




Sandia National Laboratories

Operated for the U.S. Department of Energy by
Sandia Corporation

Date: 8/28/2009

To: SNL Records Center
Technical Review: Greg Roselle
QA Review: Steve Davis

Martin Nemer
Sandia National Laboratories
Carlsbad Programs Group
4100 National Parks Highway
Carlsbad, NM 88220

From: Martin Nemer 

Subject: Adequacy of MgO reactivity test (EPA re-certification question 1-C-2) and interpreting MgO reactivity test results above 96 mol %

On February 11th 2008, EPA issued a letter to DOE approving the planned change request (PCR) for reducing the MgO excess factor from 1.67 to 1.2 times the amount of emplaced carbon. In the letter the EPA stipulated two conditions, one of which was "*DOE must annually verify the reactivity of MgO and ensure that it is maintained at 96% as assumed in DOE's supporting documentation*" (Reyes, 2008). Sandia National Laboratories, Carlsbad Programs Group, (Sandia) developed a methodology for meeting the EPA's requirement that could be performed by a commercial laboratory within a reasonable cost and turn-around time.

Sandia originally developed a methodology for testing the mole percent of reactive constituents in Martin Marietta (MM) MgO in order to support the DOE's PCR on reducing the MgO excess factor from 1.67 to 1.2 (Moody, 2006). As part of the PCR, Sandia submitted a report to EPA titled "Analysis of Martin Marietta MagChem 10 WTS-60 MgO" (Deng et al., 2006), which explained how the MM MgO was tested and our assumptions used in stating that 96 mol % of MM MgO was reactive periclase plus lime. EPA responded "*DOE provided information on the potential reactivity of the MgO at 96% from the current supplier. EPA found the information reasonable, and requires DOE to ensure that the MgO reactivity remains at 96% by regularly testing MgO samples*" (Attachment A of Reyes, 2008). Additionally, in section 3.1 of EPA's report titled "Review of MgO-Related Uncertainties in the Waste Isolation Pilot Plant" (Attachment B of Reyes, 2008), EPA stated "*Deng et al. (2006a) used the chemical analysis results, the LOI, and thermogravimetric results that indicated the weights of water in the hydrated WTS-60 MgO, and reasonable assumptions regarding the nonreactive phases in the MgO to calculate the amounts of reactive periclase and lime.*"

Given EPA's acceptance of the methodology used in the PCR, Sandia continued to refine the testing methodology in order to provide Washington TRU Solutions (WTS) with a procedure that could be performed by a commercial laboratory at a reasonable cost and turn-around time. A procedure was delivered to WTS on November 14th 2008 (Nemer, 2008). The procedure has been extensively tested on 46 shipments of MM MgO. The resulting mol % of periclase + lime was found to be 98 ± 1 mol %. The results can be found in Deng and Nemer (2009).

WIPP: 1.4.2.5:TD:QA-L: 543889 ^{RECERT: gcl 912109}

Information Only

The main technical difference between the original procedure submitted in the PCR and the current procedure (Nemer, 2008) is the hydration temperature. The hydration temperature is the temperature at which the MgO sample is hydrated in de-ionized (DI) water to form brucite. In the original procedure submitted in the PCR the MgO was hydrated at 90 °C for at least three days (Deng et al., 2006. section 3.2). In the current procedure (Nemer, 2008) the MgO is hydrated at ≈ 250 °C in DI water for two hours. The hydration temperature was increased in order to reduce the hydration time, to allow a commercial laboratory to test the MgO reactivity in a reasonable amount of time.

