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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES FOR ADVANCED MATERIALS

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ABSTRACT

During this quarter the determination of hydroxyl in solid magnesium oxide was studied by chemical decomposition and emission and mass spectrographic techniques. Other detectable elements were also determined with the mass spectrograph, and these data are compared with available independent results.

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by

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INTRODUCTION

The first 6 months of this research program were spent analyzing a number of MgO samples by several techniques to establish the accuracy of the mass spectrographic technique and to discover which elements were particularly prone to error. The two elements that proved most difficult to determine with reasonable accuracy were H and C; H (or OH) was believed by the project monitor to be the more important impurity in MgO and therefore was studied intensively during the period covered by this report.

Several other MgO samples, both powdered and solid, were analyzed with the mass spectrograph. These results are compared with available independent analyses. The agreement was fair in most instances, but was quite good for a single crystal supplied by Dr. Sibley of Oak Ridge.

EXPERIMENTAL WORK

Hydroxyl Determination

The determination of hydroxyl in MgO has proved to be a far more difficult task than anticipated at the beginning of this research program. Previous work by Dr. Leipziger under NASA Contract 950992 showed that low blanks, of the order of a ppmw in refractory and precious metals (equal to a hundred or more ppma), could be obtained on the mass spectrograph. The same investigator reported that hot-extraction techniques were of doubtful value because they tended to give results higher than those obtained by mass spectrography.

Work performed under the present contract and discussions with the former Technical Representative, Dr. M. H. Leipold, produced conflicting interpretations of the chemistry of hydroxyl in MgO. One set of data obtained by heating, but not decomposing, MgO in a graphite crucible showed that reproducible and very low amounts of hydroxyl were determinable in at least one MgO sample (OP 243). This same sample, when partially decomposed by reduction with graphite, had an apparent hydroxyl concentration about 200 times higher, if extrapolated to complete decomposition. Further, the hydroxyl content based on H (m/e =1) as determined by mass spectrography was almost 100 times higher than the thermal-decomposition value. Thus, the spread, expressed as ppma of H, was from 3 to 50,000.

Such a wide spread in the data for one sample certainly indicates the need for further work. The techniques employed so far, which have led to the above results, are described in the following sections.

Thermal Analysis

The quartz-tube graphite-crucible technique has been described in previous reports (Letter Reports Nos. 5 and 6, and the Second Quarterly Progress Report). As used in the work conducted during this period, the apparatus consists of a quartz tube with a detachable base that holds a split graphite pedestal on which is mounted the graphite reaction crucible. Above the crucible is a funnel that directs the sample as it is pushed from the side arm into the crucible; the funnel was then tilted away from the hot reaction zone. Induction heating was used, with the coupling being to the graphite crucible. An optical pyrometer was used to measure the temperature inside the crucible.

During the previous quarter's work, it was shown that nearly quantitative recovery of H from brucite, $Mg(OH)_2$, was possible. Also, large amounts of H were released from powdered MgO. Little or no actual decomposition of the oxide ($MgO + C \longrightarrow Mg + CO$) occurred, suggesting to Dr. Leipold that OH present as Mg·OH [not $Mg(OH)_2$], i.e., OH bound in the crystal structure as a substitute for an oxygen atom, was not being released. At his suggestion, the experiments during this quarter were designed to accomplish the complete removal of hydroxyl (as H_2) by breaking the Mg-O bond. Solid samples were used, either crushed or as chunks, to minimize adsorbed H_2O on the surface.

The first solid MgO analyzed was a sample of Fisher M-300 B-3 that had been isostatically cold pressed at 90,000 psi (BMI No. S-0460). This material has a density considerably less than theoretical. The sample had been stored in a polyethylene vial, but was not protected from the air. The pressed material was broken, and a sample consisting of eight random pieces, each of about 1/8-inch cross section, weighed 0.5303 g. After this sample had been loaded into the side arm of the reaction vessel, the system could be evacuated to only 20 microns pressure with the diffusion pump. The gas was 98 volume percent H_2O, 1 percent CO_2, and 1 percent CO.

Pumping had to be continued for several hours with infrared lamp warming of the sample to 70C before the pressure could be held constant. The apparatus was attached to the portable pumping system, and the empty crucible was heated to 2200 C for 1.5 minutes while pumping. The crucible was cooled to room temperature and the reaction vessel isolated from the pumps. The isolated vessel was then heated to a crucible temperature of 2000C for 1.5 minutes. Analysis of the gas obtained in this blank showed 0.00029 cc-atmosphere* of H_2 [equivalent to 0.26 microgram or 0.5 ppmw of $Mg(OH)_2$] , 0.0101 cc-atm of CO, and 0.00003 cc-atm of H_2O.

