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MASTER

CHEMICAL AND PHYSICAL STABILITY OF REFRACTORIES FOR USE
IN COAL GASIFICATION

Final Report, May 1, 1976—July 31, 1980

Ry
Abbas Fakhr
Gordon L. Lewis
Delbert E. Day

September 1, 1980

Work Performed Under Contract No. AS02-76ET10544

Ceramic Engineering Department and Materials Research Center
University of Missouri-Rolla
Rolla, Missouri

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U. S. DEPARTMENT OF ENERGY



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Final Report

May 1, 1976 - July 31, 1980

Prepared by

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September 1, 1980

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EXECUTIVE SUMMARY

The dimensional stability, density, porosity, flexural strength and thermal expansion of eighteen cement-bonded, dense and lightweight refractory castables and three phosphate bonded refractories were determined before and after exposure to conditions chosen to simulate those at the cold face ($\sim 250^{\circ}\text{C}$) of a refractory lining in a coal gasification vessel. Chemical reactions occurring in the refractories during exposure were determined by XRD, DTA/TGA and SEM and correlated with the above properties. The variables investigated were (1) exposure time, 60 days maximum, (2) temperature, up to 538°C , (3) pressure, 6.9 MPa maximum, (4) gas composition, particularly CO/steam ratio (0.1, 1, and 3.0) and presence of 1 Vol% H_2S , (5) degree of saturation and (6) liquid versus vapor contact.

Of all the variables investigated, the degree of saturation of the test atmosphere was the single most important factor affecting the properties after exposure. In dry atmospheres, the properties were close to those for specimens heated to the same temperature in air. In 100% saturated atmospheres, however, the dense cement bonded castables typically had a flexural strength two to three times higher than that before exposure and a significantly lower porosity. Conversely, the flexural strength of the phosphate bonded refractories was only 1/2 to 1/5 of that before exposure. The exposure time was not particularly important since the chemical reactions occurring in the refractories during exposure, which are responsible for these changes in properties, are relatively rapid and appear to be nearing completion within a few days, ≤ 10 . All of the refractories were structurally intact after the 60-day maximum exposure to both dry or saturated conditions.

The principal chemical reactions in the cement bonded castables were between the cement bond phases and steam, CO, and CO_2 . No evidence was found of any reaction involving the various refractory aggregates. In dry atmospheres, the principal reaction was the formation of CaCO_3 which had no discernible effect upon the properties investigated. More extensive chemical reactions occur in 100% saturated atmospheres where the calcium aluminate cement phases reacted to form CaCO_3 and boehmite

($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and some portion of the CaO was leached from the refractory. The increase in flexural strength of the dense castables correlated well with the additional bonding expected from the interlocking network of boehmite crystals as observed by SEM. The minimum percent saturation needed for boehmite formation varied from ~10 to 20%, depending upon the gas composition, but no increase in flexural strength was observed below ~40% saturation. No specific chemical reactions were found in the phosphate bonded refractories after exposure to either dry or saturated conditions, but attack of the phosphate bond phase(s) by saturated steam is considered the likely reason for their lower flexural strength after exposure to saturated atmospheres.

These results indicate that the degree of saturation of a coal gasifier atmosphere is a more important process design parameter in selecting refractories for use in coal gasification than gas composition (within limits), or pressure. If the gasifier design or operational requirements (including start up or shut down) are such that saturated conditions (dew point temperature) will exist for an extended period (few days) at some point in the refractory lining, then cement bonded castables appear preferable to phosphate bonded refractories. High alumina, cement-bonded castables had no decided advantage over intermediate alumina castables at cold face temperatures, the performance of these two classes of refractories being comparable. In certain cases, a small amount of silica in the refractories, either from the aggregate, cement, or as free silica, was beneficial to high flexural strength under saturated conditions.

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I. INTRODUCTION

Commercialization of the numerous, high-pressure coal gasification processes currently under study is dependent upon the availability of refractory materials which can provide long term thermal, mechanical, and chemical protection for the metal pressure-confinement vessel; i.e., prevent overheating and chemical attack of the metal gasifier vessel. There are many excellent reviews of existing and proposed gasification processes^(1,2) and the potential problems associated with the use of refractories in these processes⁽³⁻⁶⁾ where the temperature, pressure, and gas composition may vary considerably. Generally, temperatures of 100-2000°C, pressures of 100 kPa to 10 MPa, and atmospheres containing CO, CO₂, CH₄, H₂, steam, and small amounts of H₂S, NH₃, alkali vapors and organic compounds may be encountered.

The refractories used in some related petrochemical applications provide a rough guide to the design engineer for refractory selection and use in coal gasification since some of the process parameters are similar. However, there are important differences in the process parameters which make it difficult to reliably predict the service performance and life-time of refractories that might be used for coal gasification. Knowledge of the behavior of refractories under conditions simulating those encountered in coal gasification is important to the reliability of operation since premature failure of the refractory lining will usually require gasifier shut down.

A. Objectives

This investigation was commenced on 1 May 1976 with the following objectives:

- a. to achieve an understanding of the general types of chemical reactions occurring in monolithic refractories when exposed to conditions representative of those at the cold face of the refractory lining in coal gasification vessels,
- b. to assess the relative importance of these reactions to those physical/chemical properties required for long-service life, and
- c. to identify those refractory systems providing optimum service performance.

The evaluation of the corrosion resistance, especially the bond phases used in monolithic refractories, to the high pressure/temperature gases and liquids found in coal gasification was of particular importance.

B. Tasks

The investigation consisted of the following tasks, some of which depended upon the results of previous tasks.

Task I. Exposure System Design and Construction: The first task was to design and construct an experimental exposure system capable of duplicating the conditions at the cold face of a refractory lining in a coal gasifier and sufficiently versatile to operate with a wide variety of gas compositions, pressures, and temperatures.

Task II. Screening of Commercial Refractories: The objective was to survey the performance and properties of a large number of commercial and experimental refractory compositions considered candidates for use as refractory linings in coal gasifiers. Particular emphasis was placed on identifying any classes of refractories which might be totally unsatisfactory.

Task III. Exposure Time: This task consisted of investigating the durability of selected refractories (based upon results from Task II) to atmospheres representative of those at the cold face of a lining in coal gasifiers for ≤ 60 days.

Task IV. CO/Steam Ratio: The purpose of this task was to determine the effect of CO/steam ratio upon the reactions found in cement and phosphate bonded castables, steam and CO being major constituents in gasifier atmospheres.

Task V. Degree of Saturation: This task consisted of determining the dependence of the chemical reactions occurring in dense and light-weight (insulating) castables upon the degree of saturation of the atmosphere and to correlate these reactions with changes in the physical and mechanical properties of the refractories.

Task VI. Liquid versus Vapor Corrosion: In this task, the corrosion resistance of castables to condensed liquids and saturated vapors and the relative severity of liquid versus vapor corrosion was determined. Light-weight insulating castables were of particular interest because of their higher porosity (internal surface area) which could make them more susceptible to chemical attack.

Task VII. Pressure/Temperature Cycling: The aim of this task was to determine the effect of repeated boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) formation and decomposition (by repeated pressure/temperature cycling) upon the mechanical strength of selected cement-bonded castables. The boehmite formation/decomposition reaction is accompanied by volume changes which might be detrimental to the mechanical strength and structural integrity. Changes in the operating temperature or gas composition in a gasifier,

as during start up or shut down, or temperature upset, could decompose previously formed boehmite so it was of interest to know whether the strength of the refractory was affected.

Task VIII. Hydrothermal Reactions of Calcium Aluminate Compounds and Commercial Cements: The objective of this task was to determine the time, temperature, and pressure dependence for the reactions found in calcium aluminate cements (formation of CaCO_3 , boehmite and CaO dissolution) and to investigate the reaction of CA^* and CA_2 individually in hydrothermal atmospheres relevant to coal gasification.

II. EXPERIMENTAL PROCEDURES

A. Raw Materials

Based upon the experience acquired from monolithic refractory linings used in related process vessels⁽⁵⁻⁸⁾, cement and phosphate-bonded refractories were investigated. Eighteen calcium aluminate cement-bonded refractory castables (dense high alumina, dense intermediate alumina, and insulating), three dense, high alumina phosphate-bonded ramming mixes, and five neat calcium aluminate cements were tested. These refractories cover the spectrum of commercially available products currently available for use as lining materials in coal gasifiers. Their overall chemical composition is listed in Table I where CC denotes a Commercial Cement-Bonded Castable, CPRM denotes a Commercial Phosphate-Bonded Ramming Mix,

*Cement terminology used where C = CaO , A = Al_2O_3 , S = SiO_2 , $\bar{\text{C}}$ = CO_2 , etc.

and C denotes a Commercial Refractory Cement. The compositions designated as UMR were prepared in our laboratory and contained 70 to 75% aggregate and 25 to 30% of one of the commercial refractory cements.

B. Specimen Preparation

The castables were cast into slabs 30.5 by 7.6 by 1.3 cm, cured for 24h in air at 100% relative humidity at 20-25°C, and dried at 110°C for 24h. These slabs were cut (diamond saw) into 7.6 by 1.3 by 1.3 cm rectangular bars. The phosphate-bonded refractories were hand rammed into 7.6 by 1.9 by 1.9 cm bars, dried in the molds at 110°C for 24h, and fired in air at 538°C for 18h prior to exposure.

C. Pre- and Post-Exposure Analysis

The weight and length of each specimen were measured before exposure. After exposure, the specimens were inspected visually for any surface deterioration, dried at 110°C for 24h, and the weight and length remeasured. The modulus of rupture (MOR) was measured in three point bending (ASTM C268-70) using a span of 5.08 cm and a crosshead speed of 0.5 cm/min. Parts of fractured specimens were used to measure the bulk density and apparent porosity according to ASTM C20-74 except that the samples were saturated with kerosene under vacuum. The MOR, bulk density, apparent porosity, and weight and length changes were also measured for control specimens of each refractory as-cast and dried at 110°C and fired in air at 260 and 538°C. The properties reported herein are the average of at least seven specimens. The crystalline phases in the refractories before and after exposure were identified by XRD*. The exposed specimens

*X-ray diffraction, Siemens Diffractometer, Karlsruhe, Germany.

Table I. Chemical Analysis of As-Received Refractories and Cements

No.	Identification	Al ₂ O ₃	CaO	Weight Percent					Total	Remarks
				SiO ₂	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	MgO		
<u>Dense, High Alumina Castables</u>										
1	CC-1	95.0	4.5	0.1	0.2	--	--	--	99.8	Greencast 94, A. P. Green Refractories
2	CC-2	93.0	6.0	0.5	0.1	0.1	--	--	99.7	KAOTAB, Babcock & Wilcox
3	CC-3	93.7	5.6	0.1	0.3	--	--	--	99.7	CASTOLAST G, Harbison-Walker
4	CC-4	93.6	5.4	0.03	0.3	trace	--	0.1	99.43	PURO-TAB, Kaiser Refractories
5	UMR-1	93.4	5.4	0.1	0.13	--	--	0.1	99.13	70% Tabular Al ₂ O ₃ * + 30% CA-25** cement
6	UMR-2	91.3	7.8	0.1	0.1	--	--	--	99.3	70% Tabular Al ₂ O ₃ * + 30% Secar**250
7	UMR-3	91.3	7.4	0.3	0.13	trace	--	0.1	99.23	70% Tabular Al ₂ O ₃ * + 30% C-3**
8	UMR-4	87.1	10.1	1.7	0.5	--	--	--	99.4	70% Tabular Al ₂ O ₃ * + 30% Refcon**
9	UMR-6	88.7	5.1	5.1	0.1	--	--	0.1	99.1	95% UMR-1 + 5% SiO ₂ ⁵
10	UMR-7	84.0	4.9	10.1	0.1	--	--	0.1	99.2	90% UMR-1 + 10% SiO ₂
<u>Dense Intermediate Alumina Castables</u>										
11	CC-5	55.0	5.0	36.0	1.2	1.5	--	--	98.7	LO-ABRADE, A. P. Green Refractories
12	CC-6	57.4	5.5	33.5	1.3	1.7	--	--	99.4	RC-3, General Refractories
13	UMR-5	58.6	8.4	29.6	1.3	--	--	--	97.9	75% Mulcoa and Mulgrain*** + 25% Refcon Cement
14	UMR-8	63.8	4.8	28.3	1.0	--	--	0.1	98.0	75% Mulcoa and Mulgrain*** + 25% CA-25

Table I. Chemical Analysis of As-Received Refractories and Cements (Continued).

No.	Identification	Al ₂ O ₃	CaO	Weight Percent					Total	Remarks	
				SiO ₂	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	MgO			
<u>Insulating Castables</u>											
15	CC-7	59.0	4.5	33.0	0.8	0.7	--	--	98.0	KAST-O-LITE 30, A. P. Green Refractories	
16	CC-8	53.8	2.9	40.5	0.9	0.63	--	--	98.73	CERLITE 75, C. E. Refractories	
17	CC-9	46.7	9.1	40.2	1.6	1.0	--	0.1	98.7	LITECAST 60-25, General Refractories	
18	CC-10	34.5	9.3	52.5	--	--	--	--	96.3	VSL-50, A. P. Green Refractories	
<u>Phosphate-Bonded Ramming Mixes</u>											
19	CPRM-1	96.0	0.1	3.0	0.3	0.1	--	0.1	99.6	Greenpak 90-P, A. P. Green Refractories	
20	CPRM-2	96.5	0.04	2.7	0.5	--	--	--	99.74	90 RAM HS, C. E. Refractories	
21	CPRM-3	89.5	--	6.0	--	--	3.7	--	99.2	BRIKRAM 90-R, General Refractories Co.	
<u>Calcium Aluminate Cements</u>											
22	C-1	79.0	18.0	0.2	0.3	--	--	0.4	98.9	CA-25 Cement, Aluminum Co. of America	
23	C-2	72.0	26.0	0.2	0.1	--	--	0.1	98.4	Secar 250, Lane Star Lafarge Co.	
24	C-3	72.0	24.5	0.7	0.3	--	--	0.4	97.9	C-3, Babcock and Wilcox	
25	C-4	58.0	33.5	5.6	1.5	--	--	--	98.6	Refcon, Universal Atlas Cement	
26	C-5	44.0	36.0	8.6	8.5	--	--	0.7	97.8	Lumnite, Universal Atlas Cement	

*The Tabular T-61 alumina aggregate (Alumina Co. of America) contained the following fraction (wt% of aggregate): -8 to +14 mesh = 20, -14 to +28 mesh = 18.6, -28 to +48 mesh = 15.7 and -48 mesh = 45.7.