Sandia has solid evidence showing that the increase in hydration temperature has improved the accuracy of the test, without sacrificing precision or introducing appreciable experimental artifacts. We have learned that the MM MgO probably did not completely hydrate when placed in DI water at 90 °C for 3 days. Because the MM MgO didn't completely hydrate, the mole percent periclase + lime results submitted as part of the PCR are lower than results obtained from the current test procedure (on different lots), which implies that the results submitted in the PCR are conservative. X-ray diffraction (XRD) analysis of a sample that was hydrated at 90 °C for 7 days is shown in Figure 1, which still shows the presence of a small periclase peak (i.e. periclase that did not completely hydrate within 7 days). Figure 2 shows the same lot after hydration for 12 days at 90 °C, no periclase peak is visible. When the MgO was hydrated at 235 °C for 4 hours in a Parr acid-digestion bomb, the MgO completely hydrated as shown in Figure 3. Loss-on-ignition (LOI) testing on this lot was performed for two different lengths of hydration times at 90 °C and at 235 °C for 4 hours. The results are shown in Table 1. Based on the results in Table 1, we believe the increase in temperature to the current 250 °C has accomplished an equivalent reaction as heating at 90 °C for sufficiently long times. Thus we believe that increasing the hydration temperature has increased the accuracy of the test procedure.

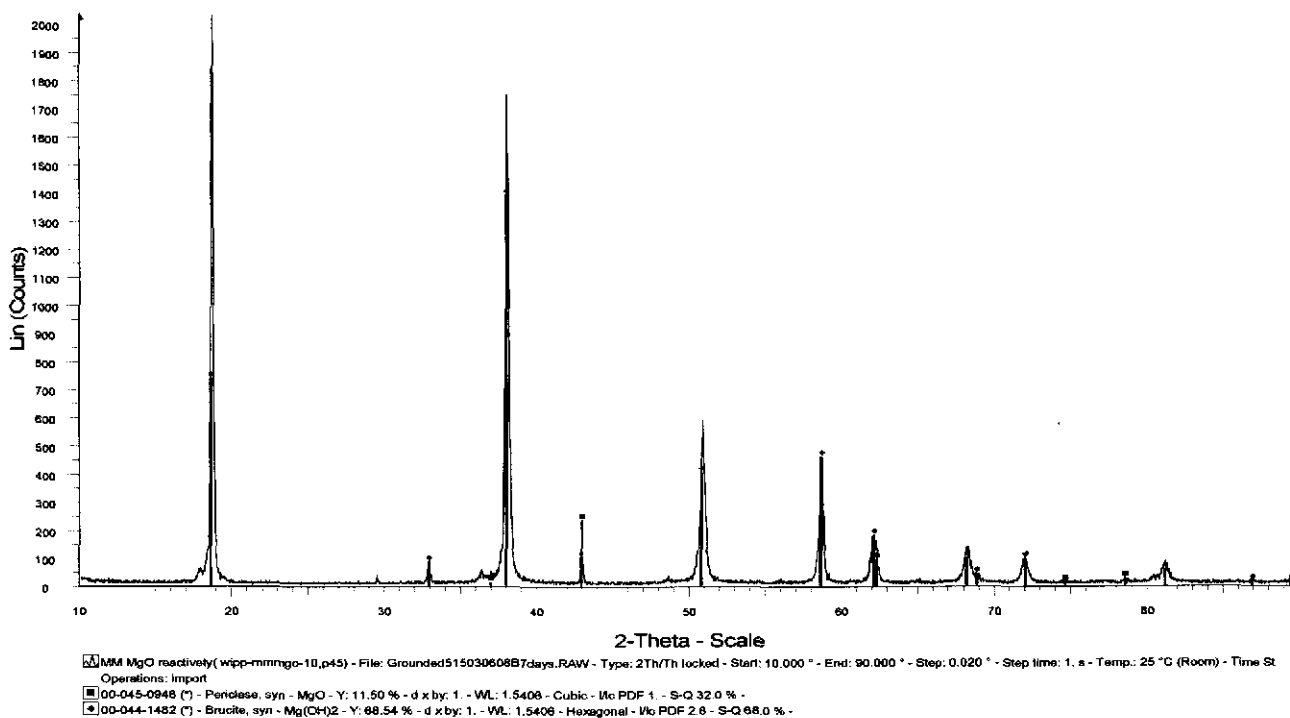


Figure 1. XRD of MM MgO, shipment 515030608, after hydration in DI water at 90 °C for 7 days. A small periclase peak is still visible at $2\theta \approx 43$ °. This XRD can be found in supplemental binder MM MgO-XRD-1 under the tab MM MgO Reactivity. This sample is described in scientific notebook WIPP-MM MgO-10 on pg. 45.

