4.0 MgO Hydration Experiments Conducted at SNL-ABQ

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Abstract

Magnesium oxide (MgO) backfill material in WIPP will reduce the solubilities of actinide elements, and remove carbon dioxid (CO_2) generated by microbiologic activities and water (H_2O) from brine, by a series of reactions involving carbonation and hydration of MgO. To provide the reaction rate constants of MgO in the repository to performance analysis (PA), a series of experiments have been carried out. This report outlines the MgO hydration rate measurement procedures, data reduction, extrapolation methods and on-going experiments. Hydration rates have been determined in brines and in vapor phase, representing the inundated conditions and humid conditions in the repository, respectively.

In addition to completing the samples generated in the previous experiments, a new experiment has been initiated to obtain the intrinsic hydration and carbonation rate constants. The purpose of this initiative is to have the generic reaction rate data for the PA to minimize the impact from possible changes of MgO suppliers. This phase of the experiment is an on-going effort, and primary data are expected by June, 2001.

Introduction

The primary purpose of MgO backfill at WIPP is to control actinide solubilities by buffering the concentration of carbonate ion (CO_3^{2-}). A secondary benefit of MgO backfill is its capability to react with water to form brucite:

$$MgO + H_2O = Mg(OH)_2 \quad (1)$$

Considering the large mass of MgO to be emplaced at WIPP, a large amount of water can be consumed by this reaction (Bredehoeft and Hall, 1996; Papenguth et al., 1998; Krumhansl et al., 1999, Papenguth and Zhang, 2000).

To develop information for PA to evaluate the effects of MgO hydration, we conducted experiments to test two relevant WIPP conditions. MgO hydration rates under *inundated conditions* were determined from experiments with MgO pellets immersed in solutions. MgO hydration rates under *humid conditions* were determined from experiments with pellets suspended over saturated solutions of various salts selected to provide different vapor pressures. The experiment matrix was structured to provide information to determine the effects of brine chemistry on hydration rates, to help develop a mechanistic

conceptual model of MgO hydration. Consequently, WIPP brine simulants were not used in the experiments. Instead, salt solutions or simple mixtures were used.

Experiments were conducted at a range of temperatures between 30° and 90°C. Elevated temperatures were necessary because rates of reactions are slow, probably requiring decades for complete reaction at room temperature. Results from elevated temperature experiments were used to develop WIPP-relevant hydration rates for WIPP repository temperatures of 27-28°C by using standard geochemical extrapolation techniques.

Experimental Approach

Humid condition experiments were conducted at 30°, 40°, 50°, 60°, 70°, and 90°C by suspending MgO samples over saturated solutions of K_2SO_4, $BaCl_2 \cdot 2H_2O$, NaCl, KI, $NaBr \cdot 2H_2O$, and $MgCl_2 \cdot 6H_2O$. Those solutions provide relative humidity (RH) values of approximately 95, 90, 75, 70, 50, and 35%, respectively, although each varies by several percent over the 30° to 90°C temperature range (Figure 1). This series of experiments consisted of a test matrix of 36 vessels (6 RH conditions × 6 temperature conditions). Solids were sampled periodically from the test vessels. For the humid-conditions experiments, extent of hydration was determined using a thermal-gravimetric technique optimized for this system. A key assumption with that technique is that the only mineralogic change occurring during hydration is brucite formation; formation of carbonate-bearing phases, due to reaction with atmospheric CO_2, must not be appreciable, or extents of hydration may be overestimated. Results from experiments conducted as long as about 643 days were used.