For the next analysis, the container was pumped out while still on the mass spectrometer, the swinging funnel was placed in the loading position, and the pieces of MgO were pushed from the side arm into the crucible by means of a Pyrex-covered iron bar inside and by an external magnet. The funnel was moved out of the heat zone, and the sample was heated to 2000C for 1.5 minutes.

Analysis of gas evolved from this MgO sample (Run M-1) showed a total of 147 cc-atm of gas with the following composition, in volume percent: H_2, 17.9; CO, 33.4; H_2O, 46.5; and CO_2, 2.19. The H_2 amounted to 26.3 cc-atm , which is equivalent to 12.82 weight percent $Mg(OH)_2$ in the MgO. During the heating a white solid deposited on the side walls of the container in the immediate vicinity of the hot crucible. This material was not identified.

To determine the reproducibility of the apparatus and method, another sample of the same MgO weighing 0.5136 g was loaded and analyzed as described above, except that no blank was run because the blank for Run M-1 was so low as to be insignificant. This analysis, designated Run M-2, showed a total of 152 cc-atm of gas containing 16.7 percent H_2. This is equivalent to 25.4 cc-atm of H_2, or 12.85 weight percent of $Mg(OH)_2$.

The sample used in Run M-2 was unloaded from the apparatus and allowed to stand unprotected from the atmosphere for 64 hours. For Run M-3 a portion of this sample was reweighed and again loaded. Only 0.2758 g of the original sample was used because two of the pieces were contaminated with black specks of a foreign substance.

The apparatus containing the sample for Run M-3 was placed on the mass spectrometer and evacuated for approximately 1 hour. No degassing could be detected on the micromanometer when the pumps were isolated. A mass spectrometer analysis showed only those components normally present in the instrument background.

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* Cubic centimeters at standard pressure and room temperature (cc-atm).

The same procedure used for Runs M-1 and M-2 was applied to the analyses described below except that the temperature was raised on some of the runs. The blank run at 2000C showed only 0.0021 microgram of H_2, which is equivalent to 0.06 microgram of $Mg(OH)_2$. This is 0.22 ppmw based on a 0.27 g sample. The sample was transferred to the crucible and ignited to 2000C. The total H_2 evolved was 0.08 microgram. After subtracting the blank, this is equivalent to 8 ppmw $Mg(OH)_2$ versus the 12.8 percent originally found indicating very little additional evolution of H_2. The only other materials detected in this analysis were CO and a trace of CO_2. A dark residue appeared on the side walls of the container in the immediate vicinity of the hot crucible.

The gases were pumped from the container and the sample was heated to 2200C. The only gas detected in this run was CO, indicating that no additional hydroxyl compounds were being evolved after raising the temperature 200C. Optical-pyrometer temperature measurements become more difficult due to an increase of the dark residue noted above.

The final heating was made at 2500C or higher. Since a blank had not been run at this higher temperature, the blank for 2000C was used. Only 2 ppm $Mg(OH)_2$ was found. The amount of dark residue on the walls around the hot crucible increased, and temperature reading became even more difficult. As the residue increases, the apparent temperature for a given power setting decreases; thus, the temperature given above actually may have been higher.

These experiments, designed to determine the efficiency of the original extraction of hydroxyl at 2000C, indicated no significant release of components on additional extraction at 2000C, or when the temperature was raised to at least 2500C. However, no significant decomposition of MgO occurred.

A sample designated as Fisher M-300, OP243 (BMI No. 91940) was analyzed twice by the procedure outlined above for Runs M-1 and M-2. These analyses are reported as Runs M-6 and M-7. The physical appearance of this sample was quite different from the sample reported above. This MgO had a glazed or translucent surface. Another difference was revealed during pump-down. This sample showed no degassing after approximately 20 minutes of pumping and no infrared lamp heating was needed during evacuation.

The pressed sample was broken into pieces and 0.4986 g was loaded (Run M-6). The blank for this run gave 0.0018 microgram of H_2, which is equivalent to 0.052 microgram or 0.1 ppmw of $Mg(OH)_2$.

