of deduced results.

B.3 THEORETICAL EVALUATIONS OF STEEL CASING CORROSION AT THE WIPP

Equilibrium thermodynamics provides a basis for establishing some limits on corrosion, including constraints imposed by the equilibrium concentrations of corrosion products, such as the aqueous solubility of iron and the equilibrium fugacity of volatile product species such as hydrogen. In simplified terms, in chemical systems where constituents can neither be added to or removed, reactions cannot ordinarily proceed beyond equilibrium. Thus, if the amount of available water is known, establishing the equilibrium solubility of iron constrains the total mass of iron that can be removed from solid, metallic form. Such a calculation is important to determining if casing can be dissolved to create a vertical pathway from brine reservoirs located in the Castile, through the repository horizon, to an exit pathway in the Culebra. Similarly, establishing the equilibrium hydrogen fugacity helps identify when corrosion of steel is expected to cease in a closed system.

B.3.1 Details of the Thermodynamic Calculation Methods Used

To perform thermodynamic calculations, balanced equations must be written for the relevant reactions and reliable thermodynamic data, such as free energies of formation, must be available. For the materials involved here (aqueous solutions and iron-based alloys), a number of relevant reactions have been hypothesized. The free energy of each reaction was calculated by subtracting the molar free energies of the reactants from the products. The equilibrium constant, K, was calculated from the Nernst equation and the relationship between the free energy of reaction and equilibrium constant ($\Delta G = -2.303\ RT\log K$) was used to calculate concentrations of interest. All calculations were performed for a temperature of 25 °C.

The stepwise progression of calculations is shown below:

Step 1, Calculate Free Energy of Reaction:

$$\Delta G(\text{reaction}) = \Delta G(\text{products}) - \Delta G(\text{reactants}) \qquad (1)$$

Step 2, Formulating the Equilibrium Constant:

For a reaction $A^a + B^b = C^c + D^d$:

$$K = (C^c)(D^d)/(A^a)(B^b) \tag{2}$$

where items in parentheses are molar concentrations (chemical activities) or partial pressures (fugacities).

Step 3, Relating Free Energy to K:

$$\Delta G(\text{reaction}) = -2.303\ RT \log K;\ \text{at } 250C; \tag{3}$$

$$\text{with } \Delta G \text{ in calories } \text{Log } K = \Delta G/1.364 \tag{4}$$

Step 4, Calculating Equilibrium Concentrations of Interest:

Calculate K from Log K and substitute the result into Step 2 (along with other known or assumed concentrations) to calculate the concentration or fugacity of interest.

Thermodynamic data are available in published tabulations and in the open literature. In this investigation, the tabulation available in Geological Survey Bulletin 1452 (Robie and Waldbaum, 1978) has been used as the primary authority. Tabulated data presented as Appendix VIII, Standard Free Energies, Enthalpies and Entropies in "Introduction to Geochemistry" (Krauskopf, 1967) has been used as a secondary source. During calculations, care has been taken not to mix data bases.

B.3.1.1 Calculating the Solubility of Iron in WIPP Formation Waters

The solubility of steel casing in WIPP ground waters is a consideration when investigating whether or not a pathway can be created by corroding and dissolving the casing along its entire length from the Castile brines to the Culebra. In a free flowing system, or a system where free space exists around the dissolving substance, the dissolving surfaces may become isolated from precipitated phases and solubility controls may not impose effective restraint on dissolution. However, in physical situations where flow is very slow or nonexistent, and where dissolving or corroding surfaces are not surrounded by a lot of free space, then solubilities will control the amount of iron that can exist in the aqueous phase, and hence how much can be dissolved. The second situation is a close approximation to the conditions expected at WIPP. At WIPP it is only conceivable that casing corrosion and diffusion could create a hydraulic pathway along the entire length of the casing if the Castile reservoirs possess enough dissolving capacity. If instead of being dissolved and mobilized, iron is simply oxidized (corroded) and left in-place, then the positive volume change in solids that accompanies oxidation will tend to decrease porosities and permeabilities associated with plugged casing locations. If these WIPP brines cannot dissolve and mobilize enough steel to create a meaningful connection, then kinetic phenomena such as corrosion rates do not need to be examined. In either case, evaluating the solubility of iron in various environments sheds light on water-casing interactions and increases understanding of how plugged boreholes might behave over long time periods.

The solubility of steel in the WIPP ground waters has been calculated after simplifying the chemical system (See Section B.3.2 Assumptions, and Section B.3.4 Limitations)by taking iron metal to represent steel and pure water to represent brine. Balanced equations have been written for the dissolution of iron metal to form a series of potential corrosion products. The concentration of iron in equilibrium with each potential controlling solid (i.e., the iron saturation level associated with each potential solid corrosion product) has been calculated and this value taken to be the potential maximum concentration that could occur in the ground water. The reasonableness of the calculations was assessed by comparing the results with easily established natural limits on the system (such as the stability of water, See Sections B.3.3 and B.5.0 for discussion).

Iron solubilities were calculated for the iron-water system using the following reactions:

(direct oxidation of iron) $(Fe^0) = Fe^{2+} + 2e^-$ (5)

Note that Eq (5) is a partial reaction common to all equilibria examined. The remaining reactions were formulated assuming ferrous iron as the only iron species in solution. Proper arrangement of the partial reactions allows calculation of dissolved quantities controlled by simultaneous contact with iron metal and iron-bearing corrosion phases. Substitution of (Fe^{2+}) into Eq (5) allows the pe^- or Eh to be calculated ($pe^- = -\log e^-$ $pe^-/17 \sim$ Eh.)

(Control of dissolved iron concentration by ferrous hydroxide precipitation)

$$(Fe^{2+}) + 2H_2O = Fe(OH)_2 + 2H^+ \tag{6}$$

(Control of dissolved iron concentration by the iron-magnetite buffer)

$$3(Fe^0) + 4\ H_2O = Fe_3O_4 + 8H^+ + e^- \tag{7}$$

(Control of dissolved iron concentration by goethite precipitation)

$$(Fe^{2+}) + 2\ H_2O = FeOOH + 3H^+ + e^- \tag{8}$$

(Control of dissolved iron concentration by ferrous hydroxide precipitation)

$$(Fe^{2+}) + 3\ H_2O = Fe(OH)_3 + 3H + e^- \tag{9}$$

The potential affect of sulfide on iron solubility was calculated using a range of sulfide: sulfate ratios, observed concentrations and pH's and the additional equations:

$$(Fe^{2+}) + 2HS^- = FeS_2 + 2H^+ + e^- \quad (10)$$

$$H_2S = HS^- + H^+ \quad (11)$$

$$Fe^{2+} + HS^- = FeS + H^+ \quad (12)$$

B.3.1.2 Calculating the Equilibrium Hydrogen Fugacity for Potential Corrosion Reactions of Steel Casing in WIPP Waters

In a chemical system where reacting components are not free to enter or leave the system, Le Chatelier's Principal holds, and once equilibrium concentrations are reached, the concentration of reactants and reaction products remains constant. Prior to reaching equilibrium, adding to the concentration of reactants drives the reaction forward while adding to the reaction products inhibits the reaction from proceeding. Combining the definition of equilibrium with LeChatelier's Principal leads to the inference that upon reaching equilibrium among steel, water, and corrosion products, corrosion of the casing will effectively cease. In contrast, in a chemical system where reacting components are free to leave the system, there is no such control on the extent of reaction. Without the buildup of reaction products, LeChatelier's rule implies that the corrosion reaction will proceed aggressively forward and will continue until the supply of either water or casing is exhausted.

Corrosion-produced hydrogen is an important component in the simplified system iron-water. Hydrogen is a corrosion product of all reactions in the simplified system, and as a gas it is highly mobile and capable of escape if flow paths exist. As a result, calculation of the equilibrium hydrogen partial pressure is useful for evaluating whether or not casing corrosion will proceed unchecked, or will be slowed by the approach to equilibrium. If hydrogen nucleates as a gas, it is assumed fugitive from the system and unchecked corrosion may be expected. If confining pressures exceed the hydrogen partial pressure, then hydrogen is not expected to nucleate as a gas and will not be able to flee the system. In such a case, equilibrium relations can be expected to constrain corrosion. The stepwise process used to calculate equilibrium hydrogen partial pressures for relevant corrosion reactions is described below.

Balanced reactions have been written for potential corrosion reactions, and their corresponding free energies have been summed. The equilibrium hydrogen partial pressure has been calculated for each reaction, assuming that water and all solid products are pure phases (See Sections B.3.2 and B.3.4). When the equilibrium hydrogen partial pressure exceeds the confining pressure supplied by the overlying brine column, hydrogen has been taken as a fugitive (or perfectly mobile) species, and corrosion is expected to be unrestrained.

Hydrogen partial pressures were calculated for the simplified iron-water system using the equations below. Note that it is important that hydrogen ions associate to form molecular hydrogen ($2H^+ = H_2$).

$$Fe^0 + H_2O = Fe(OH)_2 + H_2 \qquad (13)$$
$$Fe^0 + 4H_2O = Fe_3O_4 + 4H_2 \qquad (14)$$
$$Fe^0 + 2H_2O = FeOOH + 3/2\ H_2 \qquad (15)$$

The potential effects carbonate and sulfide were evaluated with the reactions:

$$Fe^0 + CO_2 + H_2O = FeCO_3 + H_2 \qquad (16)$$
$$Fe^0 + 2H_2S = FeS_2 + 2H_2 \qquad (17)$$
$$Fe^0 + H_2S = FeS + H_2 \qquad (18)$$

B.3.2 Simplifying Assumptions

Simplifying assumptions are routinely used during thermodynamic calculations because data for materials of the exact composition of interest are rarely available under the conditions of interest. Calculations commonly proceed by approximating the composition of materials, applying various thermodynamic mixing models, and approximating the conditions under which the reactions occur. In addition, thermodynamic calculations often invoke such fundamental concepts as equilibrium and ideality to ground the calculations in rigorous derivations and to simplify mathematical treatment. Assumptions made during theoretical calculations are discussed below.

B.3.2.1 Fundamental Assumptions

Equilibrium: The principals of equilibrium thermodynamics have been applied in all calculations. Equilibrium has been assumed to exist among all components of reactions considered.

Temperature: All reactions are assumed to occur at 298 oK

Ideality: All reactions are assumed to be ideal

Pressure: Reactions are assumed insensitive to pressure

Control: Water is assumed in excess and its constituents, rather than the reacting solids, are assumed to exert control on e.g. pH

B.3.2.2 Assumptions On Composition

The key components when considering the corrosion of borehole casing in WIPP brines are the steel which comprises the casing, and the fluids which represent the corrosive environment. Steel is an iron-based alloy which commonly contains carbon and minor amounts of other metallic elements (Cr, Mo, Va, Bi, Cu etc) to create a specialized material with properties that are well-suited to an intended application. The steel pipe which is commonly used for casing oil and gas boreholes is a low carbon steel (commonly AISI 1045; Westinghouse, 1996). The simplifying assumption applied to steel borehole casing is to represent its composition as pure iron. The potential thermodynamic effects of minor elements in the steel have been neglected.

Brine is an aqueous solution containing high levels of dissolved material. It is acknowledged that the chemical behavior of brine deviates substantially from ideality and that brine is not pure water. To avoid complex mathematics that would require the aid of computers, brine has been taken as pure water. These and other assumptions pertaining to composition are summarized below.

Steel: Steel is assumed to be pure iron

Products: Dissolved iron is assumed to exist as ferrous ion only. Corrosion products are assumed to be pure phases. Solid solution effects have been neglected

Brine: Brine is assumed to be pure water

Volatiles: Water and its components are assumed to comprise the volatile environment except where specifically noted. When other volatile phases are assumed present, they are assumed pure and in equilibrium with water and its components

B.3.3 Calculational Results

Calculational results presented in this section are intended to provide enough detail to support the discussions and conclusions presented in later sections. Each step of a given calculation is not necessarily provided, although narrative summaries are included where these are potentially helpful in understanding the reasoning and methodology. Calculations of iron solubility assuming a number of potential controlling solids are presented first (Section B.3.3.1), followed by calculations of hydrogen pressures associated with related reactions (Section B.3.3.2).

B.3.3.1 Iron Solubility Calculations

As noted earlier, iron solubility calculations are intended to assess whether the possibility exists for corrosion to create a vertical pathway from the Castile Brine Reservoir horizon (taken to be at a depth of 899 m; Rechard, 1995) to the Culebra aquifer (taken to be at a depth of 216 m). Corrosion along the length of the casing may occur from waters associated with the brine reservoirs, formation waters and aquifers such as the Culebra, as well as the brine introduced inside the casing during abandonment. Waters in the Culebra and Castile have been reported to coexist with hydrogen disulfide and carbon dioxide gases, thereby creating a range of potential corrosion environments (Popielak et al., 1983; Lambert and Robinson, 1984). In the following sections, the potential to dissolve iron in the presence of H_2S gas is examined first, followed by the potential in carbonate and then pure water environments.

The results of the calculations for ternary equilibria involving iron metal, an iron bearing phase and aqueous species can indicate solubilities that may exceed the aqueous solubility of the iron bearing phase alone. In the present analysis, such a result is taken to indicate that dissolution of iron occurs at the iron-water interface, followed by precipitation of the iron-bearing phase at a distance from the interface. This process leads to a conservative result by assuming that dissolution occurs under local equilibrium conditions (the presence of iron) that may not apply in areas where precipitation occurs (the absence of iron). In the calculations discussed here, reactions possessing the lowest free energies are generally considered dominant when more than one reaction is possible. Tests of reasonableness, such as being within the stability field for water or possessing reasonable densities, are used to evaluate the results.

B.3.3.1.1 Sulfide Controlled Solubilities. Sulfide corrosion products found on iron, and for which thermodynamic data are compiled, include pyrite and troilite (See Videm and Kvarekval, 1995; and Robie and Waldbaum, 1978). The solubility of iron metal in equilibrium with water and each of these phases is analyzed here.

Pyrite: Ferrous iron concentrations in equilibrium with pyrite are calculated first for a Salado-like environment and then for the Castile. Oxidation of iron metal, and the aqueous solubility limit of ferrous iron as controlled by the presence of pyrite, may be calculated by using equations (5),and (10).

From Eq(5): $\log K = 13.818 = \log [Fe^{2+}] - 2pe^-$.
From Eq (10): $\log K = -18.494 = \log [Fe^{2+}] + 2\log [HS^-] + 2pH + 2pe^-$

To solve the equation, estimates of the HS^- concentration and pH are required.

