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A HISTORICAL REVIEW OF WASTE ISOLATION PILOT PLANT BACKFILL DEVELOPMENT

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ABSTRACT

Backfills have been part of Sandia National Laboratories' [Sandia's] Waste Isolation Pilot Plant [WIPP] designs for over twenty years. Historically, backfill research at Sandia has depended heavily on the changing mission of the WIPP facility. Early testing considered heat producing, high level, wastes. Bentonite/sand/salt mixtures were evaluated and studies focused on developing materials that would retard brine ingress, sorb radionuclides, and withstand elevated temperatures. The present-day backfill consists of pure MgO [magnesium oxide] in a palletized form and is directed at treating the relatively low contamination level, non-heat producing, wastes actually being disposed of in the WIPP. It's introduction was motivated by the need to scavenging CO_2 [carbon dioxide] from decaying organic components in the waste. However, other benefits, such as a substantial desiccating capacity, are also being evaluated. The MgO backfill also fulfills a statutory requirement for assurance measures beyond those needed to demonstrate compliance with the United States [U.S.] Environmental Protection Agency [EPA] regulatory release limits. However, even without a backfill, the WIPP repository design still operates within EPA regulatory release limits.

INTRODUCTION

The WIPP is a mined repository for defense related transuranic nuclear wastes [TRU] located at a depth of about 650 meters in thick bedded rock salt of the Salado Formation, in the Delaware basin of southeastern New Mexico, United States of America [USA]. Almost since its inception WIPP backfills have been called upon to address a variety of long-term repository performance issues (1,2). Typically, these issues involved controlling either the hydrologic or chemical environment for long after the repository closed (centuries to millennia). Although the relative importance of backfill purposes and needs have changed over time, a list of potential WIPP backfill functions includes:

1. Controlling radionuclide migration by scavenging specific radionuclides;
2. Buffering the chemical environment to lower radionuclide solubilities, scavenge gases (notably CO_2), or minimize canister and waste corrosion;
3. Providing a hydrologic barrier to divert or impede groundwater access;
4. Dissipating radiogenic heat and provide radiation shielding (for defense high level waste [DHLW] only);
5. Providing a "sink" to chemically bind limited amounts of groundwater projected to enter the repository in certain scenarios;
6. Providing these functions with regard to cost-effectiveness, operational safety, and operational simplicity.

Over the last two decades the WIPP mission has changed significantly. These changes, in turn,

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altered the design needs for the backfills and, hence, the materials being evaluated. From the early 1970's until 1988 it was intended that the WIPP would be a dual-purpose facility. Part of the mine was to be used for the permanent disposal of low contaminant level TRU. A different part of the mine was to be used for testing DHLW borosilicate glass disposal concepts, but not for the permanent placement of this waste type. In 1988 Congress discontinued DHLW testing in the WIPP.

Backfill requirements for these two types of waste are distinctly different. A DHLW-specific backfill must address the full suite of fission products plus actinides typical of defense-related nuclear fuel reprocessing and waste processing activities. For several centuries after placement the repository environment near a DHLW canister experiences high beta-gamma radiation doses and temperatures in the range 100-200 degrees Celsius [°C] (3). DHLW is also a relatively resilient, uniform, vitrified inorganic material and will not undergo major changes in phase chemistry except when large amounts of brine entire from an outside source. Thus, backfill-waste interactions are limited to those components indigenous to the external brines, those that could slowly leach from borosilicate glass, or those derived from corroding waste canisters (iron or titanium).

Had DHLW testing remained in the WIPP mission it is likely that cylindrical waste canisters about three meters long and about half a meter in diameter would have been placed individually in vertical holes drilled in separate test rooms. Molecke(4) defined four potential DHLW backfills:

1. low density (1.3 gram per cubic centimeter[g/cm^3]) bentonite poured into the annulus around a DHLW canister;
2. low density (1.4 g/cm^3) bentonite(70%) - sand (30%, by weight) mix poured into the annulus around a DHLW canister;
3. high density (2.1 g/cm^3) bentonite (70%) - sand (30%) annular compacts;
4. crushed rock salt.

