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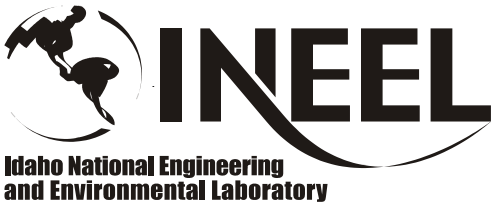

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DIGGING FOR TREASURE--UNIQUE FATE AND TRANSPORT STUDY

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ASTRACT

In 1970, scientists at the National Bureau of Standards (NBS), now called the National Institute of Standards and Testing (NIST), implemented the most ambitious and comprehensive long-term corrosion behavior test for stainless steels in soil environments. This study had historic significance since the NBS 1957 landmark corrosion textbook compiled by Romanoff did not include stainless steels, and this 1970 research set forth to complete the missing body of knowledge. To conduct the test, NIST scientists buried 6,324 coupons from stainless steel types, specialty alloys, composite configurations, multiple material forms, and treatment conditions at six distinctive soil-type sites throughout the country. Between 1971 and 1980, four sets of coupons were removed from the six sites to establish 1-year, 2-year, 4-year, and 8-year corrosion rates data sets for different soil environments. The fifth and last set of coupons (approximately 200 at each site) remains undisturbed after 32-years, providing a virtual buried treasure of material and subsurface scientific data. These buried coupons and the surrounding soils represent an analog to the condition of buried waste and containers. Heretofore, the samples were simply pulled from the soil, measured for mass loss and the corrosion rate determined while the subsurface/fate and transport information was not considered nor gathered. Funded through an Environmental Management Science Program (EMSP) proposal, the Idaho National Engineering and Environmental Laboratory (INEEL) operated for the U.S. Department of Energy by Bechtel-BWXT Idaho, LLC (BBWI), is chartered to restart this corrosion test and concurrently capture the available subsurface/fate and transport information. Since the work of retrieving the buried metal coupons is still in the planning stage, this paper outlines the interdisciplinary team of scientists and engineers and defines the benefits of this research to long-term stewardship, subsurface science, and infrastructure protection programs.

INTRODUCTION

National Bureau of Standards Test

The National Bureau of Standards (NBS), which is now called the National Institute of Standards and Technology or NIST, has had underground corrosion studies since 1910, when it was authorized by Congress to study the deterioration of underground pipelines. These studies became the NBS 1957 landmark corrosion textbook compiled by Romanoff (1). Photographs of the samples in a trench typifies the configuration of coupons in a trench as shown in Figure 1. Since the Romanoff text did not include stainless steels, in 1970, NBS scientists implemented the most ambitious and comprehensive long-term corrosion behavior test for stainless steels in soil environments to complete the missing body of knowledge. They buried in trenches, 6,324 coupons from stainless steel types, specialty alloys, composite configurations, multiple material forms, and treatment conditions at six distinctive soil-type sites throughout the country. The six sites are shown in Figure 2. During the first eight years of the study, only four of five planned removals were completed. They retrieve coupons after one, two, four and eight years for each of the six sites. The reports on the corrosion rate data were published in 1976 (2) and 1981 (3). The fifth and last set of coupons (approximately 200 at each site) remains undisturbed after 32-years, providing a virtual buried treasure of material and subsurface scientific data.

