

Corrosion Resistant Alloy Canisters for Nuclear Waste Disposal in Horizontal Drillholes

Submitted to International High-Level Radioactive Waste Management (IHLRWM) Conference, Barrier System Performance, Design, and Modeling
April 14-18, 2019 | Knoxville, TN | Knoxville Convention Center

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CORROSION RESISTANT ALLOY CANISTERS FOR NUCLEAR WASTE DISPOSAL IN HORIZONTAL DRILLHOLES

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ABSTRACT: The disposal of spent nuclear fuel and other high-level radioactive waste in deep horizontal drillholes is an innovative system. Canisters for the disposal of nuclear waste made of highly corrosion resistant nickel-chromium-molybdenum (Ni-Cr-Mo) alloys can remain perforation-free for tens of thousands of years. A distinctive feature of Ni-Cr-Mo alloys is a durable, protective (passive) film that is self-forming and reforms quickly if damaged mechanically or chemically. A time-interval method to track the evolution of the environment was used to analyze an engineered barrier system design. Early conditions were found to be moderately oxidizing and at highest temperatures. This was followed by lower temperature, benign anoxic and reducing conditions. Canisters that perform well in the initial 100 years and enter the anaerobic period in good condition, survive for tens of thousands of years. Significant attributes of disposal in deep horizontal drillholes, such as fully saturated rock, without boiling to form liquid/vapor and without a wet/dry/wet cycle, are identified.

I. INTRODUCTION

The disposal of spent nuclear fuel and high-level radioactive waste in deep horizontal drillholes is an innovative system to meet the pressing national and international need for the safe and reliable disposal of nuclear waste.^{1,2} Holes are vertically drilled one to three kilometers (several thousand feet) deep into or below a low-permeability geologic formation, then slowly turned nearly horizontal to create a disposal section that extends for up to three kilometers (nearly two miles) along the geological formation. Canisters containing the waste are emplaced along this horizontal disposal section. The drillholes are then backfilled with bentonite and sealed with rock and bentonite.

The metal canister is the only absolute, non-permeable barrier in the multibarrier system.³ It prevents radionuclide transport until there has been a through-wall perforation. Since canister perforation is the greatest risk for the disposed waste, highly corrosion-resistant alloys (CRAs) are selected to mitigate the risk of corrosion. Nickel-chromium-molybdenum (Ni-Cr-Mo) alloys along with titanium are the most resistant metals to localized corrosion in hot, chloride environments. These alloys also have strong mechanical properties and ease of fabrication and welding.

There is a sound technical basis for the selection of Ni-Cr-Mo alloys for canisters in deep horizontal drillholes. A wealth of corrosion performance information was developed in support of the proposed Yucca Mountain repository for use of Alloy 22, a Ni-Cr-Mo alloy.³⁻⁷ This corrosion-resistant passive metal was selected for use in the high temperature, oxidizing, chloride environment. There is also a wealth of corrosion performance information for metals in reducing environments from other international repository programs. For deep horizontal drillholes, both sets of information are relevant, since after emplacement the canisters are exposed to an early, high temperature, moderately oxidizing environment followed by a cool-down and exposure to an anoxic and reducing environment.

A time-interval method that aided the analysis of the proposed Yucca Mountain repository⁸⁻¹⁰ has been applied more recently to a proposed repository in the Opalinus Clay of northern Switzerland.¹¹ This method was also used in the analysis of an EBS design for the disposal of cesium/strontium (Cs/Sr) nuclear waste capsules in a deep horizontal drillhole.¹² The Cs/Sr capsules are a form of legacy waste from the United States nuclear defense program. The results of the analysis have significant positive implications for the prediction of canister life and EBS corrosion performance in deep horizontal drillholes.

Procedures and supporting information for materials selection and lifetime predictions for canisters for nuclear waste disposal have been reviewed for a number of international nuclear waste programs.^{3,5,13,14} Key approaches to the analysis comprise a) the determination of the evolutionary path of the environment from the canister emplacement

through 10,000 years or more, b) the selection of materials for corrosion resistance to the evolving environment, and c) the analysis of the corrosion performance over time.

When the horizontal drillhole is in fully saturated rock alkalinity is near neutral to mildly alkaline. The evolutionary path of the environment is from an initial period of high temperature, moderately oxidizing conditions to mild temperature, anoxic and reducing conditions. Radiation from the nuclear waste heats the engineered barrier system (EBS) and surrounding rock, and the horizontal disposal section goes through a heat-up and cool-down cycle. For a thermal simulation, heating to maximum temperature followed by the start of the cool-down period occurred within 5-10 years after canister emplacement, and the maximum canister wall temperature was 170°C.¹⁵ The thermal pulse period is followed by a slow cool-down to the ambient temperature of 60°C at the drillhole depth.

An important distinction of the deep horizontal drillhole system is that the boiling of water is suppressed by the hydrostatic pressure at the depth of the drillhole. There is no liquid/vapor present or wet/dry/wet cycle. For all other international repositories that are below the water table, there is a period of unsaturated conditions due to the thermal pulse.³¹⁶¹⁷ The evolution of the degree of saturation will cause change in the chemistry of the environment near canisters.³ In the unsaturated case, the analysis of the evolution of the environment is more complex and with higher uncertainty than for fully saturated conditions.

II. DEEP HORIZONTAL DRILLHOLES FOR NUCLEAR WASTE DISPOSAL

The horizontal drillhole disposal system is designed for a variety of waste types, and canister size is determined by the specific fuel type. For disposal of Cs/Sr capsules, canisters are on the order of 12 cm in diameter and 60 cm in length. For the disposal of spent nuclear fuel assemblies, the canisters are wider and longer, with each canister holding one fuel assembly. Each assembly is placed in a cylinder with an end plate already attached; then the other end plate is positioned and sealed, thus forming and filling the canister.

Figure 1 shows the vertical and horizontal drillhole sections.² The vertical section is 1-3 km (several thousand feet) deep into or below a low-permeability geologic formation. From there, the horizontal disposal section extends for up to 3 km (nearly 2 miles).