TRU waste differs from DHLW in that it is a highly heterogeneous mix of organic and inorganic materials: lab trash (cellulose, plastic, rubber, glassware), equipment and construction debris (metal, concrete glass, wood), stabilized sludges (diatomaceous earth, hydrous iron-aluminum-silicon oxides), Portland cement, and calcium sulfate [$CaSO_4$] onto which machine oils and organic solvents had been sorbed. Small amounts of plutonium [Pu] contamination are the principal long-term concern and traces of americium [Am] is also a minor short-term issue. In contrast to DHLW, radioactive decay processes will only raise TRU waste temperatures by a few degrees. However, TRU is not as resilient as DHLW and the presence of a minimal amount of free brine may initiate microbial degradation. Decay processes have the potential for causing large changes in the physical form of the waste while generating significant amounts of CO_2, N_2 [nitrogen], H_2S [hydrogen sulfide], and CH_4 [methane](5,6). In addition, the leachates from these materials may contain a host of soluble organic compounds derived from microbial activity. All these compounds, together with the iron from the waste containers (208 liter [1] (i.e. 55 gallon) drums and still larger steel boxes), may interact with backfill materials. Initially, crushed salt or crushed salt - bentonite mixes were considered for contact-handled TRU backfills, and bentonite-sand mixes were considered for remote-handled TRU backfills(7).

A second important change in the WIPP approach involved the perception of what constituted a step toward achieving compliance. Initially, a multibarrier philosophy was followed with the objective of constructing as many redundant barriers to radionuclide migration as possible: effective shaft seals, resilient waste forms, low corrosion rate canisters, and backfills(2). A number of rather obvious choices were made regarding early potential backfill materials. Salt was considered because of its abundance, high thermal conductivity, and known plasticity under pressure. Bentonite had been used for years commercially as a swelling grout and was also known to have a high ion exchange capacity. Sand was chosen as an inexpensive bulking agent that could increase the thermal conductivity of sand-bentonite mixes. However, the multibarrier philosophy did not provide a model for understanding how individual barriers might act in concert, or a methodology for minimizing overall repository construction costs. Further, about the closest the multibarrier concept came to providing design parameters were occasional limits on backfill thermal conductivities that were intended to prevent DHLW canisters from reaching various arbitrarily chosen temperatures. Chemical criteria for backfill success were generally not enumerated.

In the early 1990's Sandia and the DOE initiated a series of iterative performance assessment (PA) calculations that addressed some of the disadvantages of the multibarrier approach to backfill development. The methodology to be followed in PA calculations is specified in the Code of Federal Regulations(8,9). In 1992, Congress awarded licensing authority for the WIPP to EPA as part of the "WIPP Land Withdrawal Act" - Public Law 102-579, 1992. To meet the requirements dictated by the EPA, the DOE developed the Compliance Certification Application [CCA], which included PA calculations and a detailed assessment of site characteristics(10). The CCA was submitted to the EPA in October 1996. The EPA certified the compliance of the WIPP with its regulations in May 1998.

Promulgation of the regulatory requirements described above had several important effects on WIPP backfill research. First, the required PA calculations provided a tool that allowed researchers to judge the benefits derived from including, or deleting, various components from the design and to evaluate their relative impact on contaminant releases. In particular, a buildup of CO_2 was identified as a condition that would have a large potential negative impact on overall system performance. A MgO backfill was chosen to prevent this from happening. Secondly, the possibility of human intrusion scenarios had been considered from the early 1980's. However, implementation of quantitative PA rankings highlighted these scenarios as having the greatest potential for radionuclide releases (though predicted levels were still significantly below EPA-stipulated safety limitations). Thirdly, the regulatory requirements mandated the use of an engineered barrier as an assurance requirement for the WIPP and described how assurance requirements would be implemented in calculations(9,11).

By using the iterative PA approach, it was determined in 1995 that the most important aspects of performance to control through engineered barriers were brine pH and carbonate ion concentration. Using a backfill that controlled these parameters resulted in a significant decrease in actinide solubilities. Inclusion of MgO also simplified the chemical environment considered by the PA models, thus making the multiple calculations required for the PA a more tractable task. The net effect is that releases through the various potential paths are significantly reduced through the use of a MgO backfill.