WIPP: 1.4.2.5:TD:QA-L: 543889

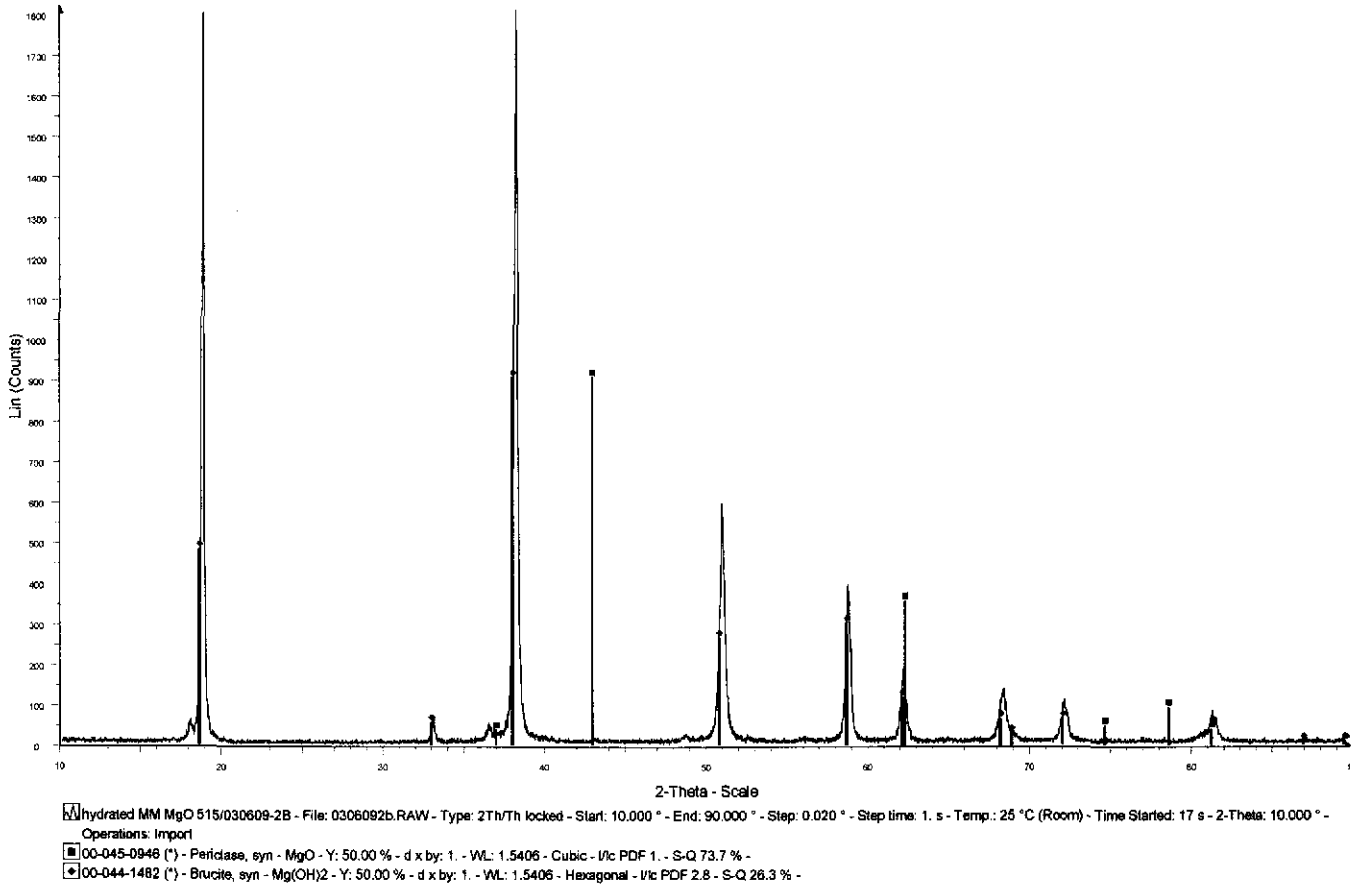


Figure 2. XRD of MM MgO, shipment 515030608, after hydration in DI water at 90 °C for 12 days. No periclase peak is visible at $2\theta = 43^\circ$. This XRD can be found in supplemental binder MM MgO-XRD-1 under the tab MM MgO Reactivity. This sample is described in scientific notebook WIPP-MM MgO-10 on pg. 36.

