WPO48997

Sandia National Laboratories
Operated for the U.S. Department of Energy by
Sandia Corporation
Albuquerque, New Mexico 87185

date: December 10, 1997

to: E. James Nowak, MS1320 (6831)

Jim L. Krumhansl

from: Jim L. Krumhansl, MS0750 (6118) John W. Kelly, MS1320 (6832)
Hans W. Papenguth, MS1320 (6832) and R. Vann Bynum, MS1320 (6831)
Hans W. Papenguth

subject: MgO Acceptance Criteria

Introduction

The use of MgO as a backfill in the Waste Isolation Pilot Plant (WIPP) has received approval from the Conceptual Model Peer Review Panel (CMPRP) based on the outcome of laboratory tests performed over the last 18 months. In order for the MgO backfill to perform as we have publicly stated, commercially acquired MgO backfill material must meet several criteria. First, the MgO material must have sufficiently high bulk density so that enough backfill can be physically emplaced in the repository. Second, the MgO backfill must have sufficient purity so that enough MgO reactant is present in the repository to react with CO_2 gas generated. Third, the MgO material must react with CO_2 at a sufficiently high rate. We have been requested by Mr. Don Allen (Westinghouse Waste Isolation Division) to advise him on a specification for that third point, so that a specification on CO_2 reactivity can be included as part of the technical purchasing requirements.

To develop a reactivity specification, we surveyed the MgO industry to gain an understanding of standard reactivity tests. Building on these findings, a procedure was developed and then calibrated with the samples of the same MgO materials used in the past 18 months of testing and presented to the CMPRP in May 1997. This memorandum documents the outcome of this calibration activity and presents the formal test procedures. In summary, the recommended technical purchasing requirement is to demonstrate at least a 20°C peak temperature rise after mixing a specified mass of MgO pellets with diluted phosphoric acid in a stirred glass beaker.

Test Rationale

Three types of MgO are produced commercially by varying process parameters, and especially temperature. Light-burned MgO, hard-burned MgO, and dead-burned MgO are produced at increasing kiln temperatures for different commercial applications. As process temperature is increased, the resulting MgO becomes denser and harder, leading to decreased reaction rates with water and carbon dioxide, together with increased bulk density. For the WIPP, the most acceptable material is the hard-burned MgO, because its bulk density is sufficient to enable a sufficient amount of MgO to be emplaced in the repository, yet it provides a sufficient rate of reaction to take up carbon dioxide.

Different test procedures are used to evaluate the reactivities of MgO produced at different temperatures. For the light-burned MgO, a weak acid is used to test reactivity. For the hard-burned MgO, however, the time required to complete such a test on non-pulverized material is disruptive to the manufacturing process. Moreover, pulverizing hard-burned MgO to conduct a reactivity test with weak acids is not desirable for WIPP material because it is the pellet form which will be emplaced in the WIPP. A more desirable test used in the MgO industry on hard-burned material is to measure the temperature rise stemming from reaction on MgO pellets with phosphoric acid. That test is recommended herein.

In the WIPP, the motivation for emplacing MgO is to decrease actinide solubilities by significantly decreasing the carbonate ion concentration through the precipitation of magnesium carbonate mineral phases and controlling the pH to a region of low actinide solubility. In an aqueous environment, MgO is believed to undergo a series of reactions preceding its reaction with the carbonate ion: (1) hydration of MgO to form $Mg(OH)_2$, or brucite; (2) dissolution of $Mg(OH)_2$; and (3) reaction of the dissolved Mg ions with carbonate ions. The reaction step that is most critical for the WIPP is the third step, the carbonation reaction. It would be most relevant to the WIPP, to design a test based on the carbonation reaction to use as a reactivity criterion for WIPP MgO. However, as was learned from the experiments supporting the CMPRP, those tests are quite slow, requiring months rather than minutes. An alternative test is to measure the hydration reaction, which can be done much more quickly. To provide the most relevant test criterion for the WIPP, however, requires that the hydration reaction must be the rate-limiting step. It is likely that the hydration reaction is the rate-limiting reaction because we did not observe a brucite layer forming at the surface of the MgO pellets in the CMPRP experiments. In any case, the carbonation reaction [i.e., the combination of $Mg^{2+}_{(aq)}$ and $CO_3^{2-}{}_{(aq)}$] is irrespective of the source of the $Mg^{2+}_{(aq)}$ or of the $CO_3^{2-}{}_{(aq)}$ ions, but is likely to be dependent on the concentration of the ions. Therefore, measuring the rate at which the reactant is supplied to the system is a reasonable acceptance test.