Salado: Assuming ideality, the bisulfide concentration in a Salado room seep should be less than ~0.3M (if total sulfur is reported as HS; Rechard, 1995). At pH = 8, substitution of pH and HS^- concentrations and rearrangement and addition of Eq's (5) and (10) yields:

$$Eq(5) + Eq\ (10) = -4.676 = 2\log [Fe^{2+}] - 1.046 + 16; \qquad (19)$$

Hence: $\log [Fe^{2+}] = -9.815$, and $pe^- = -11.816$ (therefore, Eh = -0.699 v)

This result for Eh is below the 1 atm stability field of water, indicating that when iron metal and pyrite coexist, HS must be present at much lower concentrations than assumed here. Taking 0.01M HS as a practical lower limit, the same calculations yield ferrous iron concentrations of :

$$\log[Fe^{2+}] = -8.338, \text{ and } pe^{-} = -11.078 \text{ (therefore, Eh = -0.655 v).}$$

These conditions are still well below the 1 atm stability limit of water.

The lowest theoretical HS- concentration in equilibrium with iron metal, pyrite and water may be calculated and substituted into Eq (10). At the lower stability limit of water, pe^- equals pH, and the sulfide concentration is estimated:

From Eq (5): $13.818 = \log [Fe^2] -2(-8)$, so $\log [Fe^{2+}] = -2.18$;
Substituting into Eq (10): $2\log [HS^-] = -18.94 - (-2.18)$, so $\log [HS^-] = -8.156M$.

At pH = 8, the calculated HS- concentrations are so low that if steel casing corrosion is appreciable in the Salado, it is likely to be controlled by another corrosion reaction.

Castile: The Castile brines have been characterized to the point where calculations are somewhat less parametric and more definitive. Sampling of the gas phase coexisting with brine from borehole WIPP12 showed that H_2S comprises about 20 mole percent of the gas. The minimum pH and pressures associated with the brine reservoir are 6.4 and 14 MPa, respectively. Assuming ideality, fugacity equals partial pressure and may be calculated as:

$$P_i = (P_{tot})\, X; \tag{20}$$

where X is the mole fraction. For H_2S:

$$Pi = (138 \text{ atm})(0.20) = 27.6 \text{ atm}$$

Substituting values for pH and fH_2S into Eq (11) yields

$$-7.997 = \log [HS^-] - 6.4 - \log (27.6),$$

so that: $\log [HS^-] = -0.56$, or $[HS^-] = 0.10M$.

Substituting into Eq (19) and solving for the equilibrium ferrous iron concentration yields:

$$-4.676 - 2\log [HS^-] - 2pH = 2\log [Fe^{2+}],$$
$$-4.676 - 2(-0.56) -2(6.4) = 2\log [Fe^{2+}],$$

and: $\log [Fe^{2+}] = -8.89$ M.

Substituting these ferrous iron concentrations into Eq (5) produces a pe^- of -11.35 or an Eh of -0.67v, still below the 1 atm stability field of water.

Troilite: As an alternative to pyrite, calculations can be performed using troilite (FeS) as the controlling corrosion product (See Videm and Kvarekval, 1995).

$$\mathrm{Fe} = \mathrm{Fe}^{2+} + 2e^- \qquad \log K = 13.818 \qquad (5)$$

$$\mathrm{Fe}^{2+} + \mathrm{HS}^- = \mathrm{FeS} + \mathrm{H}^+ \qquad \log K = 6.055 \qquad (21)$$

Combining Eq's (5) and (21) so that both Fe and FeS control ferrous iron yields:

$$\log K = (13.818) - 6.055 = 7.763 = 2\log[\mathrm{Fe}^{2+}] + \log[\mathrm{HS}^-] + \mathrm{pH}$$

Salado: For Salado brines a practical lower concentration limit of 0.01M may be used for $[\mathrm{HS}^-]$ and the pH range 6 to 8 evaluated. The results for log ferrous iron concentrations are 0.88 M at pH = 8 and 1.88 M for pH = 6. The resulting Eh is -0.38v, at pH = 8, which lies within the 1 atm stability field of water.

Castile: For Castile brines, the previously calcuated HS- concentration of 0.70 M and the observed pH of 6.4 were substituted into the equation. The results predict a log ferrous iron solubility of 0.76 M.

B.3.3.1.2 Carbonate Controlled Solubilities: Siderite ($\mathrm{FeCO_3}$) is the stable corrosion product of iron following exposure to carbon dioxide-rich brines. The reaction cited by Xia et al. (1989) is reaction of iron with the carbonate ion. The equilibrium ferrous iron concentrations established for these reactions (see Eq 16) are calculated below:

From Eq (5): $\log K = 13.818$,
also: $\mathrm{H_20} + \mathrm{CO_2} = \mathrm{CO_3^{-2}} + 2\mathrm{H}^+$, $\log K = -18.130$,
and: $\mathrm{Fe}^{2+} + \mathrm{CO_3^{-2}} = \mathrm{FeCO_3}$, $\log K = -10.69$.

Arranging terms and summing yields gives:

$$\Sigma \log K = -13.937 = 2\log[\mathrm{Fe}^{2+}] + \log[\mathrm{CO_3}] - 2\mathrm{pH}$$

Data from brine seeps and brine reservoirs show that $\mathrm{CO_3}$ concentrations are in the range 0.11 to 0.16M (1992 PA). Taking the lower end of the range and substituting yields gives:

$$-13.937 = 2\log[\mathrm{Fe}^{2+}] + (-0.796) - 12;$$

so that:

$$\log[\mathrm{Fe}^{2+}] = -0.571 \text{ M}$$

Substitution of $[\mathrm{Fe}^{2+}]$ into Eq (5) yields an associated Eh of -0.42 v which approximates the lower stability limit of water.

B.3.3.1.3 Corrosion Controlled by Simple Oxides and Hydroxides (Data from Robie and Waldbaum, 1978): Aqueous oxidation of iron metal can be examined using Eq (5), (6), (7), (8), and (9). Ferrous hydroxide, $Fe(OH)_2$, is a corrosion product (Eq 6) reported by Telander and Westerman (1992), although magnetite (Eq 7) and goethite (Eq 8) are also cited in the literature.

Magnetite Control: Examining the iron-magnetite reaction first, Eq (7) can be written in its component parts as:

From Eq (5): $Fe = Fe^{2+} + 2e^-$, $\log K = +13.818$,
and from Eq (7): $3Fe^{2+} + 4H_20 = Fe_3O_4 + 8H^+$, $\log K = -30.245$.

Rearranging and summing yields gives:

$$\log K = 44.06 = 4\log[Fe^{2+}] + 8pH.$$

At pH=6: $\log[Fe^{2+}] = -0.98$ M;
at pH=8: $\log[Fe^{2+}] = -4.99$ M.

The attending Eh's (calculated by substituting ferrous iron values into Eq 5 and solving for pe^-) are in the range -0.425 to -0.55v. At the reference pH's, these values are near to, but below, the stability field for water.

Ferrous Hydroxide Control (Data from Krauskopf, 1967): The most commonly cited corrosion product for iron is ferrous hydroxide. The corrosion results from reaction of iron with protons and hydroxides of water (Manfredi et al., 1989). Recomposing Eq (8) into its component parts gives:

From Eq (5): $Fe = Fe^{2-} + 2e^-$, $\log K = +14.883$,
from Eq (8): $H_20 = H^- + OH^-$, $\log K = -13.996$,
and from Eq (8): $Fe^{2+} + 2(OH) = Fe(OH)_2$, $\log K = +14.736$.

Rearranging, balancing (2 waters) and summing gives:

$$\log K = -27.845 = 2\log [Fe^{2+}] - 2pH.$$

At pH = 6: $\log [Fe^{2-}] = -7.923$;
at pH = 8: $\log [Fe^{2+}] = -5.922$.

The attending Eh's are in the range -0.67 to -0.61 v.

Goethite Control (Data from Robie and Waldbaum, 1978): Goethite (See Eq 9) is assumed to form from a corrosion reaction similar to ferrous hydroxide. Following the same procedure as above:

From Eq (5): $Fe = Fe^{2+} + 2e^-$, $\log K = +13.818$,
and from Eq (9): $H_20 = H^+ + OH^-$, $\log K = -13.996$,
and: $Fe^{2+} + (OH) + 1/2\ O_2 = FeOOH$, $\log K = +44.218$.

Rearranging and summing gives:

$$\log K = -43.331 = 2\log[Fe^{2+}] - pH.$$

At pH=6, $\log [Fe^{2+}] = -18.665$;
at pH=8, $\log [Fe^{2+}] = -17.665$.

As with previous calculations, the attending Eh's are calculated to be below the stability field of water.

B.3.3.2 Partial Pressures of Hydrogen Over Controlling Equilibria

A number of different solubilities have the potential to apply to casing corrosion at WIPP. Several relevant reactions have been written and presented in the section above. In reality, complex equilibria will likely be involved and the degree of control exerted will depend on compositional variabilities such as brine composition and over-pressures of coexisting volatile species (e.g. carbon dioxide, hydrogen sulfide, hydrogen etc.).

B.3.3.2.1 Corrosion Inside the Casing: Of the reactions written above, corrosion inside the casing is expected to be closest to the simple iron-water reactions because abundant carbonate and sulfide cannot be assumed to be present in the corroding water. At equilibrium in this system, the corrosion reactions can be recomposed to show hydrogen as a reaction product [See Eq (13)-(18)]. The equilibrium hydrogen fugacity (or partial pressure) can then be calculated as described in Section B.3.1.2.

In this simplified system, the reactions most commonly associated with corrosion are represented in Eq (13) and Eq (15). These reactions also give the lowest free energies, hence they are inferred to be the most stable, and therefore the controlling reactions. The partial pressure of hydrogen associated with these reactions is in the range 40- 45 atm, as shown below.

From Eq (13): $\log K = 1.628 = \log(P_{H2}) - 2\log(P_{H20})$, (Krauskopf, 1967)
$1.628 = \log(P_{H2}) - 2\log(1)$,
$P_{H2} = 42.4$ Atm.

From Eq (15): $\log K = 2.654$ (Krauskopf, 1967) to 2.50 (Robie and Waldbaum, 1978);

For: $\log K = 2.654 = 3/2 \log (P_{H2})$,
$(2.64) \times (2/3) = 1.769 = \log (P_{H2})$,
$P_{H2} = 58.8$ Atm

For:

$$\log K = 2.50 = 3/2 \log (P_{H2}),$$
$$(2.50) \times (2/3) = 1.666 = \log (P_{H2}),$$
$$P_{H2} = 46.4 \text{ Atm}$$

These calculations would seem to suggest that in the simplified system, when corrosion is of concern, the partial pressure of hydrogen will be in the range of 40-50 atmospheres, where the reaction stops. It should be noted, however, that magnetite has infrequently been noted as a corrosion product by some experimenters (See Telander and Westerman, 1992). If magnetite is truly present, and if it is present in quantities sufficient to control reactions, then the hydrogen pressures could be higher. In the simplified system (no solid solutions and unit activity of water), the iron-magnetite reaction is calculated to produce equilibrium hydrogen pressures of the order of 650 atm.

B.3.3.2.2 Corrosion Outside the Casing: Outside the casing, formation waters commonly contain carbonate, and in the Castile reservoirs, sulfide.

Carbonate: If carbon dioxide is assumed continuously present (i.e. there is an inexhaustible supply) at air concentration values (0.033%), then the hydrogen pressure in equilibrium with siderite (see Eq 16) may be calculated to reach 483 atmospheres. It should be noted that the continuous supply of CO_2 may be generated in the repository, with the carbon dioxide supplied by microbial action.

Sulfide: The composition of brines taken from the Castile are reported by Popielak et al., 1983. The maximum documented sulfur concentration is reported as 590 mg/l. This equates to approximately 0.06 moles/l sulfur as HS^-. Summing equations (5) (10) and (11) and substituting for HS^- and pH gives a log hydrogen disulfide fugacity of +0.775 atm at pH = 6 as shown below:

$$\log K = -7.997 = \log [HS^-] - pH - \log f_{H2S} = -0.1.222 - 6 - \log f_{H2S} = +0.775$$

Under these conditions the troilite and pyrite reactions yield extremely high equilibrium hydrogen pressures. For example, from the troilite reaction, $Fe + H_2S = FeS + H_2$, the equilibrium hydrogen pressure is calculated as:

$$\log K = 11.878 = \log f_{H2} - \log f_{H2S}$$
$$\log f_{H2} = 11.878 + 0.775 = 12.65 \text{ Atm.}$$

Thus, equilibrium hydrogen pressures associated with casing corrosion have the potential to range from a low of 40 atm to a high in excess of 1012 atm. The controlling reaction will ultimately be determined by the relative abundance of reactants and the prevailing geochemical environment. For example, Figure B-3 (from Garrels and Christ, 1965) displays the rather limited conditions within redox-pH space where sulfide corrosion products can exist. Figure B-4 shows that siderite (FeCO3) has a somewhat more substantial stability region; however, as carbon dioxide is consumed, the field becomes dominated by ferrous hydroxide. Accordingly, the equilibrium hydrogen pressure assumed to dominate casing corrosion is derived from the simplified water-iron reactions.

B.3.4 Limitations

The calculations summarized above have utilized a number of assumptions and simplifications (See Section B.3.2). Accordingly, while the results are good indicators of how elements of a plugged borehole will behave, they should not be taken as quantitatively definitive.

Two assumptions central to the calculations are those concerning the reaction of pure phases and equilibrium. For example, water has been assumed to be pure water, while in actuality the corroding solutions will be brines in which the chemical activity may be expected to be somewhat less than 1. This compositional effect will result in underestimates of calculated solubilities and equilibrium hydrogen pressures. Partial or complete compensation of this error may come from having assumed pure solid reaction products, while the iron-bearing minerals assumed as pure solid phases will likely incorporate some degree of solid solution with the iron, e.g., by metals such as magnesium. Similarly, pure iron has been used to approximate steel casing. The free energies of various steels has not been modeled, and the general effect on free energies and equilibrium constants is unknown.

Equilibrium has been assumed throughout the system. Lack of equilibrium may lead to incomplete reaction causing the results of the calculations described here to be overestimates. Lack of equilibrium may also result in a lack of solubility control allowing supersaturated solutions (i.e. higher concentrations) to persist, if they are somehow generated. In addition, the calculations employed here do not account for galvanic effects that might occur across different domains of steel alloys or between passivated portions of the casing and areas that remain unclad by corrosion products.

To address these limitations the calculational results are supplemented with empirical results from experimental corrosion studies between low carbon steel and brines. These are described in the next section.