EARLY RESEARCH ON DEFENSE HIGH LEVEL WASTE BACKFILLS

Prior to being concluded in 1988, DHLW backfill development focused on assessing performance in the high temperature environments adjacent to canister-sized electric heaters designed as surrogates for DHLW containers. An extensive program of in-situ tests underground in the WIPP was supported by a wide range of developmental laboratory tests(7). The in-situ tests involved placing electrically heated canisters (maximum thermal output of 1.5 kilowatt [kW], top surface temperature 190° C) in vertical floor holes in the salt and then surrounding them with various backfills. In some cases brine was added to the test emplacement to evaluate its impact on canister corrosion and backfill physical properties.

Post-test analyses of the crushed salt backfill were relatively easy. No chemical changes in the rock salt were anticipated and, even when brine was artificially introduced into the backfill, interactions with the mild steel were confined to a few millimeter thick skin on the canister surface. The mechanical compaction of the crushed salt backfill was, however, quite striking. Creep deformation of the hole walls compressed the backfill and encapsulated the heaters so tightly that it proved difficult to remove samples for post-test analysis. The resulting backfill had less than 1% porosity(12) and, hence, should have properties similar to the undisturbed rock salt.

Bentonite backfills had the potential for being more geochemically reactive and were characterized in greater detail(13). A significant concern was whether bentonite exposed to high temperature steam would loose its ability to expand when later wetted by cooler brine(14). A loss of expansion capacity could adversely impact bentonite backfills by decreasing both radionuclide sorption and its ability to swell and seal cracks. At a mineralogic level, this equates to an irreversible collapse of the interlayer spaces as observed by X-ray diffraction. However, even samples exposed to the hottest temperatures showed normal interlayer spacing and no development of a collapsed 10-angstrom phase was apparent. No difference was noted between the clay-sand mixtures and the pure bentonite. In short, in spite of early fears, the heated bentonite remained stable.

Bentonite from the hottest parts of the test was often discolored, ranging from a pinkish tinge to brick red along cracks. During test canister recovery, a distinct odor of hydrochloric acid [HCl] was noted. This odor was eventually traced to the hydrolysis of magnesium chloride in the injected brines and accounted for the localized dark red coloration along the vapor exit channels. Although the red clays had normal X-ray patterns, transmission electron microscopy (TEM) studies were initiated to assess if breakdown products were present in amounts below the X-ray diffraction detection limit (about 5%). However, these studies also failed to identify any new phases. Thus, in spite of the bright coloration, only a minute amount of clay apparently broke down to produce the hematite pigment. No adverse synergism between the canister and the clay backfill were noted and even low density bentonite-based backfills were compacted to form a dense cover around the canister surfaces. However, unlike the crushed salt, the bentonite backfill was only compacted to about 75% of its theoretical maximum density during the three-year test period. In situ thermal conductivity's ranged from 0.28-0.43 Watts per meter degree Kelvin [W/m°K] for bentonite-sand mixtures up to 1.12 W/m°K for compacted salt(15). Earlier field studies report a thermal conductivity of 0.25 W/m°K for pure bentonite and up to 1.25 W/m°K for high density sand bentonite mixes(16).

The supporting laboratory program for bentonite backfills(17) dealt primarily with three issues: (1)

swelling losses due to dehydration, (2) gamma radiation effects, and (3) brine-bentonite interactions. Compacted bentonite pellets (1.8 g/cm^3) were dehydrated at temperatures up to 320° C for periods as long as 500 days. The volume change was then noted when the pellet was wetted with brine. Two brines were used for testing: (1) a simple NaCl [sodium chloride] fluid, such as might arise if fresh water gained access to the repository and became saturated with rock salt, and (2) brine A, " a brine which might intrude into the WIPP waste horizon by percolation through an overlying zone containing potash "(18). The loss of swelling noted in brine A (NaCl with high Mg, K [potassium], moderate sulfate) was significantly more than in the saturated NaCl brine. However, even in Brine A, temperatures of 250° C or higher were needed to seriously diminish bentonite expansion.