Calibration of MgO Reactivity

In our presentation to the CMPRP in May 1997, we utilized a representative MgO backfill material. That material, known in the industry as a hard-burn material, was acquired from National Magnesia (Moss Landing, California) and is designated as "MAG Plus 00HB Kiln Run 3/8xDown". It contains a range of sizes of MgO pellets composed of 1-2 micrometer MgO crystallites fused together in rough spheres with about 50% porosity. For the experiments conducted in support of the presentation to the CMPRP, we utilized several sieve cuts extracted from the material acquired from National Magnesia: Pellets with diameters from 0.5 to 1 mm, and pellets with diameters from 2 to 4 mm. Based on experiments conducted with those two sieve fractions, we demonstrated to the CMPRP that the MgO in either size fraction was sufficiently reactive with CO_2 to sufficiently reduce the concentration of carbonate ion in the repository. Because that material in those particular sieve fractions was demonstrated to produce acceptable results for the WIPP, we used portions of that same material to establish an acceptance criterion for reactivity.

The method used to evaluate MgO reactivity is outlined in detail below in the following section. Briefly, 300 mL of 20% concentrated phosphoric acid is mixed with 18 g of MgO pellets. The mixture is stirred using a magnetic stirrer and the temperature rise is noted over a 40-minute time period.

Our initial tests were designed to evaluate the relative reactivities of different size fractions. Tests were conducted with the "as received" samples of MAG Plus 00HB Kiln Run 3/8xDown and the 2-4 mm sieve fraction demonstrated that the bulk material, with the full range of pellet diameters, resulted in a slightly greater temperature rise than the relatively coarse pellets in the 2-4 mm diameter range. Subsequent tests were conducted with the 2-4 sieve fraction, because that material was shown to provide acceptable reactivities to the CMPRP. Test results of eight replicate experiments are summarized in Table 1 and a full record of the data is presented in appendix A.

The recorded maximum temperature rises ranged from 22.0 to 23.4°C, with a mean and standard deviation of 22.9 and 0.52°C, respectively. The deviation in the eight experiments is probably related to differences in stir rates and beaker dimensions. Given that a temperature rise test may be affected by differences in test geometry and stir rates that a supplier might select, it seems reasonable to stipulate that any successful candidate material should result in at least a 20°C temperature rise following the test procedures described below.

Table 1
Temperature Increases from MgO - Phosphoric Acid Interactions

Run number	Initial Temperature (°C)	Maximum Temperature (°C)	Temperature Rise (°C)	Time to Max. Temperature (min)
1	25.0	48.1	23.1	34
2	25.0	48.4	23.4	33
3	25.0	47.8	22.8	31
4	25.0	48.1	23.1	34
5	25.0	48.2	23.2	32
6	25.0	47.0	22.0	36
7	25.0	47.2	22.2	34
8	25.0	48.3	23.3	34
mean		*47.9*	*22.9*	*33.5*
std. dev.		*0.52*	*0.52*	*1.5*

Detailed MgO Acceptance Test Procedure

Equipment Needed:

1. A drying oven able to sustain a temperature of approximately 100°C.

2. An NIST-traceable partial-immersion thermometer (or electronic equivalent) able to measure temperatures from 20°C to at least 55°C, with increments of 0.1°C, for measuring MgO solution temperature rise. A second NIST-traceable full-immersion thermometer (or electronic equivalent) with increments of 1°C for measuring room air temperature. A third NIST-traceable full- or partial-immersion thermometer, depending on oven configuration (or electronic equivalent) with increments of 1°C for measuring oven air temperature.

3. A means of supporting the thermometer in a 400 mL beaker so that the fluid level will be at the immersion mark on the thermometer.

4. An analytic balance accurate to within ± 0.01 g, calibrated with NIST traceable standards.

5. A plastic-coated magnetic stir bar 1-3 inches in length and a stir plate to drive it.

6. A source of deionized water.

7. A source of ACS Reagent Grade 85% phosphoric acid.

8. 400-mL glass beakers.

9. Stopwatch (optional).

10. Scientific notebook (or suitable alternative which provides permanent archiving of recorded information).

Procedure:

1. Mix one liter of 20% ± 0.1% phosphoric acid (by weight) from deionized water and reagent grade 85% phosphoric acid. After mixing, allow the temperature to return to within 3°C of room temperature (20 to 30°C).

2. Dry at least 60 g of as-received MgO pellets. The sample should be either dried overnight or until it is verified that the center of the MgO mass has been at approximately 100°C for at least half an hour. Verify the drying temperatures using an NIST-traceable thermometer. Pellets should be at room temperature (20 to 30°C) before being tested.

3. Weigh 300 ± 0.5 g of 20% phosphoric acid into a glass 400 mL beaker. Record the weight in the scientific notebook.

4. Place a piece of insulating cardboard on the stir plate and then place the beaker on the cardboard. Put a stir bar in the solution and initiate stirring so that a dimple about 1-2 cm deep forms in the center of the beaker.

5. Put the thermometer in the phosphoric acid to the immersion line and fix it in this position so that it cannot change during the remainder of the test.

6. Note the temperature and do not proceed until it has stabilized (e.g., does not change by more than 1°C in two minutes). Record the temperature once it has stabilized.

7. Weigh 18.00 ± 0.1 g of pre-dried as-received MgO pellets. Record the weight in the scientific notebook (or suitable alternative).

8. Add the MgO to the phosphoric acid and note the starting time of the experiment to the nearest second. Alternatively, start the stopwatch.