The sample was heated to 2000C and no white residue formed around the side walls, as had been observed with the previous sample. Analysis of the evolved gas showed it to be CO and H_2, the latter equivalent to 2 ppmw $Mg(OH)_2$, net. The duplicate run for this sample (Run M-7) had a blank equivalent to 0.17 microgram or 0.4 ppmw of $Mg(OH)_2$ and the sample showed a net of 2.7 ppmw $Mg(OH)_2$. A trace of some compound, possible acetylene, was observed in both gas samples at mass 26. The samples were reweighed after both Runs M-6 and M-7. Each lost 0.4 percent of its original weight. This compares with a 23.9 percent weight loss for Run M-2. A dark residue deposited on the side walls of the container for these runs in about the same amount and location as for the previous runs. Water was not detected in these runs, while approximately 45 percent of the gas released from Runs M-1 and M-2 was water. The data for these runs are summarized in Table 19.*

A sample of pressed MgO designated as Kanto MgO, OP 366 (BMI No. S-0432) was analyzed using the procedure described above. Duplicate analyses gave 133 and 144 ppmw of $Mg(OH)_2$. Data for these analyses are shown in Table 23 (Runs M-8 and M-9). Little if any actual decomposition occurred under the conditions used for these runs. The reproducibility of this method has been established and the blanks are low and fairly constant, but the accuracy remains in doubt until the MgO is dissociated completely to ensure complete liberation of any hydroxyl in the sample. Experiments were therefore performed in an effort to convert the MgO to CO and Mg.

Most of the previous analyses were made at a temperature of 2000C for 1.5 minutes; however, it became obvious that either a higher temperature, a much longer time at the same temperature, or an increase in both temperature and time would be required to complete the above reaction. The apparatus and technique was modified to permit these changes. To obtain a greater cooling capacity around the reaction vessel, deionized water was frozen and added to the cooling water during the reaction. The temperature of the cold bath was reduced to about 0C before the blanks or

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* The tables in all reports under this contract are numbered sequentially.

samples were heated and the bath was stirred continuously. A new quartz-tube apparatus was fabricated, which includes a larger sample-storage arm. This sample-storage arm is large enough to contain both the sample and a supply of graphite to cover the sample after it is dropped in the crucible.

A preliminary feasibility run was made with powdered MgO covered with powdered graphite, Grade 38, produced by the National Carbon Company. It was preconditioned by igniting in a muffle furnace at 900C for 45 minutes. The MgO sample was Fisher M-300 (OP 243, BMI No. 91940). All subsequent experiments were run with this same sample. The powdered MgO was obtained by grinding the pressed MgO in a hardened-steel mortar. Powdered MgO weighing 0.1193 g was placed in the graphite crucible and 0.2 g of the powdered graphite was distributed over the sample. Blanks could not be determined because the sample and graphite had already been loaded in the crucible. The system was evacuated and heated to 2800C for 4 minutes. The evolved gas was analyzed with the mass spectrometer. Because the quartz tube was not degassed at 2800C, the hydrogen results probably are not significant. The amount of CO that should have been produced (had the reaction proceeded to completion) is 0.0830 g, but only 0.0480 g was actually found, indicating a 58 percent decomposition of the MgO. A small amount of graphite was found in the bottom of the apparatus after the reaction. These encouraging results suggested that a careful analysis for hydroxyl of the same MgO material be made. Results of this and subsequent experiments are shown in Table 24.

A sample weighing 0.1088 g was loaded into the front part of the sample storage arm and 0.2 g of graphite (the same as used before) was placed in the back portion. The system was evacuated and degassed at 2800C, and blanks were obtained for H_2 and CO at 2000C and 2800C. The sample was dropped in the crucible, but no graphite was added. The sample was heated to 2000C for 1.5 minutes as in previous runs; analysis of the gas collected showed 3 ppmw $Mg(OH)_2$, which is in agreement with previous results (see Table 19).

Approximately one-half the graphite was added to the crucible, covering the sample completely, which was more than the theoretical amount required for complete decomposition of the MgO. The temperature was raised to 2800C for 3 minutes, the power was turned off, and additional ice was added to the cooling bath until the temperature of the water dropped to about 0C. The temperature of the bath rose to slightly above room temperature during a 3-minute run at 2800C. This cycle of a 3-minute heating followed by cooling was continued until a total reaction time of 12 minutes had been obtained. The temperature was raised very slowly each time in an effort to prevent graphite loss from the crucible, as had been observed during the feasibility run. These efforts were not successful, as graphite was again observed in the bottom of the quartz tube after the reaction. Results of these conversion runs are shown in Table 24 and are designated as Run C-1-2. Only a 2.6 percent conversion of the MgO was obtained and 38 ppmw of $Mg(OH)_2$ was found.