B.4. RESULTS FROM EMPIRICAL STUDIES INVESTIGATING STEEL CORROSION IN BRINE WITH RELEVANCE TO WIPP

As noted above, while simple thermodynamic calculations are useful, they cannot be relied on to present a complete picture of how casing will corrode under repository conditions. To provide more reality to the theoretical analysis, data has been obtained from the literature from investigations of low carbon steel corrosion in brine environments. Other parameters of interest included volatile environments (air saturated, de-aired, carbon-dioxide and hydrogen sulfide-enriched) and the presence of portland cement materials.

These studies do not determine the steady state composition of ferrous iron in brine. Rather, they investigate the rate at which iron oxidizes and the mechanism through which corrosion occurs.

B.4.1 Corrosion of Low Carbon Steel in Aerated Environments

Corrosion of casings at WIPP may include environments where oxygen is available. Thus, brines put into casings at abandonment will initially be air saturated, and formation waters from shallow depths may be in contact with air to some degree. In either case, the subject of oxic corrosion of low carbon steel casing is relevant.

In the presence of air saturated brines, steel undergoes oxic corrosion. Eq (14) can be recomposed as:

$$2Fe + 3/2\ O_2 + H_20 = 2FeOOH \tag{22}$$

This reaction is written to describe the consumption of oxygen; however, at equilibrium it is thermodynamically equivalent to Eq (14). Oxic corrosion strips Fe randomly from exposed surfaces. Each surface location has an equal potential for reaction, so the mechanism is called uniform or generalized corrosion. With all other compositional aspects held constant, the presence of oxygen may be the strongest driver for corrosion; however, other species which promote oxidizing environments also contribute substantially.

Acidity: The acidity of the corroding medium can be a very important parameter to corrosion rates of steel. Acid environments are oxidizing environments. Reference to Eq (2) through (12) shows that elevated concentrations of hydrogen ion (e^-) lead to elevated concentrations of ferrous ion [Fe^{2+}]. The effect of pH on oxic corrosion rates of low carbon steel is exemplified by Figure B-1, taken from Manfredi et al., 1989 who performed experiments on low carbon steel in brine at temperatures associated with heat producing nuclear wastes (up to 1500 °C). Moderate temperature elevations of this type generally accelerate kinetic reactions unless reaction mechanisms change, with a 100 °C rise in temperature generally doubling or tripling reaction rates (Sienko and Plane, 1966). These short term elevated temperature experiments therefore simulate more then 100 years of corrosion. The results show that short-term corrosion rates are much higher, by an order of magnitude or more, than the rates likely to occur over long time periods. In addition, the experiments reveal that the pH sensitivity of low carbon steel corrosion rates varies with acidity. In low pH regions (pH= 0 to 3), corrosion rate increases steeply as pH decreases. In contrast, in the more neutral range (pH 4-10) shows a moderate corrosion rate that lacks sensitivity to pH. At higher pH's, corrosion is low and corrosion may be more influenced by local aberrations in chemistry of the steel or surface energies etc.

Effect of Concrete: The presence of concrete complicates the picture somewhat. As a cladding material, concrete has the potential to change the corrosion of low carbon steel from a generalized to a localized mechanism. This potential is created because concrete adheres to the surface of low carbon steel preventing uniform access of brine, while the concrete is non-uniform with respect to density and composition and can therefore introduce chemical micro-environments. During corrosion of steel by brine in the presence of concrete, oxygen exerts influence on the overall corrosion rate and chloride exerts influence on where corrosion is initiated, since high chloride concentrations initiate corrosion (Andrade et al., 1990). Where oxygenated waters have access to steel surfaces, corrosion rates are higher. Where steel surfaces are in contact with elevated chloride concentrations, more corrosion sites are initiated. Where the corrosion environment includes both saturated and unsaturated areas (dry and wet areas or interfaces), anodic corrosion is especially aggressive (Aguilar et al., 1990). Corrosion rates for low carbon steel surrounded by both dense and cracked concrete are depicted in Figure B-2 (Andrade et al., 1990). For ease of comparison, a conductance of 11mA/cm2 is equal to about 0.1 mm/year. Accordingly, short term corrosion rates reported for concrete encased low carbon steels in aerated brines reach as high as about 11 mm/yr.

B.4.2 Corrosion of Low Carbon Steel In the Presence of CO_2 and H_2S

It is quite likely that the dominant corrosion environment for low carbon steel casing at WIPP will not be an air saturated or oxygen-rich environment. With increasing depth, communication with surface air becomes impossible. With time, air entrained during drilling and abandonment is consumed by corrosion or biota and the environment becomes anoxic. At the WIPP, the gases carbon dioxide and hydrogen disulfide are commonly associated with brine reservoirs (Popielak et al.,1983) and possibly formation waters such as the Culebra (Lambert and Robinson, 1984; Myers, 1991). Accordingly, review of low carbon steel corrosion experiments involving brines and CO_2 and H_2S has been conducted.

In the presence of some oxygen, carbon dioxide- rich brines induce corrosion rates of 1-3 mm/yr in low carbon steel (Andrade et al.,1990). Production of carbonate scale on steel surfaces leads to pitting corrosion as opposed to uniform corrosion. In de-aired experiments with brine and carbon dioxide, corrosion mechanisms and rates are similar (Xia et al.,1989). Early production of $FeHCO_3$ passivates corrosion, but within weeks, the $FeHCO_3$ was converted to the thermodynamically stable $FeCO_3$, passivation ended and corrosion at 1-3 mm/yr resumed (Xia et al., 1989).

In anoxic brine containing hydrogen disulfide, corrosion of low carbon steel is complicated by passivation (Telander and Westerman, 1992). At the onset, corrosion is driven aggressively by the thermodynamic stability of iron sulfides, i.e. iron sulfides are highly favored over iron metal. At elevated partial pressures of hydrogen sulfide, however, a dense sulfide coating (reportedly mackinawite; Videm and Kvarekval, 1995) inhibits access of the corroding medium to the steel surface. As a result, corrosion virtually ceases. At lower partial pressures (below about 5 atm; Westerman personal communication), the passivating sulfide coat does not form.

The combination of hydrogen disulfide and carbon dioxide at low partial pressures creates an environment that is likely to be similar to a Castile brine reservoir that has been vented to the atmosphere. Corrosion of low carbon steel in just such an environment has been investigated (Videm and Kvarekval, 1995). Figure B-3 reproduces their experimental results and shows low carbon steel corrosion in the range of 1-3 mm/yr.

B.5. DISCUSSION OF FINDINGS

B.5.1. Corrosion Rate

The empirical corrosion rates presented for oxic and anoxic conditions, whether or not additional gas species such as carbon dioxide and hydrogen sulfide are present, appear to have an upper range near 1-3 mm/yr (For example, compare Andrade et al., 1990; Aguilar, et al., 1990; Videm and Kvarekval, 1995). These initial rates may slow with time as suggested by Manfredi et al. (1989), and Telander and Westerman (1992), and an uncracked concrete coating will undoubtedly inhibit corrosion (Andrade et al., 1990). It may be argued that better estimates of rates could be obtained from more detailed researching of hydrocarbon steel casing compositions followed by performing site-specific corrosion experiments directly on those compositions. While it is certainly true that corrosion rates can be specified with reasonable accuracy for specific steels in brines of a given chemistry, the uncertainties associated with the variability of corroding environments at WIPP make it more reasonable to adopt the published, upper range for generic low carbon steel in brine as the expected corrosion rate.

The estimated rate of 1-3 mm/yr is a very aggressive rate, but it appears to comport well with oil field observations made during exploration in the Delaware Basin. As reported by the New Mexico State Land Office, corrosive failure of casings in the Salado is common though not pervasive (See Bailey memo in La Venue, 1991). Most commonly, these failures are reported to occur within several years of emplacement of the casing, although breaches within months after emplacement are not unheard of. Setting aside the fact that most failures appear to occur near Nash Draw, where aqueous environments in the Salado and shallower formations will be most oxidizing and corrosive (Lambert and Robinson, 1984; Myers et.al, 1991), as shown below simple division shows that the rate of 1-3 mm/yr would account for most casing failures. The common maximum wall-thickness of the surface casing is about 11 mm, while the common thickness associated with intermediate casing is about 9 mm. The intermediate casing is the pipe that would be placed in the Salado (Westinghouse, 1996), where failures are reported (Bailey, 1991). Dividing 9 mm by several (e.g. three) years would give an annual corrosion rate of 3mm/yr.

This apparent agreement lends confidence to the selection of 3 mm/yr as a conservative but applicable corrosion rate; however, the coincidence does not mean that corrosion will necessarily occur at 3 mm/yr in every environment encountered by the borehole casing.

Corrosion rates measured under repository conditions are on the order of one thousand times slower than rates applied to the casing (Telander and Westerman, 1992). This difference may be due to different compositions of steels and/or corroding environments or to unknown experimental differences between the WIPP-specific and generic investigations. It is with the understanding that a corrosion rate of 1-3 mm/yr represents a conservative, generally applicable rate that this investigation recommends it for predicting borehole plug performance.

B.5.2 Corrosion Mechanism

Corrosion mechanisms are important because some mechanisms strip layers of iron from the surface while others bore through the steel in a focused fashion. Focused mechanisms may result in localized failures even when the corrosion reaction is controlled by a low solubility. Localized failures may have hydraulic consequence without being attended by physical collapse. Generalized mechanisms must be accompanied by appreciable solubilities or very large quantities of corroding media before failure is as significant a concern. Generalized failure will commonly be accompanied by physical collapse.

Two corrosion mechanisms are reported for corrosion of low carbon steel: uniform corrosion (e.g. Manfredi et al, 1989) and pitting corrosion (e.g. Xia et al, 1989 ; Videm and Kvarekval, 1995). Uniform corrosion is reported at low and moderate pH's (<10) under oxic and de-aired conditions (Manfredi et al, 1989; Posey and Palko, 1979) and when steel surfaces are not covered with mineral coatings. Pitting corrosion is reported at high pH's (Manfredi et al., 1989)or under elevated partial pressures of carbon dioxide (Xia et al 1989; Videm and Kvarekval 1995), hydrogen disulfide (Videm and Kvarekval, 1995) or when concrete or the degree of saturation create non-uniform corrosion environments (Andrade et al, 1990; Aguilar et al., 1990).

Corrosion mechanisms will operate in two directions. Brine placed inside the casing will corrode from the inside-out, while formation waters in the host rock will corrode from the outside-in. Internal corrosion will proceed in a relatively uniform environment. In contrast, external corrosion may experience great variability due to the cement that attaches the casing to the host rock, i.e. casing cement will inhibit access to steel surfaces to different degrees at different locations.

In addition to axial location, depth may also affect the corrosion mechanism acting on the outside of the borehole casing. Shallower depths are more likely to support oxic corrosion environments and are therefore more likely to experience generalized corrosion. Corrosion at greater depth is more likely to encounter elevated partial pressures of carbon dioxide and hydrogen disulfide, and localized pitting should be more prevalent.

B.5.3 Conceptual Models For Casing Corrosion

Information developed for low carbon steel corrosion has been synthesized with site characteristics and judgment to yield a conceptual model for casing corrosion at WIPP. The model has been assembled based on published corrosion rates and corrosion mechanisms, as well as calculated solubilities and amounts of materials. The casing corrosion model recommended for WIPP is comprised of two sub-models one in which hydrogen is fugitive, and free to leave the system, and another in which hydrogen is confined within the system. These models are described more fully below.

B.5.3.1 Corrosion When Hydrogen Is Fugitive

As noted above, depth is expected to affect corrosion by influencing the oxidation potential of the environment. Depth may also affect whether or not corrosion is thermodynamically limited. Section B.3.3.2 showed that corrosion controlled by formation of iron hydroxides theoretically ceases when hydrogen partial pressures reach 40-45 atm. The weight of the brine column inside the casing creates a confining pressure of this magnitude at depths below about 1100 feet (See Section B-5.4).

Confining pressure determines the ability of a volatile to nucleate as a free phase gas. When the physical confining pressures exceed the pressure of the volatile of interest, the volatile cannot become a free gas and the chemical potential associated with hydrogen can increase. If the confining pressure is less than the volatile's pressure (as it is above ~1100 feet), then the volatile can escape as a gas. When a reacting component can enter or leave the system it is said to be "perfectly mobile" or fugitive. This is relevant to the corrosion process because when hydrogen is fugitive development of back pressure to stop corrosion cannot occur. Corrosion will continue until all the iron is oxidized as long as there is sufficient water.

The most certain volume of water available is the brine placed in the casing at abandonment. The volume of water associated with the casing can be calculated. The dimensions of the intermediate casing are taken to be an O.D of 8.625 in. (0.21908m) and an I.D. of 7.921 in. (0.20119m) (Westinghouse, 1996). In a 1m length of casing, the internal volume is 0.0318 m^3 and the volume of steel is 0.00589 m^3. The molar volume for iron is 7.092 cm^3 (Robie and Waldbaum, 1978). Thus, in one meter of casing there are ~830 moles of iron. The volume of water in that same meter of length is ~ 31.8 liters, or with a molar volume of water of 18.068 cm^3 (Robie and Waldbaum, 1978) about 1756 moles of water per meter of casing length.

Referring to Eq (16) shows that each mole of iron reacts with 2 moles of water to create ferrous hydroxide. Thus, theoretically only 1660 moles of water are required to oxidize all of the iron in the casing. The calculated amount of water present (1756 moles) appears close enough to that theoretically required that assumptions such as ideality etc may be enough to call total corrosion into question. However, additional water is certain to be present. First, water will exist in the surface casing. Because of its proportions (O.D.= 0.3397m, I.D = 0.3179m) a similar calculation shows that the molar ratio of water to iron in the upper part of the column will be 2.76 (vs 2.11 for the intermediate casing and a requirement of 2.0 for complete oxidation).

In addition to casing water, formation waters may be available to drive corrosion. Brine flows have been reported from shallow Salado interbeds (and attributed as the potential causes for casing failures) in oil field wells (Bailey memo in LaVenue, 1991). As reported by the New Mexico State Land Office, "These water flows are characterized as strong, intermittent and spotty. Not all wells have encountered flows, but when they did, the flows were estimated at 1000-2000 barrels per day. The flows often would last 4-5 days before stopping themselves."

Two points may be made in connection with these reports. Firstly the reports of brine flow and casing failure come from locations closer to Nash Draw than to the site. Near Nash Draw, the Salado contains clastic intervals capable of supplying water at a much higher rate than the interbeds characteristic of the WIPP site. Nevertheless, if the minimum values of 1000 barrels and 4 days are taken, then the drainable volume of the interbed brines could be as high as 480,000 liters□ ,and supply about 26 x 106 additional moles of water. The combination of casing and potential formation brines are therefore more than adequate to oxidize borehole casing completely when hydrogen is fugitive.

