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Sandia National Laboratories
Waste Isolation Pilot Plant

Analysis of Martin Marietta MagChem 10 WTS-60 MgO

Haoran Deng,¹ Shelly Johnsen,¹ Yongliang Xiong,¹ Gregory T. Roselle,¹ and Martin Nemer²

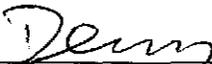
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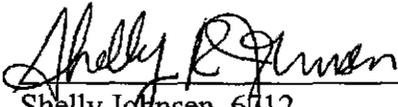
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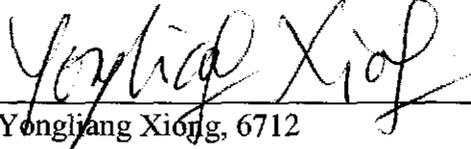
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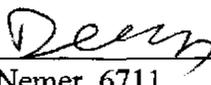
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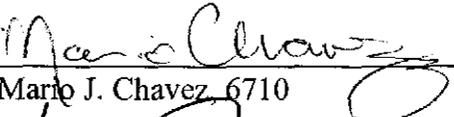
Author:  11-14-06
Shelly Johnson, 6712 Date

Author:  11-14-06
Yongjiang Xiong, 6712 Date

Author:  11/14/2006
Gregory T. Roselle, 6711 Date

Author:  11/14/06
Martin Nemer, 6711 Date

Technical Reviewer:  11/14/06
Daniel Clayton, 6712 Date

QA Reviewer:  11/14/2006
Mario J. Chavez, 6710 Date

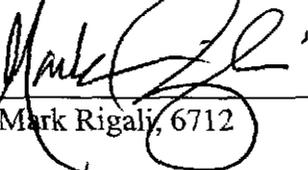
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Mark Rigali, 6712 Date

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1 INTRODUCTION

On April 10, 2006, a planned change request was submitted to the U. S. Environmental Protection Agency (EPA) requesting approval to “emplace 1.2 moles of magnesium oxide (MgO) for every mole of consumable-organic carbon contained in the Waste Isolation Pilot Plant (WIPP)” (Moody, 2006). Currently the EPA requires the emplacement of 1.67 moles of MgO for every mole of consumable carbon in the emplaced cellulose, plastic, and rubber (CPR) materials. In response, EPA wrote a letter (Gitlin, 2006) asking the U. S. Department of Energy (DOE) to address the “uncertainties related to MgO effectiveness, the size of the uncertainties, and the potential impact of the uncertainties on long-term performance.” The objective of this report is to address uncertainties concerning the amount of periclase plus lime in Martin Marietta (MM) MgO. The total mole percent of periclase plus lime in Martin Marietta MagChem 10 WTS-60 is determined to be $96\% \pm 2\%$ (one sigma), see Subsection 4.2. This number is very close to that obtained by Wall (2005), who found $96\% \pm 2.5\%$ (one sigma) periclase in Martin Marietta MagChem 10 WTS-30; Wall’s analysis was performed on a different lot, see Subsection 4.2. The results obtained herein use a number of conservative assumptions on the identity of the remaining unreactive mole percent, which are described in Subsection 4.2 and throughout.

2 NOMENCLATURE

In this memorandum, unless stated otherwise "MgO" refers to the bulk, granular material being emplaced in the WIPP to serve as the engineered barrier. MgO comprises of mostly periclase (pure, crystalline MgO – the main reactive constituent of the engineered barrier), which will consume CO₂ and water (H₂O) and form brucite (Mg(OH)₂), hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O), and – eventually - magnesite (MgCO₃). The terms "periclase," "brucite," "hydromagnesite," and "magnesite" are mineral names and should, therefore, be restricted to naturally occurring forms of materials that meet all other requirements of the definition of a mineral (see for example, Bates and Jackson, 1984). However, mineral names are used herein for convenience.

3 DATA USED IN THIS ANALYSIS

Herein we list the data and source used below in Section 4 to calculate the mole percent of periclase and lime in the MgO. Copies of spec sheets, and spreadsheets used in this analysis are located on an accompanying CD. Original (or copies) of the scientific notebooks and binders are located in the SNL records center.

Samples of Martin Marietta MagChem 10 WTS-60 MgO were analyzed by SNL from a single lot (shipment), listed as SL2980076; all analyses were performed under test plan TP 06-03, Rev. 0.

The manufacturer's analysis sheet may be found in Martin Marietta Magnesia Specialties Inc., (2006a). The relevant pieces of information from the analysis sheet are listed below in Table 1 .

Table 1. Data from MM certificate of Analysis for lot SL2980076.

Product:	MagChem 10 WTS 60
Plant Shipping No.:	SL2980076
Truck:	156/051506
Magnesium as MgO (on ignited basis) %:	98.39
Loss On Ignition %:	0.22

A typical composition for MagChem 10 (WTS-60 is a grade of MagChem 10) can be obtained from the manufacturer's specifications sheet (Martin Marietta Magnesia Specialties Inc., 2006b), a synopsis of which is given below in Table 2. In Table 2, the elements from a total chemical analysis are reported in terms of their oxide, which is common practice. This does not mean, however, that the oxides in Table 2 are the actual phases in the MgO.

Table 2. Typical composition of MagChem 10.¹

Constituent Name	Typical (wt %)	Specifications (wt %)
Magnesium oxide (MgO)	98.2	97.0 min
Calcium oxide (CaO)	0.9	1.0 max
Silica (SiO ₂)	0.4	0.5 max
Iron oxide (Fe ₂ O ₃)	0.2	0.3 max
Aluminum oxide (Al ₂ O ₃)	0.1	0.2 max

1. These results are from Martin Marietta's total chemical analysis. Magnesium, calcium, silica, iron, and aluminum are reported here in terms of the oxides above, which aren't necessarily representative of the actual phases in the MgO material.

3.1 Chemical analysis of the composition of MgO

An estimate of the amount of magnesium, calcium, aluminum, iron, and silicon in the received lot of MgO (SL2980076) was determined by Sandia National Laboratories (SNL) by dissolving samples of MgO in nitric acid. This is a lower estimate because a small fraction of nitric-acid insoluble solids remain after dissolution. The total amount of calcium, magnesium, aluminum, iron and silica (by ICP-AES analysis) that was soluble upon dissolving the MgO samples in nitric acid is shown below in Table 3; see Subsection B.1 of APPENDIX B for the experimental protocol. This data (wt %) can be found on the MgO-icp sheet of the Microsoft Excel file 90-922 results.xls. The MgO-icp sheet is a copy of data contained within the Microsoft Excel file MgO-ICP.xls, a printout of which can be found on pg.1 of scientific notebook supplement MM MgO/ICP-AES-1.

