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CHEMICAL AND PHYSICAL STABILITY OF REFRACTORIES FOR USE IN COAL GASIFICATION

Second Annual Progress Report, May 1, 1977—April 30, 1978

By
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May 22, 1978

Work Performed Under Contract No. EY-76-S-02-2904

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Rolla, Missouri

U. S. DEPARTMENT OF ENERGY

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CHEMICAL AND PHYSICAL STABILITY OF REFRACTORIES FOR USE IN COAL GASIFICATION

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I. INTRODUCTION

This is the second annual report for this project which commenced on 1 May 1976 with the following objectives:

(1) to achieve an understanding of the general types of chemical reactions occuring in refractories when exposed to conditions representative of those at the cold face of the refractory lining in coal gasification vessels;

(2) to assess the relative importance of these reactions to those physical/chemical properties required for long-service life; and

(3) to identify those refractory systems providing optimum service performance, particularly in regard to the bond phases.

The basic aim of this investigation is to establish the corrosion resistance of refractories, especially the bond phases, to those high pressure/temperature gases and liquids typically present in coal gasification vessels.

This report summarizes the data obtained and analyzed from 1 May 1977 to 30 April 1978. The large number of data sheets for each refractory and cement which accompanied previous reports, are not a part of this report, but will be made available upon request.

II. WORK COMPLETED

During this quarter, XRD and DTA-TGA analyses of samples from the 60-day exposure in the DOE* +1 Vol.% H_2S atmosphere, and from the 20-day exposure in CO/H_2O ratios=0.1, 1 and 3+1 Vol.% H_2S atmospheres were completed.

III. EXPERIMENTAL PROCEDURE

A. Materials

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*Composition is 18% CO, 12% CO_2, 24% H_2, 41% H_2O, 5% CH_4(Vol.%) plus 1% H_2S

The refractories and cements investigated during this year are listed in Table 1.

B. Test Atmospheres

The exposure tests were performed in the DOE* or CO-Steam atmospheres containing 1 Vol.% H_2S at 1000 psia. The exposure conditions were as follows.

(1) 60-Day Long-Term Exposure Test, DOE Atmosphere

Total Pressure - 1000 psia
Temperature of Unsaturated Vapor = 700°F
Temperature of Saturated Vapor = 447°F

(2) 20-Day CO/H_2O Exposure Tests

CO/H_2O ratio	Pressure (psia)			Temperature (F°)	
	Steam	CO	H_2S	Unsaturated	Saturated
0.1	900	90	10	1000	532
1.0	495	495	10	1000	466
3.0	247.5	742.5	10	1000	400

Seven Samples of each refractory were exposed to the unsaturated and saturated vapors and two samples were immersed in the water in the bottom of the steam vessel. The liquid in the bottom of the steam vessel is referred to as water although it contains various dissolved gases.

C. Pre-and Post-Exposure Characterization and Procedure

Specimen preparation, test systems, testing procedures, and pre- and post-exposure characterization were the same as described previously.

IV. RESULTS AND DISCUSSIONS

Calcium Aluminate Cement-Bonded Refractories

(1) 20-Day CO/H_2O Exposure Tests

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*Composition is 18% CO, 12% CO_2, 24% H_2, 41% H_2O, 5% CH_4(Vol.%) plus 1% H_2S

A. Weight and Dimensional Changes

Table II summarizes the weight changes* for the high alumina, intermediate alumina, and insulating castables exposed to the $CO/H_2O=0.1$, 1.0 and 3.0 atmospheres. For any given refractory the weight changes at 1000°F (unsaturated vapor) in all three atmospheres were similar. All samples showed weight losses close to those observed in previous exposures in the DOE and CO-Steam atmospheres at 1000°F. With the exception of UMR-4 and VSL-50, the weight change for all samples exposed to saturated vapor was small, about ±2.5% or less. However, samples immersed in water during exposure, showed larger weight increases in $CO/H_2O=0.1$ and larger weight decreases in $CO/H_2O=3.0$. The weight change for the refractories immersed in water for the three CO/H_2O ratios indicates that the weight loss increases with increasing CO content of the atmosphere. The present results indicate that the primary reason for this weight loss is the dissolution of CaO from the refractories. X-ray fluorescence analyses of these samples after exposure showed that the CaO content, generally decreased with increasing CO/H_2O ratio of the atmosphere. Details of this analysis and the role of CaO dissolution on various properties are discussed in Section V.

The UMR-4 samples, in the saturated vapor of the $CO/H_2O=3$ atmosphere showed significantly large weight gains. These samples, in addition to boehmite and calcite, also contained calcium formate which may account for the extra weight increase. Trace amounts of calcium formate were also found in the UMR-2 samples.

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*As cast and dried (230°F) is reference weight.

The dimensional changes in both unsaturated and saturated atmospheres were small and generally below 1%. In the unsaturated atmosphere, there was generally a slight shrinkage, while a slight expansion occurred in saturated atmospheres. Similar results were observed in previous exposures in the DOE and CO-Steam atmospheres. The CO/H_2O ratio of the atmosphere appears essentially unimportant to dimensional changes.

B. Density and Porosity

In all three of the unsaturated CO/H_2O atmospheres at 1000°F, the density usually decreased and porosity increased. These results are similar to those observed in previous exposures in the DOE and CO-Steam atmospheres at 1000°F. In the saturated $CO/H_2O=1.0$ and 3.0 atmospheres, the high and intermediate alumina castables generally showed lower densities and higher porosities as compared to the $CO/H_2O=0.1$ atmosphere, see Table III. Immersed samples had the highest porosity, particularly those in the $CO/H_2O=3.0$ test. The higher porosities of the immersed samples is consistent with their larger weight loss caused by the dissolution of CaO from the bond phases. The lower porosities for the saturated $CO/H_2O=0.1$ atmosphere test are similar to those observed in previous exposures in the DOE and CO-Steam (CO/H_2O ratio = 1.10) atmospheres. The density and porosity of the insulating castables, was essentially the same in both unsaturated and saturated atmospheres in all three CO/H_2O tests.

C. Flexural Strength

Figure 1 shows the MOR of the cement-bonded castables after exposure to the $CO/H_2O=0.1$, 1.0, and 3.0 atmospheres. As observed in previous exposures in the DOE and CO-Steam atmospheres, the high and intermediate alumina castables, generally had higher strengths in saturated atmospheres. This strength increase continues to be attributed to the formation of boehmite in the samples during exposure which provides additional bonding.

Comparison of the MOR data in Table III and Figure 1 for the saturated atmospheres, shows that the high alumina castables containing pure calcium aluminate cements (UMR-1 & UMR-2) lost strength in the $CO/H_2O=3.0$ atmosphere. This loss of strength (especially for immersed samples) is again attributed to the dissolution of CaO from the cement bond phase(s) which became progressively higher with increasing CO/H_2O ratios. The UMR-2 samples in the saturated vapor $CO/H_2O=3.0$ atmosphere also contained ~5% calcium formate.

The UMR-4 samples in the saturated vapor $CO/H_2O=3.0$ atmosphere showed a significant loss of strength. These samples, containing Refcon cement, were severally cracked during exposure. Neat Refcon cement cubes exposed to the saturated $CO/H_2O=3.0$ atmosphere were also heavily cracked. UMR-4 also contained trace amounts of calcium formate.

