

Implementation of Chemical Controls Through a Backfill System for the Waste Isolation Pilot Plant (WIPP)

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Submitted to ICEM'97, The Sixth International Conference on Radioactive Waste Management and Environmental Remediation, October 12-16, 1997, Singapore

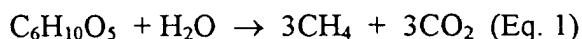
ABSTRACT

A backfill system has been designed for the 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 implementation of magnesium oxide (MgO) as the backfill material not only controls the pH of the expected fluids but also effectively removes the carbonate from the system, which has a significant impact on actinide solubility. The 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 occurring 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:



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This process, 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 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.

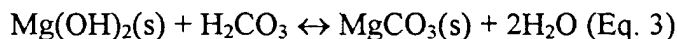
Based on there being an estimated 2.7×10^7 kg of carbon containing compounds to be emplaced in the WIPP (U. S. DOE, 1996), the fugacity of CO₂ (f_{CO_2}) could vary within the range of 0 (in the event that there is insufficient microbial action to overcome the buffering effect of the cementitious material (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 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.

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. EPA 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 this 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 for 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 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 this 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 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,
- Ca(OH)₂,
- MgO, and
- Mg(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 milder base, MgO. At the pH obtained via an Mg(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, 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 nesquehonite) 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/nesquehonite, respectively.

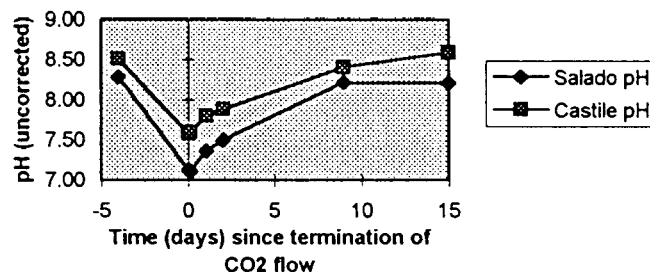
As part of our ongoing studies, the above assumptions are being confirmed. First, the ability of MgO to control the pH was confirmed. The reaction rate of industrial grade MgO was studied

via titration with both strong and weak acids by equilibrating a WIPP brine with excess MgO, adding sufficient acid to initially lower the pH into the acid region (less than pH 5) and monitoring the increase of pH as a function of time. It was found that over the course of just a few hours, the pH returned to its pre-acidification pH. These studies have demonstrated that the reactivity of the industrial grade MgO is sufficient to function effectively as a pH buffer within the repository time scale.

The ability of the MgO to react with the CO₂ in the repository is critical to the backfill functioning as designed. The scavenging of the CO₂ by the MgO can be demonstrated by the identification of solid phase reaction products. These studies were carried out by bubbling pure CO₂ into a stirred reactor of WIPP brine and MgO. After several days of reaction, the solid phase was separated and analyzed via x-ray diffraction. Depending on the specific experimental conditions, one of two new mineral phases were identified as having formed: dypingite {Mg₅(CO₃)₄(OH)₂·5H₂O} and/or nesquehonite {MgCO₃·3H₂O}. Modeling utilizing EQ3/6 (v.7.2a on an IBM compatible platform) has shown that these phases yield approximately the same chemical conditions as when the formation of magnesite (MgCO₃), which is the equilibrium phase included in the solubility calculations, is enabled. We have thus experimentally confirmed that the MgO backfill will have sufficient reactivity to function effectively as a pH buffer, will effectively remove CO₂ from the system through precipitation of relatively insoluble carbonate phases, and that the solid phases expected to be formed over a very short time-scale will yield approximately the same chemical conditions as those expected from the formation of magnesite.

Based on Scanning Electron Microscopy (SEM) evidence, the reaction of the MgO/Mg(OH)₂ with the CO₂ takes place at the surface. However, it is not known at this time whether this will be the reaction site in the repository or if this is an artifact of the lack of nucleation sites in the experimental design. The formation of a new mineral species at the surface could lead to the development of a low permeability reaction rim which could inhibit the ability of the MgO in the interior of the pellets to participate in reactions with the aqueous phase. To evaluate this phenomena two approaches were taken. In the first approach, MgO pellets were reacted with CO₂ as described above. After a reaction period of approximately four days, the introduction of CO₂ was terminated and the pH monitored. As shown in Figure 1, even after reacting with pure CO₂ for several days the MgO still exhibits the ability to control the pH within a reasonable time frame. In the case of more extensive reaction with CO₂, the reaction product is expected to fracture and create pathways to the interior due to the greater than 110% molar expansion in converting from the oxide or hydroxide to the carbonate.

Ability of Reacted MgO to Control pH



Nevertheless, the question remains whether the reaction rim formed will dramatically inhibit communication between the interior of the MgO pellets and the surrounding fluids. To investigate the presence or absence of this phenomena, a series of dye penetration tests were performed. In the first series of tests, pellets of the MgO were first reacted with CO₂ and then immersed in a dye solution. After allowing the dye to penetrate for 24 hours, the pellets were removed from the dye, set in an epoxy resin and sectioned. In all cases, the dye was visually observed to have uniformly penetrated throughout the interior of the pellet. Calculations have shown that the time necessary for diffusion along a straight path from the exterior of the pellet to the center is approximately 10 hours. Thus, even when conservatively ignoring tortuosity in the MgO pellets, the permeability could not have been increased by more than a factor of approximately 2.

In the second series of tests, the repository configuration was more closely simulated. In these tests, the MgO was placed in a porous bag to simulate the close packing that will be experienced in the repository. The bags of MgO were partially suspended in one of the WIPP brines and CO₂ bubbled through the solution. The bags were only partially suspended in the brine to simulate a partially inundated repository (i.e. a repository where there is both a brine and gas phase present). After reaction periods of 10 and 25 days, a bag of MgO was removed from the brine and placed into the dye solution for three days. At the end of the three days the bags were dried, potted in clear plastic and sectioned. In all cases good dye penetration was noted. From this we have concluded that the formation of reaction products on the surfaces of the backfill material do not have a significant, detrimental impact on the ability of the MgO to maintain the predicted chemical conditions.

During the course of these investigations, an additional interesting reaction was noted. When the MgO was added to Salado brine (one of the two possible brines at the WIPP and composed principally of NaCl and MgCl₂), a reaction product was formed which exhibits a very high strength. Analysis by energy dispersive x-ray microanalysis has shown this material to be sorel cement (typically made by mixing magnesium chloride and brucite), which is known to have strengths of up to 10,000 psi (Lewis, 1993). The formation of sorel cement may serve to effectively cement the waste materials in place, thus limiting the ability of the material to contribute to a release. This is particularly significant in the event of the direct release of materials during a drilling intrusion event.

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.

ACKNOWLEDGMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

This work was conducted under the Sandia WIPP Quality Assurance Program which is equivalent to NQA-1, NQA-2 (Part 2.7), and NQA-3 Standards.

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