Table 3. Weight percent of magnesium, calcium, aluminum, iron and silica that dissolved in nitric acid.¹

	MgO (wt %)	CaO (wt %)	Al ₂ O ₃ (wt %)	Fe ₂ O ₃ (wt %)	SiO ₂ (wt %)
Average ²	98.462	0.874	0.130	0.115	0.311
Standard Deviation ²	2.544	0.025	0.018	0.009	0.008

1. Magnesium, calcium, aluminum, iron and silicon are reported here in terms of the oxides above, which aren't necessarily representative of the actual phases in the MgO.
2. The average and standard deviation are based on 12 analyses.

For the purposes of determining a mole percent of periclase in the MgO, we will use the amount of aluminum, iron and silica from Table 3. The amount of potentially reactive lime in the MgO will also be taken from Table 3. The amount of MgO reported in Table 3 is the total amount of MgO, not all of which is periclase in the bulk material. The MgO result in Table 3 is not used in the calculation of the mole-percent periclase plus lime, calculated in Section 4. As will be described further below in Section 4, to the precision achieved in this analysis, whether the calcium is lime or not has virtually no impact on the total mole fraction of periclase plus lime.

3.2 Loss on Ignition and Thermal Gravimetric Analyses of hydrated MgO

The weight percent of water driven off from hydrated MgO during loss on ignition (LOI) and thermal gravimetric analyses (TGA) is used to determine the amount of magnesium and calcium that are in the phases periclase and lime, respectively. We assume that unreactive components do not hydrate to a significant extent, and that any unbound water will be lost at temperatures below 150 °C, as we measure the weight difference of hydrated MgO samples between heating to 800 °C and heating to 150 °C; see Subsection B.2 of APPENDIX B for more information.

In this analysis, SNL prepared samples of MgO that were hydrated at 90 °C for at least three days, which converts periclase and lime to brucite and portlandite, respectively. The samples were then dried and then subjected to the temperature protocol given above which causes brucite and portlandite to convert to periclase and lime, respectively. These results are given below in Table 4 and are used in Section 4. The results in Table 4 are calculated in the Microsoft Excel spreadsheet 90-922 results.xls, on the TGA and LOI sheet, cells B1-B23, where references to the appropriate data sources are given.

Table 4. Weight percent lost during TGA and LOI analyses.

	wt % lost (from hydrated MgO) during TGA and LOI analysis
Average: ¹	29.8946
Standard deviation: ¹	0.3771

1. The average and standard deviation are based on 8 analyses.

To ensure that calcite precipitation did not contribute significantly to the TGA and LOI analyses, SNL performed a total carbon analysis on the MgO before and after hydration by carbon coulometry. This analysis was performed under SP 12-2, Rev. 1. The results are shown below in Table 5. One sample that was re-soaked in DI water (at room temperature) for several days did show calcium carbonation; the results from this sample are not used in this analysis. These results used to produce Table 5 are located in the 90-922 results.xls spreadsheet, cells A45-F56.

Table 5. Total carbon in the MgO before and after hydration.

	Average Carbon (wt %)	Standard deviation (wt %)
dry-unhydrated MgO ¹	0.05	0.02
hydrated MgO ¹	0.07	0.01

1. The average and standard deviation are based on 6 analyses.

3.3 Qualitative chemical analyses of MgO

To gain some understanding of the phases that are present in the MgO, SNL took scanning electron microscope images and associated energy dispersive spectrum of as received MgO, and of the insoluble portion after dissolution in nitric acid; these analyses followed SP 12-17, Rev. 0. These spectra are located in scientific notebook supplemental binders WIPP-MM MgO-2 SEM/EDS supplemental binder-1 and WIPP-MM MgO-4 SEM/EDS supplemental binder-1, which are associated with scientific notebooks WIPP-MM MgO-2 and WIPP-MM MgO-4.

SEM images of particles of as received MgO and an associated EDS spectra are shown in Figure 1 and Figure 2. Figure 1 shows a typical particle of MgO; the large particle is a sintered collection of small particles; the EDS spectra shows Mg, O, and a small amount of Ca. Figure 2 shows an unusual particle; the EDS spectrum of shows Mg, Ca, Si, Fe, and O.

Images of the particles that remained after dissolving the MgO in nitric acid are shown in Figure 3, Figure 4 and Figure 5. Figure 3 shows a particle that contains Fe, O and lesser amounts of other elements. This particle appears to be some kind of iron oxide, perhaps hematite. The iron oxide may have come from the brine from which the MgO is obtained or it may have come from the processing equipment. Figure 4 shows a particle that contains Mg, Al, Fe, Cr, and O. This particle is most likely a spinel or a solid solution of several spinels, such as those listed in Table 6. Spinel form when MgO fuses with the oxides of aluminum, iron, or chromium at high temperature (Deer et al., 1992). The chromium most likely came from the steel equipment used to burn the MgO at high temperature. Spinel may have formed during the high-temperature burn, or (non-chromium spinel) may have formed naturally in the magnesium deposits from which the magnesium is mined. Figure 5 shows what may be a particle of MgO that didn't completely dissolve in nitric acid. We suspect that the appearance of particles of MgO, as shown in Figure 5, are an artifact of incomplete acid digestion, as it appears from Figure 5 that the acid had partially etched its surface (compare Figure 1 to Figure 5).

Little Si and Ca were found in the nitric-acid insoluble particles. For silica, this may be because the nitric acid-MgO mixture heats-up during the digestion due to the enthalpy of the nitric acid-MgO reaction. Silicon dioxide may gel when heated in nitric acid (Kolthoff et al., 1962). Some of the gel may have been rinsed away when filtering the particles.

