DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES
FOR ADVANCED MATERIALS

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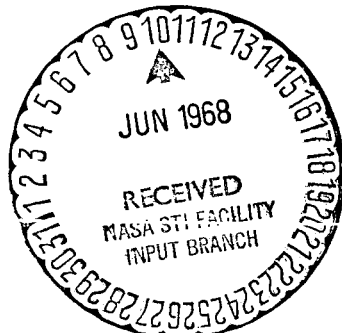
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ABSTRACT

During this quarter the laser decomposition of magnesium oxide
plus graphite was continued, and a new approach to determine hydroxyl
was begun. Mass spectrographic studies were continued, emphasizing the
analysis of refractory materials for elements other than the interstitial
elements. A Knudsen cell run was made in an attempt to establish the time-
temperature relationships in the magnesium oxide-graphite-hydroxyl system.

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by

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INTRODUCTION

The first year of this research program was devoted to studying MgO--both for "substitutional" impurities and for the "interstitial" elements H, C, and N. This work was reported in detail in the Annual Summary Report dated February 2, 1968. In the period covered by the present report, the problem of OH determination in MgO was studied, and several University of Washington refractory samples were analyzed mass spectrographically.

The OH problem has been mentioned and discussed in many previous reports under this contract. Each approach tried to date has appeared promising on first inspection, but closer investigations have revealed serious deficiencies. Of the two new techniques applied during this quarter, the Knudsen cell produced puzzling data that would be quite difficult to reduce to meaningful results. The other innovation, heating MgO in O_2, has given quite good results in the first two experiments.

EXPERIMENTAL WORK

Hydroxyl Determination

Laser Heating

The MgO used for the experiments reported below was OP 243, BMI 91940. It was finely ground, then mixed and pressed 1:1 by weight

with graphite. The apparatus in which the MgO-C pellet was heated was
a quartz tube, with a Lavite pedestal, capped by a platinum disk to
which the pellet was attached. One end of the tube was an optical flat
for use with the laser. The assembly was evacuated and heated by infrared
until no outgassing could be detected. The sample was heated by induction
to 1000 C for 6 minutes and the quantity of gas was measured and analyzed.
After subtracting the blank obtained on the graphite, it was determined
from the amount of H liberated that the sample contained 0.17 weight
percent $Mg(OH)_2$. Since the entire sample is heated by the induction
method, calculations are based on the total weight of MgO in the pellet.
(Since only a minute quantity of the MgO is heated by the laser, calcula-
tions for laser heating are based on the amount of MgO decomposed as
calculated from the amount of CO produced.)

Another sample of OP 243 was treated in the same manner except
that fine-focus laser heating was used before the induction heating.
The amount of CO liberated indicated 4000 μg of the MgO was decomposed,
but the amount of $Mg(OH)_2$ was only 85 ppmw. After evacuating the system
again, the sample was heated by induction for 6 minutes at 1000 C, and the
CO liberated indicated 7240 μg of the MgO was decomposed. Based on the
H liberated, the total sample contained 0.16 weight percent $Mg(OH)_2$. The
laser result at high energy indicated very low OH content although very
good check results were obtained on the low-temperature induction-heating
method. These results, together with results obtained earlier on Sample
BMI 91938, suggest that increased energy (high-temperature induction
heating) produces a loss of H. The focus of the laser beam was changed
to reduce the effective energy, and the following experiment was made
with the diameter of the beam at the impact point about 1/4 inch.

Another sample of OP 243 was treated the same as before and
run by laser, this time with the large-diameter beam and 60 shots. A
blank on the graphite was also run under these same conditions. Under
these conditions, about one-tenth the amount of MgO decomposed, but the
amount of H liberated indicated the sample contains 0.33 weight percent
$Mg(OH)_2$.

The same sample was analyzed by 160 laser shots with 10 joules. The fine focus was used, which produced an impact area about 1 mm in diameter. Decomposition of the MgO amounted to 3200 μg, and the $Mg(OH)_2$ was equivalent to 37 ppmw.

The above data verify the evidence from the induction-heating experiments that higher temperatures yield less H from the MgO or that a secondary reaction which consumes H is taking place. The mass spectrometer shows no products other than CO which might account for a secondary reaction. No significant amount of free water was found in any of the above experiments.