A comparison of the MOR data for the UMR-6 and UMR-7 samples in Figure 1 with the UMR-1 samples shows an interesting and increasingly evident effect that seems to be due to the presence of SiO_2. Whereas, the strength of the silica-free refractory, UMR-1, after exposure to unsaturated CO/H_2O atmospheres (at 1000°F) was always lower than the unexposed control specimens (fired to either 500 or 1000°F), the addition of 5% (UMR-6) or 10% SiO_2 (UMR-7) to the silica-free UMR-1 composition caused the exposed specimens to have a <u>higher</u> strength than the controls. Similarly, this same behavior where the strength of specimens exposed to the unsaturated (1000°F) CO/H_2O atmospheres is higher than controls fired in air is also observed for the other silica-containing refractories, RC-3 and UMR-5.

In earlier tests, the presence of SiO_2 in the refractory (introduced either as a component of the refractory grain or refractory cement) had been suspected as having a beneficial effect in terms of strength retention in unsaturated atmospheres. The MOR data for the UMR-6 and UMR-7 compositions, which were prepared specifically to test this suspicion, provides additional evidence that the mechanical properties of silica-containing compositions are less adversly affected by exposure to the unsaturated atmospheres being investigated than the high-purity, silica-free compositions. This potentially significant result is being investigated further.

(2) 60-Day Long-Term Exposure Test

Table IV summarizes the properties after a 60-day exposure in the DOE+1 Vol.% H_2S atmosphere at 1000 psia. In both the unsaturated (700°F) and saturated (447°F) vapor atmospheres, samples generally showed small weight and dimensional changes. These changes are similar to those observed previously in the DOE and CO-Steam atmospheres after exposure for 30 days. However, significantly larger weight increases occurred in the refractories immersed in water at 447°F. These increases are currently attributed to the formation of a large quantity of aragonite crystals during exposure which covered the external surface and filled internal pores in the refractory. This also believed to be the cause of the significant decrease in the porosity found for most of the high alumina castables.

The flexural strength of the refractories after the 60 day exposure was basically similar to that for the 10-30 day exposure in the DOE atmospheres. The dependence of the flexual strength upon exposure time is illustrated in Figure 2 for some selected refractories. The major change in flexural strength occurs within the first 10 days of exposure (shorter times have not been investigated) and is highly dependent upon the degree of saturation of the atmosphere. Between 10 and 60 days the change in MOR is small. While 60 days is not a major fraction of the anticipated refractory service-life in a coal gasifier vessel, there is currently no significant evidence of any larger change, particularly a decrease, in flexural strength at longer exposure times.

The change in porosity with exposure times for these same refractories is shown in Figure 3. On saturated atmospheres, the porosity of the high and intermediate alumina castables especially, decreased significantly within 10 days, but then increased, and after 60 days the porosity was essentially the same as that for unexposed samples fired in air at 500°F. The initial decrease in porosity is attributed to the filling of pores by boehmite. The subsequent increase is tentatively attributed to the dissolution of CaO from the refractory, although this may not account for the total increase in porosity. It should be noted that although the porosity increased substantially from 10 to 60 days, the flexural strength, Figure 2, remained basically constant.

Phosphate-Bonded Ramming Mix

(1) 20-Day CO/H_2O Exposure Test

The properties of the phosphate-bonded ramming mix (GREENPAK 90-P) after exposure for 20 days in the CO/H_2O=0.1, 1.0, and 3.0 atmospheres is given in Tables II and III. With the exception of samples immersed in water during the CO/H_2O=1.0 and 3.0 exposures, all weight and dimensional changes in the three CO/H_2O atmospheres were below 1%. The porosity was slightly lower in CO/H_2O=1.0 as compared to either CO/H_2O=0.1 or 3.0 atmosphere. In general, the weight and porosity changes in the phosphate-bonded refractories were significantly smaller than those observed in the high and intermediate alumina castables.

Figure 4 summarizes the MOR after exposure to all of the atmospheres investigated to date. The flexural strength in the unsaturated CO/H_2O atmospheres was always higher than in saturated atmospheres. Not unexpectedly, the lowest strength occurred in the saturated CO/H_2O=0.1 atmosphere, where the steam content (pressure = 900 psia) was highest. The importance of the degree of saturation is clearly evident and in all cases substantial reductions in flexural strength continue to be found in 100% saturated atmospheres. Note that samples B and C are no longer being investigated.

(2) 60-Day Long-Term Exposure Test

Table IV summarizes the property data for the two ramming mixes (GREENPAK 90-P and BRINKRAM 90-R) exposed to 100% saturated vapor in the DOE+1 Vol.% H_2S atmosphere for 60 days. The weight and dimensional changes were small and similar to those found in previous exposures (30 days) to the DOE and CO-Steam atmospheres containing 1 Vol.% H_2S. The flexural strength of these ramming mixes in the saturated vapor atmosphere (Figure 4) after the 60 day exposure was slightly higher then after 30 days.

V. LOSS OF LIME FROM REFRACTORIES

Evidence is now available which clearly establishes that a substantial fraction of the lime (CaO) is leached (removed) from the cement-bonded castables and neat cements during exposure and is either redeposited as $CaCO_3$ (aragonite) on and within the refractory samples and in the bottom of the metal vessel ($CO/H_2O=1.0$ and 60-day DOE atmospheres) or in solution in the water ($CO/H_2O=3.0$ atmosphere). Table V shows the Ca^{2+}ion concentration found in the initially pure distilled water used in the various exposure tests. The CO/H_2O ratio is important to lime removal since the Ca^{2+} concentration shows a large increase with increasing CO content of the atmosphere, Table V.

Further evidence of lime removal was obtained by x-ray fluorescence analysis of the refractory samples immersed in water. The CaO content of some selected refractories after various exposures, is given in Table VI and Figure 5.

The effect of the loss of CaO on the various properties of cement-bonded castables has been briefly mentioned earlier in this report. In the high and intermediate alumina castables, the weight losses in the three CO/H_2O tests increased with increasing CO content of the atmosphere and this is generally consistent with the loss of CaO found by x-ray fluorescence analysis, Table VI.

The loss of CaO is also believed to partially account for the increase in the porosity of these castables. However, except for the slight decrease in MOR of UMR-1 and UMR-2 (immersed samples), there was no change in flexural strength that could be directly attributed to this loss of CaO. While the loss (dissolution) of CaO should be anticipated to lower the strength of the refractories because of the destruction of the cement bond phases, the strengthening provided by the formation of boehmite apparently more than compensates for the destruction of the cement bond phases.

The exact mechanism for the loss of CaO from the refractories is not fully known at this time. However, it is suspected to involve the reaction of CaO initially to form $CaCO_3$ which is then subsequently dissolved in the saturated vapor (or liquid). Obviously the CO/H_2O ratio of the atmosphere is quite important to the process and greater dissolution of $CaCO_3$ would be expected in atmospheres of higher CO/H_2O ratio where the water contains a higher concentration of dissolved CO (more acid).

VI. CHEMICAL REACTIONS IN REFRACTORIES

In the DOE and various CO-Steam atmospheres between 390 and 1000°F and 465 and 1000 psia, very little, if any, reaction occurs between the gases and the refractory aggregate (alumina, aluminosilicate, silica aggregates). The principal chemical reaction in the cement-bonded castables is the decomposition of the initial calcium aluminate bond phases and their reaction with steam and CO to form boehmite, calcite, and in some cases calcium formate. In saturated atmospheres where the most evidence of chemical reaction has been observed, both boehmite and calcite form. The amount of boehmite formation is primarily dependent upon the degree of saturation, Table VII. In some instances, trace amounts of calcium formate are also found. In addition, there is evidence showing that CaO from the bond phases, either directly or after forming $CaCO_3$, is leached from the refractories and redeposits as aragonite crystals on sample surfaces and within pores. The tendency for the aragonite growth is higher in the liquid where m.m. size crystals are found, than in the vapor atmosphere. At 1000°F (for all exposures), where the atmosphere is essentially unsaturated, no evidence of boehmite is found. As determined from the property changes and analysis of the quantities of reaction products (calcite and boehmite), the kinetics of these reactions in the cement-bonded castables are reasonably rapid, being essentially complete within ten days. No additional or new reactions have been observed for exposure periods up to 60 days. There is no direct evidence indicating that H_2S(1 Vol.%) or other gases reacts to any significant extent with the cement bond phases.