**Information on various cements appears elsewhere in this Table.

***The Mulcoa 60 and Mulgrain M60 aggregate (C-E Minerals) contained the following fractions (wt%): -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, Del Monte Properties Co., La Salle County, IL 60557.

were also analyzed by DTA/TGA* from 25-950°C at a heating rate of 10°C/min using a 400 mg sample. The thermal expansion of a 5 cm specimen randomly selected from each group of exposed samples was measured continuously from 20 to 950°C and during cooling to room temperature.

III. RESULTS AND DISCUSSION

A. Task I- Exposure System Design, Construction, and Operation

A schematic diagram of the exposure test system is shown in Fig. 1. It consisted of two primary pressure vessels 15 cm I.D. by 46 cm long, a steam vessel constructed from 316 stainless steel, and a test-vessel made from 347 stainless steel. Both vessels were rated for a maximum working pressure of 6.9 MPa (1000 psi) at 538°C (1000°F). Resistance heating elements on the external surface of each vessel heated the vessel and contents to the required temperature. At the maximum working temperature and pressure, the temperature within the vessels varied only $\pm 10^\circ\text{C}$ from top to bottom and $\pm 5^\circ\text{C}$ from side to side. The vessels were connected to the other parts of the system and the control panel (located in a separate room) with 316 SS tubing.

Safety precautions and subsystems consisted of adjustable relief valves which would open in case of excessive pressure and automatically reduce the pressure to safe limits. Also, the gas handling and mixing system was equipped with several pre-set rupture discs and an emergency dump valve. In addition to the primary temperature controller, equipped with thermocouple break protection, a second controller served as a high

*Type TA-1 Thermoanalyzer, Mettler Instrument Corporation, Hightstown, New Jersey.

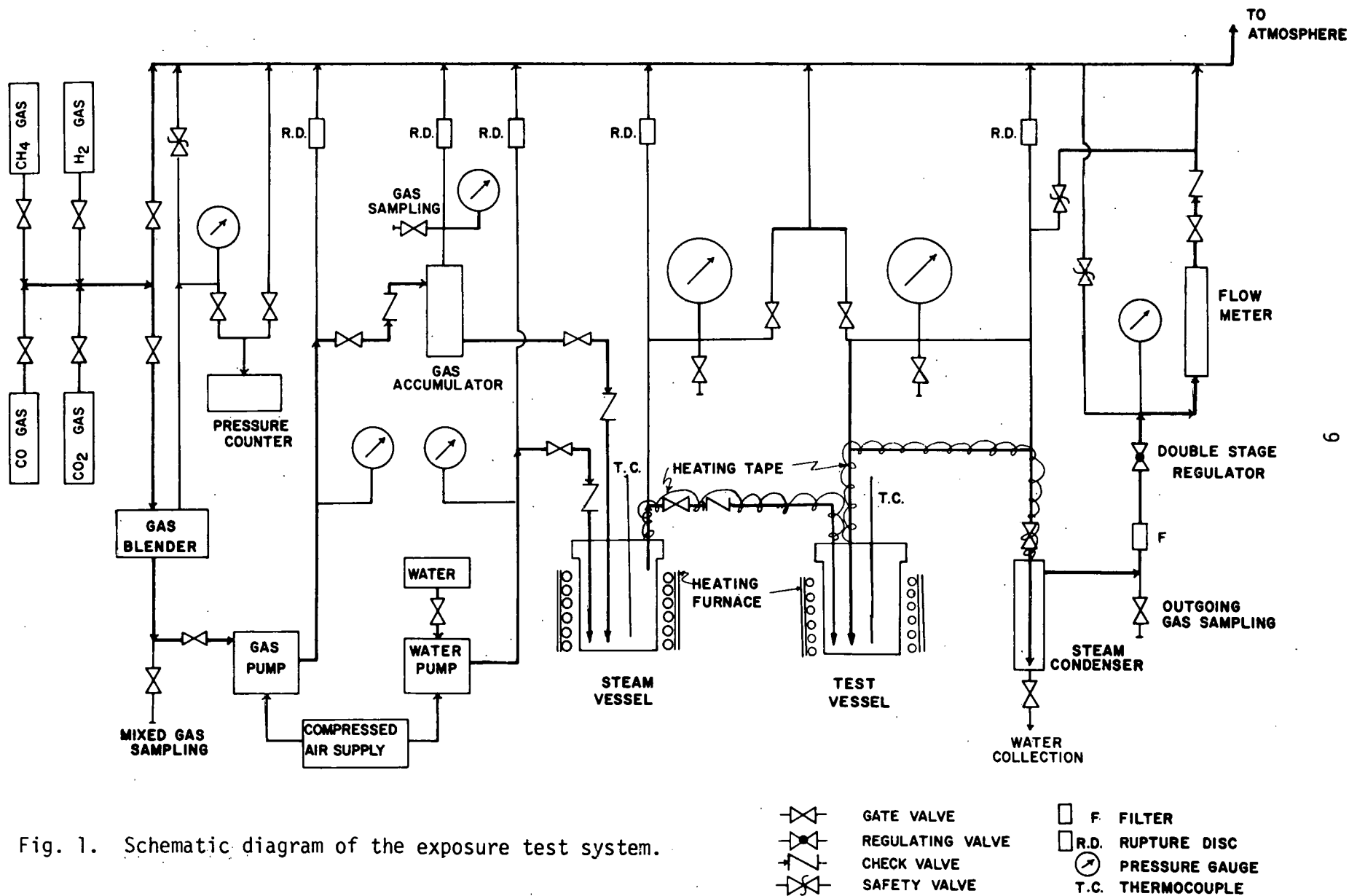


Fig. 1. Schematic diagram of the exposure test system.

temperature limit and would shut down the system totally in case of any failure of the primary controller.

The system can be operated with either a static or flowing gas atmosphere. The usual operating condition was with a flowing gas atmosphere, the flow rate controlled by a flow meter. When the pressure in the vessels dropped slightly below the selected pressure, additional gas was automatically added to the system by a high pressure gas pump operated by compressed air.

This system has been safely and successfully operated during the period of this project and remains in perfect operating condition. The longest period of continuous operation was for 60 days, but there is no apparent limit to the time of continuous operation. The system operated so dependably that direct supervision during evenings and nights was unnecessary. The pressure vessels can each accommodate 150-200 specimens of the size mentioned in section II-B.

At the beginning of an exposure test, specimens were placed in both vessels; those in the steam vessel (above water level or immersed in water) being exposed to a 100% saturated atmosphere, while those in the test vessel were exposed to an unsaturated (dry) atmosphere. Each group of specimens was separated from each other in the vessels by thin alumina plates. Distilled water was placed in the steam vessel, both vessels were purged with N_2 , pressurized, and checked for leaks. The nitrogen was exhausted and the vessels heated $\sim 50^\circ\text{C}/\text{h}$. During heating, the exhaust of the test vessel was open to the atmosphere so the water present in the unfired castables could escape. When the steam pressure in the steam vessel reached the required pressure, the remaining gases

were added from a pre-mixed mixture until the required overall pressure and gas composition was obtained. When the test vessel attained the required temperature, it was pressurized with the steam/gas mixture from the steam vessel. After flowing through both vessels, the gases exited through a steam condenser and then through a flow meter at a rate of ~ 4 L/h (STP) which provided for one complete change of the test atmosphere every 24h. Additional water was pumped into the steam vessel as needed.

Any necessary modifications in the above procedures needed for a particular Task are described at the beginning of the section describing that Task. Table II summarizes the time, temperature, pressure, gas composition, and the refractories employed in each of the 42 exposures used in this study.

B. Task II- Screening of Commercial Refractories

Seven dense high alumina castables (CC-1, 2, 3, 4, and UMR-1, 2, 3), two dense intermediate alumina castables (CC-5, 6), two insulating castables (CC-7, 8), and three phosphate-bonded ramming mixes (CPRM-1, 2, 3) were exposed to the DOE atmosphere, whose composition is given in Table II. The specimens were exposed to a 100% saturated atmosphere at 231°C in the steam vessel and an unsaturated atmosphere at 538°C in test vessel at a pressure of 6.9 MPa. The refractories were exposed to these conditions for a maximum of 30 days with samples removed at 10 and 20 days. Two tests were made, the first in the atmosphere cited above without any H_2S , exposures 4-10 in Table II, while the second used the

Table II. Exposure Test Conditions and Materials

Exposure No.	Atmosphere	Pressure (MPa) [§]	Temp. (°C)	Duration (day)	Remarks	Materials Exposed Indicated by x																									
						CC-1	CC-2	CC-3	CC-4	UMR-1	UMR-2	UMR-3	UMR-4	UMR-6	UMR-7	CC-5	CC-6	UMR-5	UMR-8	CC-7	CC-8	CC-9	CC-10	CPRM-1	CPRM-2	CPRM-3	C-1	C-2	C-3	C-4	C-5
1	Air	0.1 (atm)	110	1		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x							x	x	x	x	x
2	"	"	260	3/4		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x											
3	"	"	538	3/4		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x									
4	DOE*(without H ₂ S)	3.4	260	10	31% Saturated	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x				
5	"	"	"	20	" "	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x	x	x	x	x
6	"	"	"	30	" "	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x				
7	"	6.9	538	10	~10% saturated	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x				
8	"	"	"	20		x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x	x	x	x	x
9	"	"	"	30		x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x				
10	"	"	231	30	100% Saturated	x	x		x	x	x	x				x	x		x	x			x	x	x	x					
11	DOE with 1 Vol% H ₂ S	"	"	44	Saturated vapor					x		x						x	x		x	x	x								
12	"	"	"	44	Liquid					x									x		x		x								
13	"	"	240	5	85% Saturated					x		x						x	x		x	x	x								
14	DOE with 1 Vol% H ₂ S cyclic exposure	6.9	240 then 538	Each cycle 5 days	As #13, then heated 18h (538°C) for 5 cycles.						x		x					x	x		x	x	x								
15	DOE with 1 Vol% H ₂ S	6.9	538	10	~0% Saturated	x	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x	x	x	x
16	"	"	"	20	" "	x	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x	x	x	x
17	"	"	"	30	" "	x	x	x	x	x	x	x				x	x		x	x			x	x	x	x	x	x	x	x	x
18	"	"	371	60	13.3% Saturated	x				x	x	x				x			x			x									

Table II. Exposure Test Conditions and Materials (Continued).

Exposure No.	Atmosphere	Pressure (MPa) §	Temp. (°C)	Duration (days)	Remarks	Materials Exposed Indicated by x																								
						CC-1	CC-2	CC-3	CC-4	UMR-1	UMR-2	UMR-3	UMR-4	UMR-6	UMR-7	CC-5	CC-6	UMR-5	UMR-8	CC-7	CC-8	CC-9	CC-10	CPRM-1	CPRM-2	CPRM-3	C-1	C-2	C-3	C-4
19	DOE with 1% H ₂ S	6.9	231	10	100% Saturated vapor					x		x						x	x		x	x	x				x	x	x	
20	"	"	"	10	Liquid					x		x						x	x		x	x	x							
21	"	"	"	30	100% Saturated vapor	x	x	x	x	x	x	x				x	x			x	x			x	x	x		x	x	
22	"	"	"	60	100% Saturated vapor	x				x	x	x					x	x			x	x		x		x				
23	"	"	"	60	Liquid	x				x	x	x		x	x		x		x					x						
24	CO**/H ₂ O = 1.1 (without H ₂ S)	3.2	199	10	100% Saturated vapor	x	x	x	x	x	x	x				x	x			x	x			x	x	x	x	x	x	
25	"	"	260	10	37.5% Saturated	x	x	x	x	x	x	x				x	x			x	x			x	x	x	x	x	x	
26	"	"	538	10	~ 0% Saturated	x	x	x	x	x	x	x				x	x			x	x			x	x	x	x	x	x	
27	CO**/H ₂ O = 0.1 + 1 Vol% H ₂ S	6.9	538	20	~ 0% Saturated vapor					x	x		x					x	x			x	x	x	x					
28	"	"	278	20	100% Saturated vapor					x	x		x					x	x			x	x	x	x					
29	"	"	278	20	Liquid					x	x		x					x	x			x	x	x	x					
30	CO**/H ₂ O = 1.0 + 1 Vol% H ₂ S	6.9	538	20	-0% Saturated					x	x		x	x	x			x	x			x	x	x	x					
31	"	"	241	20	100% Saturated vapor					x	x		x	x	x			x	x			x	x	x	x					
32	"	"	241	20	Liquid					x	x		x	x	x			x	x			x	x	x	x					
33	CO**/H ₂ O = 3.0 + 1 Vol% H ₂ S	6.9	538	20	-0% Saturated					x	x		x	x	x			x	x			x	x	x	x					

Table II. Exposure Test Conditions and Materials (Continued).