Mass Spectrograph

Sample OP 243 previously had been analyzed mass spectrographically, and about 3.7 weight percent of $Mg(OH)_2$ had been found (as determined at m/e 1, 2, and 17). It was rerun twice during this report period, with special precautions having been taken to insure a good vacuum after a bake. After extensive presparking, several plates of light exposures were made in which the H-containing masses could be read. One analysis gave 0.13 percent by weight as $Mg(OH)_2$, which is in quite good agreement with the 0.16 and 0.17 percent by induction heating. The second analysis of this series gave 0.52 percent by weight as $Mg(OH)_2$. These last two mass spectrographic analyses are believed the more reliable than the original analysis [3.7 percent $Mg(OH)_2$] because more care was taken to get the good, low-intensity exposures necessary for reading high H contents.

Knudsen Cell

Because evidence had been pointing to the conclusion that higher temperatures and longer reaction times were not producing the desired effect, and in fact appeared to be detrimental to the liberation (or at least the determination) of H in the MgO + C system, it was decided to

evaluate the Knudsen cell technique. Basically the Knudsen cell enables
one to follow the composition of the gas phase above a solid under
equilibrium conditions at well-defined temperatures. As applied to the
present problem the gas was analyzed as it emerged from a small hole in
the top of a graphite crucible containing MgO (OP 243) plus C, at specific
temperatures up to about 1300 C. From previous work using induction and
laser heating it was expected that the major species would be H_2, H_2O, with
large amounts of CO and/or CO_2. However, essentially no H_2 was detected;
rather, peaks occurred at almost every mass from 12 through 70. Some
of these can be explained as such species as C, CH_4 and fragments, Mg,
MgO, MgOH, CaF, etc. But others appear to be various hydrocarbons. It
is difficult to understand how hydrocarbons can be produced and remain
at 1300 C, even given the ideal condition of free C and H in adequate
amounts. The blank run (graphite crucible only) did not show as much
hydrocarbon; therefore it must be assumed that the H in the MgO (plus
the graphite) is the source of these hydrocarbons.

The data suggest that equilibrium conditions are far different
from those employed in the past, and that equilibrium is not a desirable
condition. They further suggest that H is evolved, at temperatures up
to 1300 C, over a many-hour period, inasmuch as the Knudsen cell exper-
iments took several days to complete and hydrocarbons were still being
observed at the conclusion.

The experiment has not answered the question of importance:
At what temperature and over what time is H best extracted from MgO?
All other experiments have indicated that time periods of minutes accomplish
as much, if not more, H liberation than longer periods; in fact, further
heating has been shown to produce a decrease in the hydrogen already
extracted. In view of the difficulty of handling the raw Knudsen cell
data, and because the technique does not appear promising with respect
to the objectives of the program, no additional work will be done.

Oxygen Reaction

Upon examining the thermodynamics of the MgO system, it was calculated that the reaction $2MgOH + \frac{1}{2}O_2 \longrightarrow MgO + Mg(OH)_2$ was favored by heat, and of course by O_2. Since $Mg(OH)_2$ is known to be unstable above about 400 C, the technique of heating MgO in O_2 is theoretically a means of liberating the H.

Two experiments were made to establish the feasibility of the technique. In both cases MgO (Fisher M-300, calcined in vacuum at 700 C, BMI 91938) was used. Briefly, the sample was heated at 100 C and at 500 C in vacuum, and at 500 C with O_2 flowing. Discrete amounts of H_2O were liberated at each step; by far the largest amount came during the 500 C--no O_2 step, but a significant additional amount was obtained when O_2 was added. The complete procedure is given below; the data are presented in Table 28, and for Run 2 are shown graphically in Figure 1. (Note that the y-axis and the plot itself are three segments, with breaks between, to compress the graph.)

Procedure. A sample of MgO weighing about 10 mg was placed in a Vycor boat inside a Vycor reaction vessel. The latter was designed to pivot about an axis formed by the arms attached to the inlet and outlet gas lines. The main vessel chamber was blanked at the selected temperatures, then was rotated to allow the sample boat to slide into the heating zone. The O_2 supply was tank O_2, purified of H_2O by passing through 13X molecular sieves held at -10 C. The outlet gases passed through a liquid nitrogen trap and into the mass spectrometer inlet or, with O_2 flow, into a trapped mechanical pump.