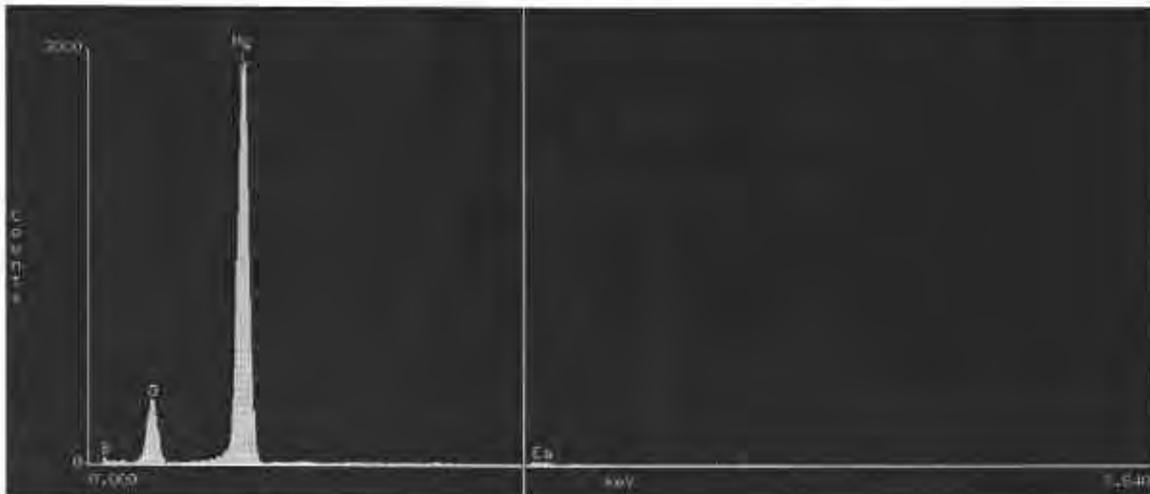
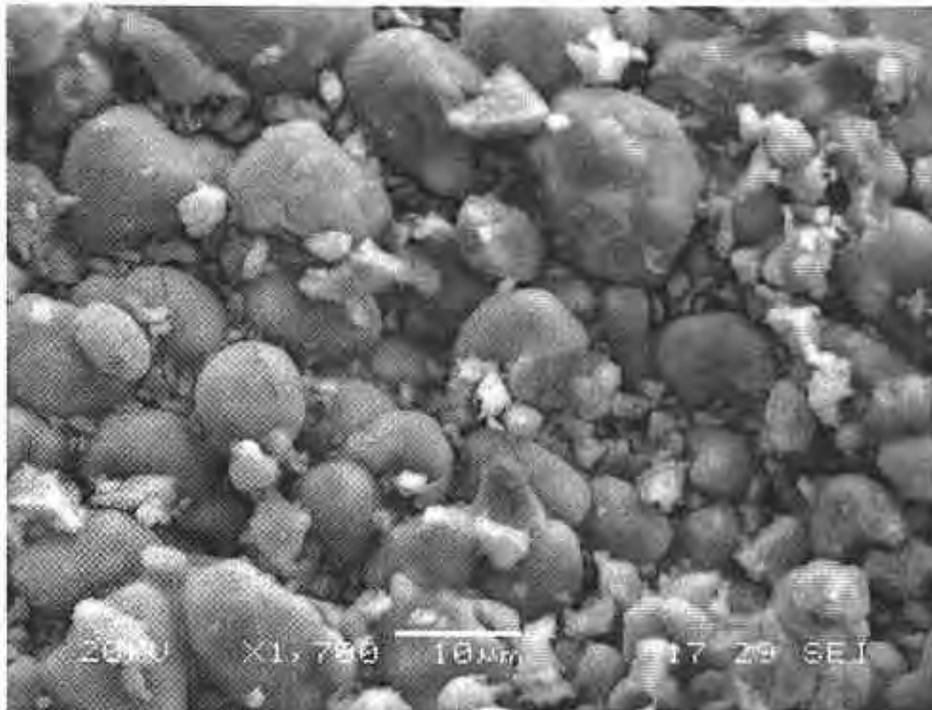


Figure 1. SEM image (top) and EDS spectrum (bottom) of as-received MgO. Small amounts of calcium are evident from the EDS spectra. The top SEM image is stored in the file 816h4i2a.bmp, the bottom EDS spectra is stored in 816h4i2a.eda. Both are located in: WIPP-MM MgO-2 SEM/EDS supplemental binder-1.

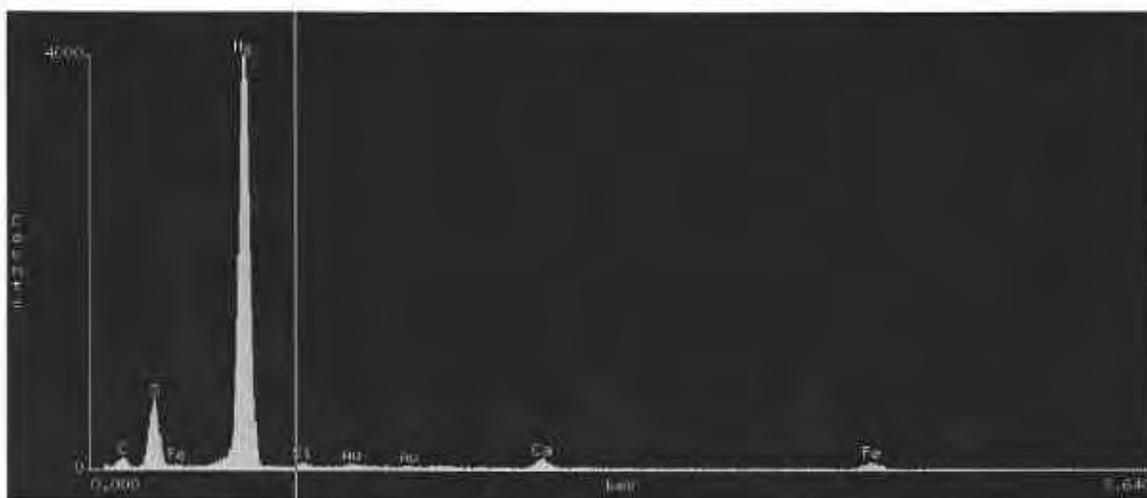
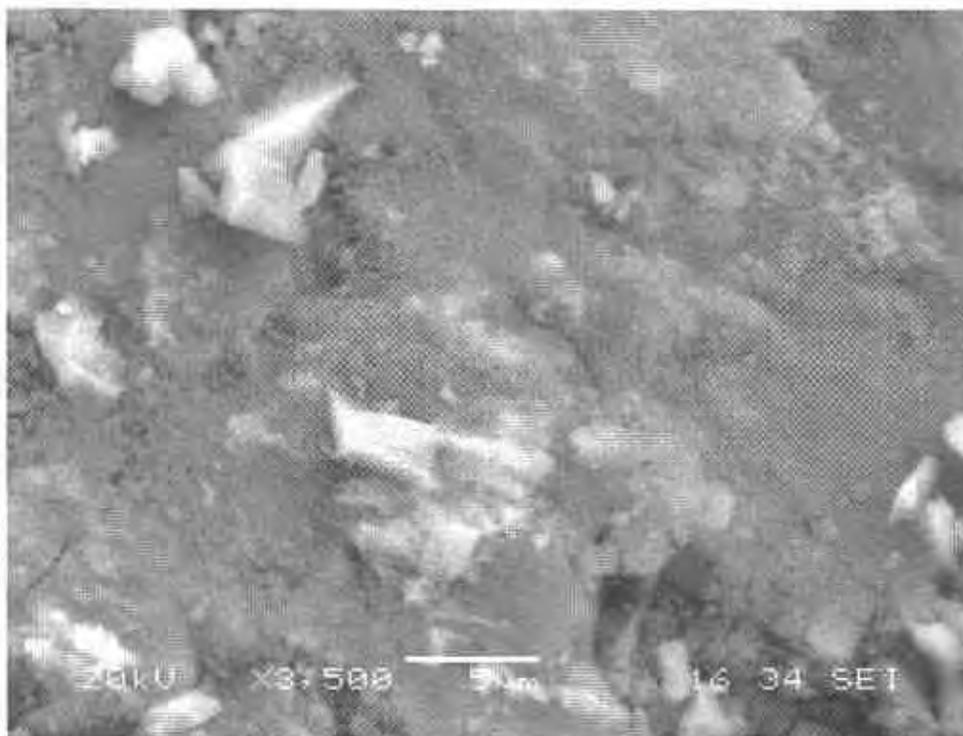