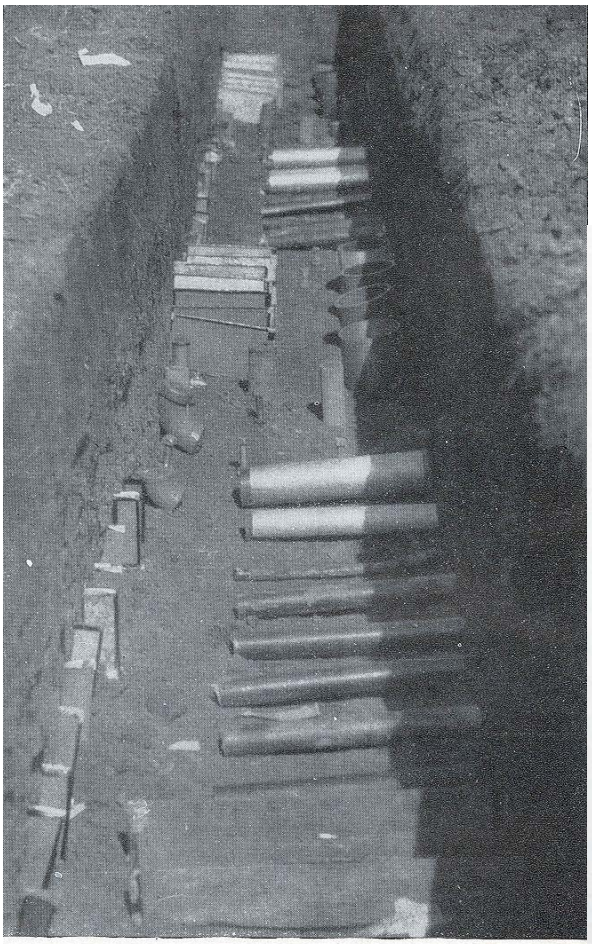

FIGURE 5.—*Arrangement of specimens buried in 1924*
Note two soil horizons.

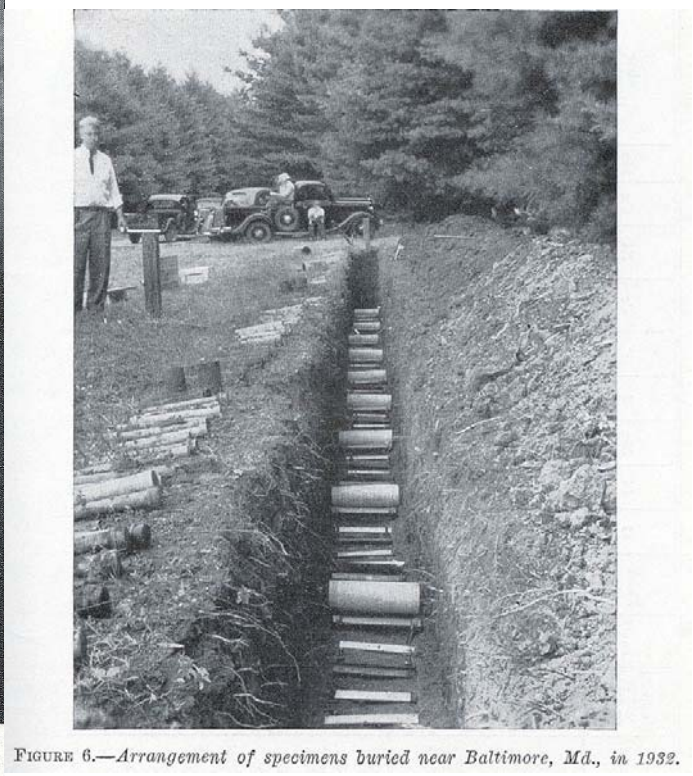

FIGURE 6.—*Arrangement of specimens buried near Baltimore, Md., in 1932.*

Figure 1. Photographs of Specimens in Trench

These coupons at the six test sites represent an analog to the condition of DOE radioactive and radiological wastes (e.g., activated metals and storage containers) and of the soils in which radioactive wastes are buried. The knowledge to be gained from retrieving and analyzing all of the metal coupons would evolve into the landmark stainless steel corrosion, behavior in soils, study, but equally valuable is the opportunity to actually measure the metallic ion fate and transport within the soils over the 32-years since burial.

Environmental Management Science Program Funded Research

Funded through an Environmental Management Science Program (EMSP) proposal, the Idaho National Engineering and Environmental Laboratory (INEEL) operated by Bechtel-BWXT Idaho, LLC (BBWI), is chartered to restart this corrosion test and to concurrently capture the treasure of subsurface/fate and transport information from one of the six NIST test sites. This proposal specifically addresses the EMSP solicitation call for research related to subsurface contamination and transport processes in the vadose and saturated zones. This research opportunity also directly applies to environmental management operational corrosion issues and long-term stewardship scientific needs for understanding the behavior of waste forms and their near-field contaminant transport. This EMSP research is a three-year effort with reports at annual intervals that include a final report.