In the first run the sample was held at 100 C for 20 minutes under vacuum, and the H_2O released was collected and measured. Presumably this is surface or physically bound water. Next, the sample was held at 500 C in vacuum, and again the released H_2O was measured. This is assumed to be water present in the sample as $Mg(OH)_2$. Finally, the sample was maintained at 500 C with about 20 torr O_2 flowing through the vessel. The H_2O released during this step is thought to be that which was held as MgOH in the sample.

The second run was similar, except that at least two heating periods were employed at each step to determine if the increases were real or were merely evidence of insufficient time in the previous step.

The data in Table 28 indicate a definite break in the elution of H_2O between 100 C, 500 C without O_2, and 500 C with O_2 present. Previous runs on this sample using the mass spectrograph and laser beam and induction heat decomposition showed about 20 percent $Mg(OH)_2$; however, the distinction between $Mg(OH)_2$ and MgOH was not made.

For Run 1 the sample was weighed after the reaction and had lost 0.0009 g. (A small amount blew out of the boat during the run and was not weighed.) The sample from Run 2 was lost during removal from the apparatus.

Table 29 shows the amount of CO_2 evolved and calculated as C and as $MgCO_3$. (No C was added to these samples.) The reproducibility is poor and no definite significance can be attached to these values. In Run 2 the evolution of CO_2 did drop on the second heating at 500 C with and without oxygen; however, at 100 C the CO_2 was nearly as high for the second heating as for the first heating.

Table 30 shows the composition of the noncondensables from Run 2 at 100 C and 500 C without oxygen. No significant amount of material was detected except for air release at 100 C. Obviously the analysis of the noncondensables was not practical for the 500 C temperature with oxygen flow.

One can raise the question "Why would this technique work while calcining in air apparently is ineffective?" The only obvious answer is that the adsorption of H_2O is very rapid and that MgO, even though free of OH at one stage in production, soon picks up OH from the atmosphere. This hypothesis can be checked by exposing the sample to moist air after having been heated in flowing O_2. It is not expected that an amount of H_2O will be picked up equal to what was released. It will be interesting to determine if the same "three types of OH" are found after air exposure of supposedly OH-free MgO, as were found in the initial runs.

Standardization of Mass Spectrographic Technique

Throughout this program the standardization of the mass spectrographic technique has been stressed. Most of the work has involved cross-check data obtained by chemical and emission spectrographic means. During this report period synthetic standards were prepared using as a base Kanto MgO, BMI S-0430, and BMI S-0429. The amounts of selected elements present in the sample, the total after the additions, and the amounts subsequently found by mass spectrographic analysis are shown in Tables 25 and 31. In most instances the agreement was good, particularly so for elements that might have been expected to be problems. The two high-weight alkalies, Rb and Cs, appear to have unit sensitivity, i.e., they are not abnormally ionized. But two low-weight alkalies, Na and K, are severely enhanced at the +1 positions, and apparently the +2 positions (m/e 11-1/2 and 19-1/2 for Na and K) require correction factors in the range of 100 to 300 for Na, and 30 to 50 for K. The reported values were obtained from the +2 lines using a correction factor of 10. Lithium, the lowest weight alkali, has a sensitivity of about 3 at the +1 position.[*]

The halogens behave in a peculiar manner. Br has nearly unit sensitivity. Cl and F have been inconsistent, Cl usually being too high and F too low as determined mass spectrographically. This was true for the standards as well.

The standards were made by adding small volumes of solutions containing water-soluble salts of the cations and anions of interest. Care was taken to moisten essentially all the powdered MgO but not to have left-over solution that could fractionally crystallize. The paste was mulled thoroughly, then muffled at as high a temperature as possible, considering the decomposition temperatures of the various ingredients and the corresponding MgX compounds (where X indicates the added anions). In the present case, this was 120 C. After muffling, the mixture was shaken in plastic vials with plastic balls for 15 to 30 minutes, then

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[*] The observed concentration must be divided by 3 to arrive at the proper result.

mixed with Ag or C as usual. This technique, long used by emission spectroscopists, probably insures a more homogeneous standard than is possible by dry mixing.

The Cl results are so far above the known addition level as to suggest that Cl was added inadvertently. The first set of standards was made with the salts RbCl, CsBr, Na_2SiO_3, KF, Li_2SO_4, and $Sr(NO_3)_2$. The second set was made using NaOH, $MgCl_2$, and MgF_2 in the hope of avoiding chance Cl pickup. However, the one unknown item is the Yb, made by dilution of a stock of Yb in unknown acid. This stock was not checked for Cl because of an oversight; either it or one of the standards will be checked chemically to determine if this is the source of unintentional Cl addition.