Figure 2. SEM image (top) and EDS spectrum (bottom) of a piece of unusual as-received MgO. Gold is from Au-Pd coating prior to imaging, carbon is from the carbon tape mount. The top SEM image is stored in the file 816h4i2a.bmp, the bottom EDS spectra is in 816h4i2a.eds. Both are located in: WIPP-MM MgO-2 SEM/EDS supplemental binder-1.

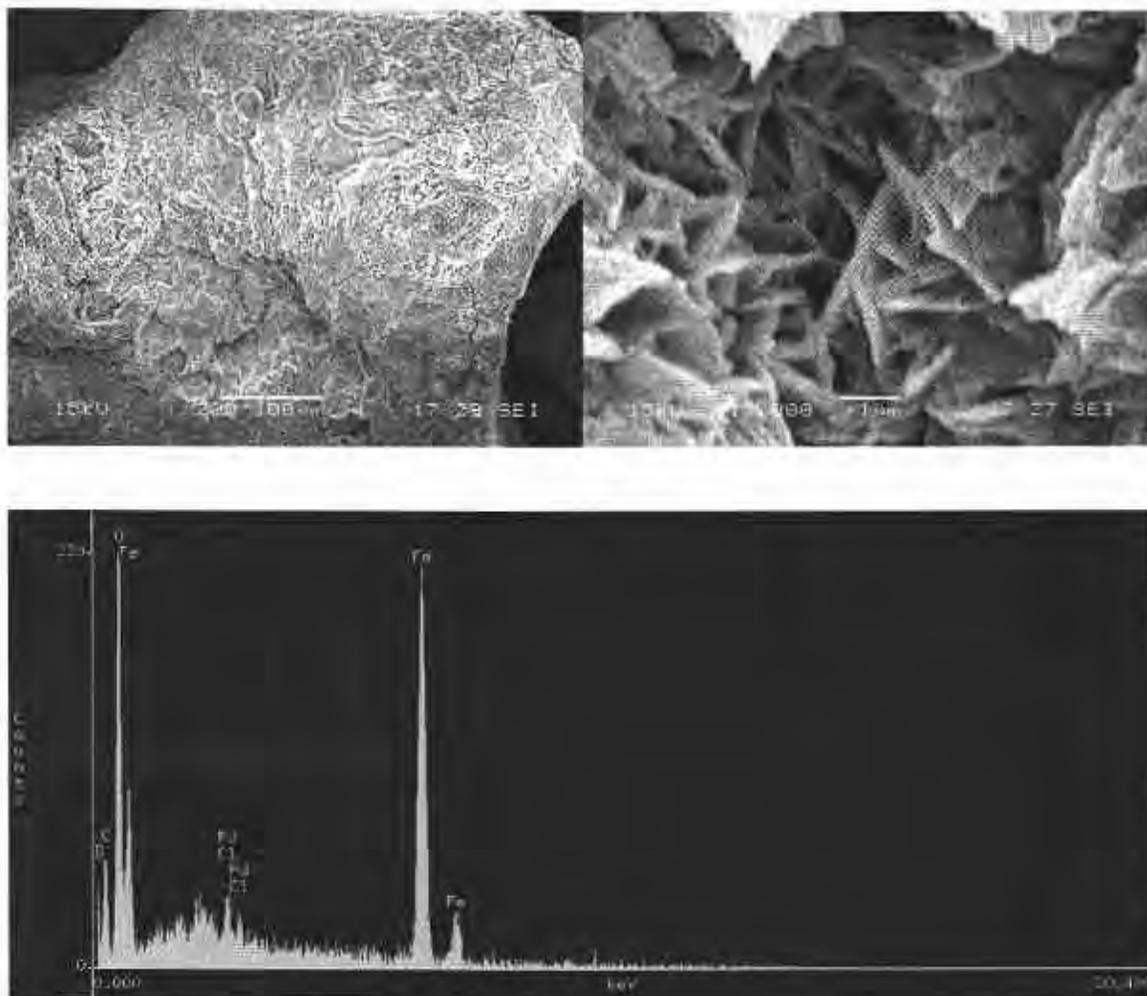


Figure 3. Low (top left) and high (top right) magnification SEM images and associated EDS spectrum (bottom) of a particle that remained after dissolving the MgO in nitric acid. Palladium is from Au-Pd coating prior to imaging, C is from the carbon tape mount. The top left SEM image is stored in the file 718h1i2.bmp, the top right SEM image is stored in the file 718h1i4.bmp, the bottom EDS spectra is in 718h1i4s1.eds. All are located in: WIPP-MM MgO-2 SEM/EDS supplemental binder-1.