In summary, at depths less than 1000 feet, hydrogen gas can nucleate and escape if a pathway exists. Corrosion failures of casing are well-known in these depths (Bailey, 1991) and will almost certainly occur in a matter of years to tens of years. These failures will provide escape paths for gaseous hydrogen and unchecked generalized corrosion can proceed. As a result, steel casings above 1000 feet are expected to corrode entirely and collapse into the hole. The time required for total collapse of the casing is not calculable from known data; however, judgment has been applied in the form of an additional order of magnitude to yield an estimate of about 100-200 years.

The physical characteristics of the corrosion debris are also not amenable to calculation. Corrosion products found on the surfaces of corroding metals are exceptionally fine (micron sized). This knowledge together with the well-known, fine-grained nature of most chemical precipitates, suggests that much of the resulting debris will contain abundant silt-sized or finer material. Not all of the debris will be disaggregated chemical precipitate, however, nor can fine materials formed initially be assured not to agglomerate and cement. These materials will comprise coarser materials, in an undetermined amount. Other material, such as pieces of rusted pipe or concrete may also be present, approximating sand or gravel materials. Collectively, the debris is expected to comprise a mixture of coarse to very fine-grained material and hydraulically resemble silty-sand, as originally proposed by EPA in 40CFR191.

B.5.3.2 Corrosion When Hydrogen Is Contained

At depths greater than about 1000 feet, hydrogen gas will not develop and hydrogen will not be a fugitive species. Because it cannot escape, hydrogen back pressure will build up inside the casing as corrosion produces ferrous hydroxide. Upon reaching the equilibrium hydrogen pressure near 40-45 atm, generalized corrosion in the simplified water-iron system will cease, probably before failure of the casing occurs.

Outside the casing corrosion will be driven by formation brines. Brines are not expected to occur in abundance within the deep Salado at the site; however, large brine reservoirs with volumes as high as 1 x 109 liters (1992 PA) may be encountered in the Castile. These brines are reportedly charged with CO_2 and/or H_2S (Popielak, 1983) and although no compositional data are available for Salado interbed brines, it is reasonable to assume a similar chemistry.

Attack by formation waters will lead to localized failure of the casing due to pitting corrosion. Pitting is almost certain to be the dominant mechanism given that casing concrete will surround the pipe and that carbonate and sulfide phases will form on some steel surfaces. The result of pitting corrosion will be a degraded casing that is locally perforated and has failed hydraulically but which has remained substantially intact physically.

B.5.3.3 Potential For Corrosion To Create Hydraulic Pathways

In inadvertent human intrusion scenarios, steel casing is assumed to intersect Castile Brine reservoirs (899 m depth), the repository (655m depth) and the Culebra aquifer (216 m depth; all depths from 1992 PA). The potential exists for corrosion of the steel to create an open path that hydraulically connects all of these features. Solubility and corrosion rate data have been used to assess this potential.

Dissolution of the entire casing would produce an open annulus in the space previously occupied by the steel. Assuming one billion liters of brine, a bounding calculation was performed to see if simple dissolution was a concern. The removal of iron by dissolution will be determined by the solubility of the most stable phase.

The water source with the greatest volume (hence capacity for dissolution) is an assumed Castile Brine Reservoir with an estimated volume of 109 liters (Popielak et al., 1983). These reservoirs have been observed to emit hydrogen disulfide gas. Brines rich in hydrogen sulfide gas react with iron to form iron sulfides such as troilite, pyrite, and mackinawite (Telander and Westerman, 1992; Videm and Kvarekval, 1995). Thermodynamic data have not been discovered for mackinawite, and estimations have not been performed for that phase. Theoretical Fe 2÷ solubilities controlled by the presence of both troilite and pyrite were calculated in Section 133.3.1.1. Estimates for pyrite (~10-8 M) are used here because the presence of carbonate destabilizes FeS (See Figure B-4) and

Castile brines contain abundant dissolved carbonate and excess carbon dioxide (Popielak et al., 19%)

In a brine reservoir with a volume of one billion liters at a pH near 6, sulfide solubility would limit dissolution and transport of iron to less than 31,000 moles {(10^9 liters) x (10^{-8} moles/liter) = 10 moles}. This amount represents all of the steel in a 1 cm length of casing (10 moles/830 moles of iron per meter of casing). This represents less than 0.5% of the distance between the reservoir and repository horizons. However, removal of 10 moles from the rock-casing interface (only) is not sufficient to create a conductive pathway to the repository.

The solubilities of metastable mackinawite and troilite (both FeS) will be higher than the thermodynamically stable phase, pyrite. However, empirical corrosion experiments where FeS phases are reported as corrosion products indicate that linear corrosion rates will not permit connection of the Castile Brine reservoir horizon and the repository during the 10,000 year period of performance. The corrosion rate selected for the conceptual model is less than 3mm/year. This is a very aggressive rate. The brine reservoirs and the repository are separated by about 250 m (250,000 mm). Using the cited corrosion rate, more than 80,000 years would be required to create a pathway by corrosion along the interface.

An alternative to vertical dissolution from the Castile is vertical dissolution coming from interbed sources that might occur periodically throughout the Salado. In order for such sources to have significance, they must occur every 35 m or less and all must contain sufficient accessible water supplies that dissolution is possible. Without the ability to disperse dissolved material away, corrosion products that might form will clog porosity.

Although it is inconceivable that dissolution and corrosion could combine to create a significant vertical pathway for flow, the capacities are more than enough to create horizontal pathways into the casing. Such pathways are inconsequential when the casing is completely filled with concrete (See Appendix C). Axial degradation may occur, but it will be separated by long columns of intact material that will resist flow and approximate the undisturbed geology.

B.5.4 Volume of Debris Produced by Corrosion

It is assumed that casing above 345 m depth (1131 feet) will disintegrate due to unrestrained corrosion (See Section B-3.3.2). It is also assumed that the corrosion product may be either ferrous hydroxide or magnetite. Corrosion products of steel occupy more volume than the original steel. Using the molar volume for iron to represent steel, Ferrous hydroxide occupies 3.73 times more volume and magnetite occupies 2.1 times more.

The volume of steel in the borehole casing above a depth of 345 m is calculated to be about 4.4.m^3.(Note: 260m of the length is assumed to be surface casing and 85 m is assumed to be intermediate casing). The volume contained by the intermediate (which extends to the top of the Salado) is 0.0059 m^3/m of length.

Conversion of all steel casing to corrosion products produces between 8 and 14.5 cubic meters of debris. This is sufficient to fill 1380-2460 m of casing (up to about 8063 feet). As a result, debris from corrosion in the uppermost part of the casing is sufficient to fill boreholes more than 8000 feet deep from their bottom all the way to the Culebra.

This debris is expected to contain both fine- and coarse-grained materials. Coarse material will be comprised of larger pieces of corroded casing that fall into the hole as a result of physical failure. The fine material will be the result of chemical precipitation of alteration phases. Based on such phenomena as precipitation in marine environments and production of shiny to dull films in corrosion experiments, it is the judgment of the investigators that the fine materials will range in size from microns to silt-sized. The initial permeability of the settled debris is expected to be in the range of 10^{-11} to 10^{-14} m^2.

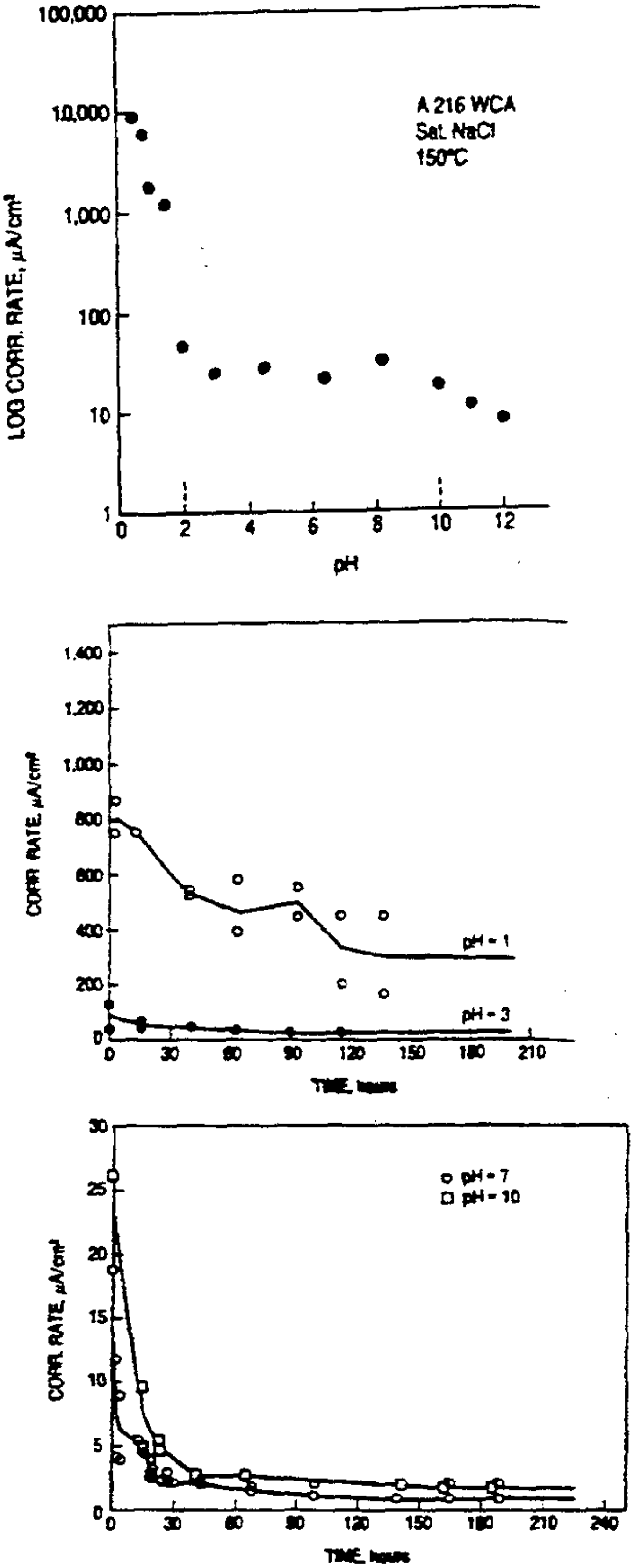
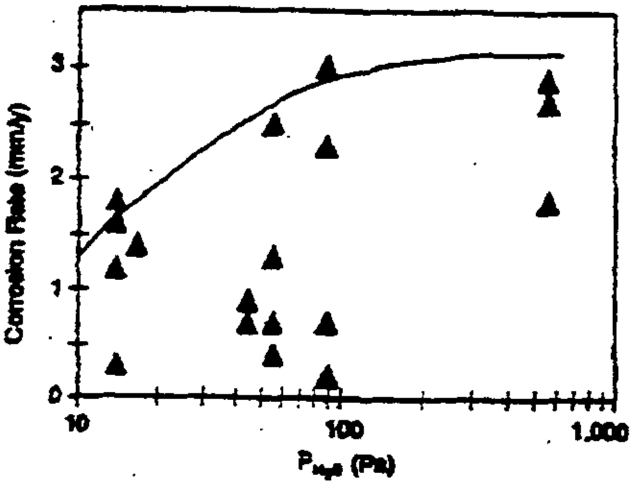
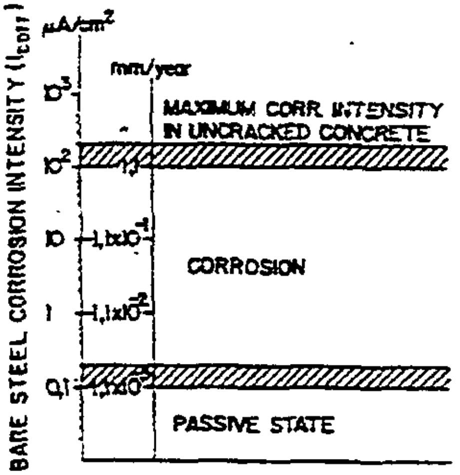


Figure B-1: The effects of pH and time on corrosion rate of low carbon steel



Corrosion rate of low carbon steel in carbon dioxide saturated solutions as a function of the partial pressure of hydrogen disulfide (from Videm and Kvarekval, 1995)



-Values of corrosion intensity in µA/cm² and in mm/year which may be measured in concrete. Below the range 0.1 to 0.2 µA/cm² the amount of corrosion is negligible. Between this range and until 100 to 200 µA/cm², corrosion is active and brown oxides develop. Values above 100 to 200 µA/cm² were never recorded in uncracked concrete.

Figure B.2

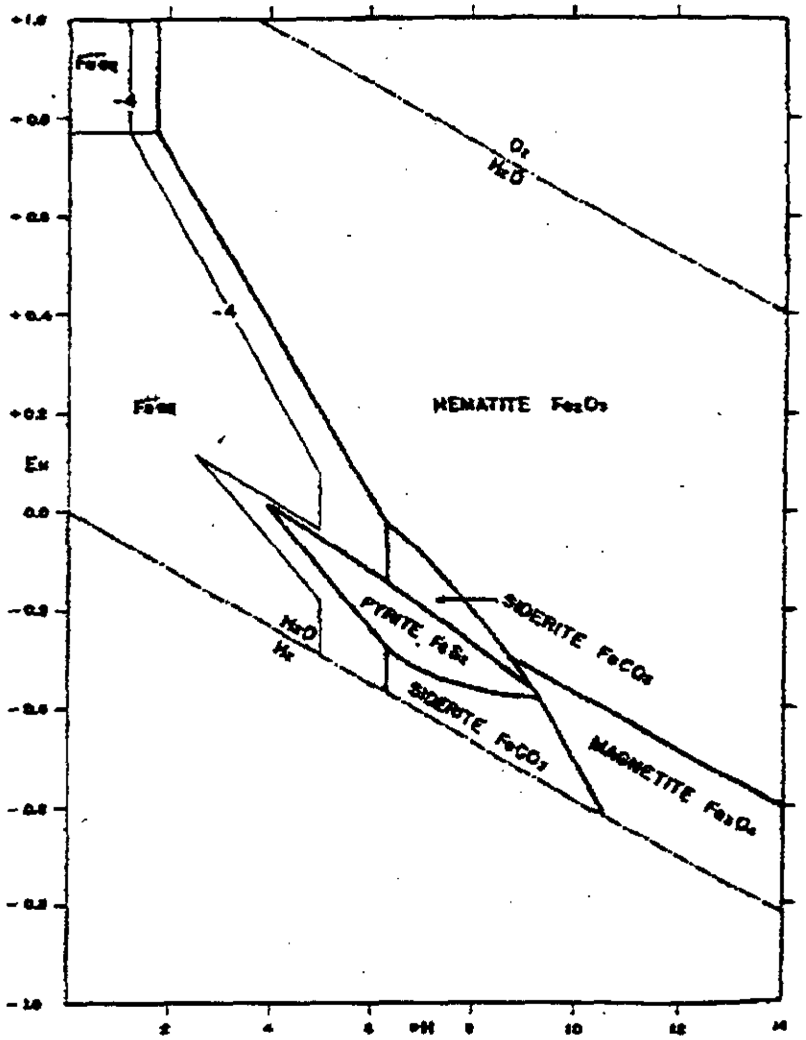


FIG B-3. Stability relations of iron oxides, sulfides, and carbonates in water at 25 °C and 1 atmosphere total pressure. Total dissolved sulfur = 10^{-6}. Total dissolved carbonate = 10^{0}. Note elimination of FeS field by $FeCO_3$ under strongly reducing conditions, and remarkable stability of pyrite in presence of small amount dissolved sulfur.