Site A

The site of choice for this EMSP effort is Site A near Toppenish, Washington because it is relatively close to the INEEL and the university team selected to assist in the project. Figure 2 shows the location of this site and other sites in relationship to the location of DOE laboratories. Site A has the Sagemoor sandy loam soil and it is similar to the soils found at the INEEL. With future funding, the other five sites could be retrieved.

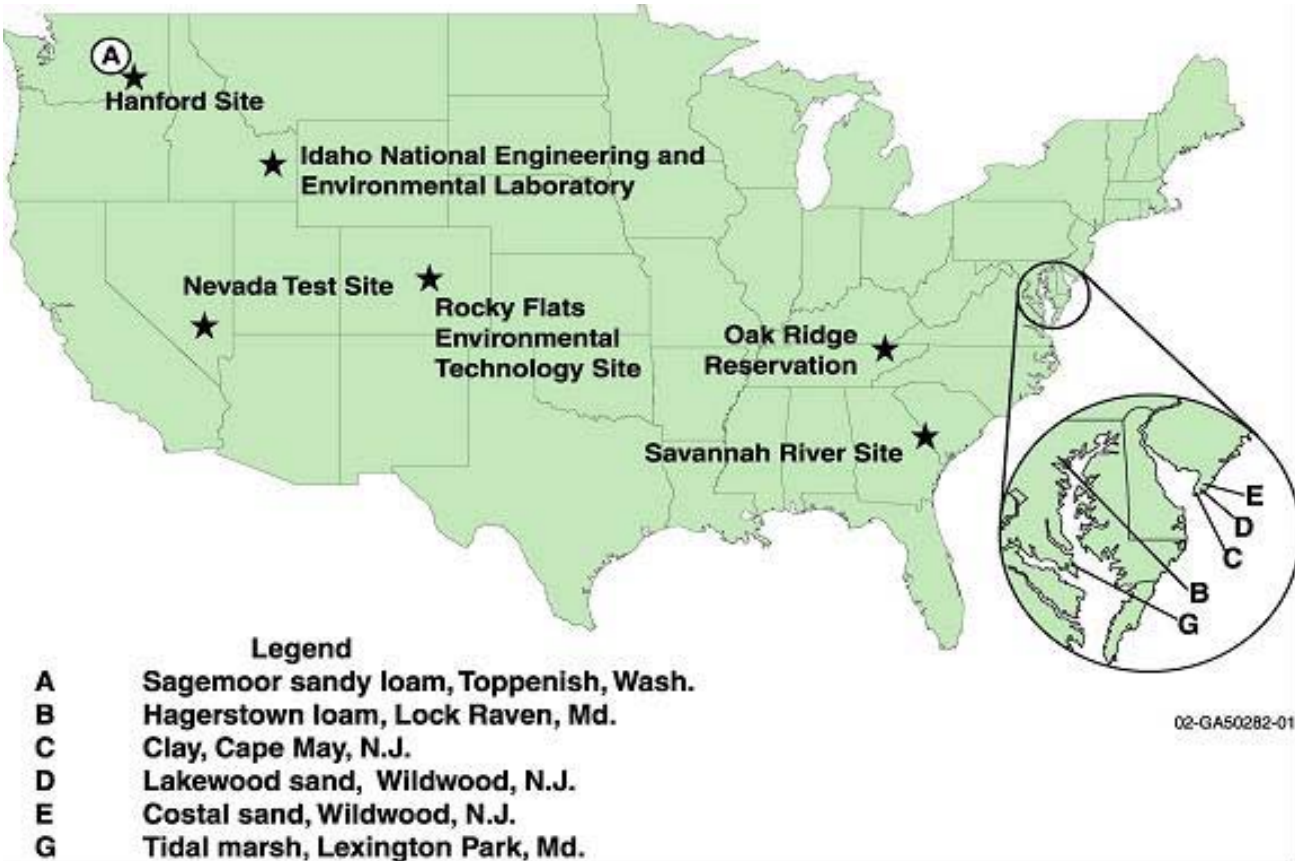

Figure 2. Map Locations of NBS Sites.