The rest of the graphite was added to the sample and the above experiment was repeated (Run C-1-3); the temperature was raised very slowly to prevent loss of graphite. The same heating and cooling cycle was used, but only an additional 7 percent conversion was obtained (a total of 9.6 percent). During the 7 percent conversion, more graphite was lost from the crucible, together with some sample. One additional heating (Run C-1-4) was made at 3300C for 2.5 minutes, but practically no additional conversion was obtained. After disassembling the apparatus it was found that the graphite crucible was empty and that all the remaining material was on the bottom of the quartz tube or on the sidewalls. Less than 10 percent total conversion was obtained.

In an attempt to prevent the loss of graphite and sample, the sample and graphite were then briquetted. A different type of graphite was used for these runs because a better pellet could be obtained with this new graphite. National Special Spectroscopic Graphite, Grade SP-1 (briquetting), was prefired at 900C for 45 minutes. A mixture of 0.040 g of this graphite and 0.081 g of the powdered MgO was pressed into a pellet.

The pellet was loaded into the sample-storage arm and the system was evacuated and degassed at 2800C. Blanks were obtained at 2000C and 2800C. The pellet was transferred to the crucible and heated at this low temperature, and the calculated $Mg(OH)_2$ content was 24 ppmw. The next reaction at 2800C for 6 minutes produced an additional 41.5 percent conversion and an additional 346 ppmw $Mg(OH)_2$.

As the temperature was being raised slowly for the next heating, a violent reaction, accompanied by sparks flying from the crucible, took place at about 800C. This lasted only a few seconds, after which the temperature was raised to 2800C for another 6-minute period. An additional 15.9 percent conversion had taken place, but no hydrogen was detected. After removal of the apparatus from the heating system, a portion of the pellet, still intact, was observed in the bottom of the quartz tube along with some powdered material. This material from the bottom of the container weighed 0.0214 g. Based on the original weight of the sample, a total conversion of 68.9 percent was obtained. If we assume that one-half the weight of residue is MgO, the conversion was 80 percent, based on the original weight of MgO minus the residue weight of MgO.

Although a new source of graphite was used for Run C-2 (with no blank data having been obtained), there is evidence that more hydroxyl is released from the sample when it is partially decomposed. If the hydroxyl release is linear with the percent decomposition, the total $Mg(OH)_2$ for Run C-1 would be 423 ppmw and 539 ppmw for Run C-2, or 465 ppmw if the assumed MgO Loss is considered.

Intimate contact of the sample and graphite is very important as can be seen by comparing Run C-1-4, at approximately 3300C in which most or all the powdered graphite placed in the crucible was lost, and Run C-2-1, at 2000C with the mixture in pellet form. A pellet of MgO and graphite produced much better conversion than did layers of each in powdered form. The major problem was a severe loss of sample and graphite from the graphite crucible. The powdered graphite was ejected from the crucible no matter how slowly the temperature was raised. The turbulence was probably due to the electromagnetic coupling of the induction heater and the graphite. The loss of part of the pellet in Run C-2 appeared to be caused by a violent reaction within the pellet.

To prevent loss of the sample, a few large pieces of carbon or graphite placed over the pellet might serve as a lid. However, this may have the disadvantage of introducing a higher blank. Extremely high temperatures do not appear to be as important as intimate contact of the graphite and MgO, although the reaction rate no doubt is dependent upon temperature as well as contact. An intermediate temperature of approximately 2200C for a longer time period certainly would be easier to control.

Interpretation of Thermal Data

Considering these data, a possible explanation of the variations in hydroxyl content with the method of determination was proposed by Dr. Leipold. Loosely bound (physically adsorbed) water can be removed simply by pumping. The isostatically cold-pressed Fisher M-300 B-3 reported above apparently contained this type of water. This sample gave off so much water when pumped at room temperature that a good vacuum could not be reached.

The second type of water may be considered to be that present as $Mg(OH)_2$. As has been reported earlier, this water is quantitatively removed at temperatures between 300 and 400C*. Brucite analyzed using thermogravimetric analysis showed a sharp weight loss at about 350C, confirming the decomposition temperature given in handbooks.

A third type of water may be present, although the experimental evidence is unclear. Perhaps the water released by the heating of MgO to around 2000C, without decomposition, is a more tightly bound water than adsorbed water or $Mg(OH)_2$ water; on the other hand, it may be either or both of these kinds of water diffusing from the interior of the solid material. This point could be clarified by a time-temperature study, but such a study seems rather unnecessary inasmuch as whichever type of water this is, it apparently is not the water of primary interest.