9. At one-minute intervals, record the temperature in the scientific notebook (or suitable alternative). Continue taking temperature measurements until the temperature starts to fall (about 30-35 minutes).

10. Perform three replicates of this procedure.

Our recommendation is that to be acceptable for the WIPP, the average maximum temperature rise observed in the three replicates must be at least 20°C.

Copy to:

WWID	D. Allen
MS 0750	J. L. Krumhansl, 6115
MS 0750	J. W. Kelly, 6832
MS 0750	H. R. Westrich, 6118
MS 1320	H. W. Papenguth, 6832
MS 1320	R.V. Bynum, 6831
MS 1322	D. S. Coffey, 6811
MS 1340	J. T. Holmes, 6832

SWCF-A:1.1.09.1.1,QA:TD:DPRP1:NF:CHEMISTRY:MGO PHYSICOCHEMICAL PROCESSES

2-4mm MgO Pellets in 20% H3PO4

Elapsed Time (minutes)	Temp(C)Exp.#1	Temp(C)Exp.#2	Temp(C)Exp.#3	Temp(C)Exp.#4	Temp(C)Exp.#5	Temp(C)Exp.#6	Temp(C)Exp.#7	Temp(C)Exp.#8	
0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	
1	25.7	25.7	25.7	25.5	25.6	25.5	25.6	25.6	
2	26.2	26.4	26.5	26.2	26.3	26.1	26.1	26.3	
3	26.7	27.0	27.2	26.7	26.8	26.6	26.5	26.9	
4	27.3	27.5	27.8	27.2	27.4	27.2	27.0	27.5	
5	27.8	28.0	28.4	27.6	27.8	27.8	27.4	28.1	
6	28.4	28.5	28.9	28.0	28.2	28.3	27.9	28.8	
7	29.0	29.1	29.4	28.5	28.7	28.9	28.3	29.5	
8	29.5	29.7	30.0	29.0	29.2	29.4	28.9	30.2	
9	30.1	30.3	30.6	29.7	30.0	29.9	29.4	30.9	
10	30.8	31.0	31.3	30.3	30.6	30.5	29.9	31.6	
11	31.4	31.8	31.9	30.9	31.3	31.2	30.4	32.2	
12	32.2	32.5	32.5	31.6	32.0	31.9	31.0	33.0	
13	33.0	33.0	33.2	32.3	32.7	32.5	31.8	33.8	
14	33.8	33.7	33.9	33.0	33.4	33.3	32.5	34.8	
15	34.7	34.6	34.8	33.7	34.1	34.0	33.2	35.7	
16	35.5	35.6	35.9	34.5	34.9	34.7	34.0	36.6	
17	36.6	36.7	36.9	35.6	36.0	35.5	34.9	37.7	
18	37.7	37.9	37.8	36.6	37.0	36.4	35.9	38.5	
19	38.7	39.2	38.8	37.7	38.1	37.2	36.9	39.5	
20	39.7	40.2	39.9	38.9	39.3	38.0	37.9	40.6	
21	40.7	41.4	41.0	40.1	40.4	38.8	39.0	41.7	
22	41.8	42.5	42.1	41.1	41.4	39.6	40.1	42.8	
23	42.8	43.6	43.2	42.2	42.5	40.5	41.2	43.8	
24	43.6	44.5	44.1	43.2	43.5	41.4	42.2	44.6	
25	44.4	45.3	44.9	44.2	44.5	42.1	43.1	45.3	
26	45.1	46.0	45.6	45.1	45.4	42.7	43.9	46.0	
27	45.8	46.7	46.2	45.9	46.2	43.4	44.5	46.6	
28	46.3	47.3	46.7	46.5	46.8	44.1	45.1	47.1	
29	46.8	47.7	47.1	47.0	47.3	44.6	45.6	47.5	
30	47.2	48.0	47.7	47.4	47.7	45.0	46.0	47.9	
31	47.5	48.2	47.8	47.7	48.0	45.5	46.4	48.1	
32	47.7	48.3	47.8	47.9	48.2	46.0	46.8	48.2	
33	47.9	48.4	47.7	48.0	48.2	46.4	47.1	48.2	
34	48.0	48.4	47.7	48.1	48.2	46.7	47.2	48.3	
35	48.1	48.4	47.6	48.1	48.2	46.9	47.2	48.3	
36	48.1	48.3	47.6	48.1	48.2	47.0	47.2	48.2	
37	48.0	48.2	47.5	48.1	48.1	47.0	47.2	48.2	
38	47.9	48.1		48.0		47.0	47.1		
42	47.3								
47	46.4								
50	45.8								
max temp	48.1	48.4	47.8	48.1	48.2	47.0	47.2	48.3	
max temp time initial	35.0	33.0	31.0	34.0	32.0	36.0	34.0	34.0	
max temp time final	36.0	35.0	34.0	37.0	36.0	38.0	37.0	35.0	
std dev max temp	47.9								
std dev max temp	0.5								

2-4mm MgO Pellets in 20% H3PO4