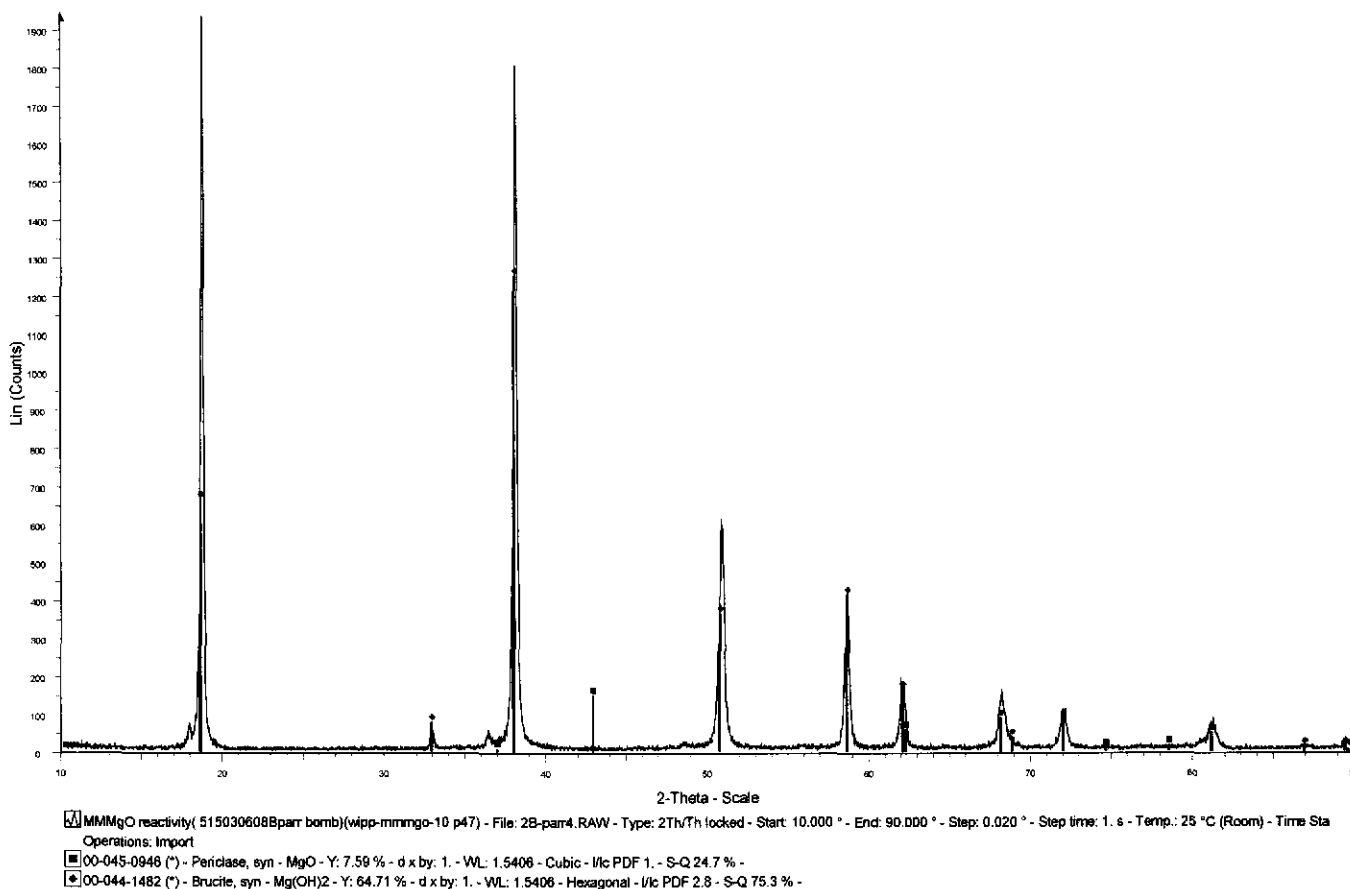


Figure 3. XRD of MM MgO, shipment 515030608, after hydration in DI water at 235 °C for 4 hours. No periclase peak is visible at $2\theta = 43^\circ$. This XRD can be found in supplemental binder MM MgO-XRD-1 under the tab MM MgO Reactivity. This sample is described in scientific notebook WIPP-MM MgO-10 on pg. 47.