Exposure No.	Atmosphere	Pressure (MPa) ^s	Temp. (°C)	Duration (days)	Remarks	Materials Exposed Indicated by x																									
						CC-1	CC-2	CC-3	CC-4	UMR-1	UMR-2	UMR-3	UMR-4	UMR-6	UMR-7	CC-5	CC-6	UMR-5	UMR-8	CC-7	CC-8	CC-9	CC-10	CPRM-1	CPRM-2	CPRM-3	C-1	C-2	C-3	C-4	C-5
34	CO**/H ₂ O = 3.0 + 1 Vol% H ₂ S	6.9	204	20	100% Sat. vapor					x	x		x	x	x		x	x		x	x	x	x								
35	"	"	204	20	Liquid					x	x		x	x	x		x	x		x	x	x	x								
36	Steam	2.8	230	10	100% Sat. vapor					x			x					x	x		x	x	x			x	x	x			
37	"	"	"	10	Liquid					x			x					x	x		x	x	x								
38	Steam	6.9	285	10	100% Sat. vapor					x			x					x	x		x	x	x			x	x	x			
39	"	"	"	10	Liquid					x			x					x	x		x	x	x								
40	"	2.8	varied	10	Various % sat.																						x				
41	"	6.9	"	10	" "																						x				
42	DOE + 1 Vol% H ₂ S	6.9	"	10	" "																						x				

*DOE Composition is 18 CO, 12 CO₂, 5 CH₄, 24 H₂, 41 H₂O (vol.%)

**Vol % Ratio

s1 MPa = 145 psia

same atmosphere to which 1 vol% H_2S was added, exposures 15-17, 19-21 in Table II.

1. Dimensional and Weight Changes

The dimensional changes for all the refractory specimens after exposure was small, <1%. The castables generally showed a slight shrinkage in the unsaturated DOE atmosphere at 538°C, while a slight expansion occurred in the saturated atmospheres at 231°C. The dimensional change for the phosphate-bonded specimens was barely measurable.

The weight loss for the cement bonded castables, Table III, was ~3% and 4-5% when fired in air at 260°C and 538°C, respectively. The weight loss of the high alumina castables after exposure to the unsaturated atmosphere at 538°C was generally smaller than that of the controls fired in the air at 538°C. The presence of 1% H_2S in the atmosphere at 538°C had little effect upon the weight loss.

In the saturated DOE atmosphere (231°C) the weight loss for all the high alumina castables was less than that at 538°C and in some cases a small weight gain occurred. Once again the presence of 1% H_2S had no major effect upon the weight change.

The weight changes for the intermediate and insulating castables after exposure were essentially the same in both the saturated and unsaturated atmosphere and were not much different from their controls fired in air. However, the weight change for these castables was significantly different when the atmosphere contained 1% H_2S , particularly in the saturated atmosphere.

All of the phosphate ramming mixes exposed to the unsaturated atmosphere at 538°C showed small weight changes, CPRM-3 having the

Table III. Percent Weight Change* Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls, fired 18h in air		DOE atmosphere, 30 days	
	<u>260°C</u>	<u>538°C</u>	<u>231°C</u> (100% saturated)	<u>538°C</u>
Dense, High Alumina Castables				
CC-1	-3.1**	-4.5	[§] +0.1/ [§] -0.9	[§] -1.9/ [§] -2.2
CC-2	-2.9	-4.7	-1.6/-2.3	-3.7/-3.8
CC-3	-2.3	-3.9	[#] nt/-0.1	-0.9/-1.8
CC-4	-3.0	-4.1	+2.0/-0.5	-1.4/-1.8
UMR-1	-3.2	-5.0	+0.2/+0.5	-2.0/-1.2
UMR-2	-4.3	-5.0	nt/-2.4	-3.6/-4.0
UMR-3	-3.0	-4.0	-1.7/+0.5	-3.8/-2.8
Dense, Intermediate Alumina Castables				
CC-5	-3.0	-4.7	-4.2/-1.9	-4.2/-4.1
CC-6	-3.2	-5.0	-5.2/-2.7	-4.4/-4.1
Insulating Castables				
CC-7	-3.4	-5.0	-5.0/+0.3	-5.0/-4.7
CC-8	-2.1	-3.5	-1.9/+1.4	-3.2/-2.9
Phosphate-Bonded Ramming Mixes				
CPRM-1	nt	nt	+0.7/+2.0	Nil/-0.3
CPRM-2	nt	nt	+1.0/+2.9	+0.2/Nil
CPRM-3	nt	nt	-3.3/-0.3	-1.2/-0.7

*Referenced to as-dried at 110°C weight for cement-bonded castables and to as-fired at 538°C weight for phosphate-bonded specimens.

**+ = Weight gain; - = Weight loss

§First number is for no H₂S present while the second is for the same atmosphere containing 1 Vol. % H₂S. This procedure also followed in Tables IV; V, VI and VIII.

#nt - not determined. Same for succeeding tables.

Table IV. Bulk Density (gm/cm³) Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls			DOE atmosphere, 30 days	
	As-Dried	Fired 18h in air		(100% saturated)	
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>231°C</u>	<u>538°C</u>
Dense, High Alumina Castables					
CC-1	2.77	2.75	2.67	2.79*/2.77	2.75*/2.77
CC-2	2.62	2.56	2.49	2.53/2.51	2.57/2.55
CC-3	2.85	2.81	2.74	nt/2.79	2.85/2.77
CC-4	2.88	2.84	2.78	2.94/2.87	2.87/2.89
UMR-1	2.75	2.71	2.68	2.75/2.73	2.73/2.78
UMR-2	2.66	2.58	2.52	nt/2.58	2.59/2.60
UMR-3	2.47	2.45	2.35	2.44/2.44	2.44/2.45
Dense, Intermediate Alumina Castables					
CC-5	2.33	2.29	2.26	2.24/2.26	2.25/2.23
CC-6	2.31	2.27	2.21	2.15/2.26	2.25/2.24
Insulating Castables					
CC-7	1.53	1.52	1.46	1.45/1.59	1.49/1.53
CC-8	1.58	1.55	1.54	1.54/1.59	1.53/1.54
Phosphate-Bonded Ramming Mixes					
CPRM-1	nt	nt	2.95	2.96/2.90	2.95/2.87
CPRM-2	nt	nt	2.92	2.94/2.99	2.96/2.91
CPRM-3	nt	nt	2.96	2.93/2.97	3.00/2.95

*First number is for DOE atmosphere without H₂S while second is for DOE with 1% H₂S.

Table V. Percent Apparent Porosity Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls			DOE atmosphere, 30 days	
	As-Dried	Fired 18h in air			
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>231°C</u>	<u>538°C</u>
	(100% saturated)				
Dense, High Alumina Castables					
CC-1	14.2%	20.0%	23.3%	13.0*/15.5%	24.3/23.7%
CC-2	18.7	25.2	27.6	28.8/28.5	28.0/28.3
CC-3	13.7	16.9	20.1	nt/16.4	21.1/23.9
CC-4	14.4	17.1	21.8	6.2/12.7	21.0/20.7
UMR-1	16.1	20.1	22.9	10.5/15.3	26.1/23.5
UMR-2	15.6	24.1	27.8	nt/17.8	27.0/26.8
UMR-3	23.3	25.1	31.2	28.0/28.2	31.6/30.7
Dense, Intermediate Alumina Castables					
CC-5	13.3	16.6	20.3	11.8/15.8	21.2/21.9
CC-6	16.1	18.7	22.8	22.3/16.7	22.6/22.3
Insulating Castables					
CC-7	42.9	46.0	48.6	53.8/44.9	52.3/50.5
CC-8	38.8	41.0	42.3	52.0/45.4	52.4/51.4
Phosphate-Bonded Ramming Mixes					
CPRM-1	nt	nt	17.3	20.6/20.6	18.2/20.1
CPRM-2	nt	nt	19.8	21.1/18.7	18.6/19.4
CPRM-3	nt	nt	16.3	21.5/18.5	16.2/17.5

*First number is for DOE atmosphere without H₂S while second is for DOE with 1% H₂S.

Table VI. Modulus of Rupture (MPa^{*}) Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls			DOE atmosphere, 30 days	
	As-Dried	Fired 18h in air		(100% saturated)	
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>231°C</u>	<u>538°C</u>
Dense, High Alumina Castables					
CC-1	19.8±2.0 ^{**}	13.4±0.9	13.0±0.4	29.2 [§] /24.4±2.6	9.0±0.9/8.2±0.9
CC-2	17.2±1.0	8.2±1.2	9.5±1.0	13.7/11.9±1.0	5.2±0.4/6.5±0.2
CC-3	21.2±1.7	17.3±1.3	18.3±0.6	nt/28.6±3.1	10.8±0.4/11.8±0.7
CC-4	22.8±2.6	16.6±1.8	15.3±2.4	33.5/37.1±1.9	11.9±1.9/12.5±5.6
UMR-1	19.7±1.3	15.3±1.2	15.2±1.0	45.7/33.6±1.4	12.4±1.4/13.9±1.1
UMR-2	20.2±2.3	8.4±1.1	12.5±2.0	nt/27.9±3.9	4.6±0.6/7.1±0.9
UMR-3	16.3±2.1	11.7±2.1	6.7±1.6	18.3/14.6±1.7	8.6±1.0/9.7±0.7
Dense, Intermediate Alumina Castables					
CC-5	19.3±3.9	12.9±2.3	12.1±1.2	24.4/16.2±1.7	17.5±2.3/12.8±1.3
CC-6	15.2±1.7	10.8±1.6	9.6±0.7	23.0/27.0±2.7	16.9±2.2/16.1±1.3
Insulating Castables					
CC-7	4.5±0.7	3.1±3.0	3.3±0.2	6.4/5.4±0.3	4.5±0.4/3.6±0.4
CC-8	6.7±0.8	5.4±0.6	6.5±3.1	6.6/3.9±0.5	7.5±0.6/6.2±0.4
Phosphate-Bonded Ramming Mixes					
CPRM-1	nt	nt	27.0±2.2	11.2/7.6±0.8	24.9±3.9/15.4±2.9
CPRM-2	nt	nt	23.5±1.7	3.2/4.2±0.9	20.8±2.8/16.6±2.2
CPRM-3	nt	nt	18.3±4.1	3.0/6.2±2.2	11.1±4.4/14.6±1.4

*1 MPa = 145 psi.

**The ± limit corresponds to one standard deviation.

[§]Standard deviation is not shown since only two specimens were tested in the DOE atmosphere without H₂S.

largest at ~1%. In the saturated atmosphere, CPRM-1 and 2 had a weight gain of 1 to 3%, while CPRM-3 continued to show a weight loss (-3.3%) which became smaller when 1% H₂S was present (-0.3%).

2. Density

As shown by the data in Table IV, the bulk density after exposure was comparable to that of the controls fired in air at equivalent temperatures. Comparison of the data for 231° and 538°C indicates that the degree of saturation of the atmosphere had no appreciable effect upon the bulk density. Similarly, the presence of 1% H₂S had no significant effect upon the bulk density.

3. Porosity

In comparison to the change in weight or bulk density, a large reduction in porosity occurred in most of the high and intermediate alumina castables after exposure to the saturated (231°C) atmosphere, Table V. On the other hand, the porosity after exposure to the unsaturated atmosphere at 538°C was close to that for the respective controls fired in air at 538°C, the insulating castables CC-7 and CC-8 being the only exception where a moderate increase in porosity was found. The change in porosity of the phosphate-bonded refractories was much less than that of the cement bonded castables and appeared less dependent upon the degree of saturation of the test atmosphere. While the presence of 1% H₂S does not appear of major significance, the porosity of the cement-bonded castables appears to be affected to a greater degree than phosphate-bonded refractories.

4. Flexural Strength

The modulus of rupture (MOR) for controls fired in air and after exposure to the DOE atmosphere at 231° and 538°C is given in Table VI.

In all cases, the MOR of the as-cast and dried (110°C) specimens equalled and generally exceeded the manufacturer's MOR value. The decrease in MOR for the controls fired at higher temperatures is normal for cement-bonded castables.

In general, the MOR of the refractories after exposure to the unsaturated (538°C) atmosphere were not too different from that of their respective controls fired in air at 538°C, the MOR being lower for the high alumina castables (except UMR-3), higher for the intermediate alumina castables, and about the same for the insulating castables and phosphate-bonded refractories (except CPRM-3). The presence of 1% H₂S did not affect the MOR of the cement-bonded castables to a significant degree, but did seem to result in generally lower strengths for the phosphate-bonded refractories.

As is clearly evident from Table VI, the largest and most significant change in MOR occurred after exposure to the saturated (231°C) atmosphere. The MOR of the high and intermediate alumina castables increased significantly, sometimes more than doubling, whereas the phosphate-bonded refractories showed a large decrease in MOR. The MOR of the insulating castables remained relatively unchanged. The presence of 1% H₂S in the saturated atmosphere produced no clearly discernible change in MOR, although more samples showed a decrease in MOR than increase.

This large increase in MOR for cement-bonded castables and decrease in MOR for phosphate-bonded refractories has also been found in other saturated steam⁽⁹⁾ and steam/CO^(8,9-12) atmospheres. As might be expected, a reasonably good correlation is found between the change

in MOR and porosity of the cement-bonded castables after exposure to the saturated atmosphere. Those castables such as CC-1, CC-4, and UMR-1 with the larger increases in MOR, Table VI, also showed large reductions in porosity, Table V, whereas CC-2 and UMR-3 whose porosity changed only slightly showed only a slight increase in MOR.