Phosphate-bonded refractories show less evidence of chemical reaction with steam and other gases than the cement-bonded castables, except in 100% saturated atmospheres where leaching (dissolution) of the phosphate binder by steam has been found.

VII. OTHER WORK

A. Thermal Expension Measurements

The thermal expansion measurements of cement-bonded castables are in progress. The measurements were temporarily delayed by the failure and repair of the furnace. No new data is reported at this time.

B. CaO Analysis, X-ray Fluorescence

The CaO analyses, which were started during this quarter, have been completed on some of the castables immersed in water during the three CO/H_2O and 60-day DOE atmospheres, as reported elsewhere in this report. This work is continuing and other samples exposed to the saturated vapor atmospheres are being analyzed.

VIII. MAJOR CONCLUSIONS

A. Long-Term Durability

With the exception of the weight and porosity changes for the cement bonded castables immersed in water during exposure, the properties of the various refractories after long-term (60-days) exposure in the unsaturated and saturated DOE atmospheres were similar to those observed in 10-30 days DOE or CO-Steam atmospheres. The major change in properties occurs within relatively short times, a few days, and depend more upon the degree of saturation of the atmosphere than upon exposure time.

B. Saturation Versus Non-saturation

Except for the CO/H_2O=3.0 atmosphere, all the cement-bonded castables showed higher strengths in saturated than in non-saturated atmospheres. This strengthening effect is due to the formation of boehmite. In the CO/H_2O=3.0 atmosphere, a large amount of CaO dissolution occurred. In the high alumina castables containing pure calcium aluminate cements, their strength decreased with increasing CO/H_2O ratios probably because of the dissolution of CaO. Phosphate-bonded ramming mixes continue to be weaker in saturated atmospheres.

C. Vapor Versus Liquid Corrosion

Depending upon the CO/H_2O ratio, the liquid conditions were generally more reactive then the vapor. When the CO/H_2O ratio is above ~1.0, dissolution of CaO occurs, thereby increasing the porosity of the castables. For $CO/H_2O < 1$, a part of CaO lost from the sample is retained as aragonite crystals thus showing no net change. In the phosphate-bonded refractories, there is generally no major differences between vapor and liquid atmospheres.

D. Effect of CO/H_2O Ratios

With increasing CO content of the atmosphere, the rate of dissolution of CaO increases, particularly for samples immersed in water. In the high alumina castables containing pure calcium aluminate cement, UMR-1 and 2, the strength tends to decrease with increasing CO/H_2O ratio. Other castables containing silica tend not to show as large a dependence of strength upon CO/H_2O ratio.

E. General Chemical Reactions

No reaction has been observed between the various refractory aggregates and the gases in the DOE atmosphere (including steam), either saturated or non-saturated. In unsaturated atmospheres only calcite is formed. Both calcite and boehmite form in all of the cement-bonded high and intermediate alumina and insulating castables exposed to saturated atmospheres. In saturated atmospheres CaO is leached from the refractories, particularly those in contact with liquid, by a process highly dependent upon the CO/H_2O ratio.

IX. FUTURE WORK

XRD and DTA-TGA analyses of the cements from the exposure tests mentioned herein continues and will be completed in May 1978, see Work Schedule in Figure 6. Work will also continue on thermal expansion measurements and lime analysis.

During the forthcoming quarter, the following work will be undertaken.

(1) Preparation and pre-exposure characterization of samples for the Third Year Exposure Tests (Figure 7) will start on 1 June 1978.

(2) First Exposure Test will start ~ June 15, 1978. This test is aimed at investigating the effect upon mechanical properties of repeated boehmite formation and decomposition (Task III).

XII. PERSONNEL

During this quarter the following personnel worked on this project:

(a) Delbert E. Day, Principal Investigator

(b) Gordon Lewis, Co-Investigator

(c) Syed F. Rahman, Postdoctoral Fellow in Ceramic Engineering (full-time)

(d) Student Research Technicians (two, part-time)

(e) S. Sinharoy, Research Associate (half-time)

Table I
Refractory Materials Used in Exposure Tests

Trade or Given Name	Manufacturer	Remarks
		Dense High Alumina Castable
Greencast 94	A. P. Green	94% Al_2O_3, CA-25 Cement*
UMR-1	University of Missouri	93% Al_2O_3 (70% of Tabular Al_2O_3** + 30% CA-25 cement*)
UMR-2	University of Missouri	91% Al_2O_3 (70% of Tabular Al_2O_3** + 30% Secar 250 cement*)
UMR-3	University of Missouri	91% Al_2O_3 (70% of Tabular Al_2O_3** + 30% C-3 cement*)
UMR-4	University of Missouri	87.4% Al_2O_3 (70% of Tabular Al_2O_3** + 30% Refcon cement*)
UMR-6	University of Missouri	88% Al_2O_3 (UMR-1 with 5% SiO_2^{+})
UMR-7	University of Missouri	84% Al_2O_3 (UMR-1 with 10% SiO_2^{+})
		Intermediate Alumina Castable
RC-3	General Refractories	57% Al_2O_3, 34% SiO_2, CA-25 Cement
UMR-5	University of Missouri	50.4% Al_2O_3, 38.4% SiO_2 (75% of Mulcoa and Mulgrain 60*** + 25% Refcon Cement*
		Insulating Castable
Cerlite #75	C. E. Refractories	54% Al_2O_3, 40% SiO_2, CA-25 Cement
Litecast 60-25	General Refractories	46.7% Al_2O_3, 40.2% SiO_2
VSL-50	A. P. Green	34.5% Al_2O_3, 52.5% SiO_2
Sauereisen No. 72	Saureisen Cement Co.	
Penguard	Pennwalt Corporation	

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*Information on various cements appears elsewhere in this Table.

**Aluminum Company of America, Bauxite, Arkansas. Tabular alumina T-61, used as grog in the high alumina castables prepared in this laboratory, contained the following fractions (wt% of the total amount of castable): -8 to 14 mesh = 14%, -14 to 28 mesh = 13%, -28 to 48 mesh = 11 %, -48 mesh = 32%

Table I Continued

		Dense High Alumina Phosphate-Bonded Ramming Mix
Greenpak 90-P	A. P. Green	95% Al_2O_3
		Calcium Aluminate Cements
CA-25	Aluminum Co. of America	79% Al_2O_3, 18% CaO
SECAR 250	Lone Star Lafarge Co.	72% Al_2O_3, 26% CaO
C-3	Babcock & Wilcox	72% Al_2O_3, 24.5% CaO
REFCON	Universal Atlas Cement	58% Al_2O_3+ TiO_2, 33% CaO
LUMNITE	Universal Atlas Cement	44% Al_2O_3+ TiO_2, 36% CaO

***C-E Minerals, King of Prussia, Pennsylvania. Mulcoa 60 and Mulgrain M60 used as grog contained the following fractions (wt% of the total amount of castable):
-4 to 8 mesh = 19%, -8 to 20 mesh = 25%, -20 to 60 mesh = 9%, -60 mesh = 17%

\+ 99.9% pure, bone dry Wedron Silica flour. Manufactured by Wedron Silica Division, Del Monte Properties Company, La Salle County, IL 60557.