Table 1. Mole percentage of reactive periclase + lime for shipment 515030608 hydrated at 90 °C and 235 °C. The data and calculations for this table can be found in Appendix A.

Hydration Time	Temp (°C)	Periclase + lime (mol %) ¹	Periclase + lime (wt % inferred by LOI) ¹	Periclase + lime (wt % XRF) ²
7 days	90	95.8 ± 0.1	95.6 ± 0.1	99.3 ± 0.01
53 days	90	99.4 ± 0.1	99.2 ± 0.1	99.3 ± 0.01
4 hours	235	98.9 ± 0.04	98.6 ± 0.02	99.3 ± 0.01

1. Calculated using the LOI results.
2. X-ray fluorescence (XRF) results from the Analysis of Shipment from Martin Marietta.

EPA in comment 1-C-2 of the first set of CRA-2009 recertification questions wrote “*DOE should provide an explanation of whether the current reactivity test would reliably detect MgO with insufficient reactive periclase plus lime (i.e. less than 96 ± 2 mole %)*” (Cotsworth, 2009). To answer this question SNL tested 6 samples of known composition using the new test procedure. Among the 6 samples, five of them are tested blind and 4 of them were also tested non blind. In each sample, a weighed portion of Alfa Aesar Puratonic MgO (99.998 wt % metals basis) was mixed with a weighed portion of Acros Al₂O₃ (99.99 wt % metals basis). The Puratonic MgO was the reactive periclase ingredient and the Al₂O₃ was un-reactive filler. The results of the blind testing are shown in the top portion of Table 2. Three replicates were run for each of the 5 blind samples. Table 2 also shows results on three non-blind samples and on the Puratonic MgO. Two or four replicates were run for each of these samples.

Looking at Table 2, one should compare the columns labeled MgO (wt % by mass) and Periclase (wt %, inferred). The column labeled MgO wt % (by mass) is the weight percent of MgO known from the masses of MgO and Al₂O₃ weighed into each sample bottle. The column labeled periclase wt % (inferred) is the amount of periclase calculated from the test procedure spreadsheet (see Appendix A). Comparing these two columns, the results show that errors are at most one percent without a clear positive or negative bias. In the blind testing performed, two of the five samples had a mole percent less than 94 mol %, thus satisfying EPA’s request to show that the test can discriminate lots that are below 96 ± 2 mol %.

Given the evidence of the preceding paragraphs Sandia strongly believes that the current test procedure provides an accurate assessment to 2 significant figures of the reactivity of Martin Marietta MgO. We believe the current procedure is adequate for testing Martin Marietta MgO.

Table 2. Results of the blind testing performed on the new MgO test procedure. The data and calculations for this table are given in Appendix A.

Sample	MgO ¹ (wt % by mass)	Periclase ² (wt %, inferred by LOI)	Periclase ³ (mol %)
Blind MgO 1	90.00	91.0 ± 0.2	92.7 ± 0.2
Blind MgO 2	99.00	99.4 ± 0.2	99.5 ± 0.2
Blind MgO 3	86.16	86.7 ± 0.3	89.1 ± 0.3
Blind MgO 4	97.00	97.1 ± 0.4	97.7 ± 0.4
Blind MgO 5	94.89	94.7 ± 0.3	95.8 ± 0.3
Previous non-blind			
Puratonic	99.998	99.1 ± 0.2	99.1 ± 0.2
1 wt % Al ₂ O ₃ (Blind MgO 2)	99.00	99.3 ± 0.3	99.4 ± 0.3
3 wt % Al ₂ O ₃ (Blind MgO 4)	97.00	97.3 ± 0.3	97.9 ± 0.4
13 wt % Al ₂ O ₃ (Blind MgO 3)	86.16	85.8 ± 0.4	88.4 ± 0.6

1. Weight percent of MgO in the sample known from the amount of Alfa Aesar Puratonic MgO weighed into the sample bottle.
2. Weight percent of periclase in the sample, calculated from the LOI results.
3. Mole percent of periclase in the sample, calculation from the LOI results.