Radiation effects studies were carried out on both dry (at 25° C) and brine saturated bentonite under hydrothermal conditions (150° C) at gamma doses up to $3x10^{10}$ rads. In both cases, post-test X-ray diffraction studies failed to yield any evidence of mineralogic changes. In the hydrothermal studies the post-test brine pH was 4.8. This is the value expected for Brine A bentonite interaction experiments at that temperature so radiolysis reactions had a negligible effect on this important parameter. Headspace gases, however, changed significantly: H_2[hydrogen], CO_2, and CO (trace) [carbon monoxide] were enriched while O_2 [oxygen] was virtually eliminated. Radiation tests on dry salt revealed a different behavior: less H_2 and CO_2 were produced and residual O_2 was present. In addition, the post-test headspace gas also contained 7 mole % N_2O_5 [nitrous oxide]. Exposure of irradiated salt to brines liberated abundant chlorine gas and produced strongly oxidizing solutions.

Bentonite stability in WIPP brines is a potentially complex subject since both K and Mg could interact with the bentonite. K uptake could lead to illitization of the clay and a loss of swelling capacity. A theoretical analysis based on published rate data(19,20) indicated that for the 10^4 year period of regulatory concern, this would be unimportant if peak temperatures stayed below 150° C, but could be significant if temperatures peaked at around 235° C. Experimental studies in simplified KCl/NaCl brines (51 days, 250° C) confirmed this but reemphasized the importance of competing ions. With Brine A, no illite appeared and instead the dominant reaction was Mg uptake. The change in clay composition was chemically similar to that followed by clays undergoing normal diagenesis in the Salado formation over millions of years(21). However, rather than producing ordered corrensite, a disordered saponitic smectite resulted.

A parallel review of bentonite stability at low temperatures indicated similar trends(22). A combination of natural analogue studies and thermodynamic calculations predicted Mg-uptake to be the dominant reaction. To a lesser extent, K and Fe [iron] enriched illite might also be expected to produce more mica-like forms. A Transition State Theory approach(23), using dissolution data from kaolinite to calibrate the rates, demonstrated that with excess brine, these reactions could be rapid enough to change bentonite to a different, Mg-rich, type of swelling clay in times shorter than the period of regulatory concern (10^4 years). However, significant production of nonargillaceous materials would not be anticipated.

High temperature radionuclide retardation studies were not carried out because of their difficulty, and because brines entering the repository during the early high radiation – high temperature phase of repository operation would quickly evaporate to dryness (thus, affording little possibility for radionuclide transport). However, if the backfill became brine saturated while still hot, there is good reason to question whether a saturated bentonite backfill would retard radionuclides. WIPP brines interacting with bentonite at elevated temperatures typically develop an acidic pH (less than 5) due to the uptake of Mg by the clays(17). Such conditions would optimize actinide solubilities and minimize their chances for sorption. Further, from hydrothermal tests with marine clays, it is evident that temperature-gradient induced transport (Soret effects) would significantly supplement isothermal diffusion through a bentonite backfill(24). At the predicted rates, significant amounts of nonsorbing components might traverse the normal thickness of a DHLW backfill barrier in just a few months.

To summarize, early DHLW backfill studies were generally successful at demonstrating that both salt and bentonite backfills would withstand the rigors of the early near-field environment. Further, where bentonite-brine reactions occur, the reaction products are also predicted to be sheet silicates with swelling and radionuclide sorptive properties similar to the original bentonite. Some doubt exists, however, regarding the effectiveness of a high temperature, brine saturated, bentonite barrier. It is, however, quite unlikely that any significant amount of brine will enter the WIPP repository during the short, early, high temperature phase of repository operation. Thus, bentonite backfills should function successfully for the full 10,000 year period of regulatory concern.

EARLY RESEARCH ON TRANSURANIC WASTE BACKFILLS

Early plans called for backfilling around contact handled TRU wastes with either crushed salt or a mix of crushed salt (70%)-bentonite (30%). Although this review focuses principally on chemical process, it is worthwhile to briefly summarize the extensive research done to characterize the mechanical and hydrologic properties of these early backfills. Initial studies on dry materials revealed that: (1) short term, dry, compaction of both mixes only increased their densities to about 80% of its theoretical maximum(25,26), (2) that the compaction rate slowed rapidly with time, and (3) that in accelerated tests increasing the temperature to 90° C had little effect on compaction rates. Materials produced in this fashion had permeabilities in the darcy (10^{-12} m^2) range (7) and would not serve as effective seals in a rock salt formation with indigenous permeabilities in the nanodarcy range.