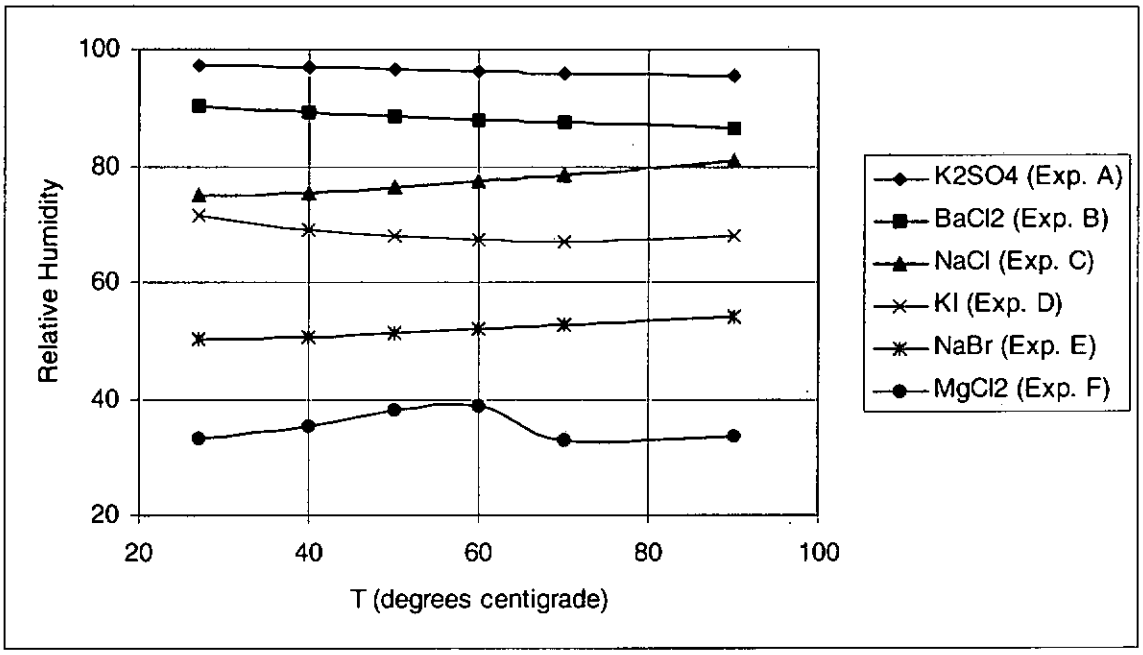

Figure 1. Relative humidity over saturated salt solutions used in humid-condition experiments. Calculated using "React" in The Geochemist's Workbench, with Pitzer equations. Note that for KI, the database contains no iodine-bearing solid phases. Therefore, vapor pressures were determined by continuing to add KI to the system until the calculation became unstable, then slightly reducing the amount added. Values calculated at room temperature were compared to values determined from expressions in the 73rd CRC handbook to ensure that they are reasonable (they closely match in all cases).

Inundated-condition experiments were also conducted at 30°, 40°, 50°, 60°, 70°, and 90°C by immersing MgO samples in solutions of DI water, 0.5M NaCl, 0.5M NaCl + 0.1M $MgCl_2$, 0.5M NaCl + 1M $MgCl_2$, 4M NaCl, 4M NaCl + 0.1M $MgCl_2$, and 4M NaCl + 1M $MgCl_2$. Those solutions provide information on the effect of ionic strength, inert electrolyte (NaCl) concentration, and magnesium concentration on hydration rates. The matrix is sufficiently broad to provide information on rates for actual WIPP brines, which are similar to the 4M + 1M $MgCl_2$ and the 4M NaCl cases, for Salado and Castile Formation brines, respectively. This series of experiments consisted of a test matrix of 42 vessels (7 solutions × 6 temperature conditions). Like the humid-conditions experiments, solids were sampled periodically from the test vessels. For the inundated-condition experiments, extent of hydration was determined using a quantitative powder X-ray diffraction technique. Results from experiments conducted as long as about 225 days were used.