References

- Cotsworth, E. 2009. "EPA CRA-2009 First Set of Completeness Comments." Letter to Dr. Moody, May 21st, 2009. Washington, DC: Environmental Protection Agency. ERMS 551444.
- Deng, H., S. Johnsen, Y. Xiong, G. T. Roselle and M. Nemer. 2006. "Analysis of Martin Marietta MagChem 10 WTS-60 MgO." Analysis, November 14, 2006. Carlsbad, NM: Sandia National Laboratories. ERMS 544712.
- Deng, H. and M. Nemer. 2009. "Results of Martin Marietta MgO testing from February 2008 to February 2009." Routine Calc. Memo, March 3rd, 2008. Carlsbad, NM: Sandia National Laboratories. ERMS.
- Moody, D. C. 2006. "Letter to E. A. Cotsworth Requesting a Reduction in the MgO Excess Factor from 1.67 to 1.2." April 10, 2006. Carlsbad, NM: DOE, CBFO. ERMS 543262.
- Nemer, M. B. 2008. "Procedure for Testing For the Periclase Plus Lime Content in Martin Marietta MgO, Rev. 1." Carlsbad, NM: Sandia National Laboratories. ERMS 550455.
- Reyes, J. 2008. "EPA 1.67 to 1.20 Excess Factor Change Approval Letter." Memo from Juan Reyes to Dr. David C. Moody, February 11, 2008. Washington, DC: Environmental Protection Agency. ERMS 549331.

Appendix A

The attached spreadsheet contains the data and results presented in Table 1 and Table 2. The methodology in the attached spreadsheets has been reviewed and documented previously (Nemer, 2008), for Martin-Marietta-MgO samples. We have modified the spreadsheets slightly as follows:

- 1) In cell B18 of each of the test-procedure worksheets used for the blind samples we have equated the amount of Al_2O_3 with the difference between 100 % and cell B50. That is, the un-reactive remainder (wt %) in the sample. This cell then impacts the mol % of periclase + lime. This may seem like circular logic, especially given that we know the weight percent of Al_2O_3 from the mass that was weighed into the sample. However it is useful to calculate this number here and compare with the known (by mass) weight percent of Al_2O_3 given in column D. Furthermore in the blind testing exercise we are comparing weight percents and not mole percent.
- 2) Cell B20 calculates the weight percent of MgO in the same manner as described in 1) above for Al_2O_3
- 3) For the materials used in the blind test experiments, the amount of impurities in the starting materials is below the level that affects the output of the spreadsheet (i.e. 3 significant figures). We cannot put zero's in for the standard deviations as this would result in dividing by zero. Thus for convenience we arbitrarily assign a value of 10^{-10} wt % for both the wt % and the uncertainty in the amounts of CaO, SiO_2 , and Fe_2O_3 . We also arbitrarily assign a value of 10^{-10} for the uncertainty in the weight percent of Al_2O_3 , although one could have equivalently assigned a value of $0.1 \text{ mg}/10 \text{ g} \sim 10^{-5}$ wt % based on the Mettler AT261 balance resolution of 0.1 mg and the original sample size of $\sim 10 \text{ g}$. Either value, 10^{-10} or 10^{-5} , is too small to be relevant for these calculations.
- 4) The worksheet titled "Summary of Blind" calculates the difference between the MgO wt % known from the mass of MgO and Al_2O_3 weighed into each sample bottle and the Periclase wt % calculated from the spreadsheets. This difference is then plotted in the "Chart of Summary" worksheet. This isn't presented in the memo but may be of interest.

Additional notes on the blind samples test: (A) Two student interns prepared two samples to be tested blind and re-labeled three previously made samples such that none of the labels on the sample bottles were indicative of their contents. The interns kept the information on the contents of the 5 samples from the staff until the test procedure was completed; (B) the three Sandia National Laboratories personnel who had performed the MgO testing throughout 2008 performed the Nemer (2008) test procedure on the 5 blind samples.