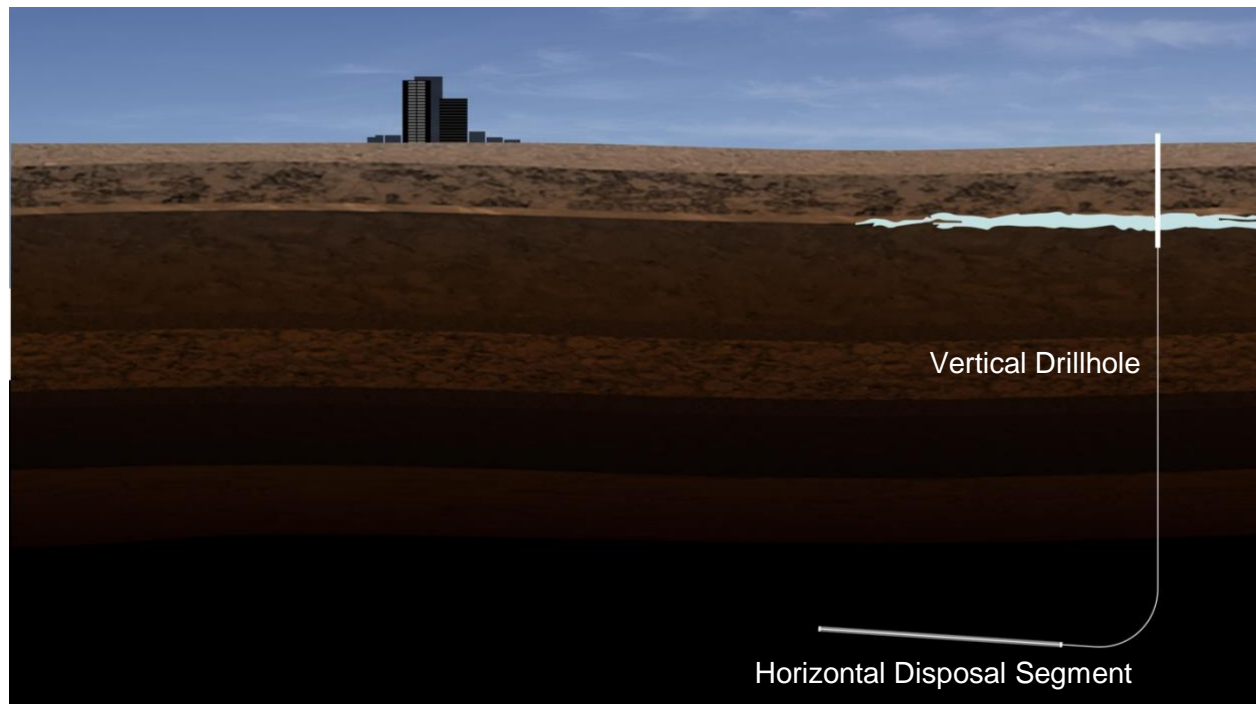


Fig. 1. Depiction of deep horizontal drillhole system

Once the hole is drilled, a continuous metal casing, typically steel, is inserted into the drillhole to add structural strength. It is common to fill the space between the casing and the wall of the drillhole with cement. Corrosion-resistant canisters containing the nuclear waste are then lowered into the casing and emplaced along the length of the horizontal disposal section. The drillhole is backfilled with bentonite or mineral-based slurries and sealed with rock and bentonite. Figure 2 shows a cross section of a Pressurized Water Reactor (PWR) fuel assembly in a CRA canister and a cross section of an EBS configuration for disposal of the spent fuel.

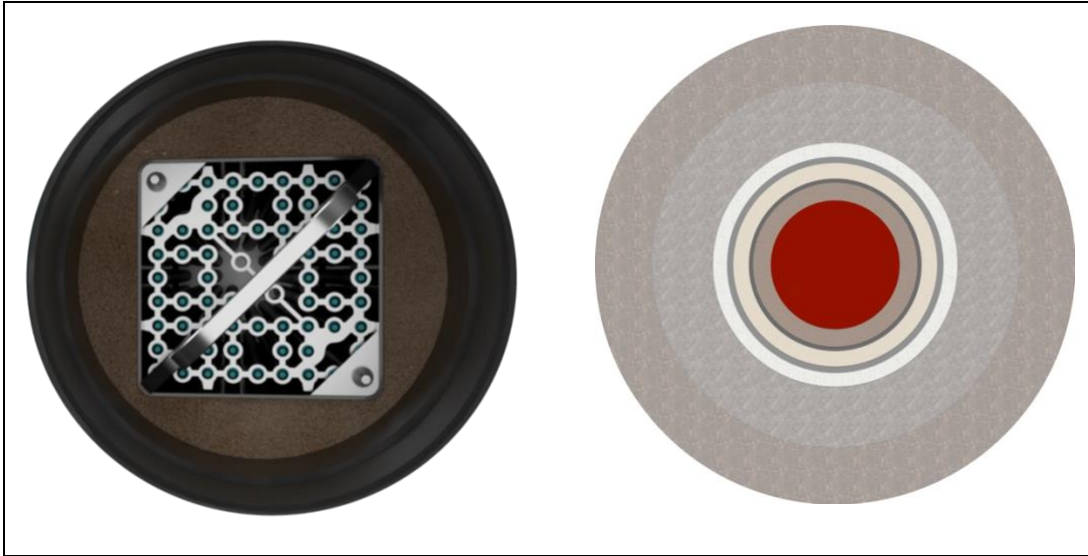


Fig. 2. Cross section of a PWR fuel assembly in a corrosion resistant alloy canister and a cross section of an engineered barrier system for disposal: PWR assembly, quartz sand, canister, casing, excavation disturbed zone, and host rock.

For perspective, a representative design of an EBS for disposal of cesium/strontium capsules is presented. The EBS comprises the engineered materials placed within a repository, including the waste form, waste canisters, buffer materials, backfill and seals. Components of the EBS are to work in combination to prevent the transport of radionuclides from the EBS to the host rock for the regulated time period and beyond. The canister is a crucial component of the EBS. Each waste capsule is emplaced and sealed in a Ni-Cr-Mo alloy canister.

A representative segment of the horizontal drillhole is shown in Figure 3. The EBS configuration comprises ten canisters, 0.6 m long \times 11.4 m outer diameter \times 9.5 mm wall thickness. Canisters are emplaced within a steel casing that is 12 m long \times 14 cm inner diameter \times 12.5 mm wall thickness. The separation between canisters along the steel casing is 0.6 m. The outer diameter of the casing is 16.5 cm, and the drillhole diameter is 21.6 cm. The depth of the horizontal section is 1 km. The metal canisters are made of Ni-Cr-Mo alloy, and the casing is made of carbon steel.

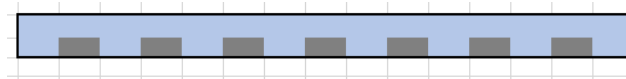


Fig.3. A short segment of the horizontal drillhole: the canisters are 0.6 m long x 11.4 cm outer diameter; along a steel casing that has a 14 cm inner diameter; the canister spacing is 0.6 m. Height is not to scale.