All experiments described here and above were conducted at SNL-ABQ using National Magnesia Chemicals (Moss Landing, California) MAG Plus 00HB 3/8xDown (i.e., 3/8-inch diameter and smaller), which is the material used by Westinghouse Waste Isolation Division (WID) for early phase of waste disposal at WIPP. This product is somewhat

unique, in that it appears macroscopically as pellets, but when viewed with scanning electron microscopy (SEM) is found to consist of MgO crystallites on the order of several micrometers in size. The crystallites are "fused" together to form hard, well-indurated pellets with porosities of about 50 percent. National Magnesia Chemicals MAG Plus 00HB 3/8xDown is no longer available. The replacement material selected by WID may have different hydration characteristics.

Because of existence of the possibility of changes in MgO vendors during the period of repository accepting wastes, a universal conceptual model of hydration and carbonation may be needed and the intrinsic rate constants should be used for performance assessment instead of that obtained from MgO provided by a specific vendor. With this in mind, we initiated a new experiment to determine the hydration rates of a high purity MgO in later June of 2000. This experiment was designed to obtain the base line of MgO hydration rate (in DI water) and then determine the rates in brines under WIPP conditions. After hydration is completed, we intend to do the same for MgO (or brucite) for carbonation rates. A conceptual model of MgO transformation in WIPP repository conditions, therefore, can be established and the parameters can be applied in PA as the base line.

In the first experiment, the intrinsic MgO hydration rate will be determined under controlled conditions with out affect from water diffusion. Obtaining the intrinsic MgO hydration rate will help to separate the effects of hydration and diffusion rates on the overall hydration process of packed MgO in the repository.

The first phase of the experiment is to measure the reaction rate of MgO in deionized water at 60, 75 and 90 °C. Utilization of elevated temperatures is to accelerate the reaction rates and the results from the elevated temperatures will be extrapolated to repository temperatures.

The MgO powder was grounded and passed to a 200 mesh sieve (74 μm in diameter) prior to contacting with water.

The MgO powder (0.20 g) was placed into a test tube containing 20.0 ml of degassed DI water. The test tube was then sealed and continuously agitated in a temperature controlled shaker. Test tubes were removed out of water bath periodically and the sampling intervals depend upon the temperature used. The contents in the test tubs were filtered and dried for XRD analysis. The test tube was removed and stored in a refrigerator if filtration couldn't be immediately conducted.

Quantification of minerals in the samples are conducted with XRD. A correlation between X-ray peak areas and the mole fraction of the two minerals, periclase and brucite, are to be established.

Results to Date

From the available data, the extent of hydration of MgO as a function of time follows an "S"-shaped profile in plots of extent of hydration as a function of reaction time (Figures 2 and 3). In the *first stage* of hydration, hydration proceeds slowly, as brucite nucleation sites develop. After a hydration of several mole percent, the rate of hydration becomes significantly faster, constituting the *second phase*. The *third stage* occurs at high extent of hydration, where the hydration rate diminishes, as the system becomes diffusion limited.