5. Thermal Expansion

The thermal expansion of high and intermediate alumina castables before and after exposure to the saturated DOE atmosphere (231°C) is shown in Figs. 2 and 3. After exposure, a sudden expansion was observed between 500°C and 600°C which varied in magnitude for different castables, being generally smaller in the intermediate alumina castables than in the high alumina castables.

After exposure to the unsaturated DOE atmosphere (538°C), high and intermediate alumina castables showed similar thermal expansion hysteresis, the expansion being almost linear up to 800°C. Above 800°C, the expansion increased but was less pronounced than in the castables exposed to the saturated atmosphere.

The insulating castables exposed to the saturated DOE atmosphere generally showed very distinct changes in the expansion rate during heating from 25 to 950°C, as illustrated in Fig. 4. Specimens exposed to the unsaturated atmosphere had comparatively smooth expansion curves.

6. Chemical Reactions

a. General

The crystalline compounds identified by XRD in each refractory prior to exposure are summarized in Table VII. Only minor or trace amounts of the calcium aluminate compounds (CA, CA₂) and hydrated

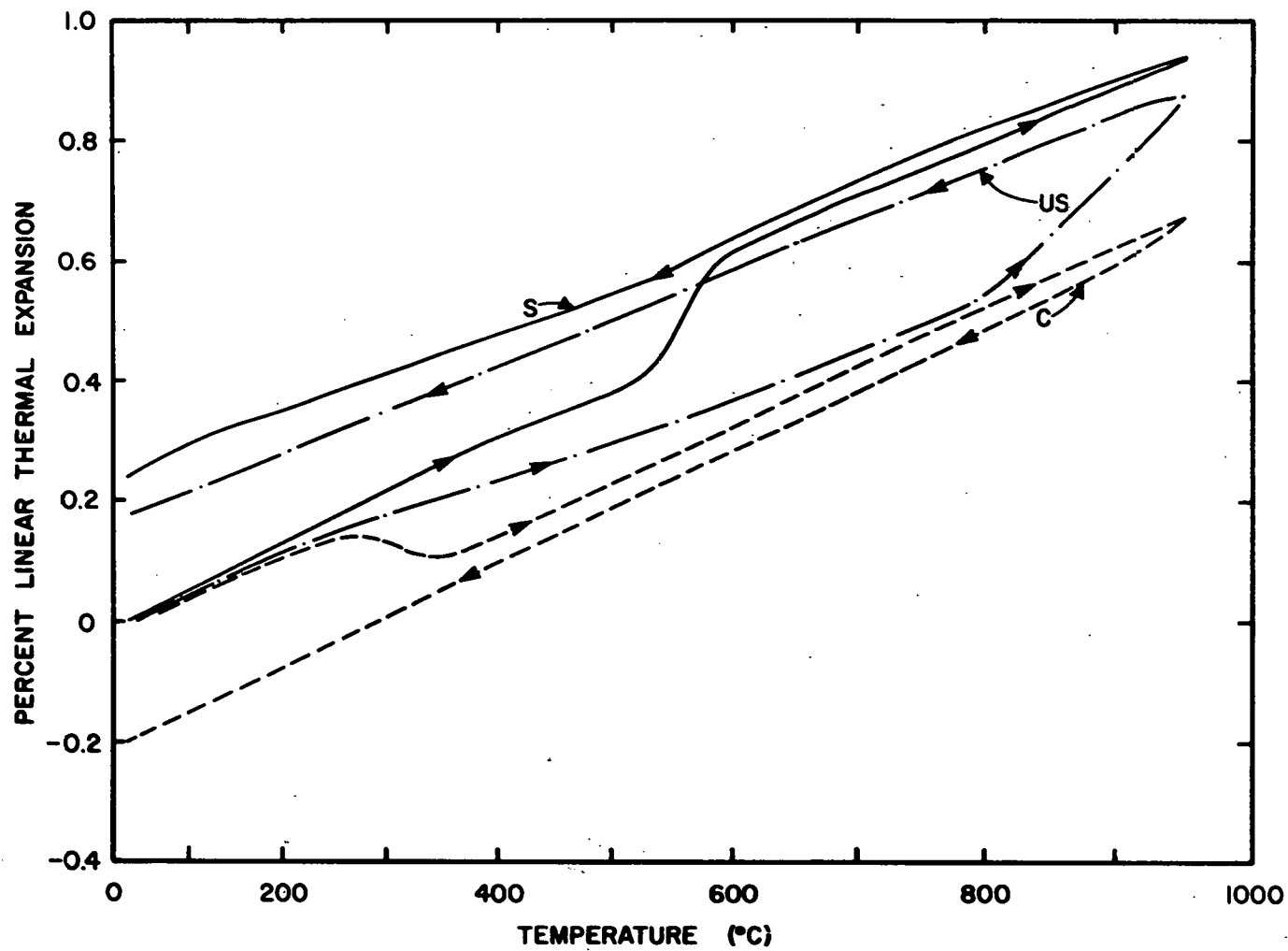


Fig. 2. Typical thermal expansion curves for high alumina castable, UMR-1.
 C -Control (as-cast and dried)
 S -After exposure to saturated DOE atmosphere at 6.9 MPa/ 231°C.
 US -After exposure to unsaturated DOE atmosphere at 6.9 MPa/538°C.

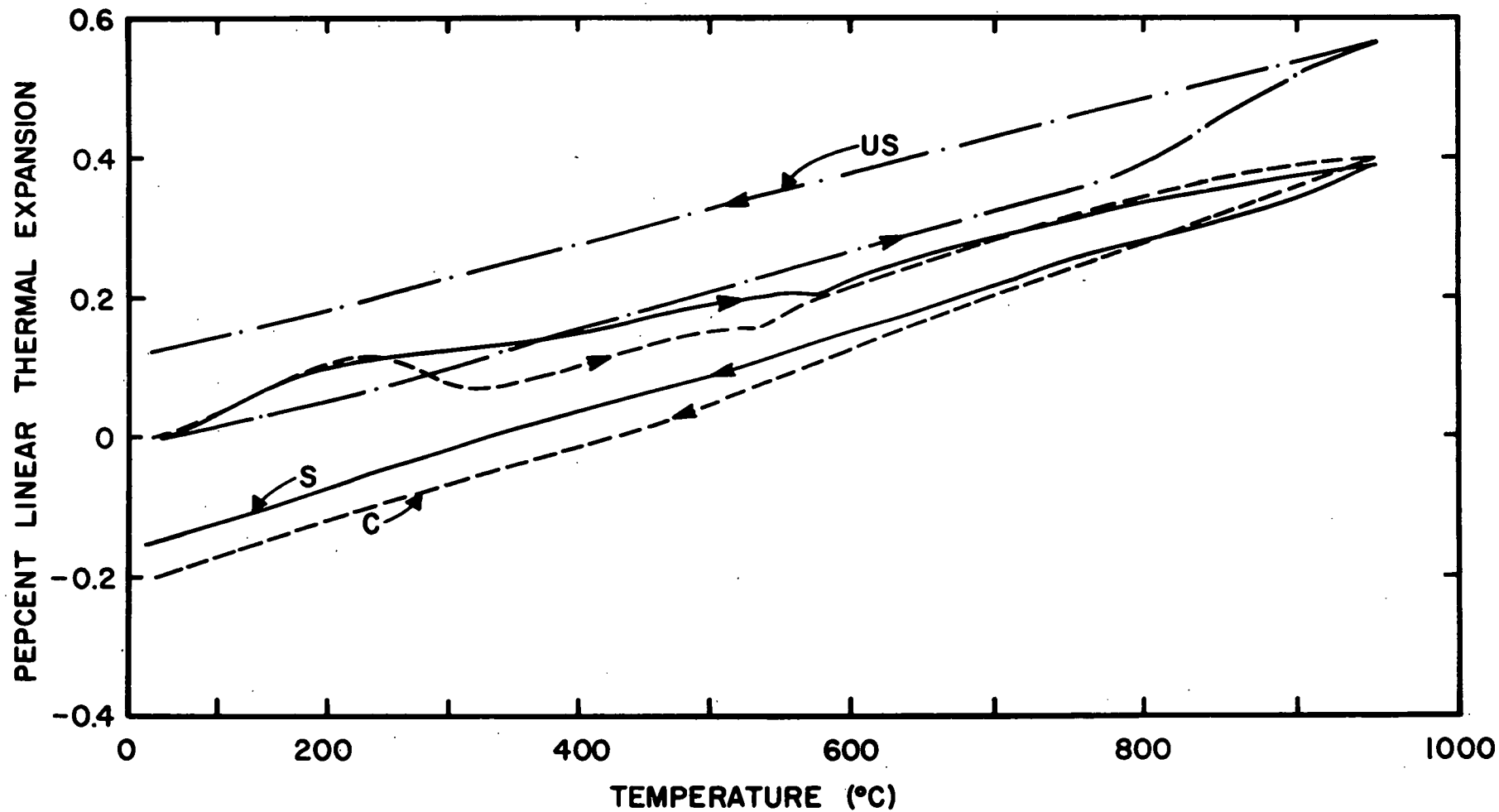


Fig. 3. Typical thermal expansion curves for intermediate alumina castable, CC-6.
 C - Control (as-cast and dried)
 S - After exposure to saturated DOE atmosphere at 6.9 MPa/231°C.
 US- After exposure to unsaturated DOE atmosphere at 6.9 MPa/538°C.

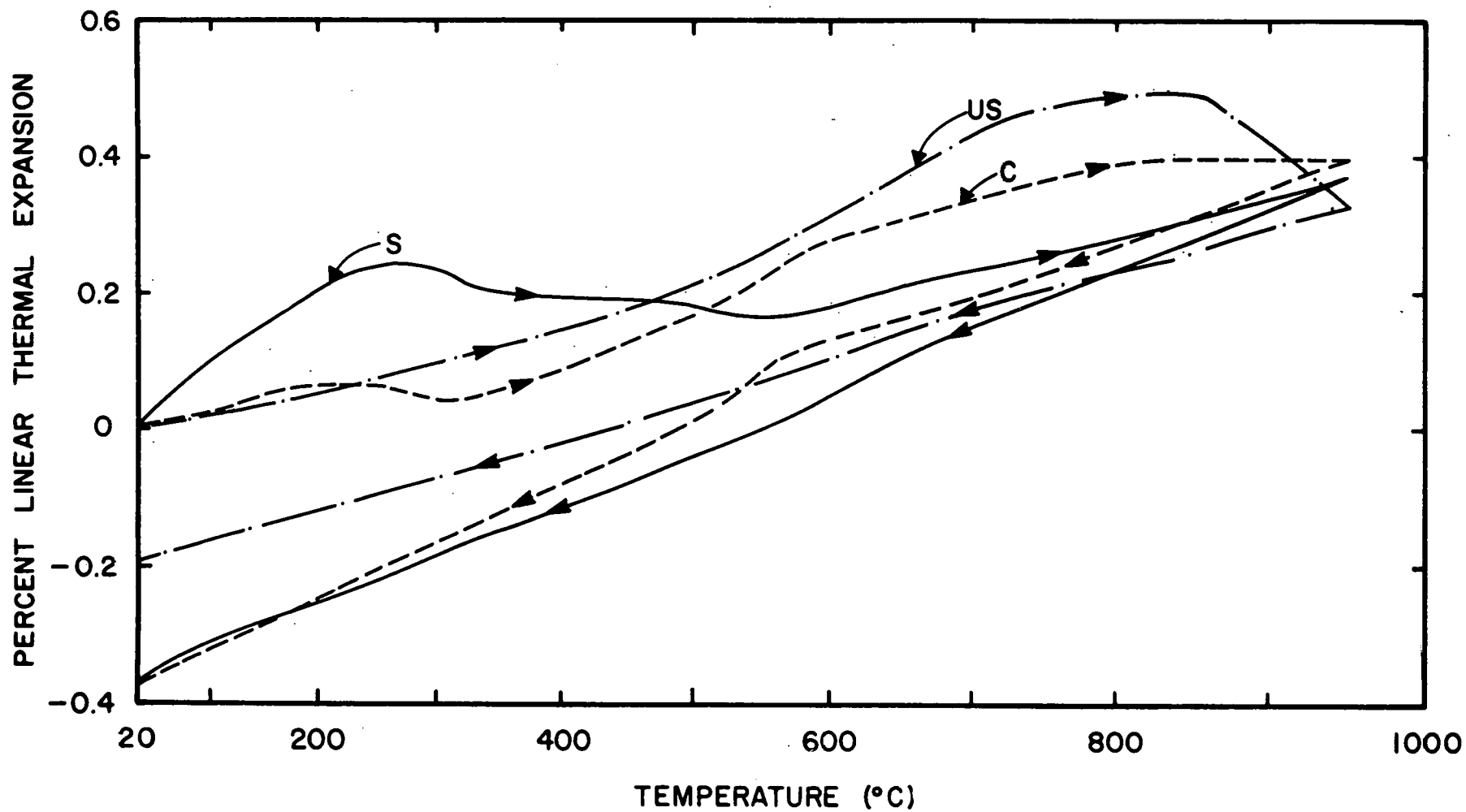


Fig. 4. Typical thermal expansion curves for insulating castable, CC-8.
 C - Control (as-cast and dried)
 S - After exposure to saturated DOE atmosphere at 6.9 MPa/231°C.
 US- After exposure to unsaturated DOE atmosphere at 6.9 MPa/538°C.