The evolution of the environment is a key determinant of corrosion performance of the EBS. Typical pore waters in the rock are a chloride brine, and chloride concentration can range from dilute to concentrated levels. Other dissolved anionic species can be present in lesser concentrations. The brines are anoxic and due to this lack of oxygen, the environment is reducing. The acidity/alkalinity ranges from near neutral to mildly alkaline.

The horizontal section of the drillhole is in fully saturated rock. There is a region of “disturbed” rock surrounding the drillhole. This rock has been cracked or otherwise affected by the excavation process. The disturbed zone typically extends beyond the drillhole wall to a distance equivalent to about one drillhole radius. For the base case, the disturbed

zone is about 10 cm thick, and undisturbed rock extends outward from there. Waters from the drillhole and surrounding rock fully saturate the disturbed rock. Process waters from drilling, installation of the casing and emplacement of canisters can contain oxygen. This introduced oxygen creates a moderately oxidizing condition in the early stages of disposal. With time, the oxygen is consumed primarily by the corrosion of the steel casing. So, there is a transition from moderately oxidizing waters to reducing waters after oxygen is consumed.

Temperature is also an important characteristic of the environment for corrosion analysis. The horizontal disposal section goes through a heat-up and cool-down cycle. Radiation from the spent nuclear waste heats the EBS and surrounding rock. The temperature decreases as the waste decays, radioactivity drops, and the rock continues to conduct heat away. The thermal evolution in horizontal drillholes was analyzed by numerical simulations.¹⁸ For a simulation with a canister diameter of 32.4 cm (12.75 in) and a drillhole diameter of 45.7 cm (18 in), the heat-up to maximum temperature and the start of cool-down occurred within 5-10 years after canister emplacement. The maximum temperatures of components were as follows: capsule 182°C, canister wall 170°C, casing 165°C, drillhole wall 160°C, and 1 m into the rock 103°C. The heat-up extends a few meters into the host rock. There was a 40-year thermal heat-up and cool-down period followed by a slow cool-down to the ambient temperature. The ambient temperature and pressure are determined by the depth of the horizontal section. For a drillhole at 1 km depth, representative values are a temperature of 60°C and a hydrostatic pressure of 10 MPa. The boiling of water is suppressed on metal surfaces within the EBS and the host rock due to hydrostatic pressure at depth. At 10 MPa, the boiling point of water is 310°C.

III. Properties and Industry Applications of Ni-Cr-Mo Alloys

A sound technical basis and proven engineering practices exist to support the design and fabrication of canisters for the long-life needed to meet nuclear waste disposal requirements. CRAs are available to meet structural and mechanical requirements. Fabrication and assembly can be done by currently available methods. There are methods available for insertion of spent fuel assemblies into canisters, transport and placement of canisters into the casing, and emplacement along the horizontal disposal section of the drillhole. Commercially available metals with extremely low corrosion rates are available. Ni-Cr-Mo alloys and titanium alloys are the most corrosion resistant CRA families. Large industrial equipment made from these alloys have been in service for many years in extremely harsh environments.

The Ni-Cr-Mo alloys are favored here over titanium for their availability in pipe and plate forms and for their fabricability and weldability. In the family of Ni-Cr-Mo alloys, Alloy 625 and Alloy 22 are at the top for their durable passivity and resistance to localized corrosion.

The properties and corrosion resistance in a number of applications are detailed for Alloy 625 in a technical information document.¹⁹ Excerpts from that source are presented here. The composition and mechanical strength of Alloy 625 enable it to withstand a wide variety of severe corrosive environments. In mild environments such as the atmosphere, fresh and sea water, neutral salts, and alkaline media there is almost no attack. In more severe corrosive environments, the combination of nickel and chromium provides resistance to oxidizing chemicals, whereas the high nickel and molybdenum contents supply resistance to nonoxidizing environments. The high molybdenum content makes this alloy highly resistant to pitting and crevice corrosion. The high nickel content also provides resistance to chloride stress-corrosion cracking.

This combination of characteristics makes Alloy 625 useful over a broad spectrum of corrosive conditions. For instance, it has been recommended as a construction material for a storage tank to handle chemical wastes, including hydrochloric and nitric acids. These strong acids represent directly opposite extremes regards oxidizing/reducing conditions. Hydrochloric acid is highly reducing, and nitric acid is strongly oxidizing. Materials that resist either one of these acids are normally severely attacked by the other.⁶

The following are empirical descriptions of Alloy 625 in industrial service in a range of hostile environments. Exposure conditions in industrial service are not as well defined or clearly controlled as laboratory tests; however, they do provide documentation of performance in real-world service where a range of environmental conditions pertain through start-up, shut-down and operation cycles. Further, the industrial service durations are relevant to deep horizontal drillholes as hostile conditions last for tens of years prior to transition to benign conditions and not hundreds of years.

CRAs are broadly used by various industries, especially those in chemical processing. These alloys provide reliable performance in the fields of energy, gas and oil, pipelines, health, pharmaceutical, and others. The use of these alloys provides:

- Excellent resistance to corrosion attack
- Stress corrosion cracking (SCC) resistance

--Ease of fabrication and welding

Production technology and metallurgy have been established and constantly developed to utilize CRA in extremely corrosive situations. Such harsh conditions include concentrations of hydrogen sulfide higher than 35%, temperatures reaching 220°C, as well as pressure nearing 152 MPa (22,000 psi). For a sour gas system (those containing hydrogen sulfide), alloys with molybdenum (Mo), like Alloy 625 which has 9-Mo, can handle severe conditions with the existence of species such as free sulfur. Moreover, nickel in the alloy plays a large role in the prevention of SCC when combined with molybdenum and chromium.²⁰

The following information addresses attributes and applications of Alloy 625 in a number of industries. The exposure conditions do not define use limits, but rather document successful service experience.

Chemical processing field The versatility of Alloy 625 under a wide range of temperatures and pressures is a primary reason for its wide acceptance in this field. Because of its ease of fabrication, it is made into a variety of components for plant equipment. Its high strength enables it to be used in thinner-walled vessels or tubing than possible with other materials. Alternatively, higher pressures can be sustained at equivalent wall thicknesses. Some applications requiring the combination of strength and corrosion resistance are tubing, reaction vessels, distillation columns, heat exchangers, transfer piping, and valves.