The water of interest, and that which is proving so difficult to determine, is the water presumed to be present in the crystal structure as an OH substituting for an O, as mentioned above. If this hypothesis is true, and if the thermodynamics of the MgO-MgOH system are such that the OH cannot be removed without rupturing the other Mg-O bonds, then it follows that only in the last experiments described above did the hydroxyl liberation (as H_2) approach the true value. Certainly the data cited in these experiments tend to confirm Dr. Leipold's contention that there is hydroxyl in MgO that cannot be determined using conventional techniques. It was for this reason that the mass-spectrographic technique was specified in the

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* Second Quarterly Progress Report, this contract.

work statement as a possible means of determining hydroxyl.

Mass Spectrograph

Because the spark employed breaks up any compound (the temperature in the spark gap has been estimated to be as high as 50,000C), the hydroxyl, no matter how it is bound in the crystal lattice, should be seen as H, H_2, or OH. As described in earlier reports, this is the case. The important question, and the one not yet answered, is, "Can the intensities of the lines at m/e 1,2, and 17 be related to the true hydroxyl content of the sample?" Dr. Leipziger, in his work at Sperry Rand, tentatively concluded that it was possible. Certainly his work on refractory metals proved that H, as determined at m/e 1, could be determined by this technique with reasonable accuracy. His values for H in two solid samples of MgO were 600 and 1400 ppma in OP 14 and OP 111, respectively; Battelle mass results* for these same samples were 2000 and 600 ppma H, respectively. The agreement is within a factor of about three, but the reversal in values obtained is disturbing.

Thermal (quartz-tube graphite-crucible) and mass data for OP 243 were 650 and 50,000 ppma H, respectively. For another sample, Fisher M-300 isostatically cold-pressed B-3 (BMI No. S-0460), the agreement was good, with the thermal and mass values being 180,000 and 200,000 ppma H, respectively. Sample OP 366 showed 200 and 3,000 ppma H, by the thermal and mass techniques.

When the MgO residues from the thermal analyses were examined mass spectrographically, the H value increased to 30,000 ppma in the case of OP 366, and decreased to 10,000 ppma for OP 243. It is difficult to understand why H or OH should increase in MgO during or after the thermal treatment, as appears to have occurred in OP 366. Adsorption from the atmosphere alone could scarcely account for such an increase, especially since the samples were protected from long exposure to the atmosphere and were baked in the spectrograph prior to analysis.

One other point should be mentioned about the mass spectrographic technique for hydroxyl determination. The blanks for H, H_2, and OH were

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* From Table 7, First Quarterly Progress Report, this contract.

about 300, 300, and < 10 ppma, respectively, as determined by sparking pure Au wire. Dr. Leipziger reported lower blanks, perhaps because his instrument was pumped with ion pumps whereas the Battelle instrument is pumped with oil diffusion pumps (Dow Corning 705 Silicone oil). The H_2 background after a bake, with the source pressure in the low 10^{-9}-torr region, is by far the predominant gas and probably comes from oil breakdown. Other masses observed are 15, 16, 28, and usually 78, attributed to CH_3, CH_4, CO, and C_6H_6. These are logical fragments of 705 silicone oil. Nevertheless, the background at m/e 1 is not the limiting factor at the levels of OH apparently present in these samples.

Emission Spectrograph

Dr. Leipold pointed out a recent article* that described an emission-spectrographic technique to determine water or hydroxyl. A ground sample is mixed with silica and arced in a large, necked electrode with a cap similar to the "boiler cap" electrode system. The OH bandhead at 3063.6A is the analytical line.

Preliminary experiments using this technique for $Mg(OH)_2$ and two samples of MgO (Fisher M-300 B-3 isostatically cold pressed and OP 366) were quite unsuccessful. The intensity of the bandhead was weak, even with a drop of water added to the sample. The response was very poor and there was a factor of only four between the ratio $\frac{\text{intensity of OH line}}{\text{weight of sample}}$ for $Mg(OH)_2$ and OP 366, yet the difference in OH content is a factor of at least several hundred. Even if these problems were solved, there is reason to doubt that the method would work with MgO because the temperature of the sample does not exceed perhaps 1500 C and, as pointed out before, hydroxyl most likely still is retained at this temperature. If the sample were completely burned there might be a possibility of using the basic technique, were it not for the problems of intensity and response.

The minerals used by Quesada and Dennen to calibrate their instrument for this technique have been ordered and will be arced in the special

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* Quesada, Antonio, and Dennen, William H., "Spectrochemical Determination of Water in Minerals and Rocks", Applied Spectroscopy, <u>21</u> (3), 155 (May-June, 1967).

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electrodes following the given procedure. The result of this experiment will determine whether or not it would be worthwhile to pursue it further.