INTERDISCIPLINARY APPROACH

This paper outlines and describes two parts of the proposed research. The first part is the interdisciplinary approach. Because of the complexity and depth of the project, an interdisciplinary approach with a team of scientists and engineers was essential. Figure 3 graphically shows this interdisciplinary approach and the benefits of the research. The research consists of the following sections:

- Research aspects
- Research team and collaborators
- Analytical tools
- Requirements analysis

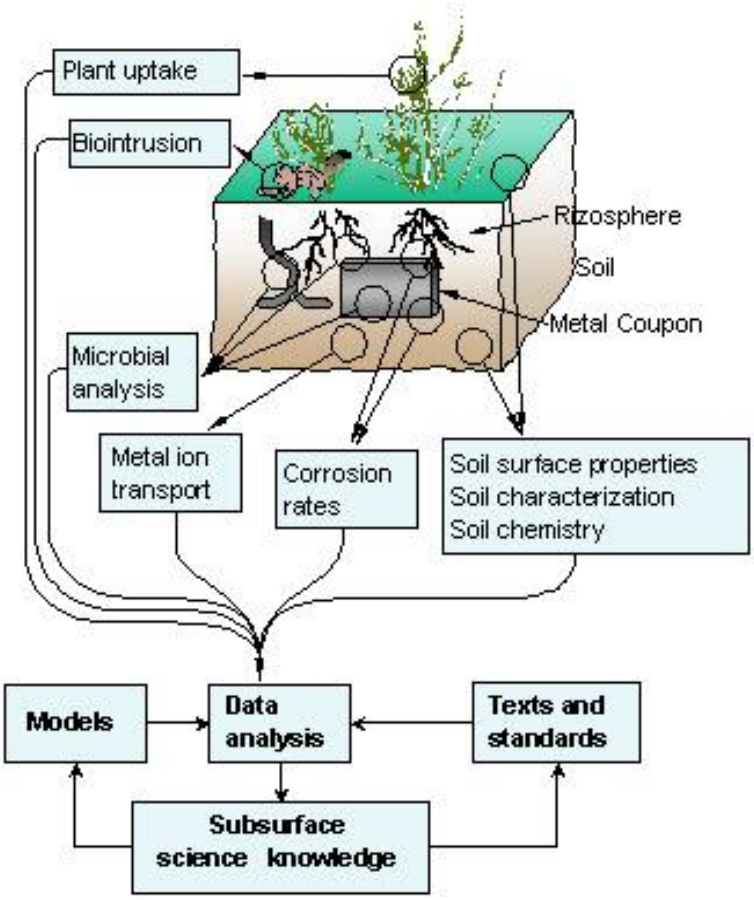

Figure 3. Interrelationship of Metal Specimens and the Environment.

Research Aspects

The project uses a an interdisciplinary research approach to correlate the complicated interrelationships between the following sciences:

- Biology
- Chemistry
- Modeling
- Materials Science
- Soils Science
- Statistics

The researchers shall determine and characterize the following:

- Corrosion rates
- Corrosion mechanisms
- Metal and weld metal integrity

- Soil chemistry
- Soil properties
- Soil microbiology
- Plant and animal interaction with corrosion products
- Fate and transport of metallic ions.

The results will provide much-needed data on corrosion rates, underground material degradation, and the behavior of corrosion products in the near-field vadose zone. The data will improve the ability to predict the fate and transport of chemical and radiological contaminants at sites throughout the DOE complex

Since the metal specimens are stainless steel, biota (plant uptake and animal movement) samples taken for metal migration will be analyzed for chromium and nickel metal—two major alloys of stainless steels. Soil samples will be analyzed for properties significant to corrosivity and to measure metal migration and attenuation. Soil core samples will be examined for hydrological and transport properties. Microbial samples will undergo DNA testing and characterization for culturable and non-culturable microbe speciation related to metal corrosion and metal migration. Metal specimens will undergo both quantitative and qualitative corrosion analyses; metal specimens will be cleaned and mass losses determined for corrosion rates; metal surface analysis will be performed and weld metal and heat-affect-zone integrity examined. Fundamental correlation between soils, microbes, materials and corrosion mechanisms can now be made that far exceeded the scientific capabilities of the 1970's when the NIST test was initially conducted, and because of the tools and electronic spectrometry equipment available today.