Sea-water applications - Benefits of Alloy 625 in seawater are freedom from localized attack (pitting and crevice corrosion), high corrosion-fatigue strength, high tensile strength, and resistance to chloride stress-corrosion cracking. It is used as wire rope for mooring cables, propeller blades for motor patrol gunboats, submarine auxiliary propulsion motors, submarine quick-disconnect fittings, exhaust ducts for Navy utility boats, and sheathing for undersea communication cables.

Nuclear field - Alloy 625 is used for reactor-core and control-rod components in nuclear water reactors. The material is selected for its high strength, excellent uniform corrosion resistance, resistance to stress cracking and pitting resistance in 260-316°C (500°-600°F) water.

Geothermal systems – Geothermal energy systems require the high corrosion resistance and strength of CRA and CRA-clad steel in highly aggressive, elevated temperature conditions. The length of casings can be up to 1500 meters and temperatures can range from 160°C to above 300°C. The exposure environments are concentrated brines and may be strongly acidic. The environments almost always contain dissolved or free carbon dioxide (CO₂) and hydrogen sulfide (H₂S) gases. While both of these gases are highly corrosive, H₂S in particular limits the materials that can be used for drilling equipment and for casing to the lower strength steels, because higher strength steels will fail by sulfide stress cracking. For the high temperature, corrosive geothermal fluids, it is suitable to use Ni-Cr-Mo alloys for reliable service.²¹ Alloy 625 and AlloyC-276 are the most suitable Ni-Cr-Mo alloys for use in high temperature geothermal fluids.²²

Mechanical Strength and Fabricability-Admirable mechanical and other properties are needed in addition to strong corrosion resistance. The mechanical properties validate that Alloy 625 is a strong, tough, ductile metal and that it maintains these properties to temperatures much higher than those for deep horizontal drillholes. Nominal room-temperature mechanical properties of Alloy 625 are for annealed rod, bar and plate: tensile strength 827-1034 MPa (120-150 ksi), Yield strength 416-655 MPa (60-95 ksi), elongation 60-30% and reduction of area 60-40%. The tensile properties from room temperature are basically unchanged to 600°C (1100F). Excellent ductility and toughness are indicated by impact strength of 66 J (49 ft-lb). The alloy is fabricable by forming, machining and welding. Alloy 625 is readily joined by conventional welding processes and procedures. Welding electrodes are Ni-Cr-Mo products designed for welding Alloy 625 to itself and to other materials.¹⁹

IV. Corrosion Resistance of Ni-Cr-Mo Alloys

IV.A. Passive Film Structure

The corrosion resistance of Ni-Cr-Mo alloys is provided by a self-forming, thin (nanometers thick) passive film. For Ni-Cr-Mo alloys, the passive film is a chromium-rich oxide. The alloys form a stable chromium (III) oxide (Cr₂O₃) film. The passive film is less than 10 nm thick.^{6 23} For Alloy 22, a protective inner Cr₂O₃ layer was always present after exposures, and an outer Ni-rich layer was often present.²⁴ After long exposure times, a thin, dense passive layer remains on the metal surface, and a thick layer of corrosion products from the alloy form an outer layer.

In laboratory tests and field exposures, as the immersion time increases the corrosion rate of Alloy 22 tends to decrease due to the formation of a more compact protective passive film.^{3,24-28} Passive films on specimens exposed

for a few days to multi-ionic electrolyte solution had similar oxide thickness as on specimens exposed for over five years to the same electrolytes.²⁴ After time, the passive film may stop growing thicker; however, the passive current continues to decrease with longer times.

High durability of the passive film on Ni-Cr-Mo alloys results from a combination of resistance to film breakdown even in highly aggressive conditions and the ability to reform (repassivate) after it has been damaged. Two methods were used to intentionally damage the passive film and then to follow the tendency for reformation: mechanical scratch-repassivation and cyclic potentiodynamic polarization tests.²⁹ To mechanically damage the passive film, a diamond-tipped scribe pressed against a rotating specimen cuts through the passive film and exposes fresh metal. The passive film reformed rapidly in 0.6 M NaCl at 80°C. In cyclic polarization, the passive film breaks down on a forward scan and then the repassivation behavior is measured on a reverse scan. Repassivation was observed for Alloy 22 exposed to 4 M NaCl at 100°C.

The durability of passive films on Alloy 22 was compared to that of two metals with lower corrosion resistance in high temperature brines.^{30 31} The alloy compositions of chromium and molybdenum in weight percent were Alloy 22, Cr-21, Mo-9; AL6XN Cr-20, Mo-6; and 316L Cr-17, Mo-2. In cyclic polarization tests in 0.6 M NaCl at 80°C, Alloy 22 repassivated readily while AL6XN did not repassivate. For Type 316L stainless steel passive film broke down under less aggressive 0.1 M NaCl at 60°C and did not repassivate.

The passive corrosion rates of all alloys were essentially equal, but the distinguishing feature is the ability to reform the passive film. These results distinguish between stable and meta-stable passivity. After mechanical damage, the film would reform rapidly on Alloy 22, but on AL6XN the film would not reform and corrosion would proceed.

IV.B. Passive Film Corrosion

Extremely low passive corrosion rates result in remarkably long projections of lives. Canisters of Ni-Cr-Mo alloys are projected to be perforation free for tens of thousands of years. Figure 4 is a semi-empirical illustration of the extremely low corrosion rate on penetration rate over time.



Fig.4. Illustration of 17,500 years to penetrate the depth of a quarter (1.75 mm). The wall thickness of canisters are on the order of a stack of 5-6 quarters.

At the corrosion rate of 0.1 $\mu\text{m}/\text{y}$, it will take 17,500 years to penetrate to a depth equivalent to the thickness of a quarter (1.75 mm). And as the canisters are not tin can-like but rather made of thick metal, equivalent to 5-6 quarters

thick, they will last a long time. Analysis of an EBS design for disposal in horizontal drillholes found first penetration of a 9.5 mm wall thickness to be 45,000 years.¹² Yet, these projections of long lives are conservative; well documented corrosion rates for passive metal are lower yet and on the order of tens of nm/y.^{4 6}

The analysis and supporting information for materials selection, lifetime predictions and performance of containers for nuclear waste disposal have been reviewed for a number of international nuclear waste programs.^{3,5,13,14} Particularly relevant is analysis and data for Ni-Cr-Mo alloys in support of the proposed Yucca Mountain repository.⁴ The analysis of corrosion performance of canisters in deep horizontal drillholes draws upon information in these sources and their supporting references. The corrosion rates are for general corrosion of the metals in the passive state.