Table II. Percent Weight Change After Exposure to CO-Steam + 1 Vol.% H_2S Atmosphere 20 Day Exposure at 1000 psia.

Sample Identification	$CO/H_2O=0.1$ + 1 Vol% H_2S 1000°F Unsaturated	532°F Saturated**	$CO/H_2O=1.0$ + 1 Vol% H_2S 1000°F Unsaturated	466°F Saturated**	$CO/H_2O=3.0$ + 1 Vol% H_2S 1000°F Unsaturated	400°F Saturated**
Dense, High Alumina						
UMR-1 (CA-25)	-2.1	+1.9 (+4.1)	-2.3	-2.9 (-2.2)	-2.0	-1.0 (-5.5)
UMR-2 (Secar 250)	-3.6	+2.4 (+1.4)	-3.8	+0.7 (-3.9)	-4.0	+1.7 (-9.5)
UMR-4 (Refcon)	-2.4	+3.0 (+2.0)	-3.5	-0.3 (-1.4)	-3.3	+3.8 (-5.2)
UMR-6 (CA-25, 5% SiO_2)	Not Tested		-4.2	-3.2 (+0.7)	-3.4	-0.6 (-3.1)
UMR-7 (CA-25, 10% SiO_2)	Not Tested		-4.1	-0.9 (+0.6)	-3.6	-0.5 (-3.8)
Dense, Intermediate Alumina						
RC-3	-5.1	-2.8 (+1.6)	-3.8	-1.3 (-4.7)	-3.5	-0.3 (-5.3)
UMR-5 (Refcon)	-5.0	-1.1 (-0.7)	-4.0	-0.4 (-3.1)	-2.7	+0.8 (-3.0)
Insulating Castables						
Cerlite # 75	-3.2	-0.6 (+3.1)	-2.7	+0.5 (+5.5)	-2.6	-0.1 (-1.1)
Litecast 60-25	-6.7	-1.6 (+5.5)	-6.2	+0.4 (+7.3)	-6.2	+1.4 (-4.6)
VSL-50	-7.0	-7.7 (-5.2)	-6.1	-6.2 (-4.6)	-6.5	-6.6 (-4.6)
Phosphate-Bonded High Alumina						
Greenpak 90-P	-0.2	-0.7 (+0.6)	-0.2	-0.4 (+3.2)	-0.2	-0.4 (+2.0)

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*Referenced to as-cast and dried (230°F) weight.

**Number without parentheses are for samples exposed to saturated vapor. Adjacent number in parentheses is for samples immersed in liquid (water) under the same exposure condition.

Table III. Comparison of Properties* After Exposure to Saturated Vapor or to Liquid (H_2O)
20 Day Exposure at 1000 psia.

	$CO/H_2O=0.1$ Atmosphere (532°F)			$CO/H_2O=1.0$ Atmosphere (466°F)			$CO/H_2O=3.0$ Atmosphere (400°F)		
Sample Identification	Density gm/cc	Porosity %	MOR PSI	Density gm/cc	Porosity %	MOR PSI	Density gm/cc	Porosity %	MOR PSI
Dense, High Alumina									
UMR-1	2.76 (2.77)	13 (13)	4660 (4610)	2.64 (2.67)	26 (20)	2910 (4720)	2.69 (2.53)	22 (26)	3320 (3590)
UMR-2	2.65 (2.63)	15 (14)	2290 (4710)	2.51 (2.55)	22 (22)	2000 (3770)	2.61 (2.38)	22 (33)	1930 (2030)
UMR-4	2.60 (2.66)	19 (17)	2450 (1750)	2.52 (2.59)	26 (22)	3120 (3570)	2.58 (2.46)	23 (28)	1410 (3100)
UMR-6		Not Tested		2.60 (2.53)	23 (18)	3300 (3330)	2.65 (2.56)	8 (24)	3990 (3950)
UMR-7		Not Tested		2.53 (2.62)	18 (20)	3540 (3190)	2.54 (2.51)	6 (22)	3980 (4210)
Dense, Intermediate Alumina									
RC-3	2.26 (2.29)	17 (16)	4470 (3960)	2.32 (2.26)	18 (20)	4610 (3880)	2.29 (2.15)	9 (22)	4060 (3570)
UMR-5	2.39 (2.41)	16 (14)	3740 (1580)	2.38 (2.38)	17 (16)	3280 (3700)	2.46 (2.33)	13 (18)	3920 (3030)
Insulating Castables									
Cerlite # 75	1.51 (1.51)	52 (52)	490 (250)	1.57 (1.68)	51 (35)	1230 (1190)	1.53 (1.51)	51 (52)	1100 (1440)
Litecast 60-25	1.19 (1.31)	56 (51)	520 (520)	1.24 (1.33)	57 (45)	1000 (880)	1.22 (1.14)	56 (60)	785 (1010)
VSL-50	0.86 (0.93)	68 (64)	120 (170)	0.84 (0.90)	70 (67)	300 (420)	0.89 (0.87)	67 (69)	280 (390)
Phosphate-Bonded High Alumina									
Greenpak 90-P	2.84 (2.84)	23 (22)	920 (1080)	2.87 (2.97)	21 (19)	1920 (1910)	2.84 (2.88)	22 (22)	1760 (1550)

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*Numbers without parentheses are for samples exposed to saturated vapor, average of seven samples. Adjacent numbers in parentheses are for samples immersed in liquid (water) under the same exposure conditions, average of two samples.

Table IV. Comparison of Properties* After Exposure to ERDA + 1 Vol.% H_2S Atmosphere 60 Day Long-Term Exposure at 1000 psia.

	Unsaturated @ 700°F				Saturated @ 447°F**			
Sample Identification	Wt. Change# %	Density gm/cc	Porosity %	MOR PSI	Wt. Change# %	Density gm/cc	Porosity %	MOR PSI
Dense, High Alumina								
Greencast 94	-1.9	2.72	26	1230	-1.4 (+4.5)	2.69 (2.72)	23 (18)	2790 (3210)
UMR-1 (CA-25)	-1.9	2.71	27	1750	+1.0 (+7.3)	2.72 (2.78)	21 (6)	4610 (5190)
UMR-2 (Secar 250)	-2.5	2.58	29	1580	-1.5 (+4.4)	2.54 (2.60)	23 (24)	3600 (2420)
UMR-3 (C-3)	-0.6	2.44	31	2110	-2.0 (+10.2)	2.35 (2.53)	32 (24)	1670 (2010)
UMR-6 (CA-25, 5% SiO_2)	nt	nt	nt	nt	nt (+4.2)	nt (2.77)	nt (16)	nt (4290)
UMR-7 (CA-25, 10% SiO_2)	nt	nt	nt	nt	nt (+6.0)	nt (2.72)	nt (14)	nt (4980)
Dense, Intermediate Alumina								
RC-3	-2.3	2.32	20	3560	-1.2 (+5.2)	2.28 (2.38)	19 (13)	3560 (4260)
UMR-5 (Refcon)	nt	nt	nt	nt	-2.2 (nt)	2.40 (nt)	17 (nt)	3570 (nt)
Insulating Castables								
Cerlite # 75	-1.4	1.51	52	1050	+1.2 (+19.6)	1.54 (1.78)	50 (37)	480 (1340)
Litecast 60-25	nt	nt	nt	nt	-2.1 (nt)	1.19 (nt)	57 (nt)	510 (nt)
Phosphate-Bonded High Alumina								
Greenpak 90-P	nt	nt	nt	nt	+1.3 (nt)	2.89 (nt)	21 (nt)	1600 (nt)
Brikram 90-R	nt	nt	nt	nt	-0.8 (nt)	2.84 (nt)	22 (nt)	1520 (nt)

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*nt represents samples not tested in that exposure condition.