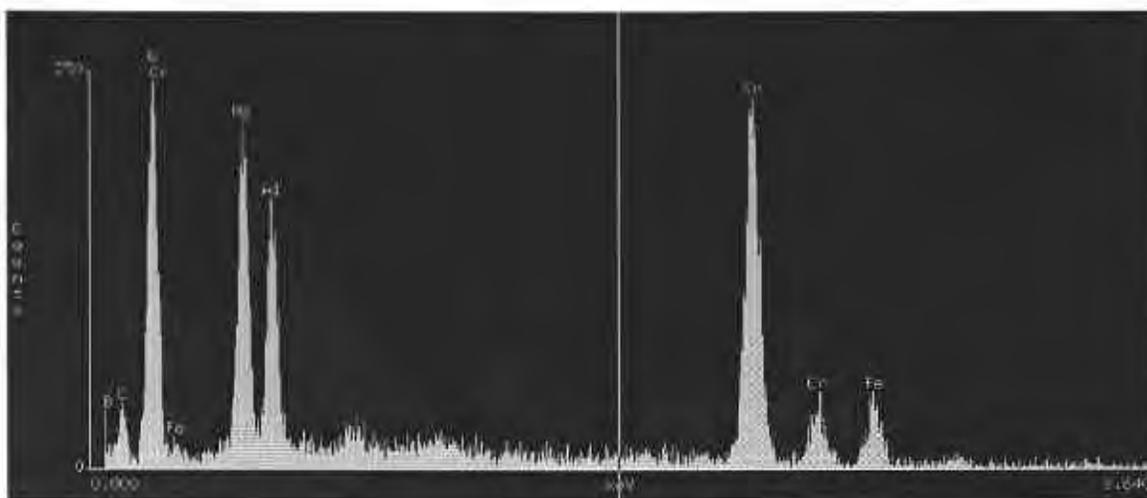


Figure 4. SEM image (top) and associated EDS spectrum (bottom) of a particle that remained after dissolving the MgO in nitric acid. Notice the conchoidal fractures in the SEM image; spinels (in general) have a lack of cleavage (Deer et al., 1992). The top SEM image is stored in the file 718h1i5a.bmp, the bottom EDS spectra is in 718h1i5as1.eds. Both are located in: WIPP-MM MgO-2 SEM/EDS supplemental binder-1.

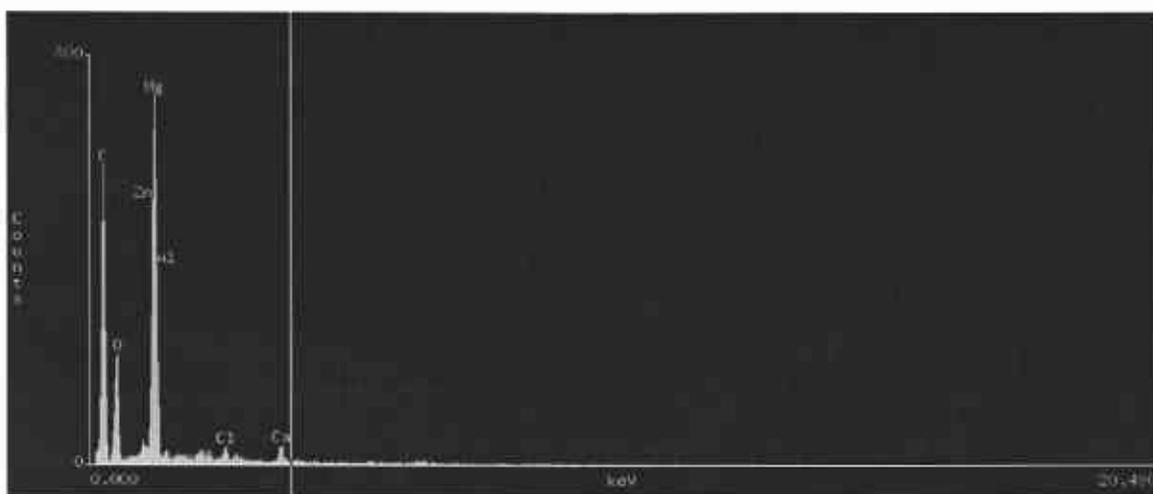
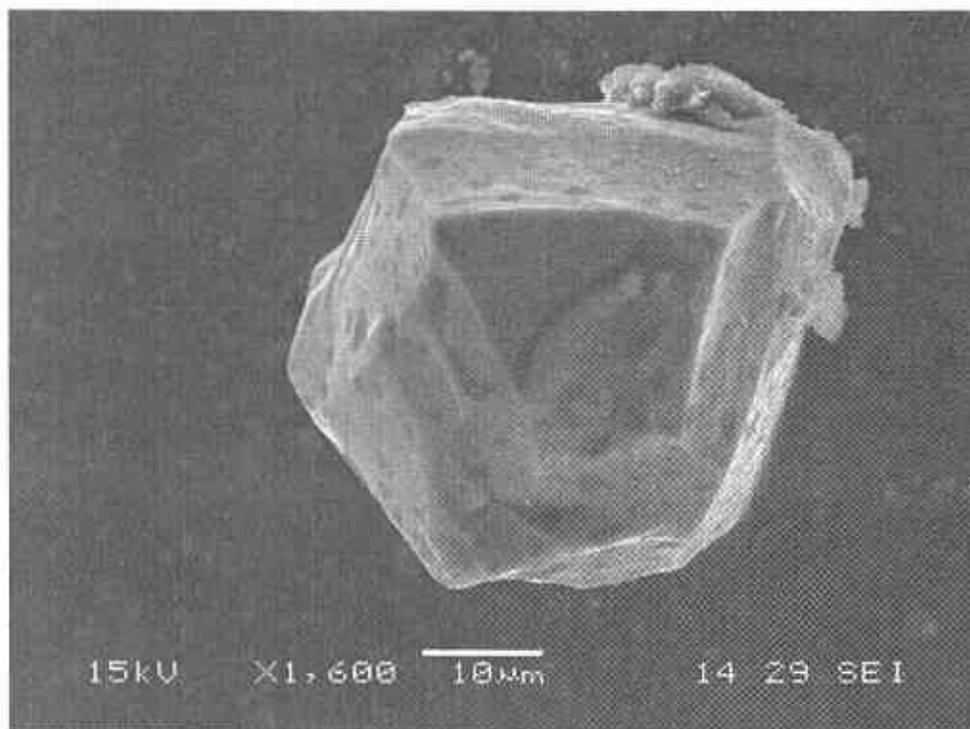


Figure 5. SEM image (top) and associated EDS spectrum (bottom) of a particle that remained after dissolving the MgO in nitric acid. The top SEM image is stored in the file 123h1i10.bmp, the bottom EDS spectra is in 1023h1i10.eds. Both are located in: WIPP-MM MgO-4 SEM/EDS supplemental binder-1.