For Alloy 22, corrosion rates are 1 $\mu\text{m}/\text{y}$ even for extremely harsh conditions. There are two primary methods to measure the extremely low corrosion rates of passive metals: weight loss and electrochemical methods. For analytical weight loss measurements, metal specimens are weighed, exposed to a control solution, and then weighed again to determine the weight loss for the time period of exposure. Electrochemical methods determine the polarization behavior of a metal over a wide range of reducing/oxidizing conditions and accurately determine corrosion rates to 0.01 $\mu\text{m}/\text{y}$ and lower. The measured passive corrosion current is then converted to a corrosion rate. Corrosion rates of the order of 10's nm/y can be determined. An array of microscopies/spectroscopies are used to measure thickness, composition, and structure of passive films. The resolution of film thickness measurements is on the order of nanometers.

The preponderance of data for the Yucca Mountain repository⁴ is for conditions much harsher than those for deep horizontal drillholes. The data still are relevant because they document the strong corrosion resistance of Alloy 22 to a wide range of environments. Alloy 22 was designed to stand the most aggressive industrial applications. Data is presented for corrosion as a function of temperature in concentrated hydrochloric acid, sulfuric acid, and the nitric acid solutions.⁶ These mineral acids range from highly reducing to highly oxidizing in nature. For temperature lower than 66°C Alloy 22 remained passive with low corrosion rates. While there is no plausible means by which these strong acid solutions could form in the EBS for deep horizontal drillholes, the results document the robust passivity of the alloy.

Near neutral, concentrated, multi-ionic solutions are more representative of pore waters in rock at the horizontal disposal zone, except that experiments were run in aerated solutions rather than the anaerobic conditions in the EBS of horizontal drillholes. In these aerated waters, even at near-boiling temperatures, the corrosion rate of Alloy 22 is only a few nm/y. Experimental evidence shows that in near-neutral concentrated multi-ionic solutions, the corrosion rate of Alloy 22 is lower than in mineral acids by several orders of magnitude.³² After 5-year immersion in aqueous electrolyte solutions simulating concentrated ground waters from pH 2.8 to 10 at 60°C and 90°C, the corrosion rate of Alloy 22 was on the order of 10 nm/y and lower.³³

General passive corrosion of Alloy 22 was examined in concentrated chloride, mixed-ion solutions at 60°C and 90°C for aerobic and anaerobic conditions. Specimens were immersed in solutions prepared by evaporation of simulated repository waters. After 5 years of exposure for this range of conditions, the mean corrosion rate was of the order of 15 nm/y and exhibited little influence from temperature, salinity, or whether the samples were immersed or in the vapor phase. The corrosion rates were low for both aerobic and anaerobic conditions.³⁴

The general corrosion rates for Alloy 22 were measured in 0.5 M NaCl and two concentrated well waters, one slightly alkaline at pH 10 and the other acidic at pH 2.7. Exposures were run at ambient, 60°C and 90°C. Corrosion rate for the 0.5 M NaCl and mildly alkaline solutions after two years was at the resolution level for the weight loss method of 0.6 nm/yr for the 24-month exposure. Corrosion rates for the acidic solution were 45.7 nm/y at 60°C and 457.2 nm/y at 90°C. For the 90°C exposure, oxide film thicknesses after 24 months were 1.7 nm and 2.4 nm at 60°C and 90°C, respectively. Under such conditions the corrosion rate was observed to be a strong function of temperature, with an activation energy of 72.9 kJ/mol.³⁵

The effect of the immersion time on the corrosion rate of Alloy 22 was examined by exposure of specimens for over 8 months in a naturally aerated, concentrated, chloride/nitrate brine at 100°C. The corrosion rate dropped from a few $\mu\text{m}/\text{y}$ initially to 0.1 $\mu\text{m}/\text{y}$ after 7 days and continued to decrease to the order of 20 nm/year for the longest immersion time.⁶

The corrosion rates of Alloy 22 as measured by electrochemical methods were summarized.⁵ Electrochemical impedance studies found corrosion rates to be approximately 200 nm/yr in aerated solution at 95°C. (Ref ³⁶) Constant potential tests in deaerated solution including 0.5 M NaCl at 95°C and pH 2.7 and 8 measured corrosion rates at less than 500 nm/y.³⁷ Other constant potential tests were run in 1M NaCl + 0.1 M H₂SO₄. At 75°C, the corrosion rate was 138 nm/y. (REFS ^{28 33}) Polarization resistance tests were run in multi-component, concentrated well water acidified to pH 2.7 at 30°C and 90°C. Corrosion rates were initially 480 nm/y and 1440 nm/y and after one-week immersion in the aerated solution decreased to 23 nm/y at 30°C and 103 nm/y at 90°C. (Ref ³⁸)

IV.C. Localized Corrosion

All passive alloys exhibit similar corrosion rates while passive; however, the durability of their passive films varies greatly depending on the alloy composition. Susceptibility to passive film breakdown and localized corrosion was measured by electrochemical tests of creviced specimens in concentrated chloride solutions.⁴ Alloy 22 was significantly more resistant to the initiation of crevice corrosion than Type 316L stainless steel.

Resistance to the initiation of crevice corrosion is a measure of the robustness of the passive film. Cyclic polarization tests measure the ability of the passive film to repassivate by forcing film breakdown at highly oxidizing conditions, reversing the scan and measuring the repassivation potential. Alloy 22 showed strong resistance to crevice corrosion and a robust passive film,

Crevice corrosion resistance was measured as function of chloride concentration for Type 316L stainless steel (UNS S31603) and three Ni alloys: Alloy 825 [UNS N08825], Alloy 625 [UNS N06625] and Alloy 22 [UNS N06022]. Comparative molar chloride concentrations with crevice corrosion resistance were 10^{-3} , 10^{-2} , 10^{-1} and 1 M, respectively. Increased chromium, molybdenum and tungsten increased the crevice corrosion resistance of the alloy in chloride solutions: Type 316L Cr-17, Mo-2.5; Alloy 825 Cr-21, Mo-3; Alloy 625 Cr-22, Mo-9; and Alloy 22 Cr-21, Mo-13.5, W-3. (Ref³⁹)

In addition to rapidly reforming the protective passive film after mechanical or chemical damage in many environments, the Ni-Cr-Mo alloys have also exhibited stifling and arrest after the initiation of localized corrosion. Stifling of crevice corrosion is the slowing down of the crevice corrosion, and arrest is the halting of crevice corrosion. The stages of initiation, propagation, stifling and arrest have been examined for Ni-Cr-Mo alloys in highly aggressive environments. With the application of applied potential to initiate crevice corrosion, these four stages were observed.⁴⁰ The crevice corrosion propagation behavior of Alloy 22 after aggressive initiation steps was examined in 5 M sodium chloride solution at 95 C. The penetration rates decreased significantly as a result of stifling of crevice corrosion and re-passivation.³⁷ Molybdenum in the alloy is responsible for stifling and modifying the morphology of crevice corrosion propagation once it has initiated.⁴¹ The propagation of corrosion across the specimen was more pronounced than its penetration. So, even though localized corrosion is unlikely to initiate, the processes of stifling and arrest can limit the corrosion damage.