**Numbers without parentheses are for samples exposed to saturated vapor. Adjacent number in parentheses is for samples immersed in liquid (water), average of two samples.

#Referenced to as-cast and dried (230°F) weight.

Table V
Ca^{2+} Concentration* in Water Remaining in Vessel After Various Exposure Tests-Saturated Conditions

	Ca^{2+} (ppm)
Distilled Water	0.04
60-Day DOE Atms. ($CO/H_2O=0.44$)	2270
52.5CO-47.5 Steam Exposure ($CO/H_2O=1.1$)	5780
$CO/H_2O=1.0$ Atms.	6350
$CO/H_2O=3.0$ Atms.	10,000

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*Determined by Atomic Absorption Spectrophotometer Utilizing Standard Direct Aspiration Technique

Table VI
Lime (CaO) Content of Refractory Specimens Immersed in Water

		% CaO			
		20-Day, CO/H_2O Atms.**			60-Day DOE Atms.**
Sample	Control*	(CO/H_2O=0.1 @532°F)	(CO/H_2O=1.0 @466°F)	(CO/H_2O=3.0 @400°F)	(CO/H_2O=0.44 @447°F)
UMR-1	5.4	3.60	1.60	0.80	na***
UMR-2	7.8	4.67	2.00	0.72	4.40
RC-3	5.5	3.73	2.43	1.28	3.06
Cerlite #75	2.9	2.40	2.53	0.67	6.45

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*CaO content of control is based on manufacturer's chemical analysis
**Atmosphere contains 1 Vol % H_2S
***na represents samples not analyzed in that exposure condition

Table VII

Modulus of Rupture of High and Intermediate Alumina Castables as a Function of Boehmite Content

EXPOSURE	HIGH ALUMINA CASTABLE		INTERMEDIATE ALUMINA CASTABLE	
	MOR (PSI)	PERCENT BOEHMITE	MOR (PSI)	PERCENT BOEHMITE
CONTROL				
500°F, AIR	2220	Nil	1570	Nil
DOE ATMS.				
500 PSIA/500°F, 30 DAYS, 30% SATURATED	2860	13	2130	14
1000 PSIA/447°F, 30 DAYS, 100% SATURATED, 1% H_2S	4870	29	3920	15
1000 PSIA/447°F, 60 DAYS, 100% SATURATED, 1% H_2S	4600	32	3560	18

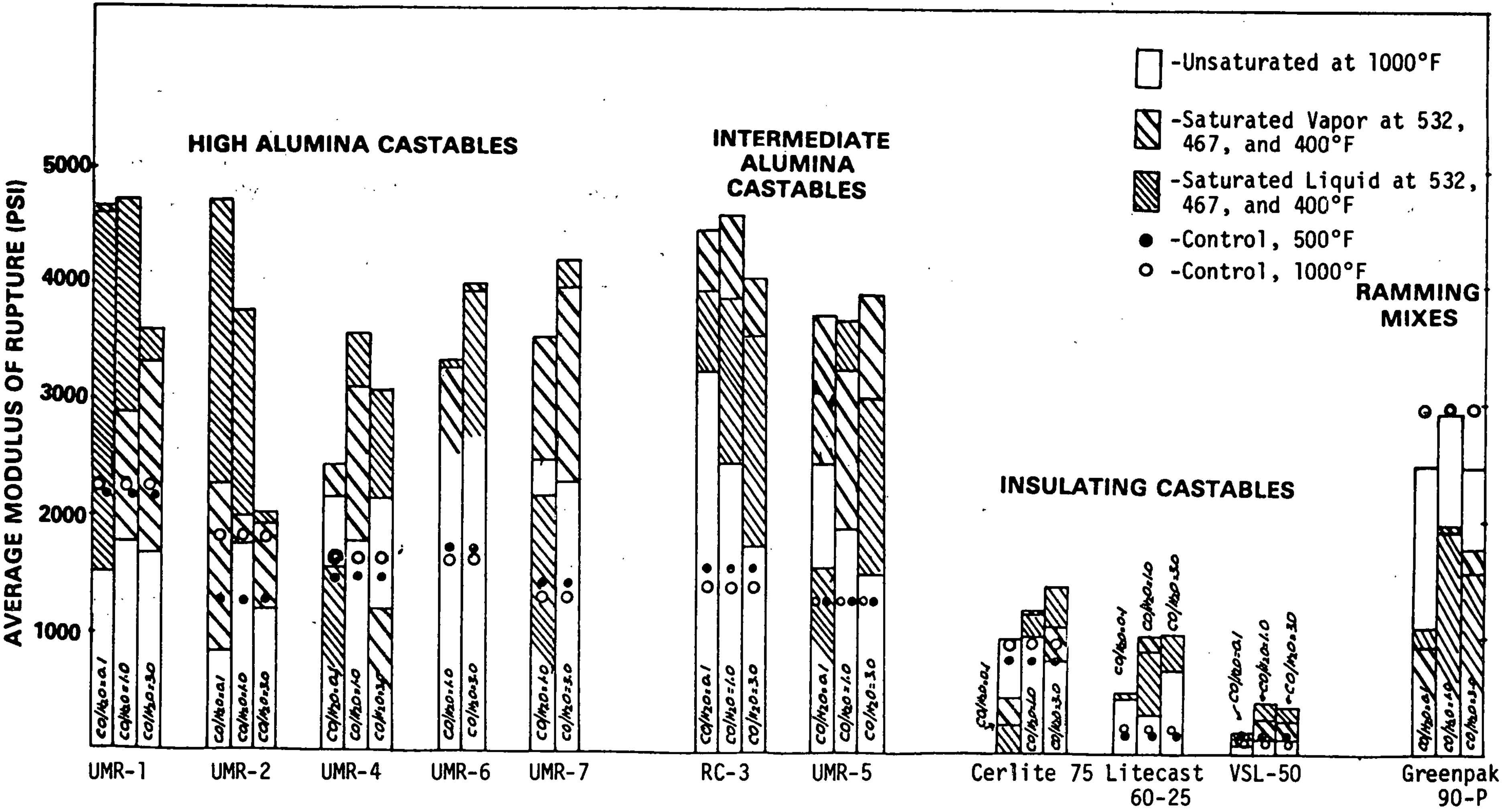

Figure 1 Modulus of Rupture of Refractories exposed to $CO/H_2O=0.1$, 1.0 and 3.0 atmospheres with 1 Vol.% H_2S, 1000 psia, 20 days