Analysis for Other Elements

mass spectrographic analyses of several MgO and $Mg(OH)_2$ samples were made during this report period. The powdered samples (three Kanto materials) were analyzed primarily for substitutional elements, and the solid samples (Kanto, Fisher M-300, and single crystal) for all detectable elements. Some analytical data were supplied with certain samples and were used as comparisons for the mass results. Also, C and N were determined chemically in the Kanto and the single-crystal samples.

The mass spectrographic technique employed was essentially that which has been reported previously. The powders were briquetted with Ag in the weight ratio MgO:Ag = 1:2 and sparked for several series of graded exposures, at both high and low mass ranges, giving three to six photoplates from which data could be obtained. The solid samples were sparked using a counter electrode of Au. The solid samples were baked overnight in the source at about 150 C, and were sparked as described above. In addition, a piece of Au was loaded in the same holder as the MgO sample to permit sparking Au versus Au, as well as Au versus MgO. The purpose of the Au versus Au sparking was to assess the residual blank of the instrument for the interstitial elements.

The results of these analyses are given in Tables 20, 21, and 22. Cross-check data, where available, are also listed. In the Kanto materials the mass results appear to be rather consistently above the supplied data. However, the variance is less than a factor of 10. The agreement for the single crystal is much better, suggesting either a more reliable supplied analysis or, more probably, a better mass analysis because the single crystal did not need to be briquetted. Note that etching (H_2O rinse) effectively removed many surface impurities. The other solid sample (OP 243) was not cross checked for enough elements to judge the agreement.

There is no apparent correlation between the mass results and the chemical or thermal data for H, C, and N. Samples having high C (as determined by combustion) give low results by mass, and vice versa. The same inconsistency can be seen in the N values. The chemical results should be valid, but on the other hand it is difficult to understand how the mass results can be so incorrect. The problem is not an instrument blank, at least for the higher values. The Au versus Au blanks on many plates averaged about 300 H, 300 H_2, <10 OH, 50 C, and <0.1 N, in ppma. Part of these blank values may be actual impurities in the Au, but because the Au is of very high purity (6-9 grade Cominco) most of the blank is no doubt residual background.

It is interesting to compare the analysis of an as-received sample with one that has been fired in the quartz tube--graphite crucible. Both OP 243 and OP 366 show a marked drop in F; other elements including Cl, S, K, Na, V, and Co drop in one sample, but not in the other. Some elements appear to be picked up, either from the mortar or from the quartz vessel.

CONCLUSIONS AND RECOMMENDATIONS

Hydroxyl in MgO received primary emphasis during this report period. The data that were generated by thermal, decomposition, and mass spectrographic techniques are confusing and badly scattered if a single form of OH or H_2O is assumed. If, however, there can be present in a solid sample three or more forms of OH or H_2O, then the data show that only a decomposition technique such as the chemical reaction $MgO + C \longrightarrow Mg + CO$ or spark source mass spectrography can be expected to yield valid results. Assuming this to be the case, the goal of this research must be the complete liberation and accurate determination of hydroxyl. It appears that two techniques discussed in detail in this report offer the most promise, and that the quartz-tube graphite-crucible technique should be the more accurate if certain problems can be solved.

Other elements, except C and N, seem to be fairly well standardized by a combination of mass and emission spectrography, combustion, Kjeldahl, wet chemical, atomic adsorption, and flame emission techniques.

NEW TECHNOLOGY

No reportable items of new technology have been generated under this contract to date.

FUTURE WORK

During the next quarter, the hydroxyl determination will receive almost exclusive attention. The three approaches--emission and mass spectrography and chemical decomposition--will be pursued until one or more is proven successful or until all are shown to be inapplicable.

Some chemical and emission spectrographic cross checks will be made of a few solid samples, especially OP 366 and OP 243.

With the transfer of this project to NASA Headquarters, the program emphasis may be shifted. According to present plans this will be discussed with Mr. Gangler in Washington, D.C., on November 16, 1967. From this meeting may come a redirection of effort to other refractories or to other phases of analytical problems such as microanalysis. Two other trips are planned during November to discuss ion bombardment microprobes as a possible means of characterizing the composition of small areas of solid refractories.