Table VII. Compounds* Initially Present in Castables (As-Cast and Dried at 110°C) and Ramming Mixes (As-fired at 538°C in Air) Prior to Exposure.

<u>Refractory</u>	<u>Compounds</u>
Dense, High Alumina Castables	
CC-1	α -Alumina, $C_3AH_6^{**}$ (tr ^s), AH_3 (tr), CA(tr)
CC-2	α -Alumina, CA_2
CC-3	α -Alumina, CA
CC-4	α -Alumina, CA
UMR-1	α -Alumina, CA
UMR-2	α -Alumina, CA, C_3AH_6 (tr), AH_3 (tr)
UMR-3	α -Alumina, CA_2
Dense, Intermediate Alumina Castables	
CC-5	Mullite, β -Cristoballite, α -Alumina, CA
CC-6	Mullite, β -Cristoballite, α -Alumina, CA
Insulating Castables	
CC-7	Kyanite, Mullite, α -Quartz, β -Cristoballite, α -Alumina, CA
CC-8	α -Quartz, Kyanite, α -Alumina, CA
Phosphate-Bonded Ramming Mixes	
CPRM-1	α -Alumina, $AlPO_4$ (Orthorhombic and trigonal, tr)
CPRM-2	α -Alumina, $AlPO_4$ (Orthorhombic, tr)
CPRM-3	α -Alumina, $AlPO_4$ (Trigonal, tr)

* Listed in order of decreasing concentration as estimated from XRD peak intensity

** Cement Chemistry Notation; C = CaO, A = Al_2O_3 , H = H_2O

str represents trace amount

Table VIII. Weight Percent CaCO_3 and Boehmite Determined by TGA
After a 30-day Exposure to DOE Atmosphere at 6.9 MPa
(1000 psia) and 231 or 538°C.

	% CaCO_3		%CaO**		%CaO	% Boehmite***
	231°C	538°C	231°C	538°C	As-Received	231°C
CC-1	5.5*/5.0*	6.8/7.3	3.3/3.0	3.9/4.3	4.5	22.3/22.8
CC-2	5.9/5.4	6.4/6.4	3.3/3.2	3.7/3.7	6.0	20.3/19.2
CC-3	nt/3.8	6.4/6.9	nt/2.3	3.7/4.0	5.6	nt ^{xx} /23.2
CC-4	3.5/3.6	7.6/8.4	2.1/2.2	4.5/4.9	5.4	23.9/32.4
UMR-1	5.2/5.1	8.0/7.8	3.1/3.1	4.7/4.5	5.4	29.1/29.1
UMR-2	nt/5.2	10.1/10.9	nt/3.2	6.0/6.5	7.8	nt/37.3
UMR-3	8.8/4.7	7.7/6.1	5.3/2.8	4.5/3.5	7.4	27.9/27.2
CC-5	2.7/4.3	3.1/2.4	1.6/2.5	1.8/1.4	5.0	8.2/13.3
CC-6	4.1/4.7	4.4/4.4	2.4/2.8	2.6/2.5	5.5	13.5/15.4
CC-7	1.5/2.6	3.4/3.2	0.9/1.5	1.9/1.8	4.5	11.5/11.9
CC-8	2.8/3.3	2.2/1.9	1.7/2.0	1.3/1.1	2.9	9.1/6.4

*First number is for no H_2S present while second number is for DOE atmosphere containing 1 Vol% H_2S .

**Calculated from wt% CaCO_3 as determined from TGA.

***No boehmite present at 538°C.

xxnt = not determined.

phases (C_3AH_6 or AH_3) were found in the cement-bonded castables. The only bond phase identified in the phosphate-bonded refractories was $AlPO_4$, either orthorhombic or trigonal (berlinite).

b. Cement-Bonded Castables

XRD analysis of the cement-bonded castables showed that all of the CA , C_3AH_6 , and AH_3 had disappeared (reacted) in both the saturated ($231^\circ C$) and unsaturated ($538^\circ C$) atmosphere in ~ 10 days, the shortest time investigated. No evidence was found for any significant reaction involving the alumina, aluminosilicate (mullite, kyanite), or silica (quartz, cristobalite) aggregate in the cement-bonded castables, the intensity of the XRD peaks for these compounds being essentially unchanged after exposure.

The major new compounds formed in the cement-bonded castables after exposure to the saturated atmosphere were boehmite (AH) and $CaCO_3$ (calcite or aragonite) as determined by XRD and DTA/TGA. Only $CaCO_3$, mostly present as calcite, but in some cases as aragonite, was detected in the castables exposed at $538^\circ C$. These results agree with other investigations⁽¹⁰⁻¹²⁾ where boehmite and $CaCO_3$ have been found in cement-bonded castables exposed to saturated steam- CO atmospheres.

In addition to the reaction of the calcium aluminate cement-bond phases to form $CaCO_3$ and boehmite, some portion of the CaO is dissolved from the refractories during exposure to the saturated atmosphere particularly. In all cases, the percent CaO in the castables after exposure, as calculated from the quantity of $CaCO_3$ present is less than the amount initially present, Table VIII. This is especially true for the castables exposed to the saturated atmosphere at $231^\circ C$. This

difference could be explained by some of the CaO not reacting to form CaCO_3 , but additional evidence of the removal of CaO from the castables during exposure to the saturated atmosphere was the higher calcium concentration in the water remaining in the vessel at the completion of the exposure. The distilled water used initially contained <1 ppm Ca, but at the completion of the exposure the Ca concentration had increased to 5000 ppm Ca.

c. Phosphate Bonded Ramming Mixes

The main change found by XRD in the phosphate-bonded refractories after exposure to the unsaturated (538°C) atmosphere was an increase in the amount of trigonal AlPO_4 present in CPRM-1 and 3, although trace quantities of orthorhombic AlPO_4 remained after exposure. Only a trace of trigonal AlPO_4 was detected in CPRM-2 after exposure, the AlPO_4 being present in the orthorhombic form as before exposure, Table VII. No new compounds were detected by XRD or DTA/TGA.

After exposure to the saturated atmosphere, the estimated amount of trigonal AlPO_4 was considerably lower in CPRM-1, but about the same in CPRM-3. No AlPO_4 in either form was detected by XRD in CPRM-2. A new compound tentatively identified as $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}^*$ was found in all three refractories. This compound probably results from the phosphate-bonded refractories coming in contact with the CaO dissolved from the cement-bonded castables since both groups of refractories were exposed simultaneously in the same vessel and the CaO content of the phosphate-bonded refractories is quite low, Table I.

*ASTM Index Card #12-27.

The XRD intensity of the α - Al_2O_3 peaks in the phosphate refractories was essentially unchanged after exposure indicating that the alumina grog did not react to any detectable extent, as found for the cement-bonded castables. However, during exposure to the saturated atmosphere some unknown portion of the phosphate bond appears to have been dissolved from these refractories since fairly large quantities of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ were found in the bottom of the steam vessel at the completion of the exposure and the water recovered contained about $\sim 5\text{ppm } (\text{PO}_4)^{-3}$.

7. Discussion

The 30-day exposure time is only a small fraction of the desired service-life for a refractory lining in a coal gasifier, but it is important to note that none of the refractories disintegrated or were otherwise totally destroyed. The loss of CaO from the cement-bonded castables and the major reduction in strength for the phosphate-bonded refractories in the saturated atmosphere could be potentially detrimental to the long-term (months to years) service performance. Other than the phosphate bonded refractories in saturated atmospheres, no reactions occurring in short times have been found which render these commercial refractories totally unsatisfactory for use in a coal gasifier.

In general, cement-bonded castables of the same type, but made by different manufacturers showed essentially the same behavior after exposure. Similarly, the results for the commercial and laboratory-prepared castables were in good agreement, indicating that investigations utilizing the latter can provide a reliable indication of the performance of commercial products. In the phosphate-bonded refractories larger differences, primarily in MOR, were found for similar products made by different (three) manufacturers.

The most significant change in properties of the cement-bonded castables was the increase in flexural strength and reduction in porosity found for most of the dense high and intermediate alumina castables after exposure to the saturated atmosphere. These changes are consistent with the chemical reactions described previously. The increase in MOR is attributed to the boehmite formed during exposure since, in a general way, the increase in MOR usually corresponded to the quantity of boehmite present. Furthermore, previous work^(13,14) has demonstrated that boehmite formed by autoclaving alumina bodies in steam, without cement, can provide substantial bonding; MOR's of 5-7 MPa were reported. An increase in MOR has also been attributed⁽¹⁵⁾ to the formation of CAS_2 (anorthite) in similar intermediate alumina castables exposed to high pressure steam. However, no XRD evidence of CAS_2 was found in the CC-5 and -6 intermediate alumina castables in the present investigation after exposure, but in Task VII, a calcium aluminosilicate compound was found by EDAX analysis of a similar castable (UMR-8).

The reduction in porosity can also be explained by the formation of CaCO_3 and boehmite within the pores of the castables. Since the specific volume of boehmite is larger than that of alumina and the external dimensional changes of these castables were small, $\leq 1\%$, it appears that the volume increase associated with boehmite formation is accommodated within the original pore volume of the castables, thereby lowering the porosity.

The sudden expansion between 500°C and 600°C in the thermal expansion curves of castables exposed to the saturated atmosphere (231°C) is

due to the dehydration of boehmite which occurs in this temperature range. The magnitude of this expansion generally corresponded to the quantity of boehmite and was absent in specimens exposed to the unsaturated atmosphere (538°C) which did not contain boehmite. The expansion above 800°C appears to be associated with the decomposition of calcite.

The significant reduction in strength of the phosphate-bonded refractories after exposure to the saturated atmosphere is attributed to a general corrosion of the AlPO_4 bond phase by saturated steam. The sensitivity of the phosphate bond phase(s) to saturated steam can be expected to vary widely with the crystallinity and composition of the bond phase, i.e., the temperature to which such a refractory is fired prior to exposure to saturated steam. Well crystallized (high fired) AlPO_4 powder has been reported⁽¹¹⁾ to show no evidence of reaction with steam in a saturated steam (47.5%)-CO (52.5%) atmosphere at 3.2 MPa/199°C.

Finally, it is important to mention all of the chemical reactions identified were between the refractory bond phases, cement or phosphate, and steam, CO, or CO_2 . No evidence was found for any significant reaction with other gases (H_2 , CH_4 , H_2S) or with the pure alumina or siliceous aggregates, such as silica volatilization by H_2 or dissolution by steam. At higher temperatures reactions involving siliceous aggregates become more likely⁽¹⁶⁾ but, for the conditions in this investigation, the chemical reactions were basically confined to the refractory bond phases.

The reader is referred to Ref. 17 for additional details.

C. Task III- Exposure Time

Several of the same commercial and experimental cement and phosphate-bonded refractories used in Task II were investigated at the same conditions

used for the 30-day screening exposure, but for periods of time between 10 and 60 days (Exp. 15-18, 21-23 in Table II). The purpose was to determine how the structural integrity, properties, and the chemical reactions found in these refractories varied with exposure time, up to 60 days.

The dimensional changes for all the refractories were small, $\leq 1\%$, and were essentially independent of exposure time between 10 and 60 days. The weight changes at 60 days were generally similar to those found in Task II at 30 days. The porosity after exposure to the unsaturated DOE atmosphere (538°C) was about the same as that after firing in air at 538°C, was similar to that found previously in Task II for the respective refractories, and was essentially independent of exposure time, Table IX. After exposure to the 100% saturated atmosphere for 30 days at 231°C, the porosity of the castables was generally less than that of the controls fired in air or after exposure at 538°C, except UMR-3. This agreed with similar decreases in porosity reported in Task II for this saturated atmosphere. After 60 days at 231°C, the porosity was consistently higher than at 30 days suggesting an increase in porosity with exposure time when the refractories are exposed to saturated vapor.

The change in porosity of the phosphate-bonded refractories after exposure at 538°C or 231°C was small and independent of exposure time.

Table X gives the MOR values for refractories used in Task III. The MOR after exposure at 538°C was essentially constant between 10-30 days and comparable with the controls, but was generally somewhat larger after 60 days at 371°C, Fig. 5. In the 100% saturated atmosphere, the MOR of the high and intermediate alumina castables more than doubled

Table IX. Percent Apparent Porosity After Firing in Air or Exposure to DOE Atmosphere With 1 Vol% H₂S at 6.9 MPa (1000 psia).

Refractories	Controls fired in air			Exposure Temperature and Time					
	110°C, 24 h	260°C, 18 h	538°C, 18 h	538°C		371°C, 13.3% Sat.	231°C, 100% Saturated		
				10 days	20 days	30 days	60 days	30 days	60 days
<u>Dense High Alumina Castables</u>									
CC-1	14.2	20.0	23.3	23.8	24.1	23.7	25.9	15.5	23.1
UMR-1	16.1	20.1	22.9	26.2	24.8	23.5	26.8	15.3	20.7
UMR-2	15.6	24.1	27.8	26.9	26.3	26.8	28.7	17.8	23.4
UMR-3	23.3	25.1	31.2	30.7	30.8	30.7	31.1	28.2	32.4
<u>Dense, Intermediate Alumina Castable</u>									
CC-6	16.1	18.7	22.8	22.5	22.1	22.3	19.8	16.7	19.3
<u>Insulating Castable</u>									
CC-8	38.8	41.0	42.3	50.9	50.6	51.4	52.0	45.4	50.1
<u>Phosphate-bonded Ramming Mixes</u>									
CPRM-1	nt	nt	17.3	20.4	19.7	20.1	nt	20.6	21.2
CPRM-2	nt	nt	19.8	19.7	19.4	19.4	nt	18.7	nt
CPRM-3	nt	nt	16.3	16.8	16.2	17.5	nt	18.5	22.1

Table X. Modulus of Rupture (MPa*) After Firing in Air or Exposure to DOE Atmosphere With 1 Vol% H₂S at 6.9 MPa (1000 psia).