Analysis of Samples

MgO

Two MgO samples from Mr. Jack Merrow, University of Washington, were analyzed by emission and mass spectrography. The results are given in Table 26. The cube was reported to be "4-9's" pure. The samples were sparked directly versus Ag and Ta counter electrodes, but the ion beam consisted of many more counter-electrode ions than Mg and O ions. The samples were therefore ground in a boron carbide mortar (the reported B values are from the direct sparking runs) and briquetted.

Al_2O_3

One of the materials specified for research in this program is Al_2O_3. Until now only MgO has been investigated in this program, but in an effort to make the research efforts as useful as possible to those working in the refractory ceramics field, other materials of interest are being studied during the remainder of the program. The single crystal Al_2O_3 supplied by Dr. W. D. Scott, University of Washington, an analysis of which is reported in Table 27, was grown from Linde polishing powder.

The analysis of this starting material is the "Given" analysis in the table, and may not represent what would be expected in a finished crystal. It appears that some of the more volatile impurities (Sn, Ag, Mn, B) were removed during the flame fusion growing, and that others (Mg, Ca) were picked up. Most of the other impurities showed good agreement between the vendor's emission spectrographic analysis of the powder Al_2O_3, Battelle's emission spectrographic analysis of the single crystal, and Battelle's mass spectrographic analysis of the single crystal. On the basis of this one sample, it appears that the analysis of Al_2O_3 does not present any unusual difficulty.

It was found, however, that mortar contamination was a serious problem because the Al_2O_3 is so hard. High and unpredictable impurities were picked up from mortars made of sapphire and tungsten carbide, probably reflecting materials previously ground in these mortars and not removed despite careful cleaning. If many samples of hard materials were to be analyzed, it would pay to reserve a new mortar for that material alone to reduce chance contamination.

CONCLUSIONS AND RECOMMENDATIONS

The major effort described in this report concerned the OH determination in MgO. On the basis of rather limited work, two techniques appear to be aimed in the right direction. These are the moderate heating of MgO-C, either by induction or by defocused laser, and the stepwise H_2O liberation using an O_2 atmosphere in the final step. Much of the previous work was performed on the premise that decomposition of MgO at high temperatures was necessary to liberate H. Not only was the reaction difficult to accomplish, it also led to an actual reduction in the amount of H_2 collected.

It is recommended that the moderate temperature release of H be studied further with the goal being the quantitative determination of OH.

NEW TECHNOLOGY

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

FUTURE WORK

The $MgO-O_2$ system will be investigated using a revised heating schedule to confirm the liberation of additional H_2O at a given temperature as O_2 is introduced into the system. Further laser-heating studies may be made if the $MgO-O_2$ technique does not prove feasible. Laser excitation of MgO in the mass spectrograph will be attempted. Preliminary studies on another project were unsuccessful because of optical alignment problems, but these have been solved.

TABLE 25. ANALYSIS OF SYNTHETIC STANDARDS BASED ON KANTO MgO[a]

(ppma)

Element	Standard A				Element	Standard B			
	Present	Added	Total	Found		Present	Added	Total	Found
Yb	--	110	110	100	Yb	--	110	110	100
Rb	--	110	110	100	Rb	--	11	11	10
Cl	50	310	360	6000	Cl	50	30	80	4000
Cs	--	32	32	30	Cs	--	3	3	3
Br	--	32	32	20	Br	--	3	3	2
Sr	--	100	100	180	Sr	--	20	20	15
Si	70	400	470	700	Si	70	160	230	300
Na	40	800	840	100	Na	40	320	360	30
K	20	800	820	500	K	20	80	100	100
F	300	600	900	100	F	300	60	360	50
Ca	30	170	200	100	Ca	30	36	66	30
S	260	300	560	500	S	260	70	330	200
Li	--	600	600	500	Li	--	140	140	300

(a) BMI No. S-0430.

