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Identification and Evaluation of Appropriate Backfills
for the
Waste Isolation Pilot Plant (WIPP)

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ABSTRACT

A backfill system has been designed for the Waste Isolation Pilot Plant (WIPP) which will control the chemical environment of the post-closure repository to a domain where the actinide solubility is within its lowest region. The actinide solubility is highly dependent on the chemical species which constitute the fluid, the resulting pH of the fluid, and the oxidation state of the actinide which is stable under the specific conditions. The use of magnesium oxide (MgO) as the backfill material not only controls the pH of the expected fluids, but also effectively removes carbonate from the system, which has a significant impact on actinide solubility. The backfill selection process, emplacement system design, and confirmatory experimental results are presented.

INTRODUCTION

The Waste Isolation Pilot Plant (WIPP) is a repository for the disposal of transuranic element (TRU) wastes. The WIPP is located in southeast New Mexico, USA in a natural bedded salt formation approximately 655 meters below ground surface. The wastes destined for WIPP are typically a highly heterogeneous assortment of materials such as ordinary laboratory refuse, construction and maintenance waste, and process wastes contained in steel drums or waste boxes.

There are many processes expected to occur within the WIPP repository which may impact the chemistry of the system, resulting in significant impacts on the actinide solubility and corresponding source term. Principal among these processes is the microbial degradation of carbon-containing materials, primarily cellulose, plastics, and rubbers. The microbial degradation of these carbon containing materials may proceed by many processes (Berner, 1980; Brush, 1990; Wang and Van Cappellen, 1996). In the WIPP repository, the available electron acceptors will soon be exhausted and methanogenesis is expected to become the dominant mechanism. Methanogenesis proceeds according to the following generalized reaction:



Methanogenesis, if indeed significant microbial action occurs at all, will lead to the production of large quantities of carbon dioxide (CO₂). The formation of CO₂ has a significant impact on the

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solubility of the actinides through one of the following processes: 1.) Upon contact with water, carbon dioxide reacts with water forming carbonic acid. Carbonic acid, although a relatively weak acid, is capable of driving the pH of the repository into the acidic range, where the solubility of the actinides is typically greatly increased. 2.) Carbonic acid undergoes dissociation in water forming carbonate and bicarbonate species. The carbonate ion is known to bind very strongly to the actinides forming stable, relatively highly soluble species. The presence of CO₂ in any significant quantity therefore drives the actinide solubility to much higher values, due to lowering of the pH or forming soluble actinide carbonate complexes.

Based on there being an estimated 2.7×10^7 kg of carbon containing compounds to be emplaced in the WIPP (U. S. DOE, 1996), the fugacity of CO₂ (f_{CO_2}) could vary within the range of 0 (in the event that there is insufficient microbial action to overcome the buffering effect of the cementitious material (which is in the waste itself or used as a sealing material) to approximately 60 atmospheres. This wide range of f_{CO_2} is accompanied by a correspondingly wide range of pH values (approximately 4-13) and carbonate concentrations. The net effect of these processes is that the actinide solubility, and thus the source term, could vary widely over an unacceptably large range.

To mitigate the detrimental effects of possible CO₂ generation, a material is required to maintain the pH of the brines in the alkaline region *and* to remove CO₂, thus minimizing the ability of the carbonate ion to participate in complexation reactions. The alkaline earth oxides (e.g. MgO) were identified as fulfilling these two functions.

The alkaline earth oxides react with water according to the following equation:



The reaction with water to form the hydroxide also potentially benefits the repository performance by maintaining a dry repository in the event of limited brine inflow. The hydroxide thus formed, in this case brucite, is available to react with any carbonic acid which may be available,



thus effectively removing the carbonate from the system due to the low solubility of MgCO₃. Through the implementation of MgO backfill, the range of chemical conditions pertinent to the performance assessment of the WIPP is constrained, and additional assurance of the repository's compliance with the applicable disposal regulations (as specified in Title 40 Code of Federal Regulations Part 191) is obtained.