The issue of adequate compaction became moot when later research demonstrated that adding less than 1 weight percent brine accelerated the compaction rate even at pressures substantially below the lithostatic load in the WIPP repository (15 megapascals [MPa]). Permeabilities in the range 1-$5x10^{-17}$ m^2 were obtained for compacted salt-bentonite mixes(27) and $6x10^{-18}$ - $3x10^{-22}$ m^2 for pure rock salt(28). Effective barriers were now predicted to form in less than a year even from crushed salt to which no bentonite was added(29). Fully saturating the crushed salt with brine prior to the test retards the compaction rate by about a factor of 10, due to trapping of brine(30). But, this would not change the basic fact that the limiting step in backfill compaction is the rate of mine closure, not the resistance offered by the backfill. Swelling pressures of bentonite-rock salt mixes in the presence of typical WIPP brines were found to be about 2 MPa, substantially below the lithostatic pressure exerted by the overlying formations(26).

Most radionuclide-retardation studies on bentonite were directed at low temperature applications relevant to TRU waste disposal, though the occasional test on previously heated clays demonstrated that such treatments did not greatly degrade their sorptive properties(31). The multibarrier compliance framework in which this research was grounded is illustrated by the following justification(2): "Assuming a linear equilibrium distribution coefficient, Kd = 2000 milliliter per gram [ml/g] for transuranics can delay their breakthrough by 10^4 to 10^5 years after release from the waste form. Similarly, the breakthrough of species for which Kd = 200 ml/g, such as fission products, can be delayed by 10^3 years." This assumes a maximum groundwater velocity of 0.0348 m/ year [i.e. 1 ft /year] and an effective porosity of 0.1 or less, and that the barrier is not fractured. It also assumes the bentonite will swell and flow plastically when wetted, thus precluding development of sustained fractures which could short circuit diffusive transport through the bulk of the backfill(7).

Early WIPP-relevant bentonite sorption studies were summarized by Nowak(31). At pH 6.7-6.8, Pu Kd values ranged between $2\text{-}3\times10^3$ ml/g and fell by a factor of 5 in a bentonite (10%) - silica sand (90%) mix. Increasing the pH to 7.1 increased the pure bentonite Kd to $3\text{-}4\times10^4$ ml/g and the Kd in bentonite-sand mixes to $3\text{-}4\times10^3$ ml/g. Am ubiquitously sorbed on all materials tested with values ranging between $4\text{-}14\times10^3$ ml/g for pure bentonite and 9×10^3 ml/g for bentonite (10%) - silica sand (90%) mixes. Hectorite-sand mixes have Am Kd values between 1.4 and 1.6×10^4 ml/g.

At that time the WIPP was still slated to receive DHLW for testing. Thus, Nowak's experimental matrix(31) also included some of the more important fission products. Cs [cesium] sorption on bentonite was similar in both high and low Mg brines with Kd values between 3 and 5 ml/g; neither Sr [strontium] or TcO_4^- [pertechnetate] sorbed at all on bentonite. Eu^{+3} [europium] Kd values ranged from 10^2 to 10^3 ml/g, with the highest values relating to a relatively pure NaCl brine at pH 6.5, and the lowest value in a high Mg brine at pH 5.5. Precipitation of $Eu(OH)_3$ [europium hydroxide] over this pH interval may partly account for the changes. However, Kd values on hectorite, a related smectite clay, only changed from 2.5×10^3 to 7.2×10^3 ml/g over the same interval. Thus, the substrate apparently exerts some influence over the Kd's even at the higher pH values.

Three year-long field studies were also performed at the WIPP to verify some of these trends(32). To document migration under field conditions Eu, Sm [samarium] and Gd [gadolinium] sources were placed beneath 55 gal drums in bentonite(30%)-salt(70%) backfill mixes underground in the WIPP. The Eu source was 20 cm above an adjacent (artificial) brine pond so that the bentonite was only dampened by the wicking activity of the backfill. Eu migration was restricted to within 10 cm of the source. The Gd and Sm sources were beneath the level of the brine pond and post-test analyses of the backfill detected these elements up 25 cm away from the sources. However, this dispersal may have resulted from agitating the brine during drum removal and sampling activities. Since neither tracer was detected in the brine the backfill clearly prevented migration beyond the lower lips of the drums for the full three-year duration of the test. The brine pond was, however, doped with both iodide [I] and Cs tracers. In backfill samples taken near the pond, the I/Cs ratio was similar to that at the source but at distances greater than 1 meter a slight discrepancy implied that the bentonite had a limited capacity for Cs sorption(32).