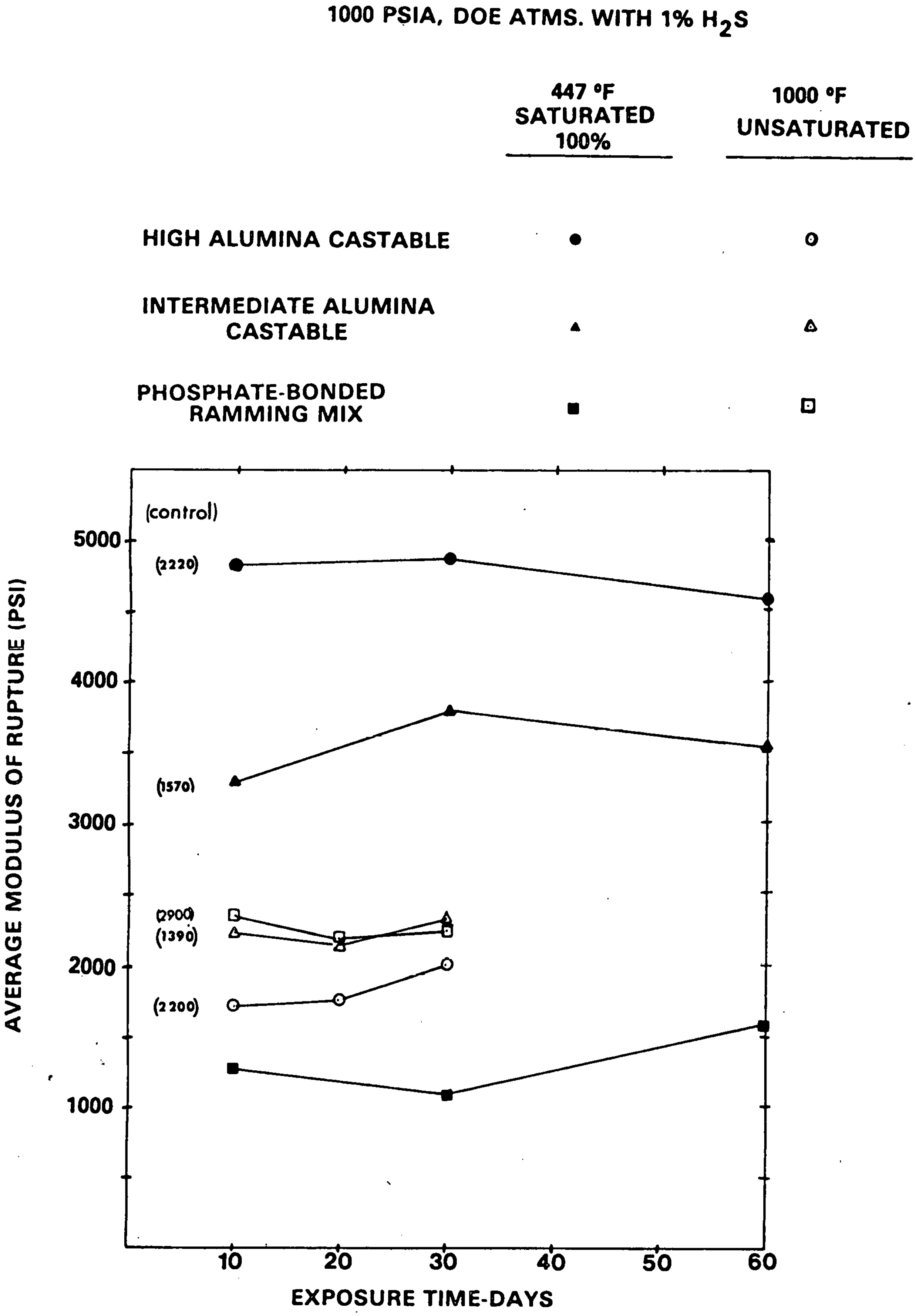

Figure 2 Modulus of Rupture as a function of exposure time

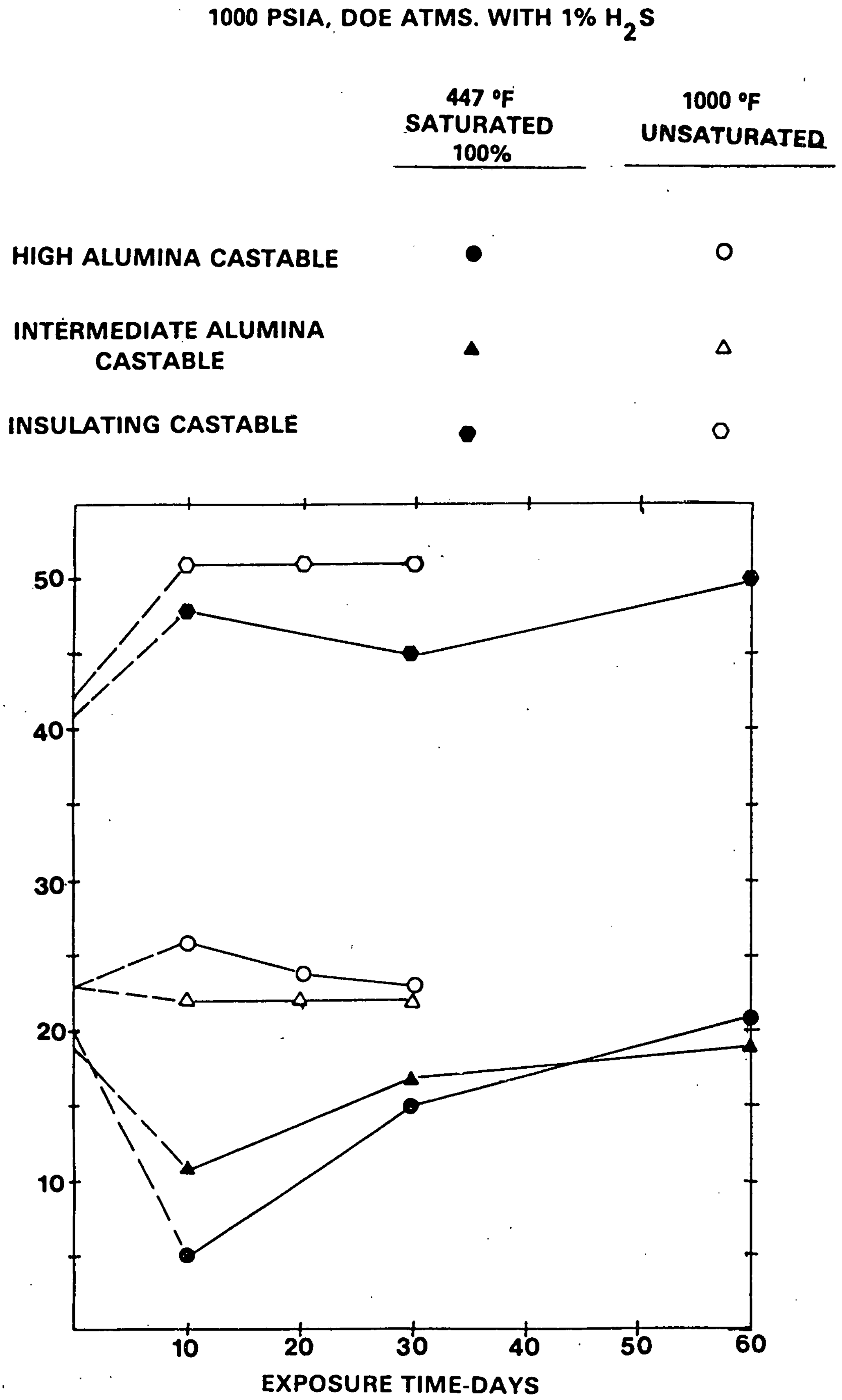

Figure 3 Porosity as a function of exposure time.