Evolution of Backfill at the WIPP

The concept of utilizing a backfill at the WIPP has been discussed in many forums with many intended objectives essentially since the idea of WIPP was first conceived (Figure 1). Early in the WIPP conceptual lifetime, backfill was envisioned for the reduction of the fire hazard within the mine (through the reduction in the potentially flammable volume available), and for subsidence

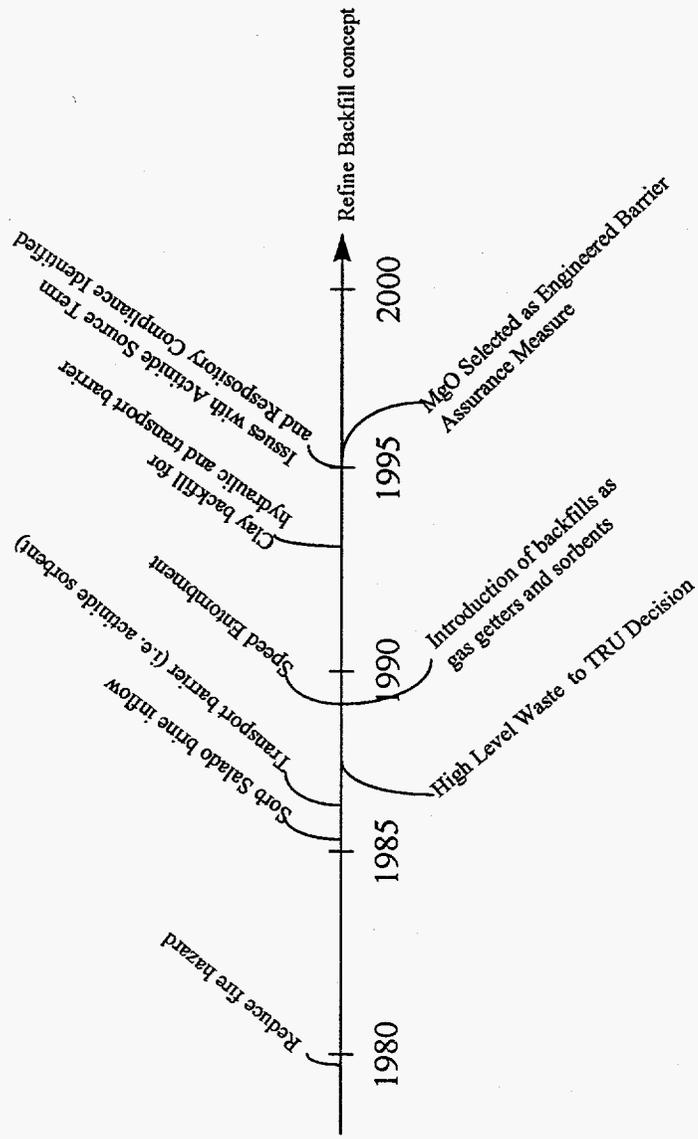


Figure 1. Evolution of WIPP Backfill Concept

mitigation. As more was learned of the system, the use of backfill was given more compliance-oriented roles. For example, in the late 1980's, salt backfill was considered in order to speed the entombment of the waste through the reduction of the void volume which had to be overcome by the salt creep of the surrounding formation salt. In the late 1980's, the disposal regulations applicable to WIPP had not been finalized (i.e. the consideration of the human intrusion scenario had not been recognized as a requirement) and the repository was anticipated to be effective for isolating the waste once the surrounding formation salt had closed in around the waste. However, it was later learned that the room closure was not significantly hastened by the presence of the backfill to justify its emplacement and the baseline design for the repository did not include any backfill material.

Toward the end of this period (approximately 1985-1990), laboratory evaluations (Lappin and Hunter 1989) were performed of the utility of clay materials for backfill. These studies included the evaluation of clay to adsorb any brine which could enter the repository from the surrounding Salado formation, and also a sorbing clay barrier to transport. These concepts were later dropped due to the discovery of pressurized brine pockets in underlying formations which dominated the release mechanisms (and would overwhelm the ability of the clay to sorb water) and the inability to assure a required minimum thickness of sorbing clay to survive the room closure process. The concept of clay backfill as a brine inflow barrier and transport impediment was revisited in 1993-1994. The concept was again dropped due to uncertainties in assuring a contiguous clay barrier and the perception that no additional measures were needed in order to demonstrate compliance with the now finalized regulations.