Refractories	Controls fired in air			Exposure Temperature and Time					
	110°C, 24 h	260°C, 18 h	538°C, 18 h	538°C			371°C 13.3% Sat. 60 days	231°C, 100% Saturated 30 days	231°C, 100% Saturated 60 days
				10 days	20 days	30 days			
<u>Dense High Alumina Castables</u>									
CC-1	19.8±2.0**	13.4±0.9	13.0±0.4	8.6±0.8	7.6±0.4	8.3±0.9	8.5±0.5	24.4±2.6	19.2±3.4
UMR-1	19.7±1.3	15.3±1.5	15.2±1.0	11.9±0.7	12.1±0.7	13.9±1.1	12.1±1.3	33.6±1.4	31.8±6.1
UMR-2	20.2±2.3	8.4±1.1	12.5±2.0	7.8±1.0	6.1±1.3	7.1±0.9	10.9±0.7	27.9±3.9	24.8±3.8
UMR-3	16.3±2.1	11.7±2.1	6.7±1.6	8.9±1.2	8.9±1.1	9.7±0.7	14.6±1.0	14.6±1.7	11.5±2.5
<u>Dense, Intermediate Alumina Castable</u>									
CC-6	15.2±1.7	10.8±1.6	9.6±0.7	15.5±1.5	14.8±1.0	16.1±1.3	24.5±2.5	27.0±2.7	24.6±2.9
<u>Insulating Castable</u>									
CC-8	6.7±0.8	5.4±0.6	6.5±3.1	6.0±0.3	6.2±0.4	6.2±0.4	7.2±0.8	3.9±0.5	3.3±1.1
<u>Phosphate-bonded Ramming Mixes</u>									
CPRM-1	nt	nt	27.0±2.2	16.2±1.7	15.0±2.1	15.4±2.9	nt	7.6±0.8	11.0±1.8
CPRM-2	nt	nt	23.5±1.7	16.6±3.0	16.8±1.8	16.6±2.2	nt	4.2±0.9	nt
CPRM-3	nt	nt	18.3±4.1	15.1±2.3	15.4±2.8	14.6±1.4	nt	6.2±2.2	10.5±1.1

*1 MPa = 145 psi.

**The ± limit corresponds to one standard deviation.

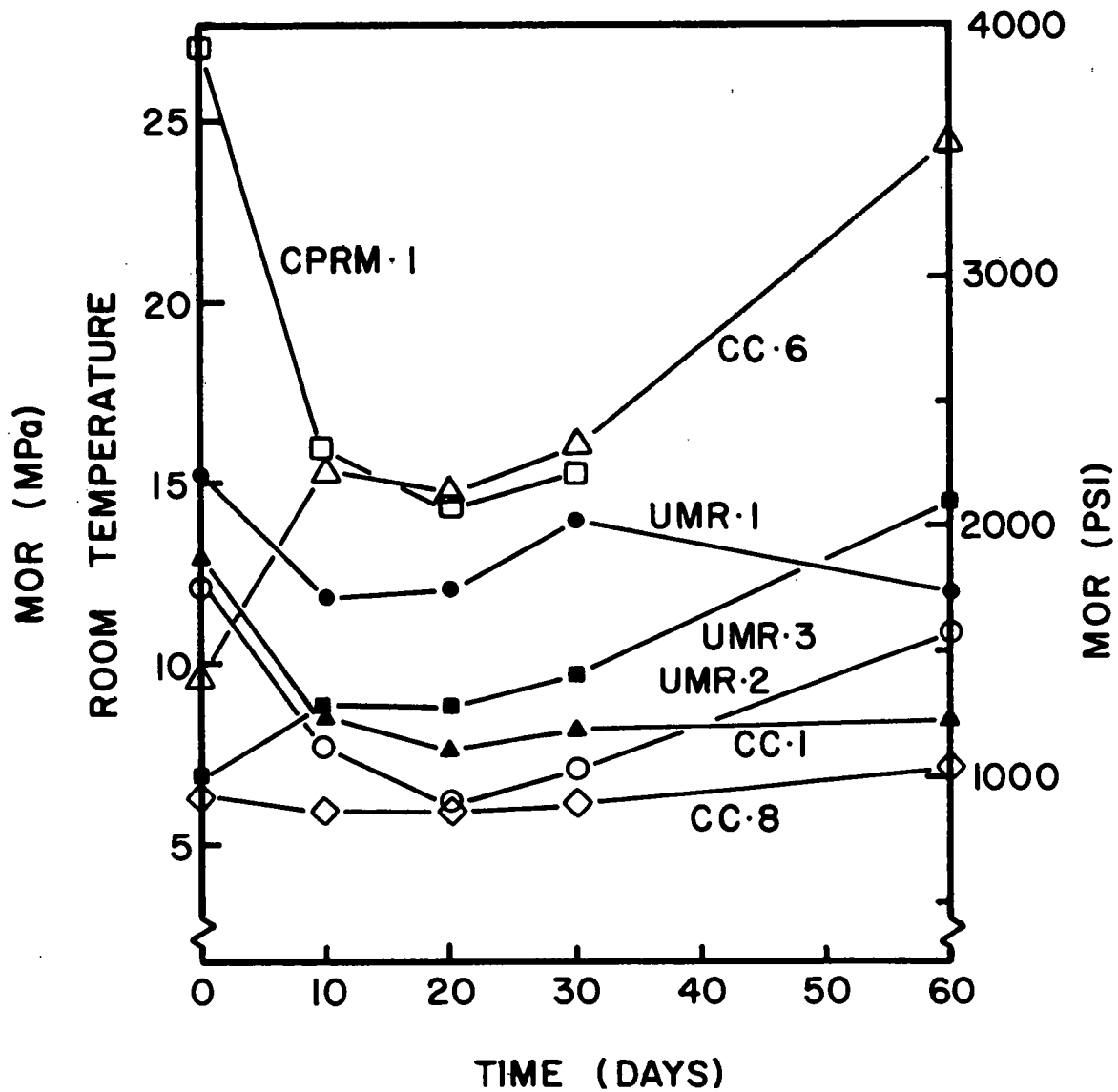


Fig. 5. Room temperature modulus of rupture after exposure. 10-, 20-, and 30-day data are for exposure to DOE (with 1% H_2S) at 6.9 MPa/538°C while 60-day data are for exposure to same atmosphere at 6.9 MPa/371°C (13.3% saturated). MOR for controls (no exposure) is after firing in air at 538°C.

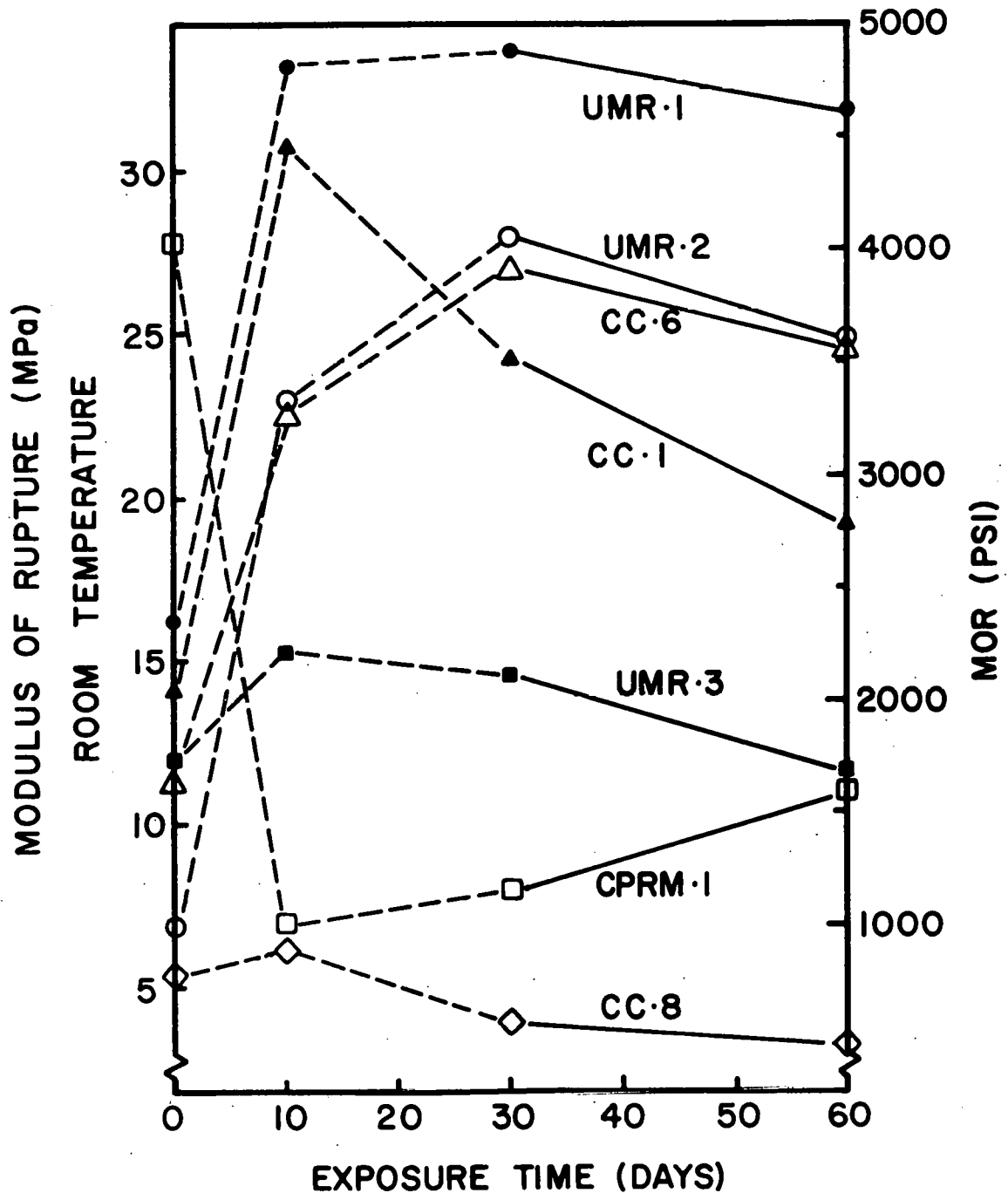


Fig. 6. Room temperature modulus of rupture after exposure. 30- and 60-day data are for exposure to 100% saturated DOE (with 1% H_2S) at 6.9 MPa/231°C while 10-day data are for exposure to 100% saturated $CO/H_2O = 1.1$ atmosphere at 3.2 MPa/199°C (Exp. #24).

Table XI. Weight Percent of CaCO_3 and Boehmite in Castables After Exposure to DOE Atmosphere at 6.9 MPa (1000 psia) - as determined by TGA.

Refractories	Exposure Temperature and Time								
	%CaCO ₃ , 538°C*			371°C, 13.3% saturated		231°C, 100% Saturated			
				60 days		30 days		60 days	
	10 days	20 days	30 days	%CaCO ₃	%Boehmite	%CaCO ₃	%Boehmite	%CaCO ₃	%Boehmite
Dense High Alumina Castables									
CC-1	6.8	6.8	7.3	7.7	0.0	5.0	22.8	5.8	25.0
UMR-1	7.5	9.4	7.8	8.3	0.0	5.1	29.1	5.7	32.0
UMR-2	9.9	10.8	10.9	11.6	4.7	5.2	37.3	9.0	34.5
UMR-3	4.1	5.5	6.1	9.3	5.3	4.7	27.2	9.1	26.5
Dense, Intermediate Alumina Castable									
CC-6	3.9	5.0	4.4	7.1	7.3	4.7	15.4	4.4	18.1
Insulating Castable									
CC-8	1.7	2.2	1.9	3.2	4.9	3.3	6.4	3.8	3.1

*No boehmite present at 538°C.

in some cases, Fig. 6. The MOR of phosphate-bonded specimens (e.g., CPRM-1) was significantly lower than the controls and the MOR of the insulating castables (e.g., CC-8) remained almost unchanged. Increasing the exposure time from 30 to 60 days in the saturated atmosphere did not produce any major change in MOR, excepting CC-1.

The present results, like those of other similar studies^(8,10-12), show the most pronounced changes in properties occur within the first few days of exposure, ~6-10, and the changes thereafter are relatively small for the conditions investigated. This point is illustrated in Figs. 5 and 6 where the MOR at 30 and 60 days is generally similar and about the same as that at 10 days. There are a few exceptions to this generalization such as CC-1 in Fig. 6 where the MOR at 60 days is lower. Similarly CC-6, UMR-2, and UMR-3 in Fig. 5 have a higher MOR at 60 days but this is due to the difference in the 60 day exposure conditions, higher saturation which caused boehmite to form in these samples, but was absent in the 10-30 day samples.

Overall, the results indicate that after a relatively short period of ~10 days, the exposure time is not an important factor affecting the properties measured in this study. This is not unexpected since the chemical reactions which are responsible for the property changes, particularly boehmite formation, are also fairly rapid and appear close to completion after ~10 days; note the small changes in the % CaCO_3 and % boehmite found for the exposure times in Table XI. While the possibility of some slower chemical reactions, that might not become evident until much longer exposure times, cannot be totally excluded,

no reactions were observed at 60 days which were different or had not already been detected at 10 or 30 days.

The reader is referred to Ref. 18 for more detailed information on the effect of exposure time.