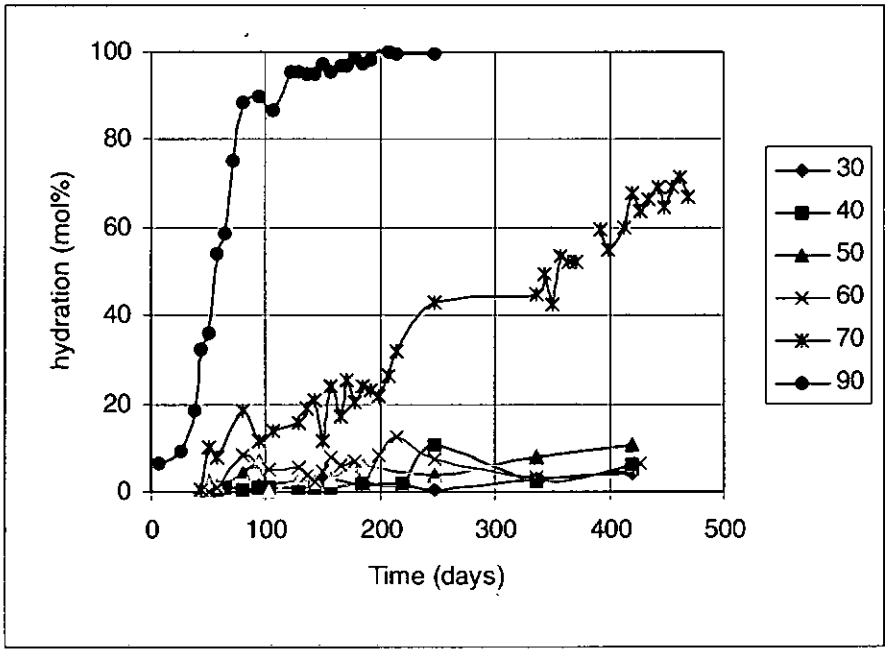

Figure 2. Example of results obtained under humid conditions. This set of experiments was conducted at 30° to 90°C, with MgO suspended over saturated solution of $BaCl_2 \cdot 2H_2O$. As described in the next section, hydration rate constants were obtained from the steep portions of curves from experiments conducted at 50°, 70°, and 90°C.

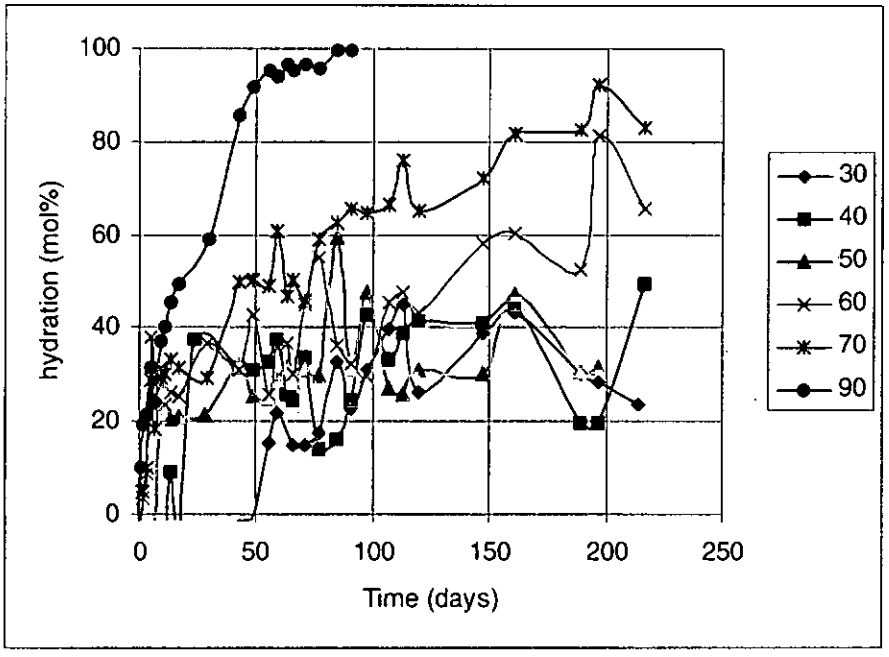

Figure 3. Example of results obtained under inundated conditions. This set of experiments was conducted at 30° to 90°C, with MgO immersed in solution of 4M NaCl + 1.0M $MgCl_2$. As described in the next section, hydration rate constants were obtained from the steep portions of curves from experiments conducted at 50°, 60°, 70°, and 90°C.

Estimation of Rate Constants

Because of limited extents of reaction observed in the lower temperature experiments and in the relatively low vapor pressure experiments, slopes could be determined with confidence from only about one-half of the experiments. We determined MgO hydration-rate constants (k) for ten sets of humid and inundated experiments, designated by rows with "T" or "P" in Tables 1 and 2. For the humid case, rate constants from 13 of 36 experiments were estimated (Table 1). Those 13 rate values are plotted to show the effect of temperature on hydration rate for four relative humidity cases (Figure 4). Note that these data are plotted using the Arrhenius format in the form $\log(k)$ versus reciprocal absolute temperature (Kelvin). For the inundated case, rate constants from 24 of 42 experiments were used (Table 2). Those 24 rate values are plotted to show the effect of temperature on hydration rate for six solution compositions (Figure 5).