4 CALCULATION OF THE MOLE PERCENT PERICLASE IN MGO

In this section we calculate a mole fraction of periclase plus lime in the MgO. This is accomplished by calculating the moles of water of hydration that were released from the MgO during TGA and LOI analyses, and by making educated assumptions on the likely phases of the unhydrated and hence unreactive material.

To determine the mole fraction of periclase and lime (the principal constituents of the MgO), the following assumptions were made:

- a) Water lost from TGA and LOI experiments (given in Table 4) came from brucite and portlandite. Because the decomposition temperatures of brucite 350-800 °C and portlandite 450-800 °C (see pg. A9 of supplemental binder WIPP-MM MgO-4 TGA supplemental binder, for portlandite see also Alarcon-Ruiz et al., 2005) overlap (at least under the conditions used), we found it difficult to separate out the water from the two compounds.
- b) Most of the calcium in Table 3 is lime that reacts with water to form portlandite. It's important to note that, to the precision achieved in this analysis, this assumption has virtually no impact on the total mole fraction of periclase + lime, only how the moles of H₂O (lost during TGA and LOI experiments) are divided up between periclase and lime.
- c) Based on the images, spectra, and discussion in Subsection 3.3, we believe that the unreactive portion of as received MgO consists of SiO₂, perhaps olivines or orthosilicates, hematite, and minerals in the spinel group and/or solid solutions of various spinels, and perhaps small amounts of MgO that were occluded in various unreactive phases. A subset of the phases considered to be representative of the unreactive material is listed below in Table 6. However, given that we do not know quantitatively how the unreactive material is distributed (in mass) between the various unreactive phases, in this preliminary analysis we assign all of the aluminum to alumina and all of the iron to hematite,

$$x_{Al_2O_3} = \frac{1}{2} x_{Al} \quad (1)$$

$$x_{Fe_2O_3} = \frac{1}{2} x_{Fe} \quad (2)$$

Here x_i is the moles of phase (or element) i per gram of dry-unhydrated sample. The moles of iron and aluminum per gram of dry sample were determined by dividing the mean results in Table 3 by their respective molecular weights. Assumptions (1) and (2) will be shown in Subsection 4.2 to be representative of a lower bound on the mole fraction of periclase, assuming that the phases in Table 6 are representative.

Table 6. Unreactive Phases assumed to be present in Martin Marietta MgO, in order of molecular weight.

Mineral Name	Chemical Formula	Molecular Weight (g/mol)
silicon dioxide (not necessarily quartz)	SiO ₂	60.084
Alumina	Al ₂ O ₃	101.960
Spinel	MgAl ₂ O ₄	142.265
Hematite	Fe ₂ O ₃	159.692
Hercynite	FeAl ₂ O ₄	173.807
Magnesiochromite	MgCr ₂ O ₄	192.293
Chromite	FeCr ₂ O ₄	223.837

4.1 Calculation Methodology

The mole fractions of periclase and lime ($X_{\text{periclase}}$ and X_{lime} , respectively) are calculated by,

$$X_{\text{periclase}} = \frac{x_{\text{periclase}}}{\sum_i x_i}, \quad (3)$$

$$X_{\text{lime}} = \frac{x_{\text{lime}}}{\sum_i x_i}. \quad (4)$$

where i is an index for periclase, lime, Si, Al, Fe, and Other. The phases considered to be contributing to equation (3)-(4) are: periclase, lime, SiO₂ (of unknown phase), alumina (Al₂O₃), and hematite (Fe₂O₃). The index "other" represents the moles of unreactive material other than Si, Al, and Fe. This is discussed further below with equation (7). The mean moles of silicon per gram of dry-unhydrated sample, x_{Si} , was obtained by dividing the results in Table 3 by the molecular weight of SiO₂.

The amount of periclase in the Martin Marietta MgO (to be used in equation (3) above) is equal to the amount of water lost during TGA and LOI analysis minus the amount of lime present

$$x_{\text{periclase}} = x_{\text{H}_2\text{O}} - x_{\text{lime}} \quad (5)$$

where x_{lime} was obtained by dividing the mean weight percent of CaO from Table 3 (see assumptions a-b above) by the molecular weight of lime (CaO), and $x_{\text{H}_2\text{O}}$ is the moles H₂O lost/g dry-unhydrated sample from TGA and LOI analysis, and is calculated from,

$$x_{\text{H}_2\text{O}} = \frac{\text{wt}\%_{\text{lost}} / 100}{1 - \text{wt}\%_{\text{lost}} / 100} \times \frac{1}{MW_{\text{H}_2\text{O}}} \quad (6)$$

Here $\text{wt}\%_{\text{lost}}$ is the weight percent lost during LOI and TGA experiments, the mean was used and is given in Table 4. The term $(1 - \text{wt}\%_{\text{lost}})$ in the denominator of equation (6) accounts for the difference between weight percent in the hydrated sample and weight percent in the dry-unhydrated sample. We need to convert to weight percent in the dry-unhydrated sample because the weight percents of Ca, Si, Al, and Fe in Table 3 are in terms of the dry-unhydrated sample weight.

For the purpose of calculating a mole fraction, the remaining unreactive weight percent (other than periclase, lime, SiO₂, hematite, and alumina) is then assigned to unreacted MgO,

$$x_{\text{other}} = \frac{\left(1 - \sum_i x_i MW_i\right)}{MW_{\text{MgO}}}, \quad (7)$$

where MW_i is the molecular weight of species i , and here i is an index for: periclase (from equation (5)), lime (from Table 3 divided by MW_{CaO}), SiO₂ (from Table 3 divided by MW_{SiO_2}), Al₂O₃ (from equation (1)), and Fe₂O₃ (from equation (2)). The calculated x_{other} is thus an upper estimate of the total moles of unreactive material (other than Fe, Al, and Si) since the molecular weight of the unreactive phases in Table 6 are all larger than that of MgO.