D. Task IV- CO/Steam Ratio

The results of Tasks II and III as well as other investigations⁽¹⁰⁻¹²⁾ indicate that CO and steam are the most important chemically reactive gas species at temperatures and pressures below 538°C and 6.9 MPa, respectively. The purpose of this task, therefore, was to investigate the effect of various CO-steam compositions. Twenty day exposure tests were made at 6.9 MPa for CO/steam ratios 0.1, 1, and 3 containing 1 vol% H₂S in both the 100% saturated and unsaturated atmosphere (exposures 27-35, Table II). These ratios basically cover those for low to high BTU gasification processes. The results were compared with those of previous exposures in the DOE atmosphere and also with the results of another exposure in CO/H₂O = 1.1 atmosphere with no H₂S at 3.2 MPa pressure and 199°C (saturated), 260°C and 538°C (unsaturated) temperatures (exposures 24-26).

Two new refractory compositions containing 5 and 10% SiO₂ additions were investigated. They are designated UMR-6 and UMR-7 and were basically 95% UMR-1 + 5% SiO₂ and 90% UMR-1 + 10% SiO₂, respectively.

The dimensional changes were similar to those observed in previous exposures, generally being $\leq 1\%$. The weight changes of the cement-bonded castables at 538°C (unsaturated vapor) were also similar to those for previous exposures in the DOE atmosphere at 538°C with no significant

difference between CO/steam ratio (Table XII). In 100% saturated vapor, all samples either showed smaller weight losses or weight increases. The weight loss of the phosphate bonded refractory in the three CO/steam atmospheres was <1%.

In the three unsaturated (dry) CO/steam mixtures at 538°C, the density of the dense castables usually decreased and the porosity increased, Table XIII. These results are similar to those observed in previous exposures in the DOE atmosphere and CO-steam with no H₂S at 6.9 MPa.

Table XIV and Fig. 7 show the MOR of the refractories after exposure to the CO/steam mixtures. As found in previous DOE exposures, the strength of the high and intermediate alumina castables was usually higher after exposure to saturated atmospheres. This is attributed to the formation of boehmite during exposure. None of the refractories showed any direct dependence of strength upon the CO/steam ratio, but there were some differences in the MOR of castables depending upon composition.

Comparison of the MOR data in Table XIV and Fig. 7 for the saturated atmospheres shows that the strength of the high alumina castables containing pure calcium aluminate cements (UMR-1 and UMR-2) was lowest in the CO/steam = 3 atmosphere. This loss of strength is attributed to the removal of some portion of CaO from the cement bond phase(s) which became progressively higher with increasing CO/steam ratio. The UMR-2 samples in the saturated CO/steam = 3 vapor also contained ~5% calcium formate, Ca(HCO₂)₂.

The UMR-4 samples in the saturated CO/steam = 3 vapor showed a significant loss of strength compared to those in the saturated CO/Steam =

Table XII. Percent Weight Change* After Firing in Air or Exposure in CO/Steam Mixtures at 6.9 MPa (1000 psia) for 20 Days.

Refractories	Controls fired in air for 18h		CO/H ₂ O = 0.1 + 1 Vol % H ₂ S		CO/H ₂ O = 1.0 + 1 Vol % H ₂ S		CO/H ₂ O = 3.0 + 1 Vol % H ₂ S	
	260°C	583°C	538°C	278°C Saturated	538°C	241°C Saturated	538°C	204°C Saturated
<u>Dense High Alumina Castables</u>								
UMR-1	-3.2**	-5.0	-2.1	+1.9	-2.3	-2.9	-2.0	-1.0
UMR-2	-4.3	-5.0	-3.6	+2.4	-3.8	+0.7	-4.0	+1.7
UMR-4	-4.6	-5.8	-2.4	+3.0	-3.5	-0.3	-3.3	+3.8
UMR-6	-4.0	-4.4	nt	nt	-4.2	-3.2	-3.4	-0.6
UMR-7	-3.7	-4.1	nt	nt	-4.1	-0.9	-3.6	-0.5
<u>Dense Intermediate Alumina Castables</u>								
UMR-5	-4.2	-4.7	-5.0	-1.1	-4.0	-0.4	-2.7	+0.8
CC-6	-3.2	-5.0	-5.1	-2.8	-3.8	-1.3	-3.5	-0.3
<u>Insulating Castables</u>								
CC-8	-2.1	-3.5	-3.2	-0.6	-2.7	+0.5	-2.6	-0.1
CC-9	-5.4	-6.4	-6.7	-1.6	-6.2	+0.4	-6.2	+1.4
CC-10	-4.5	-5.6	-7.0	-7.7	-6.1	-6.2	-6.5	-6.6
<u>Phosphate-Bonded Ramming Mix</u>								
CPRM-1	nt	nt	-0.2	-0.7	-0.2	-0.4	-0.2	-0.4

*Referenced to as-cast and fired at 110°C weight for castables and to as-fired at 538°C weight for the ramming mix.

**Weight gain = + and weight loss = -.

Table XIII. Percent Apparent Porosity After Firing in Air or Exposure in CO/Steam Mixtures at 6.9 MPa (1000 psia) for 20 Days

<u>Refractories</u>	<u>Controls fired in air</u>			<u>CO/H₂O = 0.1 + 1 Vol% H₂S</u>		<u>CO/H₂O = 1.0 + 1 Vol% H₂S</u>		<u>CO/H₂O = 3.0 + 1 Vol% H₂S</u>	
	<u>110°C 24h</u>	<u>260°C 18h</u>	<u>538°C 18h</u>	<u>538°C</u>	<u>278°C Saturated</u>	<u>538°C</u>	<u>241°C Saturated</u>	<u>538°C</u>	<u>204°C Saturated</u>
<u>Dense High Alumina Castables</u>									
UMR-1	16.1	20.1	22.9	26.3	13.4	25.1	25.7	24.8	22.0
UMR-2	15.6	24.1	27.8	27.7	14.8	26.8	22.0	24.8	21.6
UMR-4	17.8	23.8	27.0	24.3	19.4	25.3	26.0	26.2	22.8
UMR-6	17.2	22.0	26.8	nt	nt	25.4	23.3	25.0	8.0
UMR-7	19.1	23.6	26.9	nt	nt	25.9	18.3	25.3	5.8
<u>Dense Intermediate Alumina Castables</u>									
UMR-5	11.0	16.3	18.8	22.0	15.8	18.6	17.2	18.1	13.1
CC-6	16.1	18.7	22.8	22.2	16.9	20.3	18.0	22.7	8.7
<u>Insulating Castables</u>									
CC-8	38.8	41.0	42.3	52.4	52.1	48.8	51.0	46.9	51.0
CC-9	47.8	52.8	54.4	61.0	56.0	57.9	57.0	54.8	56.2
CC-10	56.0	61.8	62.9	67.7	67.9	66.8	70.2	65.4	67.4
<u>Phosphate-Bonded Ramming Mix</u>									
CPRM-1	nt	nt	17.3	20.1	22.7	19.1	21.3	20.3	21.8

Table XIV. Room Temperature Modulus of Rupture (MPa*) After Firing in Air or Exposure to CO/Steam Mixtures at 6.9 MPa (1000 psia) for 20 Days

	Controls fired in air			CO/H ₂ O = 0.1 + 1 Vol% H ₂ S		CO/H ₂ O = 1.0 + 1 Vol% H ₂ S		CO/H ₂ O = 3.0 + 1 Vol% H ₂ S	
Refractories	110°C	260°C	538°C	538°C	278°C Saturated	538°C	241°C Saturated	538°C	204°C Saturated
Dense High Alumina Castables									
UMR-1	19.7±1.3**	15.3±1.5	15.2±1.0	10.5±0.5	32.1±2.2	12.3±0.6	20.1±2.1	11.6±1.4	22.9±2.6
UMR-2	20.2±2.3	8.4±1.1	12.5±2.0	5.7±0.6	15.8±3.9	7.2±0.7	13.8±0.5	8.2±0.9	13.3±3.9
UMR-4	15.6±1.2	11.2±1.2	10.3±0.5	15.0±1.6	16.9±2.3	12.3±1.0	21.5±4.1	14.9±1.2	9.7±2.7
UMR-6	18.2±2.3	12.0±0.7	11.2±0.6	nt	nt	17.6±2.6	22.8±2.2	18.5±1.1	27.5±3.0
UMR-7	16.9±2.4	9.9±0.9	9.2±1.1	nt	nt	17.2±2.3	24.4±2.5	15.9±1.2	27.4±2.9
Dense Intermediate Alumina Castables									
UMR-5	16.3±1.4	8.9±0.6	8.9±0.5	17.0±2.3	25.8±2.9	13.2±1.5	22.6±4.4	10.7±1.7	27.0±3.2
CC-6	15.2±1.7	10.8±1.6	9.6±0.7	22.5±1.7	30.8±4.4	17.0±2.8	31.8±4.3	12.2±0.8	28.0±3.9
Insulating Castables									
CC-8	6.7±0.8	5.4±0.6	6.5±3.1	6.8±0.6	3.4±0.5	7.0±0.3	8.5±1.1	5.5±0.3	7.6±1.2
CC-9	3.0±0.6	1.3±0.2	1.4±0.3	3.2±0.6	3.6±1.2	2.3±0.6	6.9±1.9	2.6±0.3	5.4±0.6
CC-10	1.0±0.1	0.8±0.1	0.7±0.1	0.3±0.1	0.8±0.2	0.8±0.1	2.1±0.1	0.8±0.1	1.9±0.3
Phosphate-Bonded Ramming Mix									
CPRM-1	nt	nt	27.0±2.5	17.0±2.5	6.3±1.5	20.1±1.3	13.2±5.0	16.8±2.7	12.1±1.6

*1 MPa = 145.04 psi.

**The ± limit corresponds to one standard deviation.

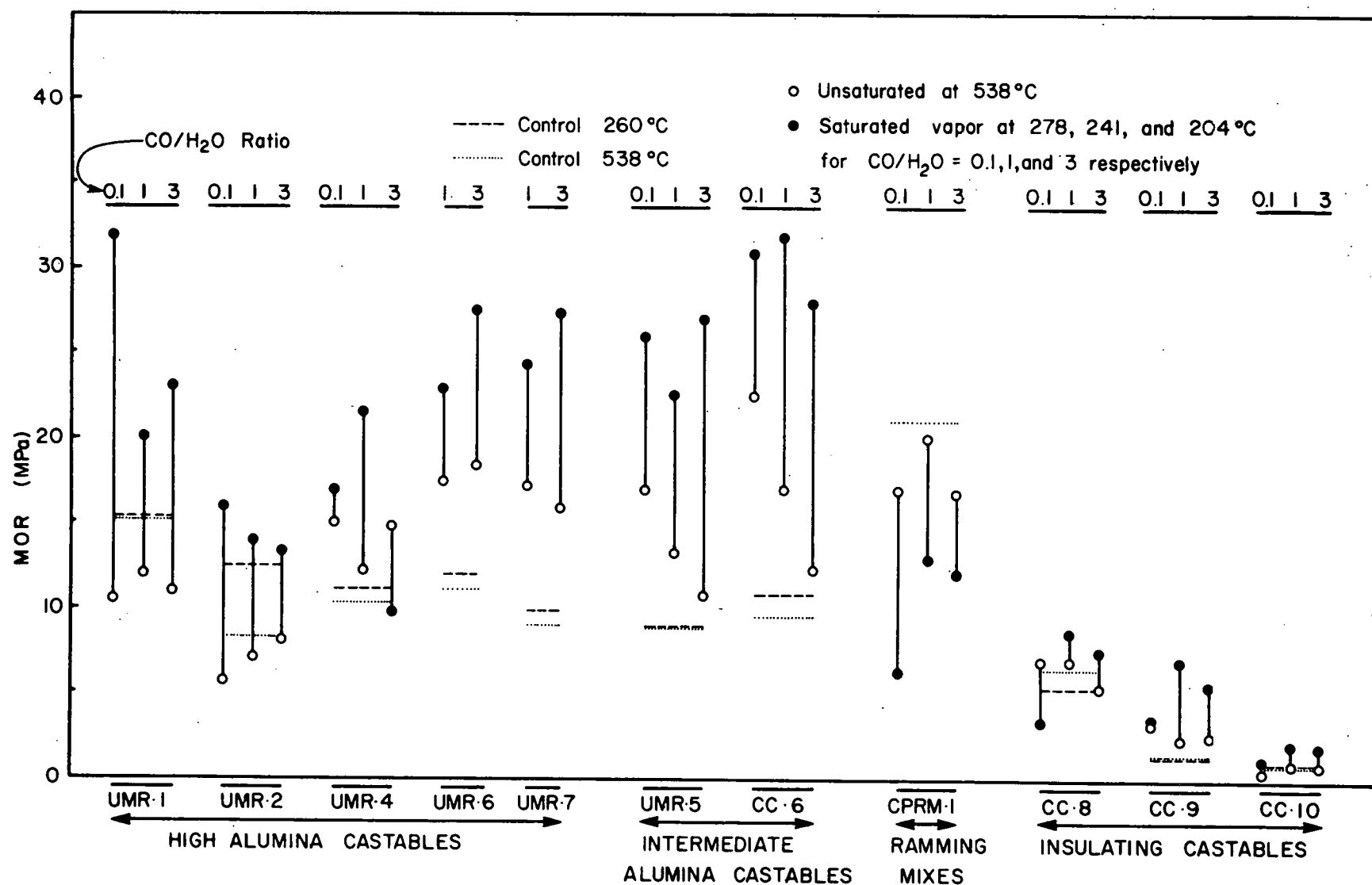


Fig. 7. Room temperature modulus of rupture of refractories after exposure to CO/H₂O = 0.1, 1 and 3 atmospheres with 1 Vol% H₂S at 6.9 MPa pressure for 20 days. Controls are for samples fired in air for 18 hours at 260 (---) and 538°C (.....).