Table 1. Experiment matrix and source of data used for parameter development for humid conditions. Usage of data are indicated by letter codes: "P" indicates data used for actual parameter value; "T" indicates data used for trend development; "C" indicates data used independent confirmation; "x" indicates data used to supplement other data to develop mechanistic understanding of hydration.

Experiment	RH Solution	RH*	30°C	40°C	50°C	60°C	70°C	90°C
A	K_2SO_4	97-96	x	x	T	T	T	T
B	$BaCl_2 \cdot 2H_2O$	90-87	x	x	T	x	T	T
C	NaCl	75-81	C	x	P	P	x	P
D	KI	71-68	x	x	T	T	x	T
E	$NaBr \cdot 2H_2O$	50-54	x	x	x	x	x	x
F	$MgCl_2 \cdot 6H_2O$	33-33**	x	x	x	x	x	x

* Estimated relative humidity (RH) values over the temperature range 27 to 90°C.
** RH for $MgCl_2 \cdot 6H_2O$ reaches a high value of about 35% at 60°C.

Table 2. Experiment matrix and source of data used for parameter development for inundated conditions. Refer to data usage letter codes in caption to Table 1.

Experiment	Solution Composition	30°C	40°C	50°C	60°C	70°C	90°C
A	DI water	x	x	T	T	T	T
B	0.5M NaCl	x	x	T	T	T	T
C	0.5M NaCl + 0.1M $MgCl_2$	x	x	T	T	T	T
D	0.5M NaCl + 1.0M $MgCl_2$	x	x	T	T	T	T
E	4M NaCl	x	x	T	T	T	T
F	4M NaCl + 0.1M $MgCl_2$	x	x	x	x	x	x
G	4M NaCl + 1.0M $MgCl_2$	C	x	P	P	P	P

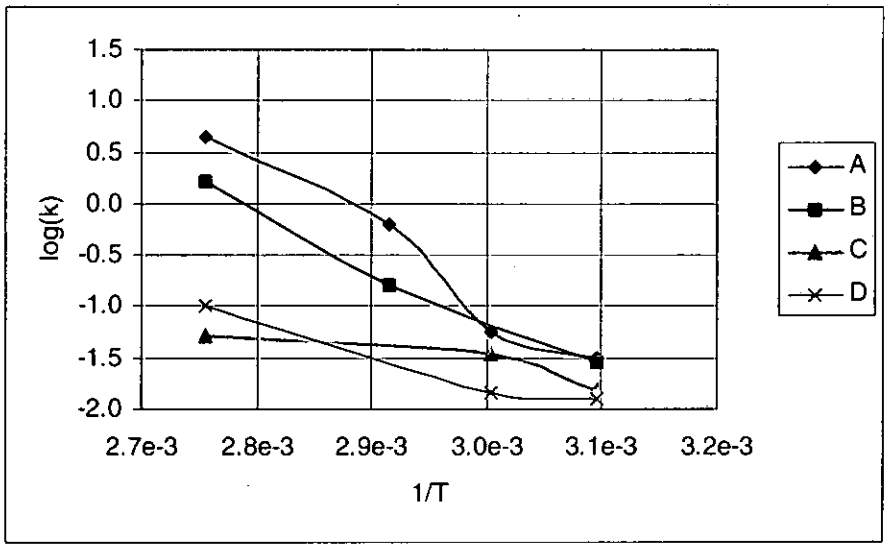

Figure 4. Hydration rates obtained from experiments conducted under humid conditions. From left to right, temperatures correspond to 90°, 70°, 60°, and 50°C, although data were not obtainable for all experiment series (Table 1). Experiment labels correspond to the following saturated solutions: "A" = K_2SO_4; "B" = $BaCl_2 \cdot 2H_2O$; "C" = NaCl; "D" = KI. The experiment most relevant to Salado and Castile Formation brines is experiment "C," conducted over NaCl.