For the purpose of reporting an uncertainty, we used the standard deviations in the experimental measurements to propagate uncertainty through equations (3)-(7). Uncertainty in linear equations was propagated using the following standard formulas. Given y , a function of means $\bar{\eta}_i$ of random variables η_i , and constants a_i and c ,

$$y = \sum_i a_i \bar{\eta}_i + c, \quad (8)$$

then if the uncertainties in η_i are independent,

$$V_y = \sum_i a_i^2 V_i, \quad (9)$$

where V_y is the variance of the function y and V_i are the variances in the random variables η_i , and if the uncertainties are not independent we use the upper bound

$$\sigma_y = \sum_i |a_i| \sigma_i, \quad (10)$$

where σ_y is the standard deviation of the function y and σ_i are the standard deviations in the functions η_i . Equations (9) and (10) may be found in Taylor (1982), pg. 56 equations 3.16 and 3.17. Equations (1)-(2) are functions of one random variable, hence we used equation (9). In equation (7) the uncertainties are not independent and hence we used equation (10). For other functions of random variables, i.e.

$$y = f(\bar{\eta}_1, \dots, \bar{\eta}_n), \quad (11)$$

the following rule is used,

$$V_y = \left(\frac{\partial y}{\partial \bar{\eta}_1} \delta \bar{\eta}_1 \right)^2 + \dots + \left(\frac{\partial y}{\partial \bar{\eta}_n} \delta \bar{\eta}_n \right)^2, \quad (12)$$

if the random variables are independent, and we use the upper bound

$$\sigma_y = \left| \frac{\partial y}{\partial \bar{\eta}_1} \right| \sigma_1 + \dots + \left| \frac{\partial y}{\partial \bar{\eta}_n} \right| \sigma_n, \quad (13)$$

if the random variables are correlated. Equations (12) and (13) may be found in Taylor (1982), pg. 73 equations 3.47 and 3.48.

In equation (6) there is only one random variable and hence we use equation (12), which yields,

$$V_{xH2O} = \left(\frac{\sigma_{wt\%lost} / 100}{\left(1 - \overline{wt\%lost} / 100 \right)^2 MW_{H2O}} \right)^2. \quad (14)$$

In equations (3) and (4) the various x_i terms are not independent and hence we use equation (13) which yields,

$$\sigma_{X_{\text{periclase}}} = \left| \frac{1}{\sum_i \bar{x}_i} - \frac{\bar{x}_{\text{periclase}}}{\left(\sum_i \bar{x}_i\right)^2} \right| \sigma_x + \frac{\bar{x}_{\text{periclase}}}{\left(\sum_j \bar{x}_j\right)^2} \sum_{i \neq \text{periclase}} \sigma_i, \quad (15)$$

and a similar result for lime (replacing terms labeled MgO with CaO).

4.2 Calculation Results

The results of the calculations described in Subsection 4.1 are given below in Table 7 for the mole fraction of periclase and lime, and Table 8 for the weight fraction of periclase and lime. Equations (3)-(4) were used to calculate the average mole fraction of periclase and lime, and equation (15) was used to calculate the standard deviation. For the sum of periclase and lime, the standard deviations were summed (since they aren't independent). These calculations are performed in the Microsoft Excel spreadsheet 90-922 results.xls (see APPENDIX A). The Reported Value column shows the values that we are reporting.

Table 7. Mole fraction of periclase and lime in dry-unhydrated MgO.

	Average (mole fraction)	Standard Deviation (mole fraction)	Reported Value mean \pm σ (mole fraction)
periclase	9.52×10^{-1}	1.82×10^{-2}	0.95 ± 0.02
lime	6.31×10^{-3}	4.04×10^{-4}	0.0063 ± 0.0004
periclase+lime	9.58×10^{-1}	1.86×10^{-2}	0.96 ± 0.02

Table 8. Weight fraction of periclase and lime in (dry-unhydrated) MgO.

	Average (weight fraction)	Standard Deviation (weight fraction)	Reported Value mean \pm σ (weight fraction)
periclase	9.48×10^{-1}	1.72×10^{-2}	0.95 ± 0.02
lime	8.74×10^{-3}	2.53×10^{-4}	0.0087 ± 0.0003
periclase+lime	9.56×10^{-1}	1.74×10^{-2}	0.96 ± 0.02

By fitting the un-reacted weight percent into phases with lower molecular weights (i.e. SiO_2 , Al_2O_3 , hematite, and MgO) compared to other possible phases listed in Table 6, we have calculated a lower estimate of the periclase mole fraction than if we had assumed species with larger molecular weights such as magnesiochromite and chromite. Although these phases were not confirmed experimentally, chromium was common in the un-dissolvable portion of the MgO as described above in Subsection 3.3.

The weight fraction of periclase in Table 8 is $\sim 2\%$ lower than the specification given in Table 2 and 3.5% lower than the result in Table 3 (from the dissolution of MgO in nitric acid). One must remember that the MgO reported in Table 2 and Table 3 is not necessarily in the phase periclase. The difference in the results from Table 8 and Table 3 is probably a good upper-bound estimate of the amount of magnesium tied up in unreactive phases. This is consistent with the results of equation (7), which gives the weight fraction of other = 3.8% (see Subsection 4.1); this is calculated in cells T40-T42 in the 90-922 results.xls spreadsheet.

Wall (2005) performed a similar analysis on a lot of WTS-30, which was not the same lot as analyzed here. In her analysis she found a mole percent of $96\% \pm 2.5\%$ (one sigma) periclase. In Wall's analysis, it was assumed that all of the water lost from LOI came from brucite, and that the remaining weight percent is unreacted MgO. The result obtained by Wall is very close to the result given above in Table 7. This is not surprising since the minor unreactive constituents (Fe, Al, Si) given in Table 3 add up to less than 1 wt%, much of which is SiO_2 , whose molecular weight is close to that of MgO.

The mole percent of periclase in Table 7 and Table 8 are equal to two significant digits. If we had assumed that all of the MgO material was either periclase or unreacted MgO (i.e. no Ca, Si, Fe, Al), then the mole fraction and weight fraction would be equal since in that case there would only be a single molecular weight. Because the total weight percent of the other components (Ca, Si, Fe, Al) is small, the contributions of the other components (Ca, Si, Fe, Al) are perturbations on this result, hence the small difference between the weight and mole percent.

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APPENDIX A. CALCULATIONS IN THE 90-922 RESULTS SPREADSHEET

The spreadsheet 90-922 results.xls is organized as follows. Cells A1-E8 contain the weight percent (in the hydrated sample) of water lost from TGA experiments on hydrated MgO. The scientific notebook and page number are given in columns C and D. Cells A13-F19 contain the weight percent (in the hydrated sample) of water lost from LOI experiments on the hydrated MgO using a Fisher programmable furnace. A run of Fisher Mg(OH)₂ FCC/USP is included for each technique, for comparison purposes. The manufacturer claims an LOI on this material of 30.2 % (Fisher Chemical, 2005) under the same temperature protocol that is described in Subsection B2 of Appendix B; however the manufacturer does not give an associated uncertainty for this number. In cells A21-B22 the average and standard deviation of both the TGA and LOI experiments (combined) are calculated.