Research Team and Collaborators

The project has known experts on the team. The team has researchers from:

- National Laboratories: the INEEL, biologist, chemists, metallurgist, soil scientists, systems engineers; Savannah River Site (SRS), metallurgists, and NIST, statisticians and metallurgist.
- Universities: Boise State University, soil scientists and Ohio State University, welding metallurgist. Also selected graduate students shall assist the project and gain valuable research experience.
- Private Industry: Diversa Corporation, microbial speciation; GoldSim, modeling, and Edward Escalante, original researcher of the NBS study and retired metallurgist.

The INEEL and the SRS proposes to support two graduate students to work along with their staff members. We expect as many as twelve publications in technical journals, corrosion texts, and national standards. Follow-on studies are expected to be generated if the opportunity or funding to complete the remaining five NIST sites arises.

Analytical tools

The INEEL and the SRS have the typical scientific laboratory analytical tools or equipment. However, there are a plethora of tools to be used by the research teams that were not available to the scientists in 1970 when this test was started. Some of the unique tools and equipment include:

- Non-intrusive soil physics equipment: ground penetrating radar, magnetics, modified local induced polarization, and seismic refraction.

- Electronic microscopy equipment: laser-based optical and chemical imaging, secondary ion mass spectroscopy, energy dispersive x-ray analysis, environmental scanning electronic microscope, scanning electrochemical microscopy, vertical scanning interferometry, and reflectance infrared and Ramman Spectroscopy.

Requirements Analysis

Since this research project has multiple scientific disciplines and with only one chance at retrieving the data, the project planning has to be perfect and complete, therefore a systems approach was used to define the project requirements. The ultimate requirement of the research addresses the hypothesis statements of the proposal, but to aid defining the roles and responsibilities, tasks and deliverables, the project manager and project engineer conducted a requirements assessment on the project with the team members. This assessment built a bridge from the proposed project title down to the tasks and deliverables element provided by each team member. An example of this assessment breakdown or decomposition is shown in the following Figure 4, Pie Chart Breakdown.