TABLE 19. HYDROXYL ANALYSIS OF SOLID MgO

Run	Temperature, C	Sample Weight, g	Hydrogen in Sample, cc atm	Equivalent $Mg(OH)_2$ in Blank, g	$Mg(OH)_2$ in Sample, g	Hydrogen in Sample	
						As $Mg(OH)_2$, ppmw	As H, ppma
			Fisher M-300, B-3, BMI No. S-0460				
M-1	2000	0.5303	26.3	0.26×10^{-6}	0.068	12.8(c)	18.4(d)
M-2	2000	0.5136	25.4	0.26×10^{-6}(b)	0.066	12.8(c)	18.4(d)
M-3	2000	0.2758(a)	0.00090	0.06×10^{-6}	2.26×10^{-6}	8.	12.
M-4	2200	Ditto	ND	0.06×10^{-6}	--	<0.01	<0.014
M-5	2600	"	0.00020	0.06×10^{-6}	0.58×10^{-6}	2.	3.
			Fisher M-300, OP 243, BMI No. 91940				
M-6	2000	0.4986	0.00038	0.05×10^{-6}	0.93×10^{-6}	2.	3.
M-7	2000	0.5327	0.00063	0.17×10^{-6}	1.45×10^{-6}	3.	4.

ND Not detected.

(a) Sample Runs M-3 through M-5 are repeated runs on the same sample without opening the container.

(b) Assumed to be same as in Run M-1.

(c) Weight percent.

(d) Atomic percent.

TABLE 20. ANALYSIS OF FISHER M-300

(ppma)

	OP 243(a)			Isostatic	
	As Received		After Heating(b)	As Received(c)	
Element	Mass	Chem	Mass	Mass	Chem
H	50,000.	3. (as H)(d) 650. (as H)(e)	10,000.	200,000.	180,000. (as H)(d)
H_2	300.		1,000.	10,000.	
OH	300.		500.	30,000.	
Li	1.		0.1	<1.	
B	300.		15.	100.	
C	30,000.	170.	3,000.	10,000.	
N	3,000.		30.	100.	
F	2,000.	1,330.	30.	500.	
Na	300.	290.	<2.	300.	
Al	100.		30.	10.	
Si	300.		3,000.	300.	
P	30.		10.	10.	
S	300.	85.	50.	1,000.	
Cl	300.	595.	10.	300.	
K	300.	8.	<1.	30.	
Ca	5,000.	2,680.	2,000.	2,000.	
Ti	50.		20.	30.	
V	1.		0.4	10.	
Cr	3.		0.5	0.3	
Mn	30.		15.	20.	
Fe	170.		100.	100.	
Co	10.		0.2	3.	
Ni	10.		3.	3.	
Cu	10.		5.	5.	
Zn	10.		0.5	3.	
As	1.		<0.1	2.	
Br	3.		<0.2	20.	
Mo	100.		<0.4	<0.4	

(a) BMI No. 91940.

(b) Average of analyses of residues from Runs M-6 and M-7 (Table 19).

(c) BMI No. S-0460; cold pressed at 90,000 psi.

(d) From Table 19.

(e) From Table 24.

TABLE 21. ANALYSIS OF KANTO SAMPLES

(ppma)

Element	$Mg(OH)_2$ (a)		MgO(b)		Calcined MgO(c)	OP 366(d)		
						As Received	After Heating	
	Mass	Given	Mass	Given	Mass	Mass	Run M-8	Run M-9
H	--	--	--	--	--	3,000. } 200 (as H)(f)	30,000.	30,000.
H_2	--	--	--	--	--	500.	300.	300.
OH	--	--	--	--	--	200.	100.	100.
Li	<2.	--	<2.	--	<0.2	1.	≤0.1	<0.1
B	100.	--	20.	--	10.	20.	5.	20.
C	60.	2,200.(e)	2,000.	570.(e)	60.;7400(e)	3,000.;400(e)	30,000.	1,000.
N	60.	2,500. 7,500.(e)	600.	195. 86.(e)	20.;500(e)	300.;29(e)	10.	3.
F	50.	--	200.	--	6.	300.	10.	10.
Na	20.	--	40.	--	<2.	3.	<3.	3.
Al	10.	22.	10.	60.	20.	100.	10.	10.
Si	200.	55.	200.	29.	100.	500.	500.	500.
P	20.	10.	20.	8.5	6.	3.	3.	3.
S	200.	17.	1,000.	--	30.	500.	500.	300.
Cl	600.	17.	600.	45.	20.	30.	30.	10.
K	20.	--	20.	--	<2.	10.	3.	2.
Ca	20.	15.	50.	30.	20.	10.	10.	20.
Ti	20.	--	20.	--	20.	3.	10.	10.
V	<1.	--	<1.	--	0.6	0.3	<0.1	<0.1
Cr	≤2.	--	≤2.	--	1.	1.	3.	0.1
Mn	2.	1.1	2.	3.	1.	1.	3.	0.3
Fe	20.	3.5	20.	11.	20.	20.	20.	5.
Co	<2.	--	<2.	--	0.6	0.3	1.	0.3
Ni	3.	--	3.	--	1.	1.	15.	5.
Cu	3.	--	3.	--	0.3	0.5	10.	0.5
Zn	10.	--	10.	12.	1.	2.	4.	1.
As	2.	0.4	2.	0.2	<0.2	<0.1	<0.1	<0.1
Br	<1.	--	<1.	--	<0.4	<0.6	1.	0.4
Zr	<0.5	--	<0.5	<0.25	<0.5	<0.5	<0.5	<0.5
Mo	<0.4	--	<0.4	--	<0.4	<0.4	<0.4	<0.4
Ba	<0.6	--	<0.6	6.	<0.6	<0.6	<0.6	<0.6
Pb	<1.	1.5	<1.	2.	<1.	<1.	<1.	<1.