In cells A24 through C36, the molecular weights of all possible phases (compounds, elements) are calculated. Column A gives the molecular formula, column B gives the mineral name, and column C gives the molecular weight in (g/mol).

In cells A40 through Y42, equations (1)-(7) are solved along with propagation of uncertainty. Row 41 contains the results on the mean values, and row 42 contains the uncertainty. Cell B41 is calculated using equation (6), cell B42 is calculated using equation (14). Cells C41-D42 show the amount of lime and are self explanatory. Cell E41 is calculated from equation (5) and uncertainty in E42 is calculated using equation (9). Cells F40-L42 are self explanatory. In cells M40 through P42 we use equations (1)-(2), and assign $x_i = 0$ for the other phases. Uncertainty is propagated using equation (9). Cells Q40-S42 are self explanatory. Cell T41 is calculated using the numerator of equation (7). Uncertainty is propagated in cell T42 using equation (13). Cell U41 then completes equation (7) and uncertainty is propagated cell U42 using equation (13). Then the total moles/g sample is summed in cell V41, with uncertainty in V42 (which isn't used) from equation (13). The mole fractions of periclase and lime are given in cells W41 and X41 respectively, using equations (3) and (4). The uncertainty in these cells is calculated in W42 and X42 using equation (15). The sum is calculated in Y41 and the uncertainty in Y42 using equation (13).

APPENDIX B. EXPERIMENTAL PROTOCOL

B.1 Dissolution of MgO in nitric acid

Below is an overview of the procedure used to dissolve MgO in nitric acid and then perform ICP-AES analysis on the resulting liquid. The exact procedure for each sample is located in the scientific notebook:

Prepare solution A: MgO HNO₃ solution for Ca, Al, Fe, Si analysis:

- 1) Grind the 5-6 g of MgO sample by mortar and pestle.
- 2) Weigh out 1g (0.9-1.1g) of the ground sample into a 100 ml volumetric flask
- 3) Rinse the volumetric flask with 40-50 ml DI water and make sure all the sample is washed into the volumetric flask.
- 4) Add 9 ml of concentrated HNO₃ into the flask.
- 5) Pipette 100ul of 1000ppm Sc standard into the flask.
- 6) Add DI water in the flask until the meniscus is at the 100 ml line.
- 7) Shake the flask well.
- 8) Most of the MgO sample will be dissolved by the nitric acid. But some black particles are not dissolvable (most likely spinel see Subsection 3.3). Let the MgO sample-HNO₃ solution settle for 2-3 hr, the black particles may be observed at the bottom of the flask.

Prepare Solution B: MgO HNO₃ solution for Mg²⁺ analysis:

- 1) Pipette 1000ul of the top clear solution from solution A into a 100ml volumetric flask.
- 2) Rinse the volumetric flask with 40-50 ml DI water and make sure all the MgO sample-HNO₃ solution is washed into the volumetric flask.
- 3) Pipette 5000ul of concentrated HNO₃ into the flask. Add the HNO₃ slowly with continuous swirling.
- 4) Pipette 100ul of 1000ppm Sc standard into the flask.

- 5) Add DI water in the flask until the meniscus is at the 100 ml line.
- 6) Shake the flask well.

B.2 TGA and LOI analysis

Below is an overview of the procedure used to prepare and analyze samples for TGA and LOI analysis. The exact procedure(s) for each sample are located in the scientific notebooks.

For the sample set labeled 90-922-1 through 90-922-4 (see APPENDIX A for location of data in spreadsheet), the samples were prepared for TGA and LOI analysis as follows (see pg.97-98 of scientific notebook WIPP-MM MgO-2):

- 1) 6-7 grams of MgO sample were loaded into clean 125 ml plastic bottles.
- 2) 100 ml of de-ionized water was added.
- 3) The threads of the bottles were covered in Teflon tape.
- 4) The bottles were closed and placed into a 90°C oven.
- 5) The bottles were placed in the oven on 9/22/06. Samples 90-922-3 and 4 were removed on 9/26/06. Samples 90-922-1 and 2 were removed on 9/28/06. The difference in TGA results from these two collection dates does not appear to be significant (see Microsoft Excel spreadsheet 90-922 results.xls).
- 6) Upon removing from the oven the samples were rinsed, filtered and dried in air overnight.

The dried-hydrated MgO sample was then analyzed by TGA in a Netzsch STA 409 PC TGA/DTA DSC under argon that has been filtered for oxygen and water, and in parallel in a Fisher Programmable furnace, in air. In the TGA (which measures weight loss continuously) the temperature program was as follows:

- 1) Heat to 150 °C at 6 °C/min, remain at 150 °C for 2 hours.
 - 2) Heat to 800 °C at 3 °C/min, remain at 800 °C for 15 minutes.
-

In the Fisher Programmable furnace, the temperature program was as follows:

- 1) Heat to 150 °C, remain at 150 °C for 2 hours.

- 2) Remove sample from oven, allow to cool (for a short time ~ ½ hour), then measure weight loss.
- 3) Heat to 800 °C at 4 °C/min, allow oven to cool, remove sample from oven, allow sample to cool (1 hour), then measure weight loss.

This program is the same as used by Fisher Chemical to analyze their FCC/USP magnesium hydroxide (Fisher Chemical, 2005).

Casey, Shannon Leigh*Shannon Casey*

From: Deng, Haoran
Sent: Tuesday, November 14, 2006 1:04 PM
To: Nemer, Martin B; Chavez, Mario Joseph; Clayton, Daniel James; Rigali, Mark J; Brush, Laurence H; Vugrin, Eric D; Casey, Shannon Leigh
Subject: RE: Final version of memo
Attachments: ERMS543900.pdf; MChem%2010.pdf; 90-922 results.xls; Analysis of Martin Marietta MgO version 10.doc

Please see the attached files. This time, it is really the final vision. Thanks.

Haoran

From: Nemer, Martin B
Sent: Tuesday, November 14, 2006 9:17 AM
To: Nemer, Martin B; Deng, Haoran; Chavez, Mario Joseph; Clayton, Daniel James; Rigali, Mark J; Brush, Laurence H; Vugrin, Eric D; Casey, Shannon Leigh
Subject: Final version of memo

Attached is the final version of the memo. I give Haoran signature authority to sign for me.

Haoran please get everyone to sign the signature page. Then give to Shannon to submit to records.

Shannon: please burn a CD with the above files. After Haoran gets the signature page signed, please submit the attached report with the CD to records.

Call me if you have any questions:

505-706-4012 (cell)

Information Only

11/14/2006