Figure B.3

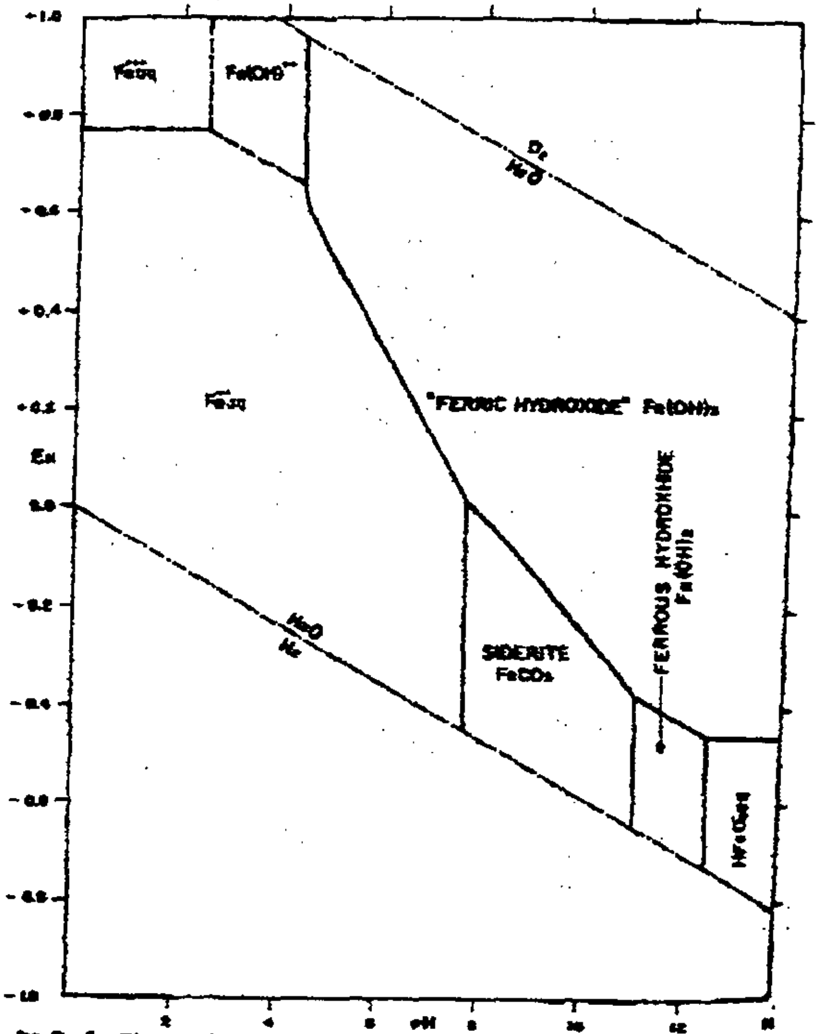


FIG. B-4 Diagram showing the relations among the metastable iron hydroxides and siderite at 25 °C and 1 atmosphere total pressure. Boundary between solids and ions: total activity of dissolved species = 10^{-6}. Total dissolved carbonate species = 10^{-2}. Dashed lines are boundaries between fields dominated by the labeled ion.

Figure B.4

APPENDIX C: DEGRADATION OF CONCRETE

C.1. INTRODUCTION

On permanent abandonment, exploration and production boreholes in the Delaware Basin of New Mexico are filled with steel casing, drilling mud and concrete plugs. This appendix contains descriptions of mud and concrete plug materials (C-2), details of how the concrete materials are expected to alter with time (C-3), an explanation of how the performance life of concrete plugs has been estimated (C-4), a description of the characteristics of alteration products and debris expected from plug degradation (C-5), and a compilation of Delaware Basin plug locations, dimensions and plugged intervals (C-5). Simplifying assumptions have been made for many of the calculations performed. These assumptions and the limitations they impose on the application of the calculations are discussed within each section of the appendix.

Many of the results of the investigation into expected concrete plug performance rely on results from the casing corrosion investigations described in Appendix B, since some form of failure by the casing is a necessary precursor to changes in performance by the concrete plug. Conservative approaches have been used when analyzing the potential for casing failure, and are also used here. As a result, in the authors' scientific opinion, predictions of concrete plug and overall system performance most likely underestimate the expected performance life of borehole plugs.

Competent emplacement of borehole plugs is an underlying assumption of the performance-life analysis described here, so that the theoretical performance life of the plugs is based on the fundamental physical and chemical properties of the plug materials in the expected service environment. With this assumption, plug performance depends primarily on the environment in which the plugs are placed, and the initial permeability and porosity of the plug, as well as the nature of the plug materials.

Conservative site specific data have been used to estimate the former, and experimental data for generic Portland cement concrete have been applied to estimate the latter. The results indicate that plugs placed above about 335 m (1100') will likely disintegrate in one or two hundred years. Plugs placed at greater depths will be much more long-lived. The best estimate for the average performance life of deeper plugs is on the order of 5000 years, with an uncertainty of one order of magnitude.

C.2 PLUGGING SCHEMES USED IN THE DELAWARE BASIN OF NEW MEXICO

A total of 194 boreholes have been drilled and plugged in the New Mexico portion of the Delaware Basin since 1988, when current plugging and abandonment regulations were instituted. During this time interval, no hole is known to have been constructed and abandoned without following the plugging requirements set forth in various regulations (see Appendix A).

Figure C.4 depicts cross-sections of several plugging schemes used in the Delaware Basin of New Mexico. The minimum plugging configuration imposed by BLM regulations (Oil and Gas Order Number 2) requires plugs to isolate the evaporate sequence (Castile + Salado formations). In practical terms in the Delaware Basin, BLM requires placement of at least two plugs with one below and one above the repository. Figure C.4 shows that the minimum standards are met by installing a deep plug (generally placed below horizons associated with the pressurized brine reservoirs in the Castile Formation) along with a shallow plug interposed between the repository and the Culebra, usually at the Rustler-Salado contact. Of the 194 boreholes, 50 are plugged in this manner (See Table C.2).

The maximum plugging configuration consists of a continuous plug throughout the Salado-Castile evaporite sequence. Regulation R-111-P applies to any hole placed in the Known Potash Leasing Area (KPLA), regardless of whether the hole is intended for oil and gas or mineral exploration. The regulation provides protection to mineralized potash areas and workings by requiring a continuous plug so that there is virtually no chance for the flooding of mines either as they are developed or during their operation. All potash exploration holes follow the practices required by R-11-P. There are only four oil and gas boreholes documented to have a continuous plug; however, over 70 applications for oil and gas holes have been denied in the KPLA since 1988 (See Burski, 1994) for fear of creating circumstances that threatened potash reserves or workings.

Between the maximum and minimum plugging schemes lies intermediate ground characterized by multiple plugs. Multiple plugs are placed when: 1) casing is cut and recovered after development, or 2) in the event that unusual circumstances are encountered (e.g., lost circulation, water-production into the casing, casing failure, delivery of excess concrete to the site etc.) .

Figure C.4 depicts several such plugging schemes documented in the Delaware Basin of New Mexico. In these schemes, additional plugs are located in the Salado and/or Castile between (or through) the brine reservoir horizon (located at ~900m depth) and the Culebra (located at ~216 m depth). Table C.2 summarizes the available borehole and plug location/dimension information. For reference, the repository is taken to be located at a depth of 655 m; thus, Basin-wide practice includes installation of intermediate plugs that lie both above and below the reference repository depth. Whether or not current practice would result in plugged intervals above or through the actual repository horizon has not been speculated upon.

C.3 COMPOSITION OF BOREHOLE PLUG ELEMENTS

For the purposes of this report a borehole plug is defined as consisting of the casing, and any material left or emplaced within the casing. Performance of the casing has been discussed in Appendix B. Materials left within the casing include drilling mud and concrete. These elements are described and discussed below.

C.3.1 Drilling Mud

Different types of mud are used at different times in well-development history. A lubricating and hydraulic control mud is used during drilling of the well. At abandonment, plugging mud is placed within the casing to provide a platform for setting internal concrete plugs at desired depths, and to provide a positive fluid pressure to control inflow of formation fluids. The plugging mud remains as a part of the plugging system, and will be referred to hereafter as "mud.".

C.3.1.1 Composition of "Mud"

The BLM regulations in Oil and Gas Order Number 2 require that drilling mud left at abandonment must have a density of 10 pounds per gallon. Density is achieved by mixing mineral solids with brine. A previous investigation (Warner and McConnell, 1990) modeled oil field muds as sodium montmorillonite with water and concluded that after settling "muds" provided significant hydraulic flow resistance. As explained below, this result cannot be translated to the current situation due to the low volume of solids used in the low density muds.

BLM requirements for "mud" density can be achieved with NaCl- saturated brine and a minimum of additional solid material. The density of NaCl brine is about 1.2 g/cm^3, or about 9.6 pounds/gallon. Addition of about 2% by volume sodium montmorillonite satisfies the BLM requirement for 10 pound "mud." A review of plugging practices in the Delaware Basin (Westinghouse, 1996) shows that BLM requirements are met in precisely this manner. Thus, in reality drilling "mud" is brine possessing a somewhat thicker viscosity than ordinary water, but without appreciable hydraulic resistance.

Discussions with drillers and mud companies have resulted in conflicting pictures of the ability of particulates to settle out from "muds." Additives are routinely placed in "muds" to prevent settlement, and there are claims that settlement will be prevented permanently, although "permanent" in the context of normal oil-field operations does no necessarily equate to "permanent" in the regulatory context. There are also anecdotes that relate to difficulties of encountering settled "muds" upon reentering abandoned holes.

The amount of montmorillonite that might settle out of the low density plugging mud will not provide a flow barrier of any consequence. The upper 345 m of casing has an ID of 31.788 cm (12.515"; Westinghouse, 1996) and an associated volume calculated as ~27 m^3. The volume of clay associated with this amount of "mud' would be 0.55 m^3 at 10 ppg. If all this clay were to settle out onto the uppermost plug (which is assumed to be located near the Salado-Culebra contact), at full density the pile would have a permeability on the order of 10^{-15} m^2, but it would extend less than 5 meters. At high hydraulic gradients and without sufficient physical support, the pile would be subject to piping and erosion. If the pile fell into the intermediate casing (ID = 20.12 cm), it would extend a length of less than 10 m or have a higher permeability. The suspicions concerning the ability of the mud to resist flow would remain approximately the same, but there would be an important additional uncertainty. Even if the settled mud column possessed low permeability and could withstand high hydraulic gradients, the pile's location may not lie between water sources of concern and the Culebra. Because of the small amounts of solids involved, the uncertainties in regard to settled mud location, and the unresolved ability of the "mud" to settle, the current analysis does not rely on settled "mud" to contribute to borehole plug performance.

C.3.1.2 Composition of Oil Field Concrete

Oil field concretes are mixed by adding water, additives and bags of cement. Precise specifications can not be given because practice varies from driller to driller. For example, specifications are written in terms of "sacks of cement." Each sack weighs 94 pounds and can be used to formulate from 1 to 2 ft^3 of concrete slurry (Westinghouse, 1996). For an assumed density for cement of 2.8 g/cm^3, and assuming conservation of volume, the calculated water:cement ratio for oil field cement pastes therefore ranges from ~ 0.3 to ~0.9. BLM requires that plugs intended for evaporite sequences must be mixed with brines saturated in indigenous salts, such as halite. Accordingly, concretes are assumed to be halite saturated.

The type (i.e. composition) of cement used to plug boreholes also varies, Class C oil field cement is highly resistant to sulfate attack, and is specified for use at some depths. Otherwise, Class H oil field cement is used. Because the cement type is variable and because no WIPP-specific experiments have been conducted, generic data from portland cement materials have been used in these analyses.

The initial permeability associated with a generic portland cement paste can be estimated from the water:cement ratio of the mix. This relationship occurs because permeability is intrinsically related to the porosity through which the permeant must move. As cements harden, they undergo water-solid reactions that form phases such as calcium-silicate-hydrate gel, tobermorite, portlandite, and ettringite. These phases form an interlocking network, with trapped porosity between the crystals. The porosity is comprised of microcracks and internal porosity, but in either case, the pore volume was occupied by water prior to the onset of cement reactions. Thus, after hardening the initial permeability is related to the original water:cement ratio. Figure C.1 (Neville, 1983) shows the relationship of permeability to porosity and permeability to water:cement for generic portland cement pastes. From the figure, it can be deduced that the initial permeability of oil field concrete plugs will be on the order of 1×10^{-19} m^2. To account for field emplacement and the increased range of water:cement, an initial permeability on the order of 10^{-17} m^2 has been judged reasonable. Data from WIPP-specific field tests on cement plugs placed in the Castile formation appears to corroborate this estimate. Measured values from these field tests were 5×10^{-17} m^2 (Petersen and Christensen, 1980; Christensen and Hunter, 1980), and, since this value is consistent with those from the water:cement ratio, this is used as the permeability of undegraded concrete.

C.4 CHANGES IN CONCRETE PERMEABILITY AS A FUNCTION OF TIME

The solid matrix that makes up concrete is composed almost entirely of amorphous to cryptocrystalline solid phases. These phases are thermodynamically unstable, and with time and exposure to water they alter into more stable and more crystalline assemblages.