The propagation of crevice corrosion can be limited by the inability to supply sufficient supporting cathodic current for continued corrosion. For example, consumption of oxygen in the environment will reduce the cathodic current and lead to the arrest of crevice corrosion.^{42 10}

When the deep horizontal drillhole is sealed, the oxygen for cathodic processes is limited to that introduced oxygen during drilling, casing installation and canister emplacement, and the oxygen is consumed primarily by steel casing corrosion. So, the availability to support crevice corrosion is short-lived. Once anoxic conditions prevail, there is no oxygen to support crevice corrosion. So, crevice corrosion will be difficult to initiate and likely to arrest if initiated.

IV.D. Microbiologically Influenced Corrosion

Microbiologically influenced corrosion (MIC) has proven to be difficult to assess over the long time intervals of interest in part because it is difficult to predict how microbial activity will adapt over repository time periods.³¹³ Further, it is difficult to assess the consequences if any of microbial activity on corrosion rates and damage evolution. A decision tree analysis was developed to determine the possibility and consequences of MIC.⁴³ The formation of biofilms on metal surfaces is a key step in corrosion from MIC.

The alloys proposed for use for the EBS system in the Yucca Mountain repository design (Alloy 22 and Ti) are not only among the most-resistant alloys for abiotic corrosion mechanisms but are among the few materials that may be immune to MIC.⁴³ However, the MIC behavior of a range of candidate nuclear waste container materials was reviewed, and it was concluded that Ti alloys may be the only materials immune to microbes.⁴⁴⁵ While immunity is not certain, Alloy 22 has high MIC resistance. The MIC resistance of Alloy 22 and Ti alloys has been examined under a range of conditions with no evidence of surface damage.⁴⁶ It has been suggested that the inherent stability of the Cr-rich oxide film on the Alloy 22 waste package surface will render it immune to MIC.⁴⁷

V. Analysis of Corrosion Performance of Canisters

V.A. Methods for Analysis

The canister to contain spent fuel and waste is a crucial component of the EBS. The metal canister is an absolute barrier to radionuclide transport until through-wall perforation occurs, and corrosion is the greatest risk for canister perforations. Corrosion behavior is determined by the combination of corrosion resistance of the alloy and corrosivity of the environment. The corrosion control strategy is to select a canister metal that has strong corrosion resistance to the changing environment over time. So, determination of the evolutionary path of the environment from the time of canister emplacement through 10,000 years is crucial to the analysis of performance. Two recent reviews assess the corrosion performance¹³ and lifetime predictions for nuclear waste disposal containers.¹⁴ Analysis of corrosion performance of Ni-Cr-Mo alloy canisters for the proposed Yucca Mountain repository was presented in the DOE license application.⁴

Archaeological analogs are found intact after thousands of years of exposure. While there are no modern alloys from these eras, the findings document that even active metals such as iron and bronze can remain intact for extremely long times when exposed to favorable environments, such as highly reducing and anoxic conditions. Beyond the empirical information, analysis of artifacts can provide support for predictions of long-term performance.^{14,13} For a carbon steel artifact after 400 years exposure, the corrosion depth of 0.8 mm and corrosion rate of 2.0×10^{-3} mm/y were determined.⁴⁸ This compared favorably with corrosion rates of 0.2 to 2.0×10^{-3} mm/y from four-year experiments under anaerobic conditions. Analysis of pit depths in archaeological bronzes⁴⁹ provided supporting information for mechanistic models of long-term performance.^{50,51}

V.B. Material Selection

Ni-Cr-Mo alloys are selected for canisters for disposal of waste in deep horizontal drillholes. The canisters are exposed to hot, multi-ionic chloride solutions. Passive metals have extremely low corrosion rates; however, localized corrosion processes such as pitting and crevice corrosion are risks to the stability of passive films and favorable corrosion performance. There is a need for high reliability for canister performance and high confidence in the technical analysis to support long life projections. Ni-Cr-Mo alloys along with titanium are the most resistant metals to localized corrosion in hot, oxidizing chloride environments. The Ni-Cr-Mo alloys are favored here for the canisters over titanium for their outstanding corrosion resistance, strong mechanical properties, and ease of fabrication and welding.

The Ni-Cr-Mo alloys are designed (a) to have a durable passive film that is self-forming and (b) to quickly reform the passive film (repassivate) if the protective film is damaged mechanically or chemically. Repassivation in hostile environments is what distinguishes Ni-Cr-Mo alloys from lesser corrosion resistant alloys. In high temperature brines, Alloy 22 repassivated readily while AL6XN and 316L stainless steel did not.³⁰ The behavior was related to the amount of Mo in the alloys. In addition to the admirable corrosion resistance, Ni-Cr-Mo alloys have structural strength to elevated temperatures much higher than those for deep horizontal drillhole waste disposal, and canisters can be fabricated and welded by conventional methods.

Both, Alloy 22 and Alloy 625 are highly corrosion resistant Ni-Cr-Mo alloys in the family of nickel alloys. There is a wealth of analysis and data for the performance of Ni-Cr-Mo alloys from nuclear waste repository programs, the science and engineering literature, field exposures and industrial service. Alloy 625 was the canister material selected for analysis of corrosion performance of a representative EBS design for nuclear waste disposal in deep horizontal drillholes.¹²

V.C. Evolutionary Path of the Environment

The analysis of the evolutionary path of the environment, determination of canister life, and assessment of corrosion performance of the EBS was carried out by dividing the full exposure time into interval periods. This method aided the analysis of the proposed Yucca Mountain repository⁸⁻¹⁰ and has been applied more recently for a proposed repository in Opalinus Clay in northern Switzerland.¹¹ Time periods are based on changes in the environment: temperature, composition, and oxidizing/reducing condition. Corrosion rates are then determined for metal behavior in the environment for each period. Corrosion metal loss is determined by the corrosion rate times duration of the period. Cumulative damage gives the penetration depth and remaining wall thickness.