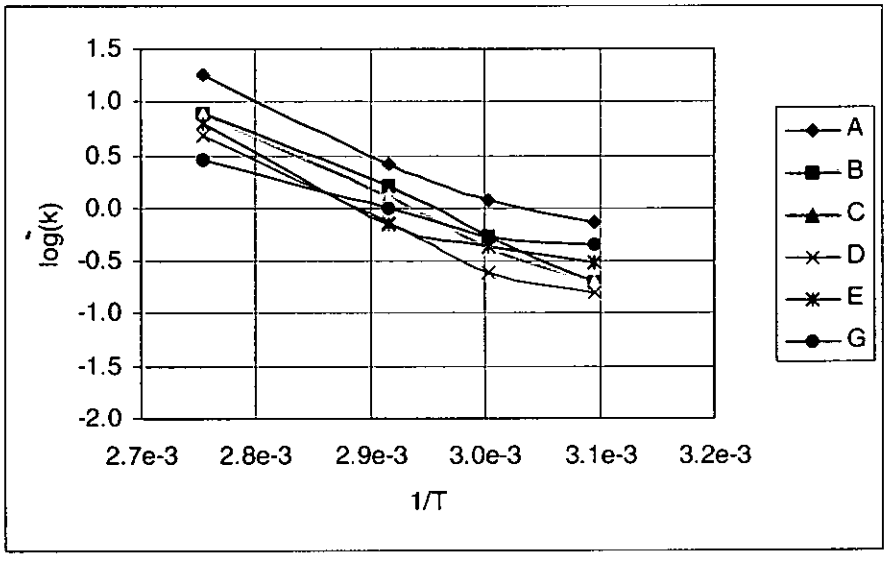

Figure 5. Hydration rates obtained from experiments conducted under inundated conditions. From left to right, temperatures correspond to 90°, 70°, 60°, and 50°C (Table 2). Experiment labels correspond to the following solutions: "A" = DI water; "B" = 0.5M NaCl; "C" = 0.5M NaCl + 0.1M $MgCl_2$; "D" = 0.5M NaCl + 1M $MgCl_2$; "E" = 4M NaCl; "G" = 4M NaCl + 1M $MgCl_2$. Note that hydration rates could not be extracted from experiment "F," which was conducted with 4M

NaCl + 0.1M $MgCl_2$. Salado Formation brine is most similar to "G," 4M NaCl + 1M $MgCl_2$. Castile Formation brine is most similar to "E," 4M NaCl.

We determined MgO hydration rate constants (k) for the ten sets of humid and inundated experiments designated with rows with "T" or "P" in Table 2 and 3.

The Arrhenius equation is used to extrapolate hydration rates obtained from relatively high temperature experiments to the WIPP repository temperature of 27°C. This equation associates the chemical reaction rate constant with the reaction activation energy. This approach has been widely used to calculate the rate constants for variety of chemical reactions. The general form of the equations is:

$$k = e^{-\frac{E_0}{RT}} \tag{2}$$

where k is the reaction rate coefficient, E_0 is the reaction activation energy, T is temperature (in K), and R is the gas constant (8.31451 J mol^{-1} K^{-1}). By plotting experimental data in the form of $Ln(k)$ vs. $1/T$, the hydration activation energy E_0 can be calculated from the slope. Resulting rate constants for the most relevant cases are listed in Table 3. Note that, assuming that those rates are valid throughout MgO hydration (this is not valid because of diffusion limitations at late stages of reaction), MgO would hydrate completely in 31, 11, and 3 years for humid conditions, inundated in Castile Formation brine, and inundated in Salado Formation brine, respectively.

Table 3. Hydration rate constants at 27°C derived from experiments.