Concurrently, other WIPP researchers were evaluating alternative backfill materials such as grouts, gas getters, and materials which might prevent the formation of some anticipated repository gases (Molecke 1990; Molecke and Nowak 1980). There was also much interest in the ability of the backfill materials to inhibit transport of the radionuclides through sorption in clay materials which are naturally present or artificially present as backfill (for example, Nowak 1978; Nowak 1980). Many other studies relating to backfill, including its mechanical properties and the materials' utility in shaft seals, for example, have been performed. A bibliography (Powers and Martin, 1993) referencing many of these early studies has been prepared and is available from the National Technical Information Service.

As the preliminary calculations for the WIPP Compliance Certification Application (CCA) were being performed during late 1995 early 1996, it was determined that a compliant complementary cumulative distribution function (CCDF) could only be assured, given the combination of other parameters and conceptual models being used at that time, when the actinide concentrations were less than approximately 10^{-5} molar. Concurrently, the experiments providing the thermodynamic parameters for the actinide source term model were still being developed, but the preliminary results, given the presence of extremely high CO_2 pressures and a wide range of pH, indicated that these relatively low actinide concentrations might be unattainable. This unfavorable situation was further compounded by the actinide source term model having difficulties addressing the extremely high CO_2 conditions and the far field transport program having preliminary indications that the presence of organic ligands reduced the retardation factors to unacceptably low levels. At that point, implementing a backfill which controlled the chemical conditions to one where the actinide solubility is low and assisted in the effective removal of the organic ligands from the system appeared necessary and a rapid evaluation and design was performed, resulting in the

implementation of MgO backfill as the design basis for the WIPP CCA. It is important to note that with the maturing of the parameters, databases, and conceptual models which occurred prior to the CCA being finalized, it was demonstrated that the repository indeed complied with the disposal regulations even in the absence of the MgO backfill and that the MgO backfill would be placed in the repository only as an additional assurance measure.

Basis for Selection of Backfill Material

There are four principal mechanisms by which a backfill could chemically control the actinide source term. These mechanisms are:

- sorption,
- redox control,
- precipitants, and
- pH and $f\text{CO}_2$ controllers

These mechanisms were evaluated to determine which mechanism (or mechanisms) would lead to the most stable repository environment and have the most significant contribution to demonstrating repository performance. A preliminary screening was performed to narrow the scope of materials which were to be evaluated. For this screening, the following qualitative criteria were applied:

- Ability to efficiently effect the desired change
- Available in bulk
- No significant health hazards
- No significant safety concerns (e.g. pyrophorics, or materials that will consume oxygen and/or generate toxic gases)
- Ability to emplace a sufficient quantity within the constraints of the existing repository design.

A description of the above identified mechanisms and the rationale for inclusion or exclusion follows.

SORPTION

The mechanism of sorption has received much attention from the international repository community, and was one of the first to be evaluated for the WIPP. However, there is a distinct difference between the WIPP and most other repository programs. The U. S. Environmental Protection Agency (EPA), the regulator for WIPP, has required that the WIPP demonstrate that it can still meet the containment criteria even when subjected to numerous human intrusion (i.e. drilling) events. That, coupled with the possible existence of pressurized brine in lower lying formations, leads to the WIPP potentially being exposed to large volumes of water equilibrating with the actinides in the emplaced waste. Unless a quantity of sorbing material sufficient to sorb all of the actinide inventory is capable of being emplaced, the sorption sites will become saturated with the actinides and the dissolved actinide concentration will return to the same level as though the sorbent were not present. The design of the repository was already fixed at the time of this backfill study and there was insufficient space available to place sufficient sorbent to tie up the

entire actinide inventory. Therefore, in the case of the WIPP, sorbents were determined not to be a viable chemical intervention capable of controlling the actinide source term.

REDOX CONTROLLERS

Another mechanism for controlling the actinide source term is through the control of the oxidation-reduction (redox) environment. The actinides have a varied and interesting chemistry, partially due to their ability to exist in multiple oxidation states, sometimes simultaneously. Each oxidation state of an individual actinide shows dramatic differences in chemistry. There is a general trend in actinide chemistry whereby the lower oxidation states exhibit significantly lower solubilities than the higher oxidation states, sometimes by many orders of magnitude. Maintaining a highly reducing atmosphere and thus keeping the actinides in the lower oxidation states can have a profound effect on the actinide source term and repository performance.