The starting point for analysis is the determination of the temperatures of the canisters and other components of the EBS over 10,000 years. A temperature profile of EBS components is shown in Figure 5 for an EBS design simulation.¹⁵¹⁸ There is a relatively rapid heat-up to maximum temperatures followed by a slow cool-down.

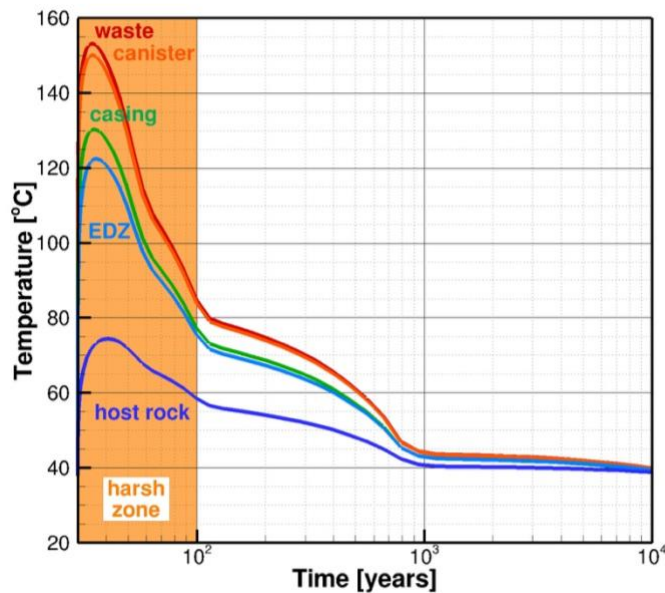


Fig.5. Heat-up and cool-down simulation for an EBS design. Demarcation highlights the early aggressive stage.

An early (about 100 years) aggressive stage is highlighted. The aggressive condition is high temperature with multi-ionic, moderately oxidizing waters. Hot, multi-ionic, oxidizing waters are highly corrosive. After the aggressive stage, the environment is anoxic and reducing. With the exception of the proposed Yucca Mountain repository, all of the international proposed underground disposal repositories and this deep isolation in horizontal drillholes system are located in the saturated zone. As a consequence, the amount of oxygen available for corrosion is limited to that introduced in the repository prior to closure because deep ground waters are invariably anoxic.³ The introduced oxygen is consumed primarily from the corrosion of the steel casing.

V.D. Analysis of Canister Corrosion Performance

Canister corrosion performance was part the analysis of an EBS design for the disposal of Cs/Sr nuclear waste capsules in a deep horizontal drillhole.¹² Each waste capsule is sealed in Ni-Cr-Mo alloy canister: 0.6 m long, 11.4 cm outer diameter, 9.5 mm wall thickness. The thermal pulse from heat-generating nuclear waste canisters and cool-down to ambient temperature were analyzed by numerical simulations.¹⁵¹⁸ For this representative case, heating to maximum temperature and the start of cool-down occurred within 5-10 years after canister emplacement. The maximum temperatures of EBS components were: capsule 182°C, canister wall 170°C, casing 165°C, drillhole wall 160°C and at 1 m into the rock 103°C. Heat-up extended a few meters into the host rock. There was a 40-year thermal heat-up and cool-down period followed by a slow cool-down to the ambient temperature of 60°C

The duration, environmental condition and assigned corrosion rate for five time periods are presented in Table 1. The evolution of the environment and corresponding effect on corrosion rates can be traced through the five periods:

- The first two years are an early transition period from moderately oxidizing to reducing conditions. Heat from the nuclear waste raises temperatures. A corrosion rate of 2 $\mu\text{m}/\text{y}$ is assigned to this aggressive period.
- From 2-20 years, introduced oxygen is consumed, maximum temperatures are reached and cool-down begins. Temperatures remain greater than 120°C. Corrosion rate of 2 $\mu\text{m}/\text{y}$ is assigned to this aggressive period.

- From 20-100 years, the environment is anoxic and reducing and temperature has decreased to 80°C. Assigned corrosion rate is 1 µm/y for this elevated temperature period.
- From 100-1000 years, the environment is both anoxic and reducing and temperature is less than 80°C. Assigned corrosion rate is 0.1 µm/y for this period.
- From 1000 to 10,000 years, the environment is both anoxic and reducing and temperature has returned to 60°C, the ambient rock temperature. These conditions will be unchanging. Assigned corrosion rate is 0.1 µm/y for this period.

The 120°C boundary relates to the greater wealth of corrosion data for Ni-Cr-Mo alloys below this temperature, yielding less uncertainty regards localized corrosion. The 80°C boundary relates to the further decreased likelihood of localized corrosion for Ni-Cr-Mo alloys. Extremely low corrosion rates prevail for the later 900-year and 9,000-year periods and beyond.

TABLE I. Corrosion behavior Nickel-Chromium-Molybdenum canisters over 10,000 years: metal penetration per period, cumulative penetration and remaining wall thickness.

Years after Emplacement	Environment	Exposure Duration y	Corrosion Rate µm/y	Alloy 625 Metal Loss per period µm	Cumulative Metal Loss µm	Remaining wall thickness mm
0-2	Early Transition	2	2	4	4	9.25
2-20	Anaerobic T > 120 °C	18	2	36	40	9.21
20-100	Anaerobic T 120-80 °C	80	1	80	120	9.13
100-1000	Anaerobic T < 80 °C	900	0.1	90	210	9.04
1000-10000	Anaerobic T = 60 °C (ambient rock T)	9000	0.1	900	1110	8.14

Corrosion damage during each period is determined from the assigned corrosion rate based on environmental conditions and the duration of the period. Results for damage in each period and cumulative damage are presented. The amounts of metal lost are 0.12 mm at 100 years, 0.2 mm at 1000 years, and only 1.1 mm penetration after 10,000 years. The starting canister wall thickness was 9.25 mm and was reduced to 9 mm after 1000 years. Wall thickness remained over 8 mm after 10,000 years. The time-to-perforate a canister was set at the time that 50% of the wall thickness remained, and for this criterion, the first canister perforation was at 45,000 years.

The assigned rates for this case are conservatively based on passive corrosion rates of Ni-Cr-Mo alloys, i.e. corrosion rates on the order of tens of nm/y in a range of environments and expected rates of 0.01 µm/y for anaerobic environments.⁵³ Analysis with more realistic rates for this representative case would significantly extend the canister life projections for deep horizontal drillhole disposal.