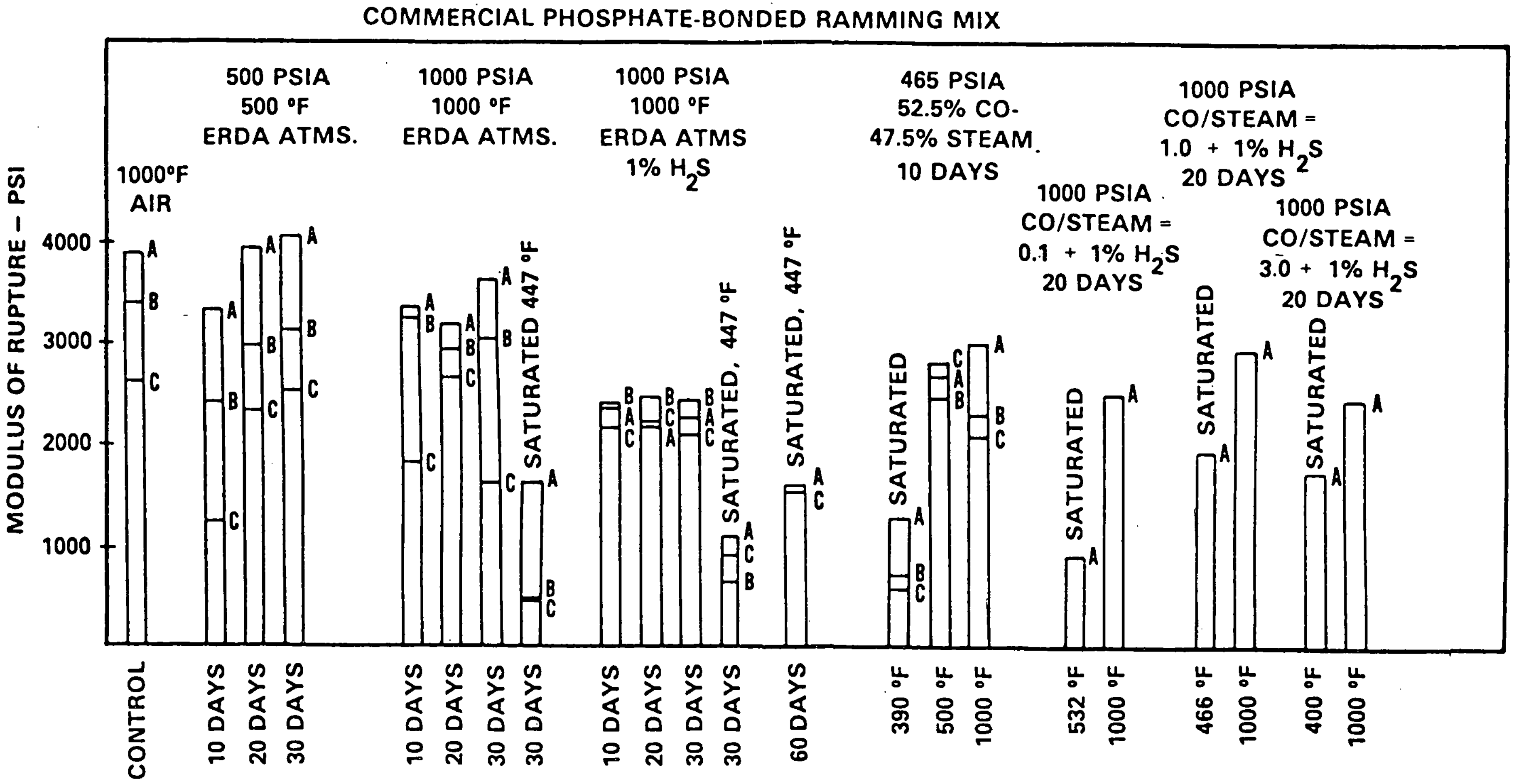

Figure 4. Room Temperature Modulus of Rupture of Commercial Phosphate-Bonded Ramming Mix.

A - GREENPAK 90-P
B - 90 RAM HS
C - BRIKRAM 90-R

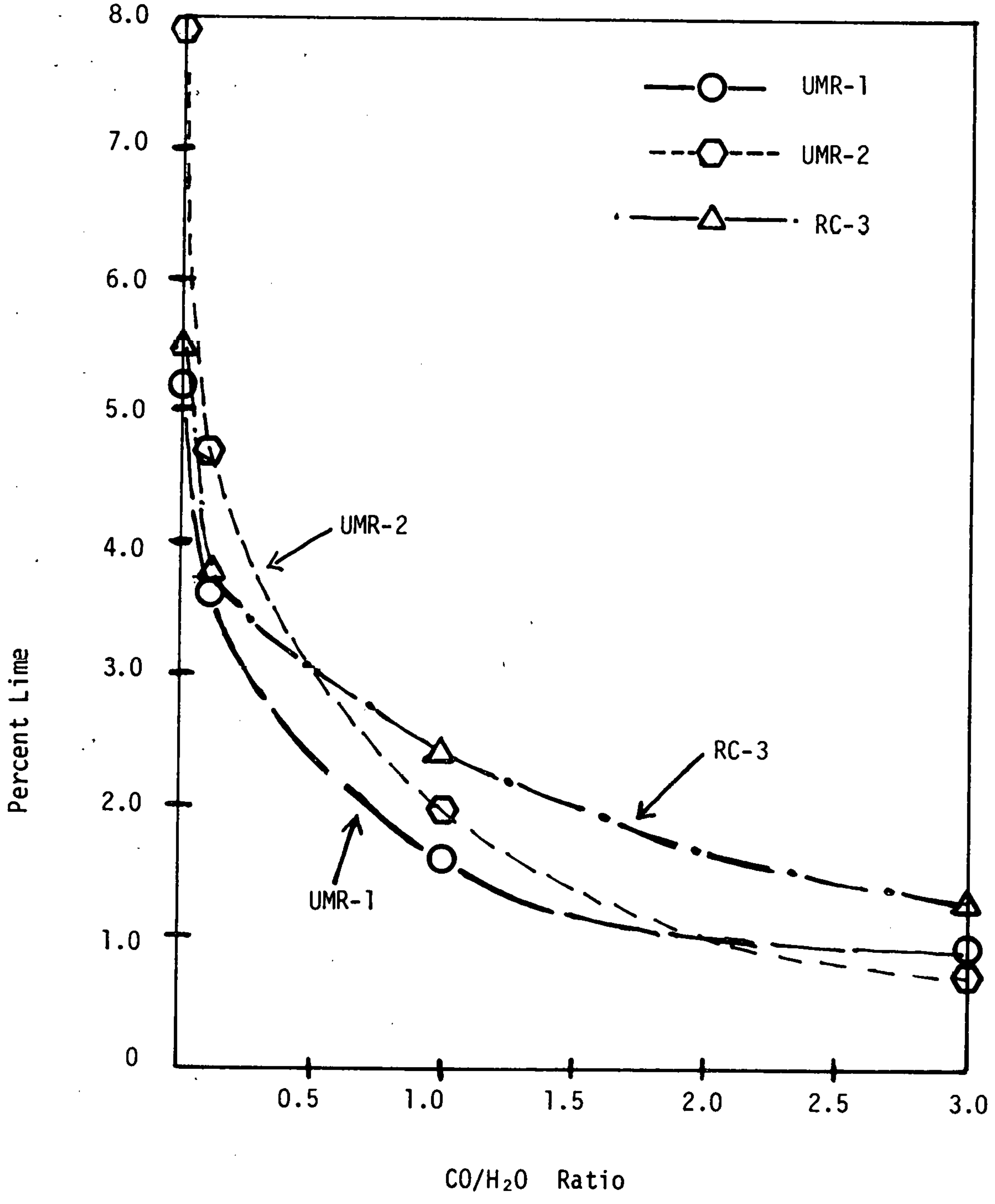

Figure 5 Percent lime versus CO/H_2O ratio of high and intermediate alumina castables.