To achieve the redox benefit to repository performance, a large quantity of an effective reductant would have to be added to the repository to ensure highly reducing conditions. As part of the waste materials and the containers holding the waste, there will be at least 1×10^9 moles of iron placed into the WIPP repository (U. S. DOE, 1996). To put this quantity of iron into perspective, this equates to an approximately 2800:1 molar ratio of iron to plutonium (which is one of the most critical elements of concern with respect to demonstrating compliance for the WIPP). Metallic iron does not always exhibit sufficiently fast reduction kinetics to provide confidence that under all conditions the actinides will be in a reduced state. Fortunately, iron also undergoes corrosion which serves as a source of iron ions. In an anoxic environment, Telander and Westerman (1996) have shown that metallic iron undergoes corrosion according to the following reaction:



As shown above, anoxic corrosion produces Fe^{2+} ions which are a very good reductant with acceptable kinetics (Clark et al., 1997). Given the large excess of available reductant, there was no justification for adding additional material, in the form of a backfill, to control the redox environment. No further evaluation of added reductants as a backfill material was performed.

The evaluations described above narrowed the range of mechanisms to two: precipitants and pH control. Both of these mechanisms were determined to be able to effect the desired impact on repository performance, the reduction of the actinide source term. To further narrow the field of potential mechanisms to implement, an assessment of the ability to have the effect reflected by the performance assessment codes utilizing existing or readily available data was performed.

PRECIPITANTS

Actinides are known to form many relatively insoluble compounds (Cotton and Wilkinson, 1988). Prominent among these insoluble compounds are the oxides, hydroxides, and phosphates. The existence of the actinide oxides and hydroxides is essentially a function of the pH of the system and is fully reflected in the existing Pitzer thermodynamic databases (Novak, Moore and Bynum, 1996) for actinides in high ionic strength solutions. The effect of precipitation of oxides or hydroxides was included in the actinide solubility models which utilize these databases and the

benefit realized via the control of the pH to a basic region. The actinide phosphates are also known to exhibit low solubilities. However, sufficient Pitzer parameters were not readily available to fully implement the beneficial effects of adding phosphate to the system. Limited Pitzer parameters for phosphates were available for actinides in the +3 oxidation state, but are not available for the other oxidation states of interest (principally the +4 oxidation state). Therefore, due to the inability to readily and fully reflect the effects of adding phosphate to the system, precipitants, except those resulting from the control of pH, were eliminated from further consideration.

pH and $f\text{CO}_2$ CONTROLLERS

Materials which can effect control over the pH or $f\text{CO}_2$ were then selected as the backfill of choice. There are numerous materials capable of controlling or buffering the pH in the repository system. Over 15 materials were screened for their ability to control the pH in the basic region. Several of these materials, in addition to their ability to control pH, are also capable of reducing the carbonate concentration through the formation of relatively insoluble carbonates. These materials include:

- CaO,
- $\text{Ca}(\text{OH})_2$,
- MgO, and
- $\text{Mg}(\text{OH})_2$

As noted previously, the alkaline earth oxides readily react with water to form the corresponding hydroxides. The removal of free water from the disposal area by the reaction with the oxides to form the hydroxides was viewed as yet another benefit which allowed the list of candidate materials to be narrowed to two: CaO and MgO.

Being in the same chemical group, CaO and MgO oxides are expected to have similar chemistries, and that is generally true. However, CaO is more reactive than MgO which results in significant differences when considering a material to be used as a chemical control for a nuclear waste repository. One of these differences is the equilibrium pH yielded by these materials. In the WIPP brines, CaO yields a pH as high as 13 or greater, whereas MgO buffers the system at a more moderate pH of approximately 9-10. This may not seem significant, but there is not a consensus in the actinide chemistry community on the ability of the actinides to exhibit amphoteric behavior. An amphoteric material, due to its ability to exhibit both acid and base properties typically has a solubility which decreases as a function of pH to a minimum, and will then increase with further increase in pH. Because the ability of the actinides to exhibit this behavior cannot conclusively be ruled out, and to avoid having to engage this debate, it was determined to take the more moderate route and utilize the weaker base, MgO. At the pH obtained via an $\text{Mg}(\text{OH})_2$ buffer, the benefits of a slightly basic solution on the actinide solubility are realized without entering a region where amphoteric behavior could be manifested. The decision to utilize MgO as opposed to CaO also yielded operational benefits. MgO has a higher allowable airborne concentration before the use of respiratory protection is required. CaO, due to its more caustic nature, requires the use of a respirator. Spills thus cause less of an operational impact.