Condition	Cross Reference	Rate Constant (mol%/day)
humid, Salado or Castile Fm. Brine	Table 1, Exp. C	0.00884
inundated, Castile Fm. Brine	Table 2, Exp. E	0.0257
inundated, Salado Fm. Brine	Table 2, Exp. G	0.1027

Note that the humid rate is approximately one order-of-magnitude slower than the inundated rates. Also, the inundated rate in Castile Formation brine (actually 4M NaCl) is about a factor of four slower than the rate in Salado Formation brine (actually 4M NaCl + 1.0M $MgCl_2$).

An important assumption in extrapolating results from high temperature is that no phase changes occur. We have no evidence that any such changes occur over the 27° to 90°C temperature range. Moreover, experimental results at 30°C can be used as an independent check to confirm that the extrapolation is reasonable, using the values in Table 3. Extrapolated and observed results match very closely for humid conditions at 425 days (extrapolated = 4 mol%; observed ~ 4 mol%) and for inundated conditions at 225 days (extrapolated = 28 mol%; observed ~ 25 mol%).

The greatest uncertainty in these results stems from the fact that the material tested may not be representative of future MgO backfill material. In the experiments, we used MgO of the same type, grade, and origin of the material initially emplaced in the WIPP (MAG Plus 00HB 3/8xDown, National Magnesia Chemicals). It was unquestionably WIPP-relevant material. That material is no longer available (Papenguth, 1999). Hydration behavior and rates of the two prospective MgO materials (Premier Chemicals, MgO produced at Gabbs, Nevada and Martin Marietta Magnesia Specialties, MagChem MC 10-20) may be different.

The MgO supplied by Martin Marietta Magnesia Specialties (MagChem MC 10-20) is a nature-formed mineral with a high purity. Hydration rate obtained from this material should be used as the base line for hydration of MgOs provided by various vendors and under various conditions.

Experiments conducted under two of three designed temperatures were completed. Totally 76 samples were collected under 60 and 90°C at 1 to 1,600 hours reaction period. Majority of the collected samples have been analyzed with XRD and also the standard periclase and brucite minerals. The quantification data are not available at the time of this report.

References

Bredehoeft, J., and Hall, P., 1996, WIPP with Magnesium Oxide Backfill. Prepared for the New Mexico Attorney General. Version 1.2, October 1996, La Honda, California: The Hydrodynamics Group, 27 pages.

Krumhansl, J.L., Molecke, M.A., Papenguth, H.W., and Brush, L.H., 1999, accepted, A Historical Review of WIPP Backfill Development. Presented at the Seventh International Conference on Radioactive Waste Management and Environmental Remediation (ICEM'99), September 26-30, 1999, Nagoya, Japan. (SAND99-0404C).

Papenguth, H.W., Krumhansl, J.L., Brodsky, N.S., Kelly, J.W., Lucero, D.A., Coffey, D.S., Wang, Y., Anderson, H.L., and Crenshaw, T.B., 1998, Behavior of MgO Backfill in the WIPP Repository. Status Report for Laboratory Research Conducted in FY 1998, Sandia WIPP Central Files, SWCF-A:1.1.01.2.7:DPRP1:NF:TD:QA:MgO Research Technical Studies, WPO#49064.

Papenguth, H.W., 1999, Evaluation of Candidate MgO Materials for use as Backfill at WIPP. SNL Memorandum to M.G. Marietta, dated November 12, 1999.

Papenguth, H.W., and Zhang, P.C., 2000. MgO Hydration Parameters for the Preliminary Panel-Closure Design-Requirements Study. SNL Memorandum to T. Hadgu, dated Nov. 30, 2000.

Schreiber, J.D., 1999, Preliminary Performance Assessment - Magnesium Oxide Hydration Sensitivity Study (M99). Sandia WIPP Central Files, ERMS# 506835.

Schreiber, J.D., and Papenguth, H.W., 1999, New Parameters to be Used in MgO Sensitivity Study (AP-060). SNL Memorandum to L.J. Dotson, dated April 14, 1999.