Alcorn et al (1992) used the equilibrium code EQ3NR/EQ6 to predict the alteration phases in portland cement that would occur upon exposure to waters ranging in composition from pure water to saline brines. The predicted alteration phases included tobermorite, quartz, gypsum, calcite, clays and zeolite, produced at the expense of soluble and unstable materials such as portlandite and hydrogarnet. The significance of the calculations is that the theoretical alteration assemblage occupies more volume than the original solids. Recalling that porosity and permeability are related, a theoretical relationship was developed to predict the change in permeability caused by the mineralogic changes:

$$\Delta_k = (k_i) \times 10^{7.39\Delta_n} - k_i,$$

where k_i is the initial hydraulic conductivity, and Δ_n is the change in porosity that derives from mineralogic alterations. (Coons, et al., 1989)

This relationship, and the predicted decrease in porosity, indicates that the permeability of a concrete plug will decrease as the plug alters geochemically, assuming that the concrete structure is not allowed to expand its external volume. It is also apparent that the initial permeability of the plug is central to determining its long term performance. If initial permeability is low, then not much change will occur. If initial permeability is high, then there is the potential to observe significant change. It is also important to note that in fast flow ("open") systems, material can be transported out of the system, causing an increase in porosity and permeability. In equilibrium flow systems, permeability should decrease significantly.

These calculated results have been verified by subsequent experiments in which waters and cement were reacted (Onofrei et al., 1992). Consistent with theoretical predictions, the experiments showed consumption of portlandite and apparent production of gypsum, calcite, tobermorite and clay-like materials which were observed as very fine-grained materials filling pores and coating surfaces of the original hardened paste. As a result, the experiments also showed the reduction of porosity and permeability predicted from theory (See Figure C.2), confirming that as time passes in physically confined systems concrete plugs may be expected to improve their performance as hydraulic barriers. This prediction is also confirmed, at least partially, from observations made on recovered plugs originally placed decades ago in potash mineral exploratory holes in the Delaware Basin. Petrographic inspection of the cores reveals some alteration proximate to surfaces where water access has occurred, but shows that original textures and mineralogy (e.g. portlandite) is present at short distances of separation (Bonen, 1995). These observations are consistent with mineralogic alteration of the concrete attending water access, followed by the subsequent inability of water to reach further into the concrete.

By contrast, at free surfaces concrete materials are not physically supported and can spall. Long term leaching experiments report that surface diffusion controlled alteration is dependent on the C_3A content of the cement and the Mg and $S0_4$ content of leachant (Walton et al., 1990). Creation of an alteration rind weakens the concrete and makes it subject to spalling (Wakeley et al., 1994). The mechanism for spalling is that the alteration phases occupy more volume than the original solids, volumetric expansion increases internal pore pressures until concrete tensile strengths are exceeded and spalling occurs. Short-term, empirical studies of ordinary concrete alteration report alteration rates in the range of 0.7 to 1 mm/year (Atkinson and Hearne, 1990) - These rates are likely to be overestimates because diffusion distance varies as the square root of time. For simplification, the time (i.e. distance) dependence and the effect of compositional changes in the leachant have been neglected when estimating spallation. This is conservative because of the two variables, diffusion is the controlling factor (the composition of the leachant is unimportant if it cannot roach the material being leached). So, for the purposes of estimating concrete plug longevity, the commonly reported leaching rates (0-5 to 1 mm/yr) are assumed equivalent to a spallation rate. Generally, spalling occurs after increments of one to several millimeters of alteration (Atkinson and Hearne, 1990) but this level of detail is inconsequential to the model. Based on this model, axial diffusion driven spallation will reduce the length of a borehole plug by 5-10 m in 10,000 years, while if corrosion produces a hydraulically conductive interface between the plug and the casing, radial diffusion and spallation would reduce the diameter of the plug by half in about 120 years. Such a reduction is judged sufficient to result in physical failure of the plug.

In summary, theoretical calculations and empirical observations show that in physically confined systems chemical alteration of concrete plugs will tend to decrease the plug's permeability. In unconfined and fast flow systems, chemical alteration will tend to increase plug permeability. Borehole plugs will generally receive radial confinement from the borehole and casing wall, however if the casing is removed from around the plug and water sources are present, failure is predicted to occur rapidly (in about 100 years), due to a combination of fast flow and diffusion-driven spallation. Axial (longitudinal) confinement for the plug comes from the plug's internal strength. Short plugs will tend to act as unconfined systems, while longer plugs will be confined, however the minimum length to approximate a fully confined system has not been determined.

C.5 FLOW-DRIVEN FAILURE OF CONCRETE BOREHOLE PLUGS

As noted above, the minimum length a plug must have to be self-supporting and approximate a fully confined system has not been determined. In an attempt to model flow driven failure, the following logic has been employed:

- The concrete plug will lose its functionality when substantial cracking results from the cumulative flow of leachant through the plug

- Cracking will occur because increased pore pressures from alteration are insufficiently offset by the internal strength of the plug's matrix, supplemented by the effects of confinement of the plug

- Substantial cracking will occur when the plug begins to lose its internal strength
- Loss of internal strength will begin when the internal matrix of the concrete is chemically attacked and loses strength
- The internal matrix of the concrete is comprised of calcium-silicate-hydrate (CSH)
- When leachants show evidence that the CSH phase is being attacked, the plug is assumed to fail. Note that concrete materials do not dissolve congruently. The first phases to dissolve are portlandite and alkali salts (Atkinson, 1985). Phases such as ettringite and hydrogarnet likely follow, and then the CSH matrix is attacked.
- Prior to failure, the plug will function with no increases or decreases in permeability caused by changes in porosity

The progression of concrete chemical alteration has been reported by Berner (1990) for both fresh water and brine leachants. The progression is charted in terms of the volume of water flow. Traditionally, geochemical studies plot the progress of alteration in terms of the water: solid ratio. It is clear that the total volume of solid is irrelevant in concrete degradation studies because much of the solid never contacts the flowing leachant. By tracking progressive alteration in terms of the number of pore volumes of water that pass through the concrete, Berner is consistent with the reasoning that only the solid that surrounds the pores interacts with the leachant. His results show that more than 100 pore volumes of leachants must pass through the concrete before there is chemical evidence that the matrix is being attacked (See Figure C.3). Clearly these results will vary somewhat depending on the composition of the leachant and the cement mix formulation.

Based on the above assumptions, and Berner's results, it has been assumed that borehole plug failure will occur after 100 pore volumes of water have passed through the plug. This volume can be converted to performance life by using Darcy's Law and assumptions about the plug's physical characteristics. Thus, for a plug with a cross-sectional area of A (m^3), length of L (m), permeability of k (m^2), and a fluid viscosity of μ (Pa.s), inlet pressure of P1 and outlet pressure of P2 (Pa) the flow rate is:

$$Q = A^*(k/\mu)^*(P_1 - P_2)/L \quad m^3/sec$$

The pore volume of the plug (V_p) is:

$$V_p = AL\phi \ m^3$$

So:

$$Q = \{(k/\mu)^*(P_1 - P_2)/L\}/\{L\phi\} \text{ pore volumes/sec}$$

Breakdown of the structure of the cement matrix is considered to start after 100 pore volumes of flow, or after:

$$t_{100} = 100*L\phi/\{(k/\mu)*(P_1 - P_2)/L\}*\ 3.154\text{x}10^7\ \text{years}$$

If the following values apply to plugs:

$L = 40$ m,
$k = 5\text{x}10^{-17}\ \text{m}^3$,
$\mu = 1\text{x}10^{-3}$ Pa.s,

then:

$$t_{100} = 1.015\text{x}10^5*\phi/(P_1 - P_2)\ \text{years},$$

with pressures in MPa.

The porosity of the plug may be taken to range from 5-40 percent, while the pressures controlling the flow will depend on the location. For a plug between the Castile and the repository the pressure below the plug will be equal to the Castile brine reservoir pressure, less any head loss between the reservoir and the base of the plug. The pressure above the plug will equal the repository pressure, plus any head increase between the repository and the plug.

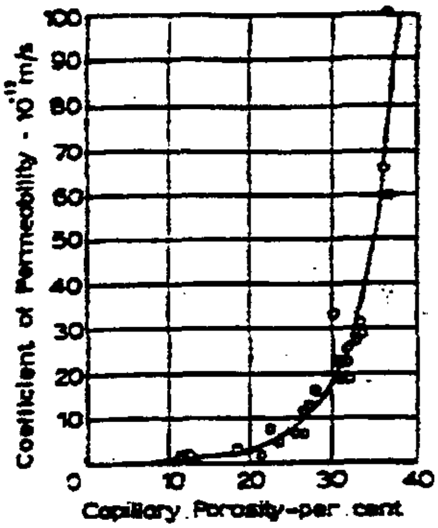
It should be noted that for the purposes of the calculations used here, the relationship between porosity and permeability is not accounted for. This simplifies the calculation but creates the somewhat illogical extension that as the porosity of the plug decreases, less and less water flux is calculated as being needed to cause failure. In the extreme, at zero porosity no flow would be necessary. The significance of this apparent inconsistency is diminished by evaluating a range of porosity that does not include zero. The lower limit of porosity for a borehole plug is judged to be 5 %. This is higher than estimated by Petersen and Christensen (2%; 1980) for the Bell Canyon test plugs, but more consistent with practical experience of field emplaced concrete structures. The upper limit for porosity is taken as 40%. This porosity conservatively reflects coarse grained (e.g. sand) particles in contact (also, see Figure C.1). Given the pressure imposed by the overlying column of water, greater porosities, while possible to engineer, would only occur with difficulty. An engineering estimate for the most likely initial porosity of concrete in a borehole plug is 10%.

C.6 CHARACTERISTICS OF DEBRIS GENERATED BY PLUG FAILURE

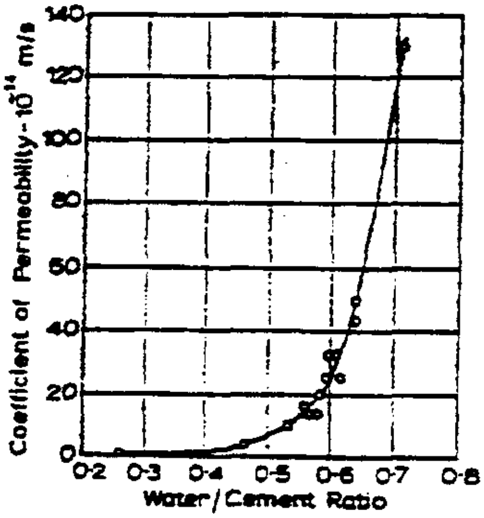
The secondary phases created during the chemical alteration of concrete are very fine (See Onofrei et al., 1992 for photomicrographs). These materials commonly clog pores in the concrete and are smaller than 100mm (See Gray, 1993). Spalled material from unloading concrete surfaces is also expected to be fine-grained. As with corrosion products, no knowledge is claimed for how the fine-grained material might agglomerate and/or cement with time.

The volume of debris that can be associated with failure of the uppermost plug is calculated as 2.89 m^3. This figure derives from the assumptions that 20 meters of the uppermost plug lies in the surface casing (ID = 31.788 cm) and 20 meters lies in the intermediate casing (ID = 20.119 cm; See Westinghouse, 1996 for plugging practices and casing dimensions) and that the disaggregated volume will be at least 30% greater than the intact volume. In addition to the volume from the degraded plug itself, the concrete materials used to cement the casing to the rock will contribute debris. The internal diameter of the borehole for the surface casing (OD = 33.973 cm) is taken to be 36.297 cm (Westinghouse, 1996). Assuming the same 30% bulking factor, the volume of degraded cement associated with disintegration of the upper 335 m (See Appendix B) of casing cement is 5.59 m^3.

Collectively, casing and plug cement debris is calculated to have a volume of 7.81 m^3. This volume is sufficient to fill the intermediate casing for a length of over 1300 m. When added to the minimum 8 m^3 of debris generated by casing corrosion, the debris pile is calculated to be at least 2600 m long (about 8800 feet). A debris column of this length is sufficient to fill an exploratory hole from its bottom (or a bridge plug set at 8000 feet depth) to above the Culebra. Thus, in the worst case, if calculations predicting plug performance life are faulty, it is inconceivable that an abandoned oil and gas borehole will perform at a level less than a pathway filled with silty-sand (See 1992 PA and Appendix D). Representative performance lives and permeabilities associated with plugged borehole intervals are summarized in Table C.1. An engineering estimate for initial porosity (10%) has been used for the example calculation.

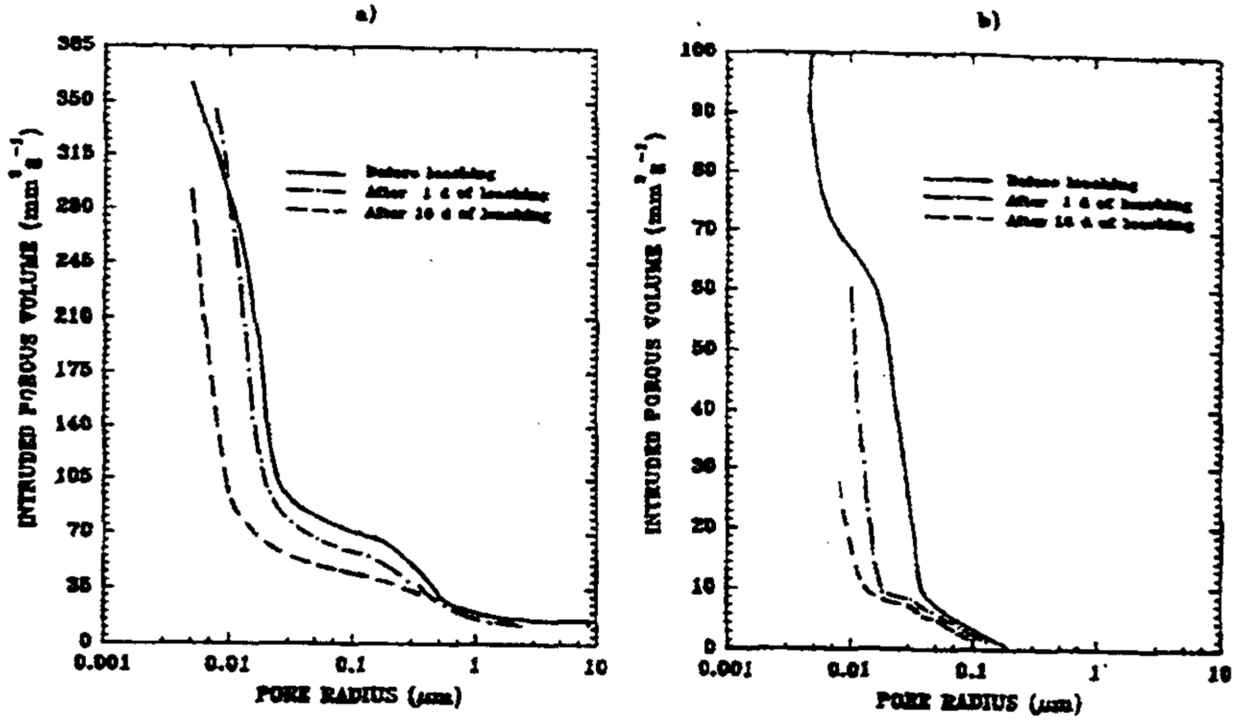


Relation between permeability and capillary porosity of cement pastes (Neville, 1981).