TABLE 26.   ANALYSIS OF UNIVERSITY OF WASHINGTON MgO SAMPLES

(ppmw)

Element	Cube		Chip	
	Mass	Emission	Mass	Emission
Li	0.01	--	0.06	--
Be	<0.02	--	<0.02	--
B	0.2	--	0.2	--
F	<0.5	--	<0.5	--
Na	<2.	--	<2.	--
Al	20.	30.	60.	180.
Si	5.	<6.[T]	50.	120.
P	<1.	--	1.	--
S	3.	--	6.	--
Cl	4.	--	4.	--
K	1.	--	1.	--
Ca	200.	450.	200.	450.
Sc	0.2	--	3.	--
Ti	<0.4	<5.	10.	5.
V	1.	<3.[T]	3.	3.
Cr	7.	6.	15.	15.
Mn	20.	15.	50.	40.
Fe	100.	100.	600.	450.
Co	0.1	--	0.2	--
Ni	2.	<6.[T]	12.	15.
Cu	1.	<3.	2.	<3.[T]
Zr	0.5	<20.	70.	150.
Mo	0.2	<3.	0.4	<3.[T]

T   = Trace.
-- = No data.

Note: Elements not reported (except H, C, N, O, and Mg) were not detected. The detection limits are 0.1 ppma, divided by the isotope fraction of the most abundant isotope of the element.

TABLE 27.   MASS AND EMISSION SPECTROGRAPHIC ANALYSIS OF Al_2O_3

(ppmw)

Element	Mass	Emission	Given	Element	Mass	Emission	Given
Li	0.004			Ag	<0.2	<3.[N]	0.5-1.5
Be	<0.03			Cd	<0.3		
B	0.1		0.6-1.5	In	<0.1		
C	(a)			Sn	<0.3		8.-16.
N	50.(b)			Sb	<0.3		
F	<0.6			Te	<0.3		
Na	2.			I	<0.1		
Mg	6.	5.	0.6-1.2	Cs	<0.1		
Si	20.	15.	7.-12.	Ba	≤0.5		
P	0.3			La	<0.1		
S	6.			Ce	<0.1		
Cl	15.			Pr	<0.1		
K	10.			Nd	<0.4		
Ca	15.	10.	0.0-0.35	Sm	<0.6		
Sc	<0.05			Eu	<0.3		
Ti	3.	3.		Gd	<0.6		
V	<0.2	<3.[N]		Tb	<0.2		
Cr	0.3	<10.[N]	0.0-0.35	Dy	<0.7		
Mn	0.5	<3.[T]	10.-20.	Ho	<0.2		
Fe	6.	10.	7.-15.	Er	<0.6		
Co	<0.1			Tm	<0.2		
Ni	2.	<10.[T]		Yb	<0.7		
Cu	1.	<3.[T]	0.8-1.6	Lu	<0.2		
Zn	<0.3			Hf	<0.6		
Ga	<0.2	<10.[N]		Ta	<6.(c)		
Ge	<0.2			W	<0.6		
As	<0.1			Re	<0.4		
Se	<0.2			Os	<0.4		
Br	<0.2			Ir	<0.4		
Rb	<0.2			Pt	<0.6		
Sr	<0.1			Au	<2.(d)		
Y	<0.1			Hg	<0.6		
Zr	<0.2	<10.[N]		Tl	<0.2		
Nb	<0.1			Pb	<0.4		
Mo	<0.4	<10.[N]		Bi	<0.2		
Ru	<0.6			Th	<0.2		
Rh	<0.1			U	<0.2		
Pd	<0.4						

(a)   Graphite binder.
(b)   Source not baked - value may not be valid.
(c)   High "less than" value due to contamination from Ta source parts.
(d) TaO^+ interference.

TABLE 28. H$_2$O RELEASED FROM MgO(a)

	Run 1			Run 2		
	H$_2$O, μg	Weight Percent, as H$_2$O	Weight Percent, as Mg(OH)$_2$	H$_2$O, μg	Weight Percent, as H$_2$O	Weight Percent, as Mg(OH)$_2$
100 C, 1st	11	0.11	0.4	42	0.35	1.1
100 C, 2nd	not run			2	0.02	0.1
100 C, 3rd	not run			5	0.04	0.1
Total	11	0.11	0.4	49	0.41	1.3
500 C, 1st	350	3.43	11.1	760	6.28	20.3
500 C, 2nd	not run			0	0.0	0.0
Total	350	3.43	11.1	760	6.28	20.3
Oxygen 500 C, 1st	126	1.23	4.0	199	1.64	5.3
Oxygen 500 C, 2nd	not run			1	0.01	0.0
Total	126	1.23	4.0	200	1.65	5.3
Total at 100 C	11	0.11	0.4	49	0.41	1.3
Total at 500 C	516	4.66	15.1	960	7.93	25.6
Overall Total	527	4.77	15.5	1009	8.34	26.9

(a) Fisher M-300 calcined in vacuum at 700 C; BMI No. 91938.