Once the decision was made to utilize MgO as a backfill, efforts focused on the emplacement design and demonstrating the efficacy of the system.

SYSTEM DESIGN

The MgO backfill will be purchased and received in two different containers: (1) a supersack typically holding several thousand pounds, and (2) a mini sack typically holding 25 pounds (11.3 kilograms). MgO is available from several suppliers in a range of grain sizes and purities. Typical purities range from 93 percent MgO for calcined dolomite to 98 percent for MgO extracted from brines. Chemical grade product (100 percent MgO) is also available. MgO is available in a variety of milled and screened grain sizes ranging from a powder (minus 325 mesh) to granular (0.5 inch by 6 mesh). The filled containers will be delivered underground using current shaft and material handling procedures and processes.

The mini sack will be 34 inches (86.4 centimeters) long, 6 inches (15 centimeters) in diameter and will be fabricated of a single layer of polyethylene or other suitable material. It will have an integral handle and hook attached into the sack closure. Six sacks will be manually placed in the external voids of each seven-pack unit just before the seven-pack is positioned on the waste stack. The mini sack will be lifted up behind the shrink wrap around the top of the seven-pack, and slid into place. Once the sacks are in place, the seven-pack will be positioned on the waste stack in the normal manner. A similar process will be used for standard waste boxes (SWB) except that the sacks will be hung from the lift clips on these units.

Super sacks, which may be up to 4,000 pounds (1,814 kilograms) will be handled and placed using normal waste handling techniques. Once each row of waste units is in place, a layer of super sacks will be placed on top of them. The super sack will have an integral slip sheet or base attachment so that it can be handled and placed in a manner that is identical to how waste units are emplaced. Typically, the space above a stack of containers will be 36 to 48 inches (90 to 122 centimeters), of which about 18 inches (45 centimeters) will contain the backfill material.

Finally, mini sacks will be manually stacked on the floor in the space between the waste stack and ribside. These sacks can be placed horizontally or vertically as may be convenient and loading rates up to 100 pounds per linear foot (148.8 kilograms per linear meter) can be achieved simply and quickly.

There are about 3,700 linear feet (1,128 linear meters) of waste stack in a panel. The supersack configuration provides about 4,000 pounds per linear foot (5,952 kilograms per linear meter) of waste stack or about 7,400 short tons (6,712 metric tons) per panel. About 10,836 waste disposal units (that is, seven-packs of drums and SWBs) will be placed in a panel and at six 25-pound (11.3-kilogram) mini sacks per unit, this will provide about 800 short tons (726 metric tons) per panel. Finally, material stacked along the ribside at 100 pounds per linear foot (148.8 kilograms per linear meter) of rib will provide about 360 short tons (327 metric tons) per panel. This gives a total of about 8,560 short tons (7,764 metric tons) per panel or approximately 85,600 short tons (77,640 metric tons) for the repository.

Backfill placed in this manner is protected until exposed when sacks are broken during creep closure of the room and compaction of the backfill and waste.

SYSTEM EFFICACY

The ability of the MgO to function as expected is subject to several assumptions. Among those assumptions are:

- the MgO will control the pH to a region dominated by the brucite/magnesite (or hydromagnesite) equilibrium,
- the MgO will react with the CO₂ generated, if any, and
- the solid phase formed upon reaction of MgO with the brine and subsequently with CO₂ will be brucite/magnesium oxychloride and magnesite/ hydromagnesite, respectively.

As part of our ongoing studies, the above assumptions are being confirmed as discussed elsewhere in these proceedings (see Papenguth et al. 1998).

CONCLUSION

Chemical intervention through the implementation of a backfill material has shown large benefits to the ability to predict long-term performance and compliance with the applicable disposal regulations. MgO has been selected as the most appropriate material, and its ability to control the pH and remove solubility enhancing carbonate from the system has been experimentally demonstrated.

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