Permeability as a function of water - cement ratio for mature cement pastes (93% of cement hydrated). From Neville, 1981.

Figure C.1



The effect of leaching time on cumulative pore size distribution measured by mercury intrusion porosimetry for: (a) ALOFX -MC grout (MC-500, 0.7/1/10), and (b) reference grout (Type-50, 0.4/1/10).

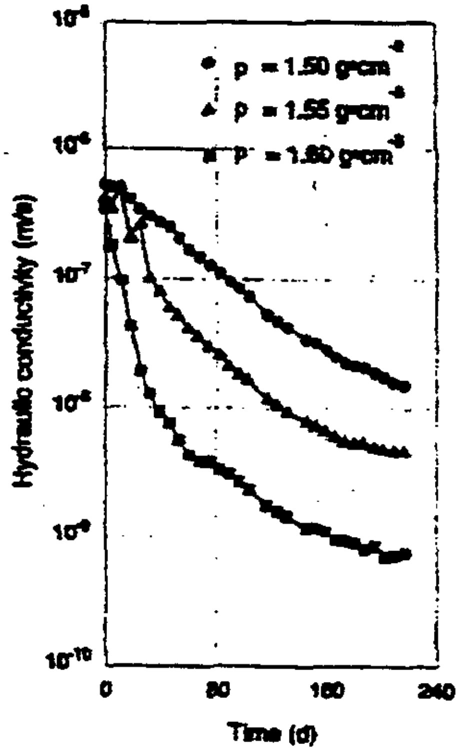
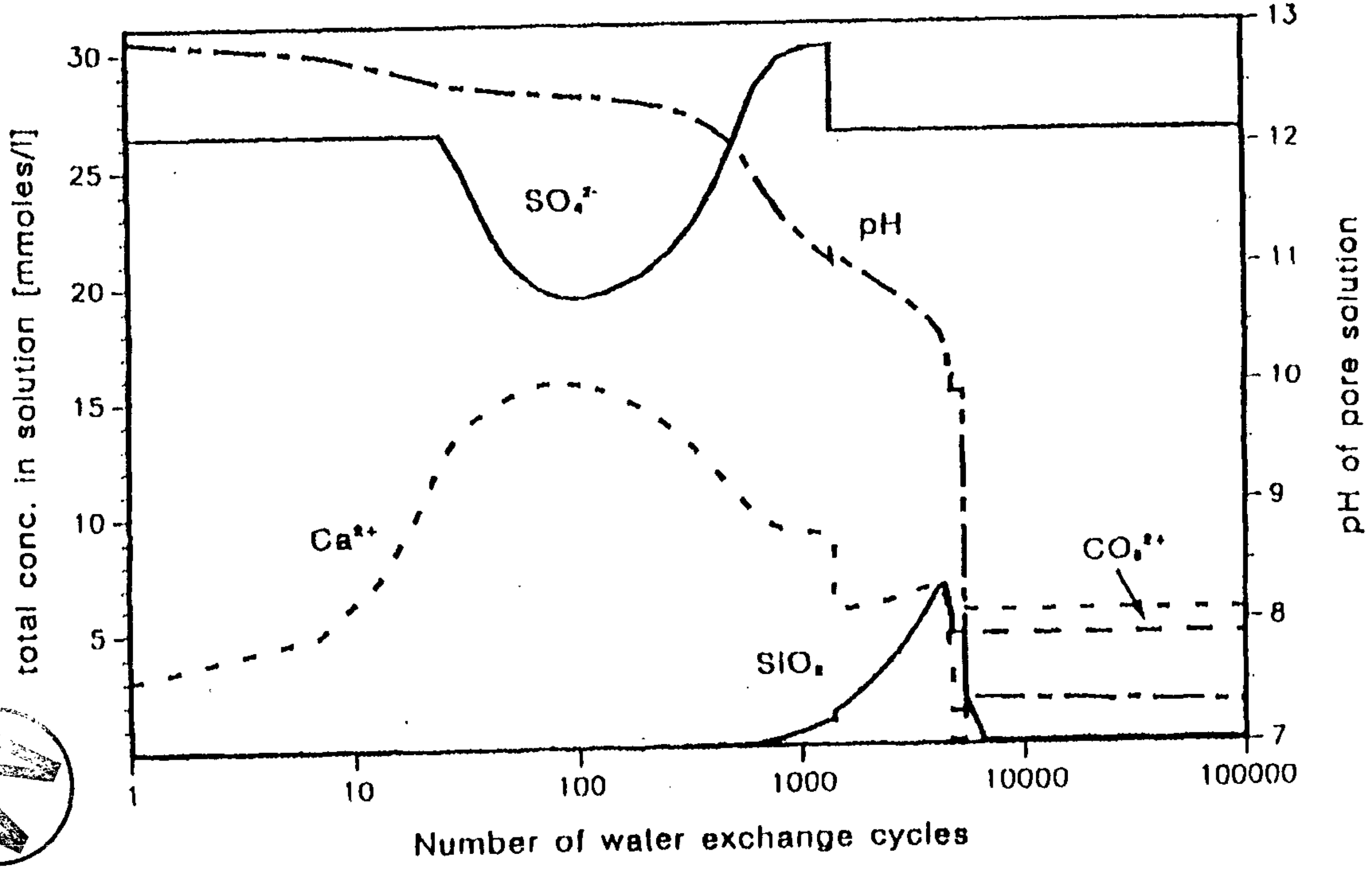


Fig C-2 Decreases in hydraulic conductivity measured in crushed, reconsolidated grout as a function of time of exposure to flowing ground water (from Gray, 1992; after Onofrei et al., 1992).

Figure C-3 Degradation of "HTS" in standard marl grundwater "MAR". After 6650 cycles calcite is the only solid phase present (T = 25 °C).



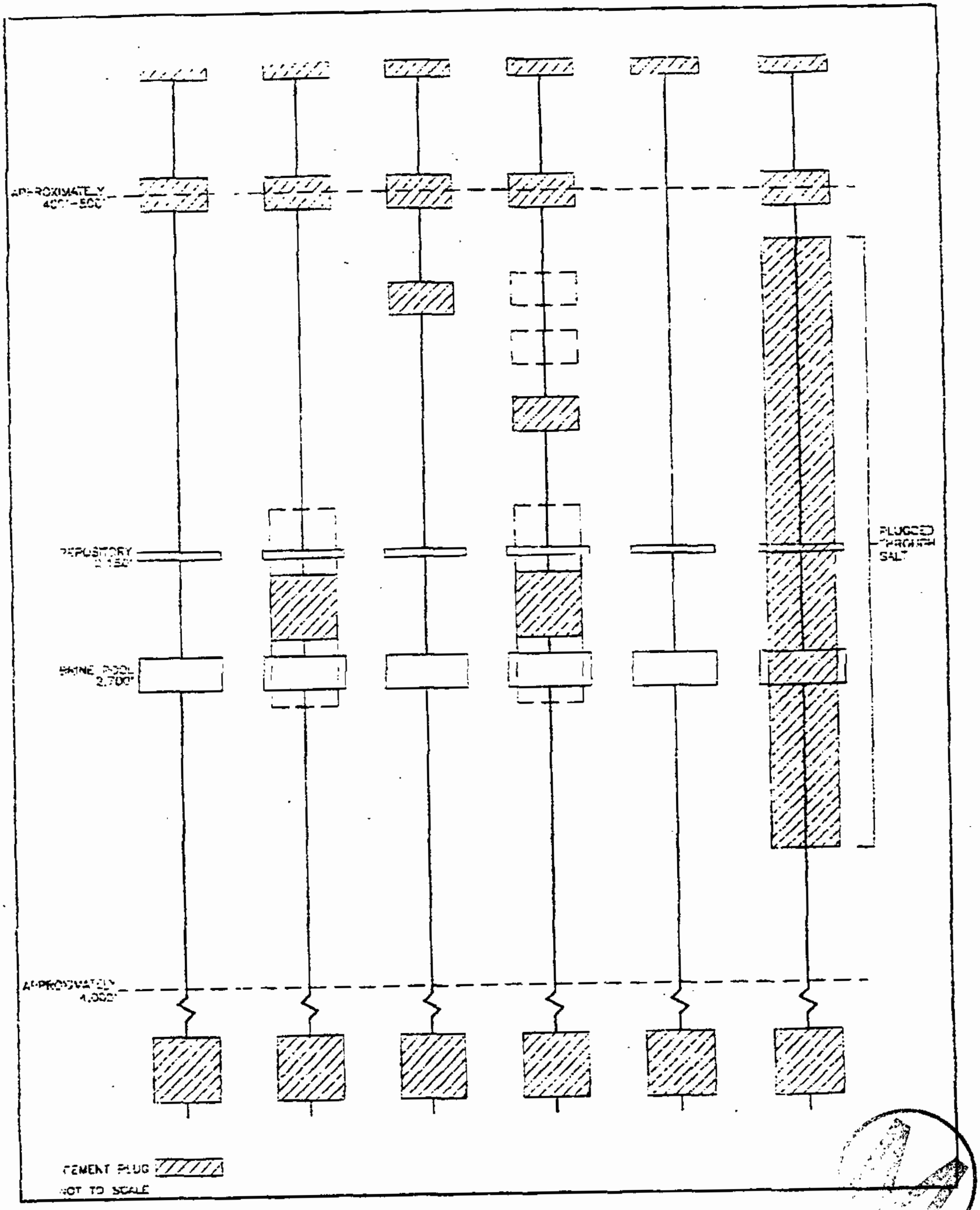


Figure C-4

Typical Borehole Plug Configurations in the Delaware Basin

APPENDIX D: CREEP CLOSURE OF BOREHOLES

D.1. INTRODUCTION

Following disintegration of the upper plug a borehole will become filled with a material whose physical properties, including permeability, will approximate those of a silty-sand. Appendix C.-- has evaluated this material. Over time that portion of the borehole in the salt sections will tend to creep closed, and in so doing will compress the fill material, and may be expected to reduce its porosity and permeability. Analyses have been conducted to evaluate this effect, and have demonstrated that, in the absence of any restraint from uncorroded casing, borehole creep closure will reduce permeabilities in the deeper parts of an intrusion borehole (that is below the repository) by about one order of magnitude in about 1000 years. Closure of the borehole above the repository will be too slow to have any significant effect.

The methodology used for these calculations is to a) calculate the time for a certain amount of borehole closure to occur at various depths, b) equate these closures to porosity reductions and c) relate these porosity reductions to permeability reductions using an appropriate correlation.

D.2. CREEP CLOSURE

Creep closure of the borehole has been calculated by RE/SPEC using a "pineapple slice" plane strain model in the Spectrom 32 code, with the MDCF model and WIPP salt parameters. Only steady state creep was included. Closure calculations were made for 5000 years at depths of 250 m (Top Salado), 450 m, 650 m (Repository) and 850 m (Bottom Salado). Far-field horizontal stresses were estimated at 1 psi/ft depth, with a back-pressure due to a column of brine (density 1.2) to the surface. No back pressure due to consolidating borehole fill is allowed for. Full details of the calculations are included in RE/SPEC's calculation file 325/3.9/01. Results are summarized in Figures D.1 and D.2.

The results, in terms of volumetric closure, are converted to a reduction in porosity for the silty-sand borehole fill as follows:

Deformation is plane strain, so:

$$V/V_o = A/A_o = (a_o + u)^2/a_o^2$$

where: V, V_o are the current and initial borehole volume,
A, A_o are the current and initial borehole cross-sectional area,
a_o is the initial borehole radius,
u is the radial deformation.

If it is assumed that all change in volume is due to loss of pore volume, i.e. the solids are infinitely stiff relative to the borehole fill, then:

$$(1 - \phi)/(1 - \phi_o) = (V_s/V_b)/\,(V_s/V_{bo}) = V_{bo}/V_b,$$

D.3. PERMEABILITY - POROSITY

It is assumed that the permeability varies with the porosity, according to the Kozeny-Carman relationship (e.g., Bear, 1972: Lambe and Whitman, 1969: Koltermann and Gorelick, 1995):

$$k = \alpha\, \phi^3/(1 - \phi)^2,$$

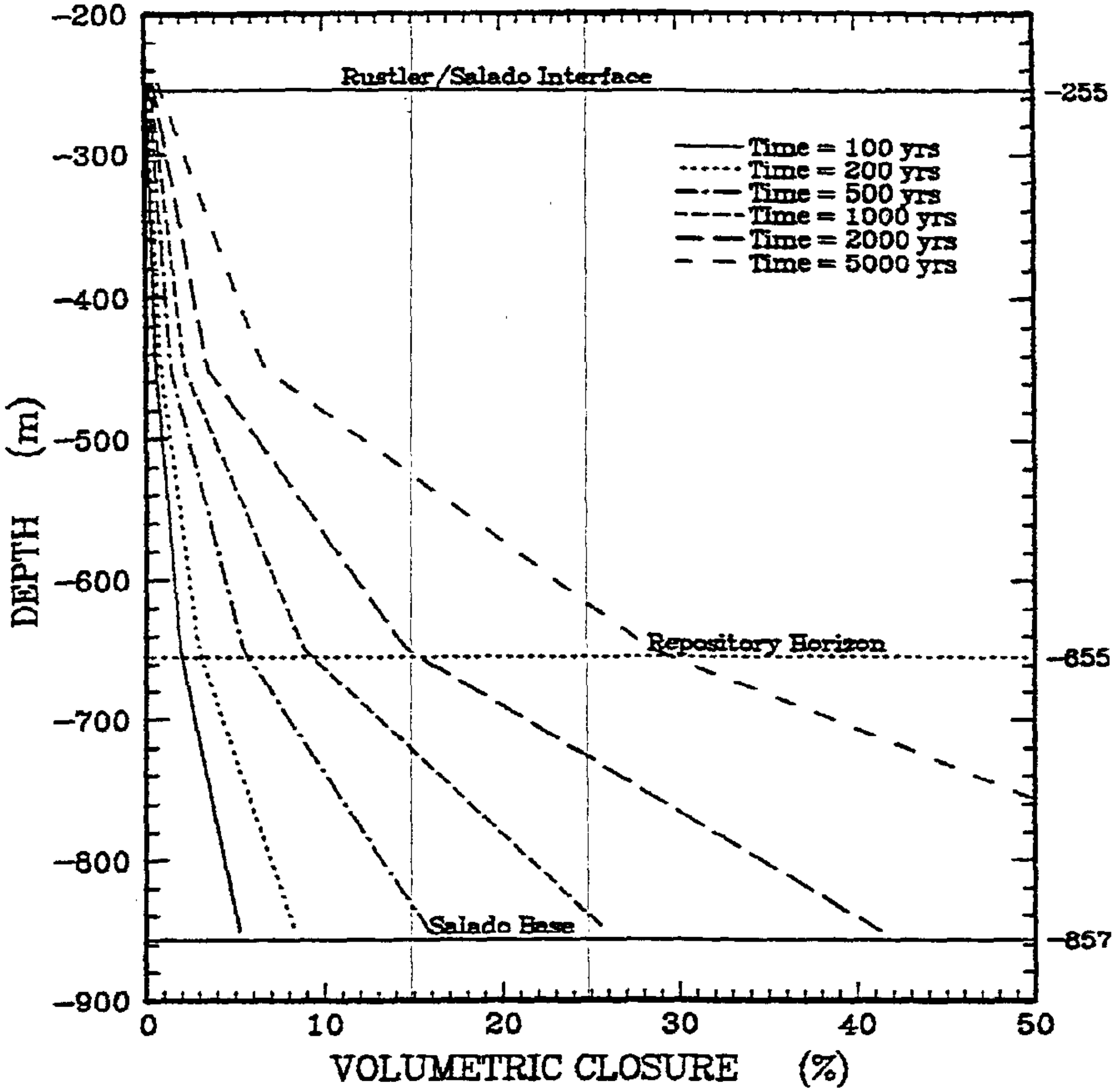
so that:

$$k/k_o = (\phi/\phi_o)^3/\{(1 - \phi_o)/(1 - \phi)\}^2.$$

D.4. RESULTS

Figure D.3 shows the volume closure required to give a one order of magnitude reduction in permeability ($k/k_o = 0.1$) for various possible values of initial porosity ,ϕ_o. This indicates that for initial porosities varying between 25% and 40% volume closures of between 14% and 23% are required. For a median initial porosity of 32% a closure of 18% is required. Figure D.1 may then be used to indicate the time required for these volume closures to occur at different depths. At the base of the Salado (850 m) 14% closure will occur in slightly less than 500 years and 23% in about 850 years. At the repository level 14 % closure will take about 1800 years, and 23 % over 3500 years. Figure D.2 indicates that the median (18%) closure will be realized for a column of about 100 metres in 1000 years and almost for the full column beneath the repository in 2000 years.

A number of points should be noted. Firstly the time values given here are calculated assuming that there is no restraint from uncorroded casing, although on the other hand they do assume uniform closure, and neglect the effect of early localized corrosion. Secondly these values take no account of consolidation due to the effect of the overlying borehole fill. Finally the creep closure calculations do not account for back stress from the consolidated fill. This is not unreasonable for the closures used here (up to 23% maximum), but will probably not be reasonable for larger closures. As a result additional closure will be increasingly resisted, making it likely that the one order of magnitude reduction in permeability from the effects of creep used here will not be exceeded with additional time.



1

Figure ~~3~~. Volumetric Closure as a Function of Depth at Six Representative Times.

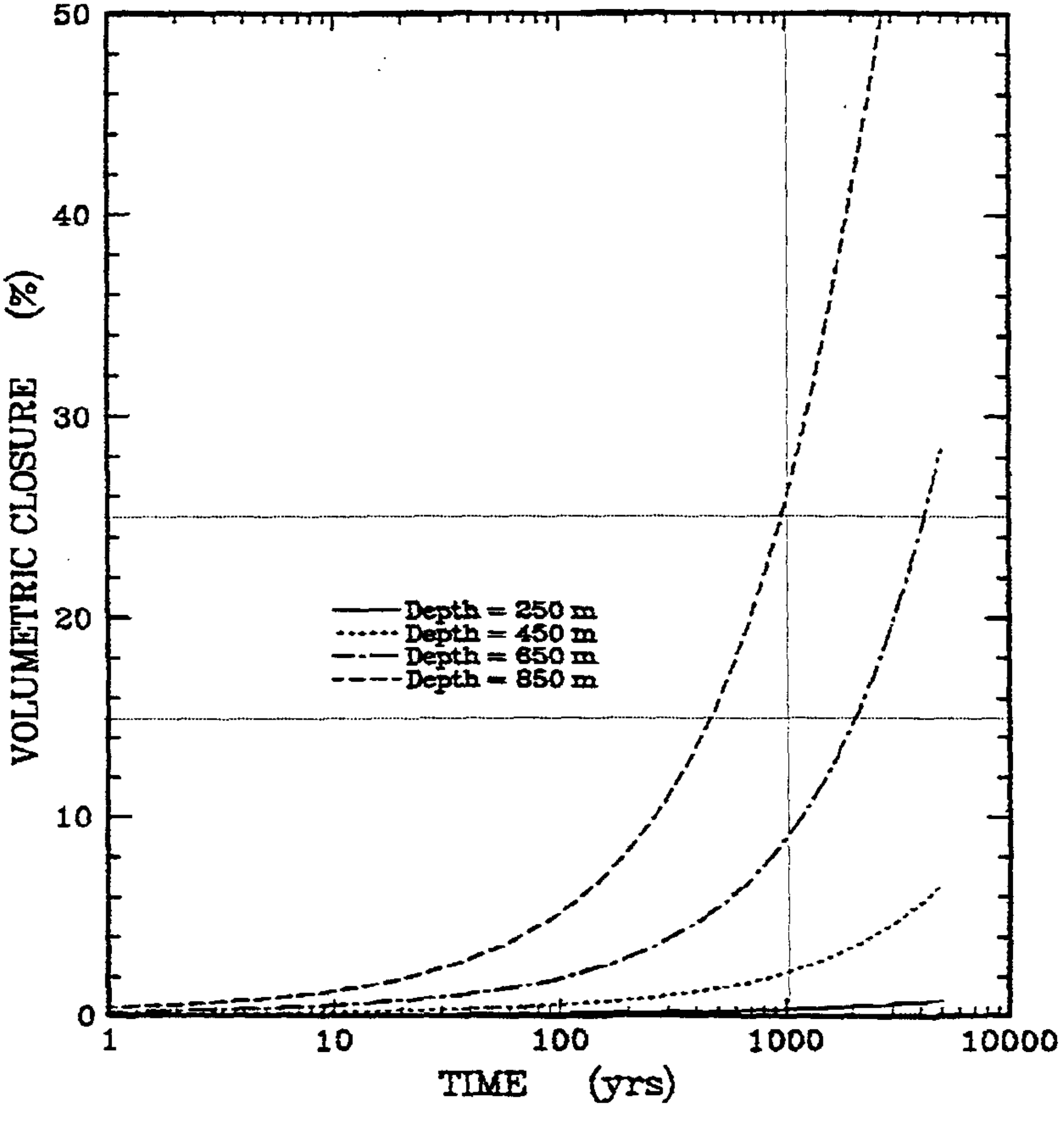
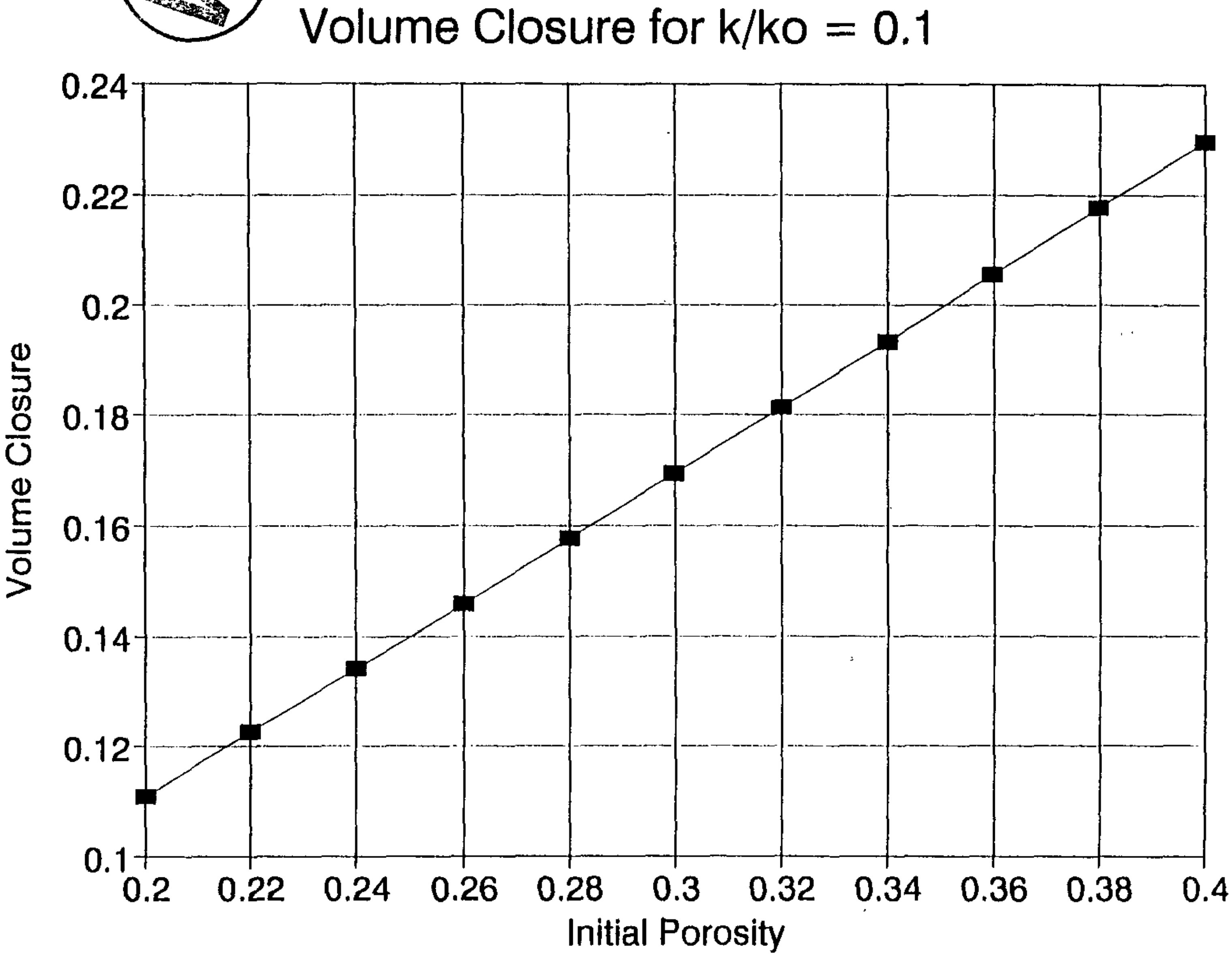
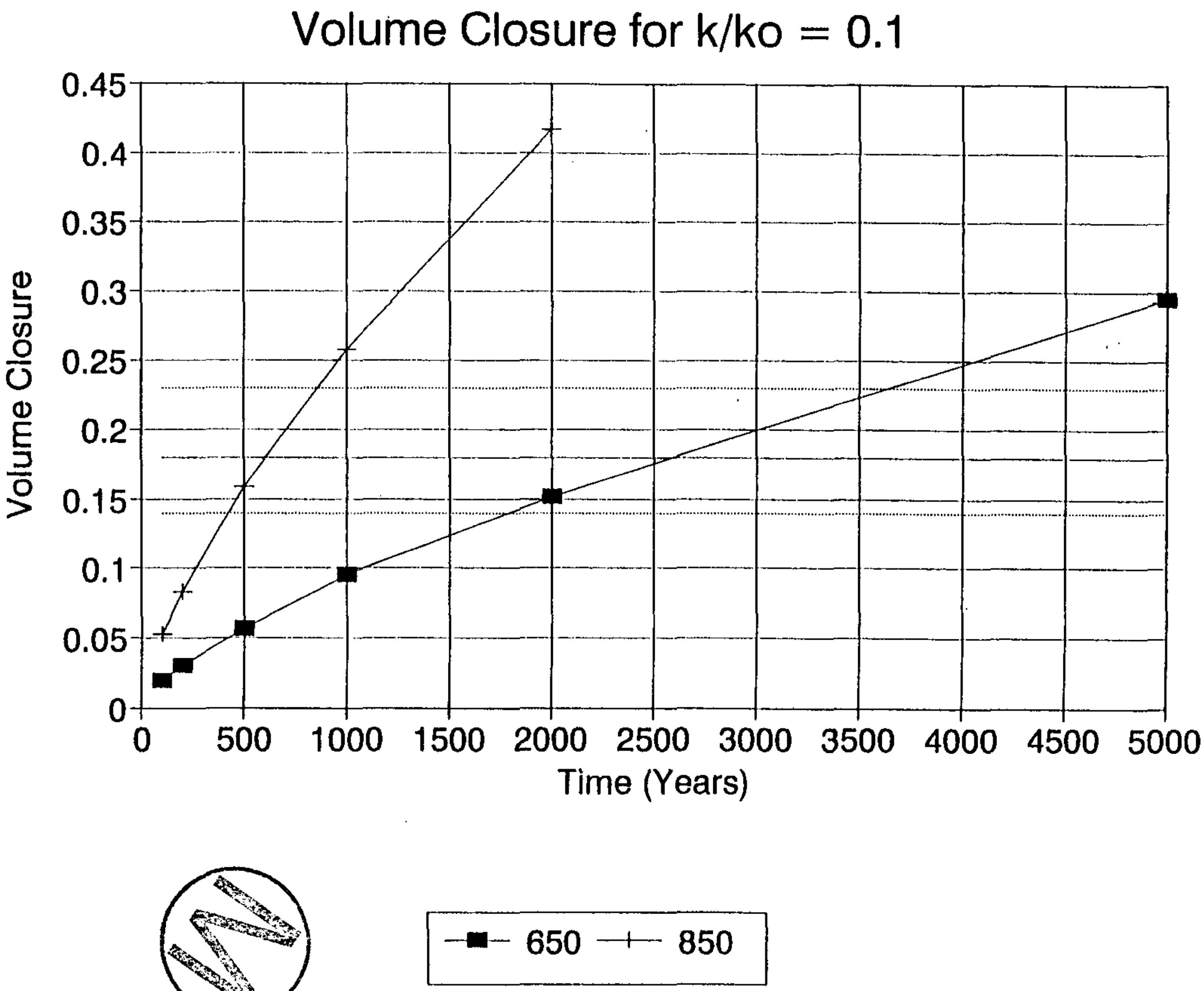


Figure 2. Volumetric Closure as a Function of Time at Four Depths.

— PRELIMINARY —



Volume Closure for k/ko = 0.1


Volume Closure for k/ko = 0.1
Volume Closure
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
Time (Years)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
650
850