VI. Attributes of Disposal in Deep Horizontal Drillholes

The analysis provides useful insights for the design of the EBS of deep horizontal drillhole systems. The major challenge is to design a system that makes it through the aggressive, initial 100 years and enters the anaerobic period

in a condition to survive for tens of thousands of years. To meet the challenge, it is necessary to select a corrosion resistant alloy that will remain passive and survive tens of years at high temperature in a moderately oxidizing, multi-ionic environment with minimal damage. Further, the fillers in the annular spaces of the canisters/casing and the casing/drillhole must be engineered to mitigate corrosion and enhance EBS performance.

Design and analysis are more tenable, since the crucial performance period of tens of years is within the realm of conventional engineering practice. There are a number of industrial and infrastructure systems that are designed for tens of years in harsh environmental conditions.

It is important to get materials selection right. A number of passive alloys, i.e. those that form protective passive films, can be passive and have extremely low corrosion rates in the drillhole environment. However, the greatest threat to passive metals for these conditions is susceptibility to localized corrosion processes. The Ni-Cr-Mo alloys are designed to have a durable protective (passive) film that is self-forming and will reform quickly if damaged mechanically or chemically. This is what distinguishes them from less corrosion resistant alloys. In addition to the admirable corrosion resistance, Ni-Cr-Mo alloys have structural strength to elevated temperatures much higher than those for deep horizontal drillholes.

The combination of canisters made of Ni-Cr-Mo alloys and horizontal drillhole environments is amenable to canister lives of tens of thousands of years without perforation. In addition, analysis for the safety case to substantiate performance is less complex and with less uncertainty than for several other proposed repositories.

An important distinction of the deep horizontal drillhole system is that the boiling of water is suppressed by the hydrostatic pressure at the depth of the drillhole. So, there is no liquid/vapor presence or wet/dry/wet cycle. The proposed Yucca Mountain repository can have waters drip onto hot metal surfaces. For all other international repositories that are below the water table, there is a period of unsaturated conditions due to the thermal pulse. In the unsaturated case, the analysis of the evolution of the environment is more complex and with higher uncertainty than for fully saturated conditions.

There are a number of beneficial attributes of disposal of nuclear waste in deep horizontal drillholes. This results from the avoidance of several complex processes;

Ni-Cr-Mo alloy canisters: Passive film is durable and reforms readily. Resistance to localized corrosion is high.

Small surface footprint: Site selection with suitable location, favorable geology and environmental characteristics contributes to the high performance of the EBS. A small footprint is amenable to local disposal in lieu of large centralized repositories.

Small Excavation Disturbed Zone (EDZ): Drilling of the drillhole causes fracturing of the host rock in the vicinity. The EDZ extends into the rock for a distance of about one half of the radius of the drillhole. For disposal of a PWR spent fuel assembly, the drillhole diameter is on the order of 36 cm, and the EDZ would extend only about 18 cm into the host rock.

Uniformity of environment: Benign conditions along the horizontal drillhole are uniform. In comparison, vertical segments can penetrate a variety of strata with differing oxidation states. Heterogeneous zones with variable oxidation states can result in localized corrosion or long-line corrosion.

Fully Saturated Rock: The absence of two-phase gas/liquid solutions eliminates aggressive corrosion processes such as droplets on hot metal surfaces and thin films of moisture in the vapor phase. Full saturation in the rock simplifies the analysis and reduces uncertainty.

Hydrostatic pressure at depth: The boiling of water at the canister surface, in the EBS and in the rock is suppressed by hydrostatic pressure even with radiation heating from the waste. Consequently, there is no liquid/vapor in the EBS or surrounding rock and no wet-dry-wet cycle for the horizontal drillholes.

Linear configuration with flexible canister spacing- Reduction of the thermal period duration and lower maximum temperatures are favored by radial heat dissipation from small diameter EBS. The linear heat load can be controlled by the spacing of canisters along the drillhole.

Environment between canisters and casing: Drilling and installation procedures can minimize the amount of oxygen introduced by waters and fluids for drilling, casing installation and canister emplacement. The canister/casing annular space is filled with bentonite or other mineral-based slurries that are formulated to chemically reduce dissolved oxygen and inhibit fluid flow.

Environment between casing and drillhole: Cement fills this annular space and modulates pore waters to be moderately alkaline. Steel corrosion rates in alkaline solution are low. Alkalinity will not persist for long repository times; however, the reduction of corrosion is beneficial during the early transition period to anaerobic conditions.

VII. SUMMARY

The metal canister is an absolute barrier to radionuclide transport until there has been a through-wall perforation. Canisters made of highly corrosion resistant Ni-Cr-Mo alloys will remain perforation free for tens of thousands of years. Corrosion performance of an EBS design was determined, and for this case, the initial canister metal thickness of 9.25 mm was reduced to 9 mm after 1000 years, and the wall thickness remained over 8 mm after 10,000 years. Time to first perforation was 45,000 years. Passive corrosion rates for Ni-Cr-Mo alloys and resistance to localized corrosion were reviewed. The corrosion penetration rates are on the order of 0.1 $\mu\text{m}/\text{y}$ and less in a wide range of environments that are much more aggressive than those encountered by deep horizontal drillholes. The Ni-Cr-Mo alloys are designed to have a durable protective (passive) film that is self-forming and will reform quickly if damaged mechanically or chemically. This resistance to localized corrosion is what distinguishes the Ni-Cr-Mo alloys from lesser corrosion resistant alloys.

For analysis of EBS performance, it is useful to break the extraordinarily long times for nuclear waste disposal into manageable periods based on the evolution of the environment over 10,000 years. For deep horizontal drillholes, early conditions are moderately oxidizing with higher temperature and followed by benign anaerobic, anoxic conditions. Ni-Cr-Mo alloys perform well in the initial 100 years and enter the anaerobic period in good condition to survive for tens of thousands of years. Significant attributes of disposal in deep horizontal drillholes include a small footprint, amenability to local disposal, fully saturated rock, no boiling of waters, the flexibility to design for lower maximum temperature and shortened durations of the heat-up/cool-down cycle, and the opportunity for “engineered environments” within the drillhole.

ACKNOWLEDGEMENTS

We acknowledge and appreciate the benefit of the extensive analysis and data from the proposed Yucca Mountain repository and other international nuclear waste programs. The authors thank their colleagues for helpful discussions and the staff of Deep Isolation Inc. for their support.

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