TABLE 29. CO$_2$ RELEASED FROM MgO(a)

	Run 1			Run 2		
	CO$_2$, μg	Weight Percent, as C	Weight Percent, as MgCO$_3$	CO$_2$, μg	Weight Percent, as C	Weight Percent, as MgCO$_3$
100 C, 1st	29			54		
100 C, 2nd	not run			34		
100 C, 3rd	not run			44		
Total	29	0.08	0.54	132	0.30	2.09
500 C, 1st	76			196		
500 C, 2nd	not run			26		
Total	76	0.20	1.42	222	0.50	3.52
Oxygen 500 C, 1st	29			200		
Oxygen 500 C, 2nd	not run			0		
Total	29	0.08	0.54	200	0.44	3.17
Overall Total	134	0.36	2.50	554	1.24	8.78

(a) Fisher M-300, calcined in vacuum at 700 C; BMI No. 91938.

TABLE 30. NONCONDENSABLE MATERIAL FROM
MgO AT 100 AND 500 C

	Total cc atmos.	Weight Percent, Based on MgO Sample	
		CO	H_2
100 C, 1st	1.244	N	T (Mostly air)
100 C, 2nd	0.004	T?	N (Mostly air)
100 C, 3rd	N		
500 C, 1st	0.0168	0.1	0.006
500 C, 2nd	0.0048	T	0.003
Overall Total	1.27	≈ 0.1	≈ 0.01
Blank	0.0013	0.01	0.0002

N = Not detected.
T = Trace.

TABLE 31. ANALYSIS OF SYNTHETIC STANDARDS BASED ON KANTO MgO[a]

(ppma)

Element	Base[a] Present		Standard C		Standard D		Standard E	
	Chem	Mass	Present[b]	Found	Present[b]	Found	Present[b]	Found
Yb	--	--	100	40	100	80	100	70
Cl	19	50	1,500	24,000	500	8,000	200	8,000
Na	--	<2	1,000	400	500	200	10,000	6,000
F	110	10	400	60	200	60	100	60

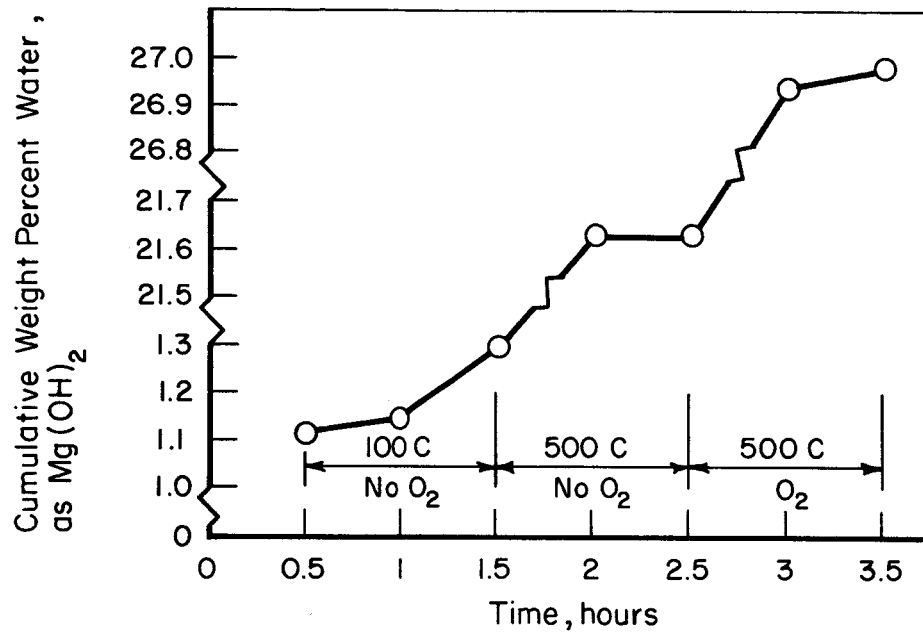(a) BMI No. S 0429
(b) Present in base plus added amount.

FIGURE I. EVOLUTION OF WATER FROM MgO AS A FUNCTION
OF TEMPERATURE AND ATMOSPHERE