(a) BMI No. S-0431.
(b) BMI No. S-0430.
(c) BMI No. S-0429.
(d) BMI No. S-0432.
(e) BMI combustion result.
(f) From Table 23.

TABLE 22. COMPARATIVE ANALYSIS OF SINGLE-CRYSTAL MgO(a)

(ppma)

	Battelle, Mass		
Element	Run 1 (As Received)	Run 2 (Etched)	Given Analysis
H	30,000	10,000	--
H_2	1,000	300	--
OH	10,000	100	--
Li	0.2	<2.	--
B	2.	2.	--
C	600.	600.	70.(b)
N	200.	100.	30.;<10(b)
F	6.	3.	--
Na	<2.	<2.	2.8
Al	100.	60.	62.
Si	20.	20.	39.
P	2.	2.	2.6
S	200.	25.	<2.5
Cl	120.	20.	--
K	<6.	<6.	--
Ca	6.	20.	47.
Ti	20.	20.	--
V	<0.6	≤0.2	--
Cr	0.6	0.6	<2.3
Mn	0.2	0.2	0.2
Fe	10.	2.	2.
Co	0.6	0.2	--
Ni	3.	10.	--
Cu	3.	<1.	--
Zn	10.	4.	4.5
As	≤0.2	≤0.2	<1.3
Br	<1.	2.	1.
Mo	<0.4	<0.4	<0.4

(a) Boule No. 8, from Dr. W. A. Sibley, Oak Ridge; material produced by W. and C. Spicer, Ltd.

(b) Battelle chemical values (combustion and Kjeldahl).

TABLE 23. HYDROXYL ANALYSIS OF SOLID MgO

	Kanto MgO, OP 366, BMI No. S-0432						
						Hydrogen in Sample	
Run	Temperature, C	Sample Weight, g	Hydrogen in Sample, cc atm	Equivalent $Mg(OH)_2$ in Blank, μg	$Mg(OH)_2$ in Sample, μg	As $Mg(OH)_2$, ppmw	As H, ppma
M-8	2000	0.5159	0.0265	0.29	68.9	133	192
M-9	2000	0.5185	0.0287	0.07	74.6	144	208

TABLE 24. DECOMPOSITION OF MgO

	Fisher M-300, OP 243, BMI No. 91940							
							Hydrogen in Sample	
Run No.	Temperature, C	Sample Weight, g	Reaction Time, min.	Theoretical CO, g	CO in Sample, g	Decomposition, percent	As $Mg(OH)_2$, ppmw	As H, ppma
Feasibility	2800	0.1193	4	0.0830	0.0480	58	--	--
C-1-1(a)	2000	0.1088	1.5	0.0756	0.00003	0.04	3	4
C-1-2	2800		12		0.00197	2.6	38	55
C-1-3	2800		12		0.00529	7.0	ND	ND
C-1-4	3300(b)		2.5		0.00006	0.08	0.1	0.1
C-1 Totals					0.00735	9.7	41.1	59.1
Totals based on 100 percent decomposition						100	423	610
C-2-1	2000	0.081	1.5	0.0563	0.0063	11.2	24	35
C-2-2	2800		6		0.0234	41.5	346	501
C-2-3	2800		6		0.0089	15.9	ND	ND
C-2 Totals					0.0386	68.6	370	536
Totals based on 100 percent decomposition(c)						100	465	670

ND None detected.
(a) Powdered carbon was not in crucible with sample.
(b) Approximate temperature.
(c) Corrected for material lost from crucible.
C-1 Powdered carbon added over MgO, except C-1-1.
C-2 Powdered carbon and MgO pressed into pellet.