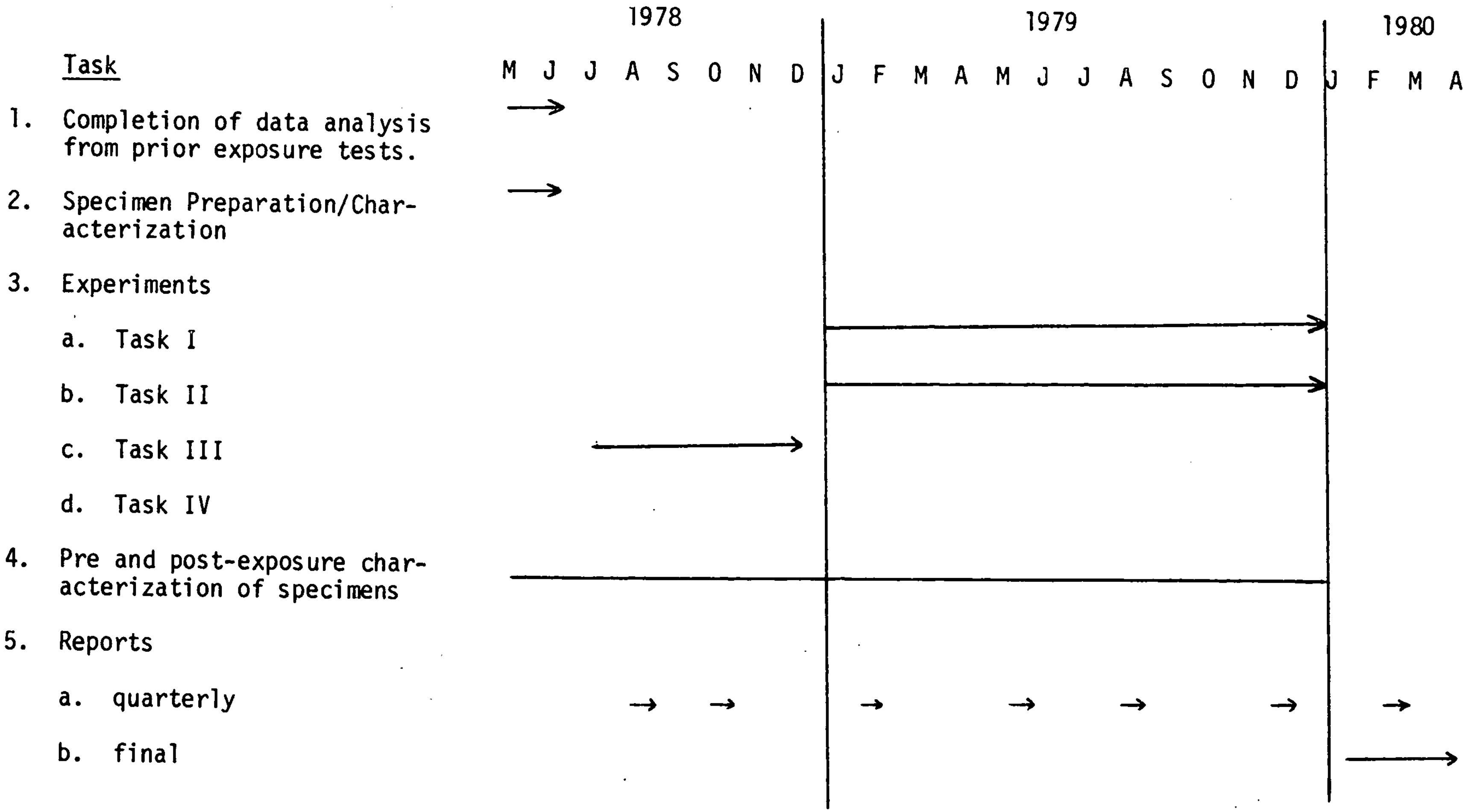

Figure 6. Work Schedule, 1 May 1978 to 30 April 1980

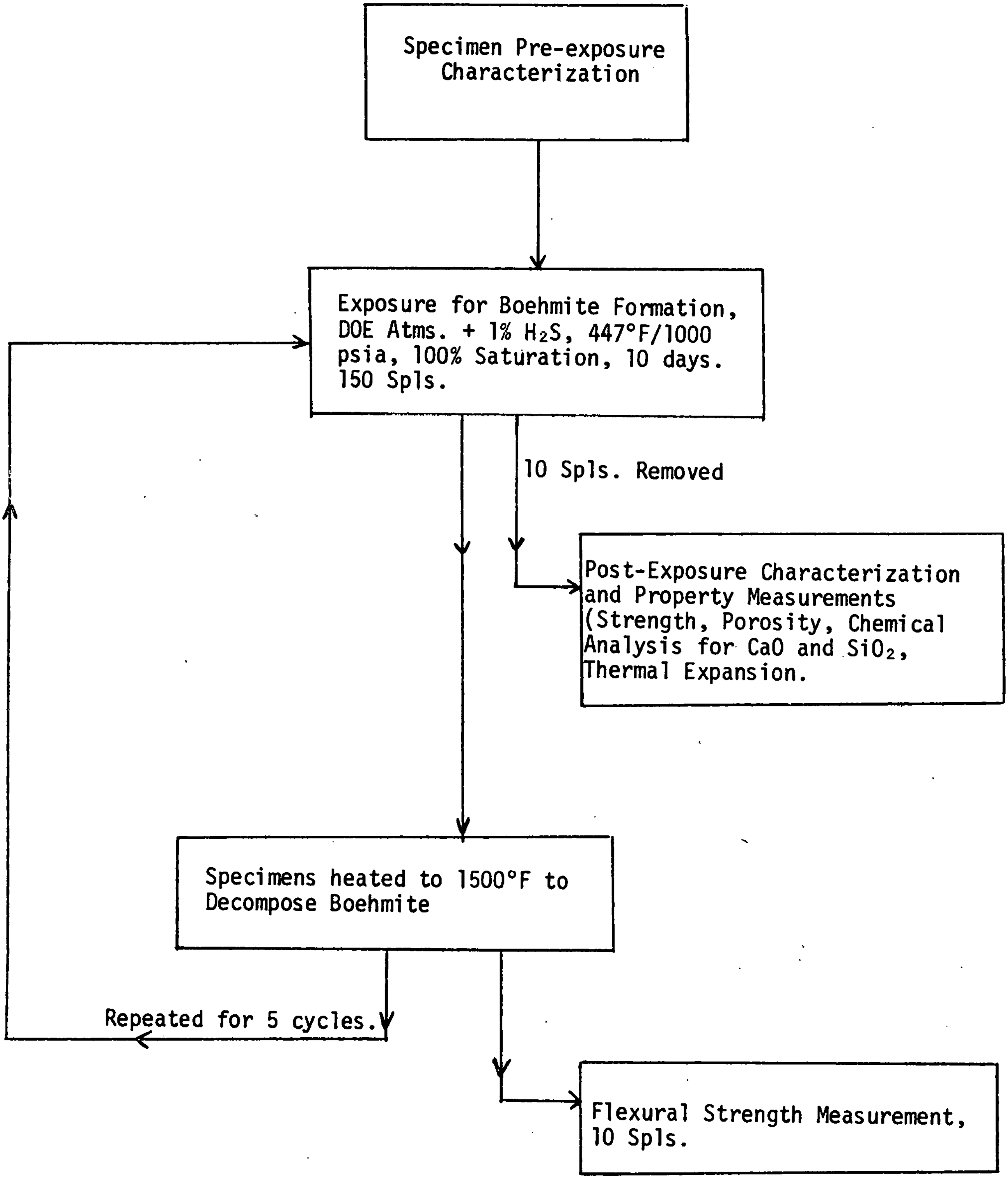

Figure 7. Flow Chart for Determining Effect of Cyclic Boehmite Formation/Decomposition on Refractory Properties, Task II.

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