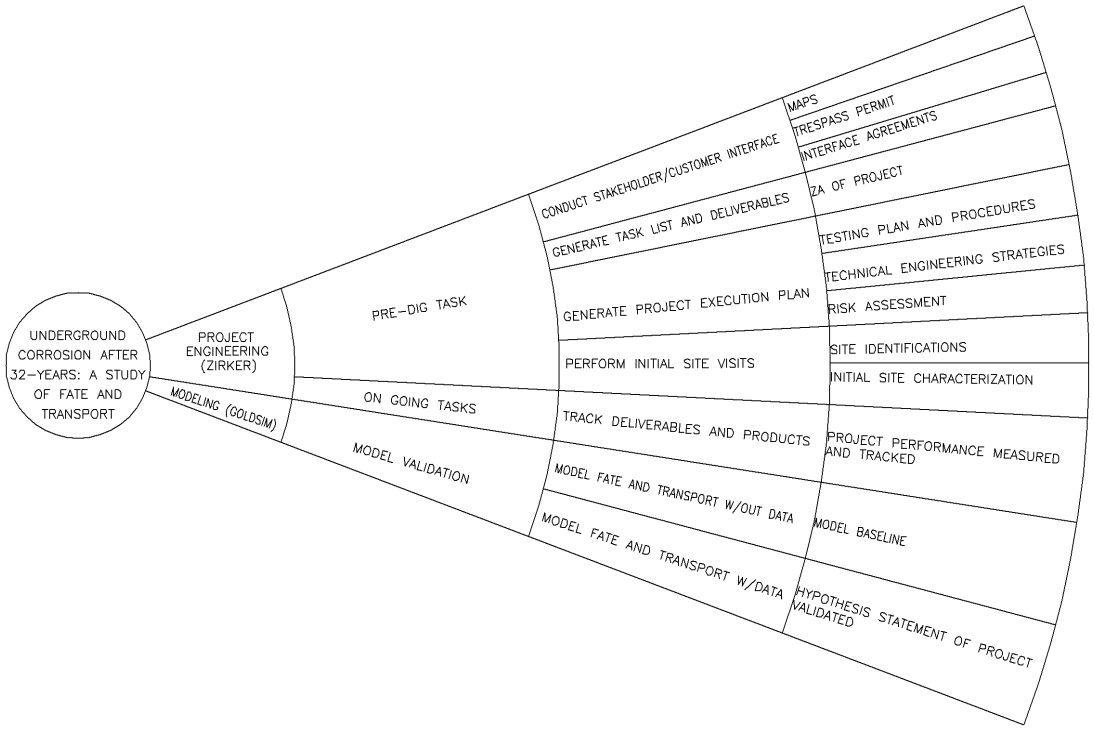

Figure 4. Pie Chart Breakdown

This iterative process developed of the disciplines develops into multiple pie sections. When all of the sections or zones were completed, they were grouped into a circular chart. This chart provided the following benefits:

- Reduced the project down to one sheet of paper and all of the participants can see the "Big Picture" of the project.
- This decomposition effort also provided a secondary function as a gap analysis tool.

- All of the deliverables are linked back to project title.
- The scientists see their place or where they fit into the whole project. They see the interdisciplinary interaction between the sciences, and this enhances the collaboration of the mainline performers.
- The project management ensures the tasks generate the deliverables that meet the project requirements.
- The project management can track the progress of the project.
- The customer sees the synergism of the interdisciplinary approach and notice the value added through the thorough planning.

END USES OF THE DATA

The second of the two parts of this paper defines the end uses of the data. Three end uses for the research data include:

- Subsurface Science
- Long-term Stewardship
- Infrastructure Protection

Subsurface Science

A growing environmental concern is the contamination of soil and groundwater by radionuclides and hazardous chemicals released from corroding metal waste forms and containers. Corrosion causes release of contamination in two ways--via leaks from aging tanks or waste containers, where contaminants become readily available for transport; and via the corrosion process itself, where the contamination becomes available for transport as the surface of the buried radioactive bulk metal waste is reduced by chemical and physical attacks. The natural processes that release these contaminants to the environment and the rates at which the releases occur are poorly understood and inadequately defined (4). Understanding the corrosion, release, and transport processes is critical to predicting soil and groundwater contamination, since a significant portion of the DOE's disposed radioactive waste is composed of activated bulk metal (non-fuel reactor components such as coolant piping, fuel end-boxes, assemblies, shims, and reflectors) or is packaged inside metal tanks and containers buried in pits and trenches during the cold war.

The research proposes to exploit the uniqueness of the historic NIST study by conducting a thorough scientific investigation to examine corrosion rates, corrosion processes, and vadose zone processes. Analysis will include the effects of soil properties, soil chemistry, microbiological processes, biota influences, and corrosion product transport and attenuation and will lead to a better understanding of coupled processes and their role in contaminant transport. As such, this site provides a ready-made, field test opportunity to obtain microbial speciation in the soils to characterize any microbial induced corrosion, on the coupons and rhizosphere, measure the biota and rhizosphere uptake and interaction with corrosion products, calculate the long-term weld metal and heat-affected zone integrity, and characterize the soil chemistry and its properties. As such, the proposed research offers the closest comparative study available for DOE waste metals and containers that have been disposed of and have been in the ground for more than 30 years.

Several DOE sites, including the INEEL, are involved in modeling the fate and transport of buried waste contaminants as part of their performance assessment. In order to improve and validate these models, a

number of related studies are ongoing. The goal is to increase our confidence in the source term release rates required by the models. Most studies limit their focus to only one parameter needed in the models (i.e. corrosion rate, infiltration rate, soil properties, contaminant migration rates, etc.) Like most vadose zone studies, corrosion rate studies are very important, but because they are generally short term, they can only provide limited information on initial corrosion rates and generally do not include vadose zone processes. Long-term studies are needed to help reduce the uncertainty in model predictions made over long time horizons (4).