To summarize, the early laboratory and in situ backfill test programs satisfied the technical needs of the current (at that time) compliance demonstration strategy by designing and demonstrating a barrier that would be redundant to other safeguards, and which could significantly reduce radionuclide releases.

TRANSITION BACKFILLS

Brush(6) and later Bynum et al.(7) summarized the transition from bentonite/crushed salt/sand backfill strategies to one based on MgO. Briefly, a combination of events were involved: (1) concerns were raised regarding the probability of maintaining a requisite thickness of bentonite around waste drums as room closure progressed; (2) it was noted that including a backfill did not greatly shorten the time before the waste could be regarded as having been entombed by the formation; (3) the chemical complexity of brine-bentonite reactions suggested that a substantial additional modeling and experimental effort might be needed to address these issues; (4) it was realized that if a drill hole penetrated a potential brine reservoir beneath the repository, the volume of brine delivered could quickly overwhelm the ability of the bentonite to sorb the brine; and (5) PA calculations focused attention on the adverse impacts of gas pressure (H_2, CH_4, CO_2) and related chemical effects such as depressed pH values. Bentonite/salt/sand mixes did little to mitigate these concerns.

In the course of addressing these new priorities a number of different functions and possible backfill materials were suggested: "$CuSO_4$, an oxidant, would corrode Fe and Fe-base alloys without producing H_2. $CaCO_3$, CaO, $Ca(OH)_2$, KOH and NaOH would remove CO_2, a potentially abundant, microbially produced gas. CaO, along with bentonite (a previously proposed backfill additive), would also remove H_2O. MnO_2, a potential electron acceptor might prevent: microbial $SO_4^=$ reduction, the concomitant production of H_2S; the reduction of H_2S with Fe, Fe-base alloys or their corrosion products to form FeS_2 (pyrite); the concomitant production of H_2(6)". In addition to variations on the theme bentonite/salt/sand, a study performed by the DOE(34) also made additions to the list of potential new backfill materials: bitumen, CaO [calcium oxide], Portland cement, while broadening the list of clays to include illite and kaolinite.

At one time during this transition period it appeared that actinide solubilities might still be great enough to present problems even in the presence of MgO with a brine pH close to 9. In this context four types of apatite were evaluated as actinide-specific getters(35). It was found that in WIPP brines hexavalent uranium-carbonate complexes caused relatively small U [uranium] Kd values (20-70 ml/g), that Pu Kd values ranged from up to 140 ml/g at pH ~ 7 but fell to almost zero by pH 9.5. Am Kd values were significantly higher reaching 3,500 ml/g near pH ~ 7. A tendency for Kd's to decrease with increasing pH was noted with Am, though two of the apatites retained Kd values in excess of 100 at pH 9.5. Np Kd values were similar (Kd typically between 500 ml/g and greater than 59,000 ml/g at pH ~ 7), but not enough data were gathered to discern pH effects. In general, actinide Kd values for the four materials followed the trend artificial hydroxyapatite >> bone meal > Florida phosphate rock > Idaho phosphate rock.

MAGNESIUM OXIDE BACKFILLS

After some deliberations the decision was made to just concentrate on resolving issues related to the build up of CO_2 and MgO was selected to perform this function(33). The Compliance Certification Application(11) PA captures only one of the positive attributes of MgO, the fact that it acts as a CO_2 sink. However, to advance the technical programs consistent with current recertification strategy there are (at least) three other positive features of a MgO backfill that are being studied for potential incorporation in future PA models: (1) certain PA scenarios involve either limited brine ingress or very slow brine delivery rates so the sizeable desiccating potential of roughly 86,500 tons of MgO may significantly impact predicted repository performance in these circumstances(36); (2) waste cementation by MgO reaction products may decrease the amount of contaminated solids that models predict would be carried to the surface in the event that a drill hole penetrated the repository; and (3) decreased porosity and permeability in the WIPP repository may limit fluid flow past contaminated waste. The general course of the MgO backfill discussion follows the trend outlined below and illustrated in Figure 1:

Initially brine encounters the MgO and hydration occurs:
(Eq. 1) $MgO + H_2O$ [water] $\rightarrow Mg(OH)_2$ [magnesium hydroxide]

Later, if microbial activity generates CO_2, hydrous magnesium carbonates will form:
(Eq. 2) $5Mg(OH)_2 + 4CO_2 \rightarrow [MgCO_3]_4[Mg(OH)_2]_1.4[H_2O]$ [hydromagnesite]

This ultimately inverts to anhydrous $MgCO_3$ [magnesite]:
(Eq. 3) $[MgCO_3]_4[Mg(OH)_2]_1.4[H_2O] \rightarrow 4MgCO_3 + Mg(OH)_2 + 4H_2O$.

Parenthetically, it should be noted that the repository is designed to contain a four-fold (molar) excess of MgO in relation to maximum potential CO_2 production. Thus, at most only about a quarter of the water incorporated into a fully hydrated backfill could ever be released to form brine during carbonation.

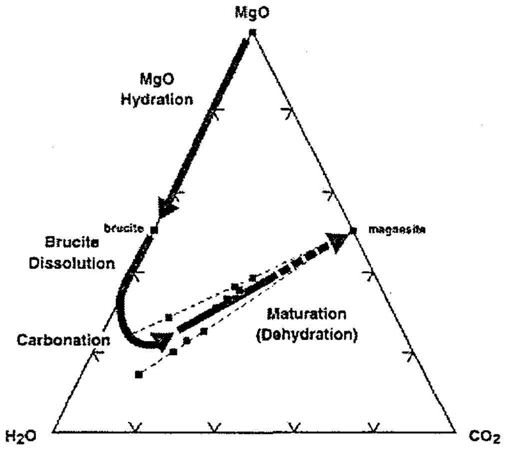

Fig. 1 Probable MgO reaction path under repository conditions

The hydration of MgO is strongly favored thermodynamically but details of the process require clarification. In particular, one set of early experiments lasting 443 days using both Salado Brine A (high Mg, K, moderate sulfate) and Castile brine (low Mg, K, high sulfate) found no evidence of

$Mg(OH)_2$ formation.

With further experimentation, it became obvious that hydration rates were markedly slowed by high Mg concentrations and, to a lesser degree, by high brine to solid ratios. The early tests were carried out with very high brine to solid ratios that are not representative of current or future WIPP scenarios. It has also been established that the hydration rate is nonlinear. First comes an incubation period when no reaction appears to take place. Then the MgO reacts rapidly until 30-40% of the mass is consumed. Thereafter, the rate again slows until the MgO is completely hydrated.

The incubation period is the feature of most immediate interest. Incubation periods were quantified at 90° C, 60° C, and 40° C and found to yield a straight line when represented as an Arrhenius plot. The activation energy obtained from this plot, 17.5 kcal/mole, suggest that the retarding mechanism was not diffusion of water through Mg-hydroxychloride coatings formed on particle surfaces. Diffusion regulated rates, such as components penetrating a surface coating, typically have activation energies less than 5 kcal/mole(23). Our value of 17.5 kcal/mole is more typical of a nucleation process requiring a degree of supersaturation before the reaction can proceed. Thus, it is not surprising that large brine to MgO ratios prolong the incubation periods. Extrapolating the incubation periods down to in situ WIPP temperatures (28-30° C) suggest that a one to two month incubation period might be needed before significant backfill hydration can start. This is fast enough to keep up with the natural influx of brine into the WIPP workings. However, if drilling penetrated a pressurized brine reservoir in the underlying Castile Formation, brine would probably fill all accessible porosity before significant hydration commenced.

The basic carbonation reaction ($CO_2 + MgO \rightarrow MgCO_3$) also has a strong thermodynamic driving force but, again, the process turned out to be relatively complex. At issue initially was whether MgO particle surfaces would react and seal off the underlying unreacted MgO, thus precluding the complete scavenging of all biogenically generated CO_2 assuming complete microbial degradation of the waste. Mass balance calculations dictated that compliance in this case required a demonstration that at least 26 mole percent of the MgO would react. Early tests to assess this possibility were undertaken(37). Although enough of the runs reached the 26 mole percent benchmark to show compliance, a few of the experiments showed a marked decrease in the CO_2 uptake rate later in the experiments.