Computer models built around mathematical formulations of geological, hydrological, chemical, and biological processes occurring in the subsurface are the best tools scientists have for predicting movement and transformation of contaminants in the subsurface and assessing future risks to human health and the ecosystem. Unfortunately, attempts to model contaminant transport through the vadose zone at DOE sites have resulted in conservative and expensive remediation decisions (4) and have fostered a lack of trust by stakeholders.

Long-term Stewardship

The data of this research provides valid data required for performance assessments. In April 2002, the Waste Area Group 7 Operable Unit 7-13/14 Comprehensive Remedial Investigation/ Feasibility Study (RI/FS) DOE/ID-10834 was issued. To support the RI/FS, the inventory of buried activated materials at the INEEL subsurface disposal area was assessed. Becker, (5) states that the corrosion rate used in the Interim Risk Assessment is highly uncertain and that developing a site-specific corrosion rate will greatly improve the quality of the Baseline Risk Assessment estimates for the INEEL radioactive solid waste disposal site containing activated metals.

Infrastructure Protection

A 1999 publication for the National Association of Corrosion Engineers, International or NACE states that losses related to corrosion in the United States are estimated to be $500 Billion per year or about 5% of the U.S. Gross National Product. (6). Additionally, a higher and undeterminable cost results indirectly from corrosion through the loss of products, life, and property by fire and explosion, over-design of structures, and shutdown of services (1). About 35% of the estimate could be saved through better corrosion control. Long duration corrosion rate results would significantly expand the base of understanding regarding the corrosion processes and could have an important impact on our national infrastructure. Because of the ongoing need to dispose of low-level nuclear waste and because the Nuclear Waste Policy Act of 1982 requires disposal of high-level nuclear waste in an underground repository, interest in long-term underground corrosion data has increased. Because corrosion is a long-duration non-linear process, obtaining accurate measurements of corrosion rates depends on taking multiple measurements during the corrosion process, not just early in the process.

The data of the research shall provide new and valid stainless steel corrosion rates that would be available for all end users to use. The corrosion rates used by the INEEL models varies widely.

- Maheras (7) applied corrosion rate parameters to model radionuclide fate and transport below the INEEL's subsurface disposal area. In doing so, the modelers assumed that radionuclides were present in the lattice structure of the metallic components (i.e., stainless steel, Inconel, and beryllium) and released to the soil through slow corrosion processes. For stainless steel, an initial value of 0.3 mil/y (i.e., 1 mm of material loss per **130 years**) was determined based on IMPACTS methodology (8). This value is an adjusted corrosion rate and was determined for the expected geometry of the reactor component.

- In 1996, Nagata and Banaee (9) performed an underground corrosion rate literature search and defined an estimated value of 1 mm of material loss per **82,200 years** for annealed 304 stainless steel.
- When asked to reexamine the literature for a more conservative estimate, Nagata (10) reported a value of 1 mm of material loss per ***4,500 years*** for plate stainless steel (304 sensitized) and projected the same value for Inconel.

Efforts to assess environmental risks and to model fate and transport mechanisms and processes tend to rely on short-duration corrosion test results as input, for the simple reason that nothing better is available. Nowhere is there a complete soil environment characterization that includes long-term corrosion rates, biota and microbiological influences, and soil chemistry and properties that couple the processes occurring naturally in the vadose zone with the migration of contaminants. A systems approach to examining the multiple, interrelated vadose zone processes has never been heretofore undertaken.

CONCLUSIONS

This paper has described the buried treasure of the project and defined the benefits to the end users. Compelling reasons for capturing this corrosion and subsurface data include:

- Accurate corrosion rates and quantifiable fate and transport data of metals in soils will add both credence and confidence in the predictive models used throughout the DOE complex and increase our ability to predict and manage contaminant transport in the vadose zone.
- Uncertainties in current data; lack of understanding of material, geological, hydrological, chemical, and biological processes and properties; overly conservative model assumptions; and our inability to monitor and model contaminant movement in the vadose zone creates confusion among stakeholders and reduces their trust in science.
- Knowing these corrosion and transport mechanisms will directly aid current and future DOE decision makers in avoiding future decisions that are deleterious to the environment, safety of the public at large, and the DOE cleanup mission.

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