X-ray diffraction and scanning electron microscope studies eventually showed that the conversion rate only slowed appreciably in accelerated tests when non-WIPP-representative, high CO_2 partial pressures (about 0.1 MPa), produced dense coatings of needle-like nesquehonite ($MgCO_3.3H_2O$) crystals on particle surfaces. At the lower CO_2 partial pressures expected in the WIPP, hydromagnesite ($[MgCO_3]_4[Mg(OH)_2]_1.4[H_2O]$) is thermodynamically favored(38). Such coatings consist of loose "card house" aggregates of bladed crystals that are ineffective at shielding the underlying MgO. Currently, our experiments out to 200 days show continued CO_2 uptake. From the CO_2 consumption rates in the later stages of these experiments, it is estimated that to reach the compliance objective of 26 mole percent conversion will take an additional 0.54 years in the 5% CO_2 atmosphere and an additional 1.76 years in a 0.5% CO_2 atmosphere.

Hydromagnesite is, however, metastable with respect to magnesite ($MgCO_3$). Papenguth et al.(37)

assimilated the scant rate data from the literature and using an Arrhenius plot suggests at in-situ WIPP temperatures (28°C) 100-300 years would be a reasonable estimate for the time needed to transform hydromagnesite to magnesite. Recent experiments in WIPP relevant brines demonstrate the impact of brine chemistry on this rate. These data suggest that in pure saturated NaCl only about 2.5 years would be needed for conversion at the in situ temperature of the WIPP workings, while in a generic WIPP weep fluid (NaCl, high sulfate, K, intermediate Mg) it might take as long as 1,500 years. The rate is of some importance to accurate compliance calculations. In addition to influencing dissolved carbonate levels, the change to magnesite will return the water trapped initially in $Mg(OH)_2$, and then sequestered in hydromagnesite, to the inventory of free brine able to transport radionuclides.

Studies regarding hydrologic and mechanical benefits of including MgO are less advanced. However, our data support some preliminary conclusions: (1) the pressure caused by hydration and swelling in a confined volume may exceed the lithostatic load at the depth of the repository; (2) hydration in a confined volume produces materials with very low permeabilities (10^{-17} m^2) even though the fill was not fully converted to $Mg(OH)_2$; (3) unconfined compressive strength of confined volume hydrated MgO is variable but falls in a range of 2 to 6 MPa when deionized water is the hydrating agent, and between 5 and 22 MPa using Salado Formation generic weep brine; and (4) tensile strength of specimens not exposed to CO_2 is 0 for simple Na-Cl-SO_4 brines but ranges from 0.2 to 1.2 MPa when the cementing media is a Mg-rich brine - which is probably due to Sorel cement formation. These latter tensile strength measurements, along with the compressive strengths, are both great enough to impart an important degree of cohesiveness to the reacted MgO that may exist adjacent to the compacted waste canisters.

To summarize, current studies have show shown that a MgO backfill can meet the compliance needs currently defined by PA calculations. It is also apparent that by including additional aspects of MgO behavior in future PA calculations the margin of compliance will be increased substantially.

CONCLUSIONS

Over the past two decades, backfill studies at Sandia for the WIPP program have provided the conceptual basis for addressing two different definitions of what constitutes acceptable long-term repository performance. Early in the history of the WIPP, acceptable long-term repository performance relied on a multibarrier concept. Bentonite, sand, and crushed salt in varying proportions were shown to possess many chemical and physical properties making them effective backfills under then WIPP-relevant conditions. Later, with guidance from PA calculations, a MgO backfill was chosen to supplant bentonite (and the no-backfill option) in order to decrease actinide solubility by scavenging biogenic CO_2 and controlling pH. In addition to verifying this scavenging ability, future studies are directed at quantifying water uptake and re-release cycles, and at the coupled hydrologic-mechanical implications of placing this material adjacent to TRU waste. Although long-term repository performance is acceptable without MgO, its presence as a backfill makes WIPP performance more robust and satisfies regulations requiring one, or more, engineered barriers(10).

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