1 and 0.1. These samples, containing Refcon cement, were severely cracked during exposure. Neat Refcon cement cubes exposed to the saturated CO/steam = 3 vapor were also heavily cracked. UMR-4 also contained trace amounts of calcium formate. These results and the higher iron content of Refcon cement (Table I) are suggestive of a CO disintegration mechanism.

A comparison of the MOR data for the UMR-6 and UMR-7 samples in Fig. 7 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/steam atmospheres (at 538°C) was always lower than the unexposed control specimens (fired to either 260 or 538°C), the addition of 5% (UMR-6) or 10% SiO_2 (UMR-7) to the silica-free UMR-1 composition resulted in the exposed specimens having a higher strength than the controls. Similarly, this same behavior where the strength of specimens exposed to the unsaturated (538°C) CO/steam mixtures is higher than controls fired in air is also observed for the other silica-containing refractories, CC-6 and UMR-5.

The presence of SiO_2 in the refractory (introduced either as a component of the refractory grain or refractory cement) is suspected as having a beneficial effect in terms of strength retention in unsaturated gases. The MOR data for UMR-6 and UMR-7, which were prepared specifically to test this suspicion, provides additional evidence that the mechanical properties of silica-containing compositions are less adversely affected by exposure to unsaturated gases than the high-purity, silica-free compositions.

The chemical reactions identified in the cement-bonded castables after exposure to CO/steam mixtures were basically the same as those in the DOE atmosphere, i.e., the formation of boehmite and calcite as the major new compounds and the solution of some portion of CaO. The CO/steam ratio does not appear to be of major importance to the refractory properties, although there is some evidence indicating that the CO disintegration reaction is favored by a high CO content as would be expected. For the CO/steam ratios likely to be present in a typical gasifier, however, there is no reason to suspect that slight to moderate changes in this ratio will have any major effect upon refractories such as those investigated.

E. Task V- Degree of Saturation

The percent saturation of the gases in a coal gasifier will vary across the refractory lining due to the temperature gradient across the lining. At the hot face, the percent saturation will be low and may approach zero depending upon the temperature, pressure, and gas composition. Closer to the cold face the degree of saturation will increase and, depending upon such factors as the thermal conductivity and thickness of the refractory, gas composition, and pressure, may approach 100% saturation. If the gasifier operating parameters and refractory design are such that the temperature at some point in the refractory lining or at the cold face is below the dew point temperature, then the refractory will be in contact with condensed liquids as well as saturated vapors.

Significant changes in properties, primarily in flexural strength, were found in the initial screening of the commercial refractories, Task II, when exposed to 100% saturated or nonsaturated (dry) gases. In dense cement bonded castables, the MOR doubled or tripled after exposure to saturated gases while the MOR of the phosphate bonded refractories decreased by a factor of 3 to 5, Tables VI and X. In the cement bonded castables this increase in MOR was attributed to the formation of boehmite (AH) which has been shown^(13,14) to provide additional bonding. Since the strength of a castable is an important factor in its erosion/abrasion resistance and ability to withstand thermal and mechanical stresses, the formation of boehmite could have practical importance to the use of such castables in coal gasifiers.

The purpose of the work in Task V, therefore, was to determine (a) the dependence of boehmite formation upon the degree of saturation, (b) the minimum saturation required for boehmite formation, and (c) the dependence of other chemical reactions upon the degree of saturation. Exposure tests 40, 41, and 42 in Table II were conducted for this purpose. Since the major chemical reactions were known to occur between the calcium aluminate cement bond phases and steam, CO, or CO₂, hydrated C-1 neat cement specimens were used for this task. Bars, 10 by 10 by 400 mm, of the hydrated neat cement (water/cement ratio of ~0.3) were cast, cured in air at 100% humidity for 24h, dried at 110°C for 24h and exposed to either the DOE atmosphere or pure steam at 6.9 MPa for 10 days using the test system and procedures described previously. The bar was contained in a horizontal pressure vessel, 450 mm long and 15 mm in

diameter, which was located in a temperature gradient furnace. The temperature gradient was controlled such that the atmosphere was 100% saturated at the ends of the pressure vessel and close to zero in the middle. After exposure, the MOR of the bar was measured at 25 mm intervals and the compounds present in every piece were determined by XRD and DTA/TGA. The results are summarized in Figs. 8 and 9 and Tables XV and XVI.

As shown in Fig. 8, the minimum percent saturation at which boehmite was detected depended primarily upon the gas composition, being ~10% saturation in the DOE atmosphere and ~20 to 30% saturation in pure steam. The maximum amount of boehmite formed also varied with the gas atmosphere, being largest in pure steam, but in both atmospheres (DOE and pure steam) the quantity of boehmite was essentially constant above ~70% saturation. The quantity of other major compounds formed in the DOE atmosphere, namely CaCO_3 and $\text{C}_4\text{A}_3\text{H}_3$, did not vary appreciably with the degree of saturation.

A general correlation exists between the MOR and the quantity of boehmite, but it is apparent from Fig. 9 that a minimum saturation of ~40% was required before any increase in MOR occurred even though boehmite forms at lower saturations. At >70% saturation, the MOR became essentially constant, as did the boehmite content. A dependence of the MOR upon the gas atmosphere is again evident from Fig. 9, the MOR being higher in the DOE atmosphere than in pure steam. The reason for the higher MOR in the DOE is not completely known, since the boehmite content is lower, but it is possible that some amount of bonding may also be provided by the CaCO_3 which forms in the DOE atmosphere. An example of

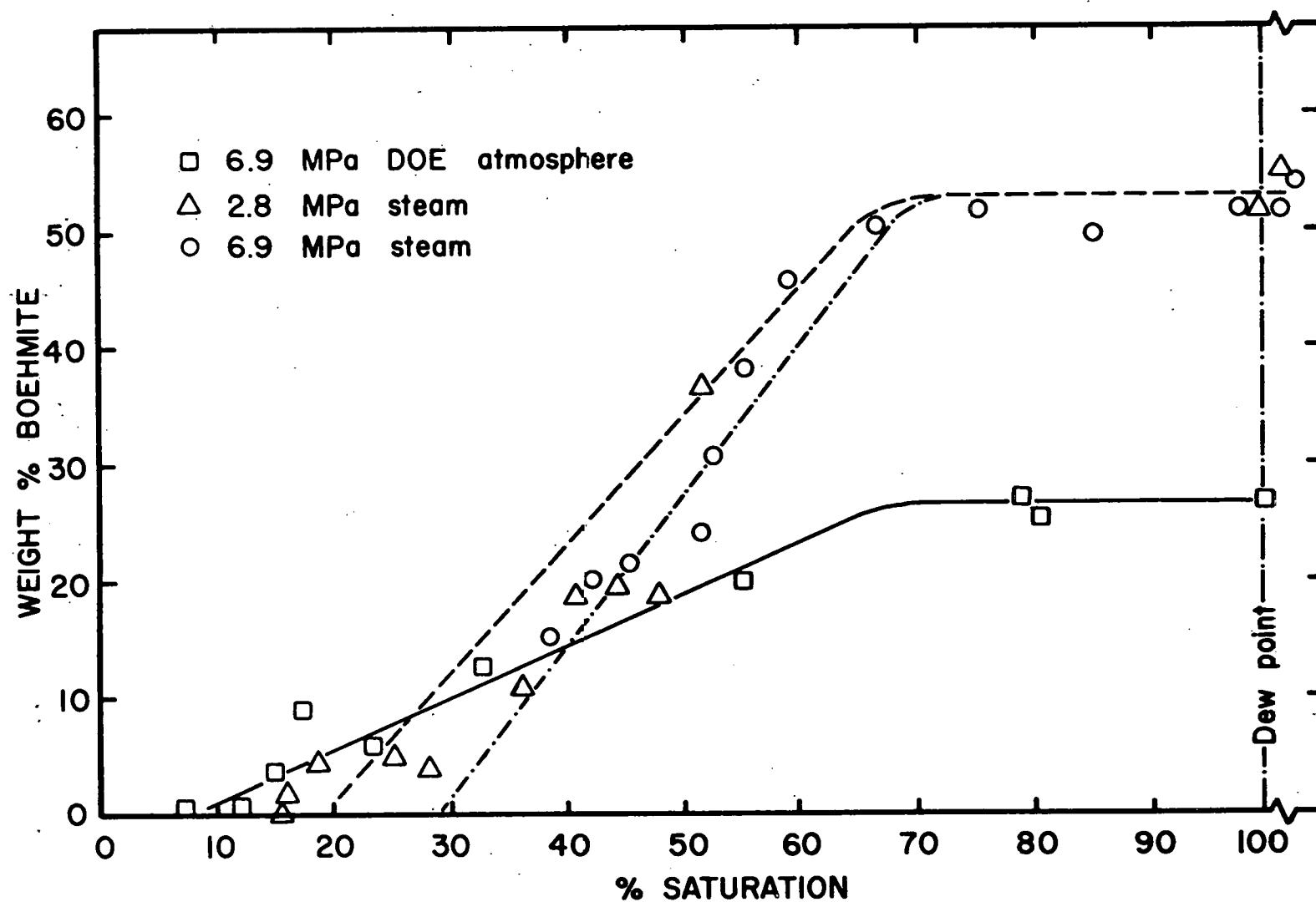


Fig. 8. Weight % boehmite as a function of the degree of saturation for C-1 neat cement exposed to DOE atmosphere and steam for 10 days.

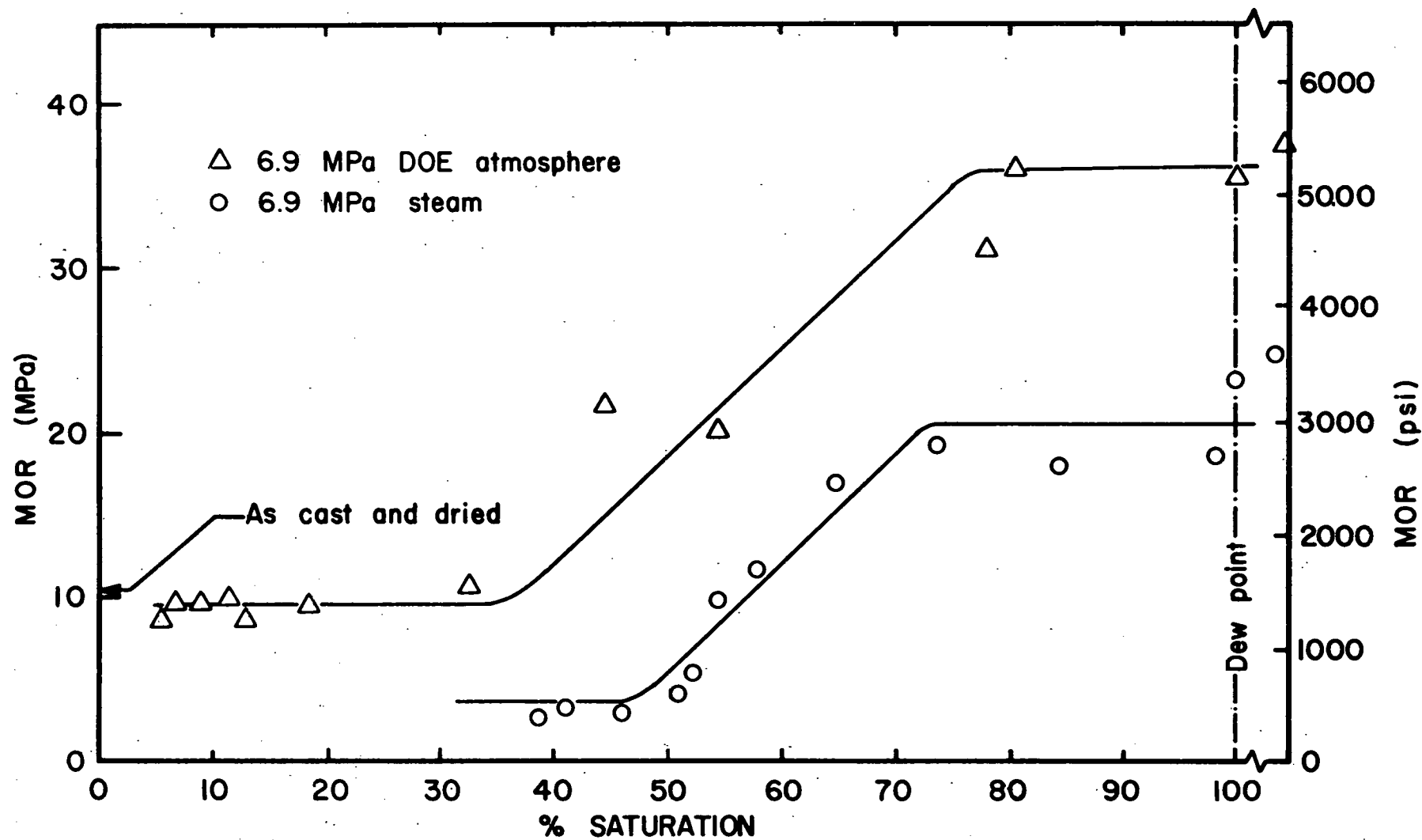


Fig. 9. Variation of modulus of rupture of hydrated C-1 neat cement exposed to DOE atmosphere and steam at 6.9 MPa for 10 days.

Table XV. MOR and Compounds Present in C-1 Cement Bar After Exposure to Steam at 6.9 MPa for 10 Days

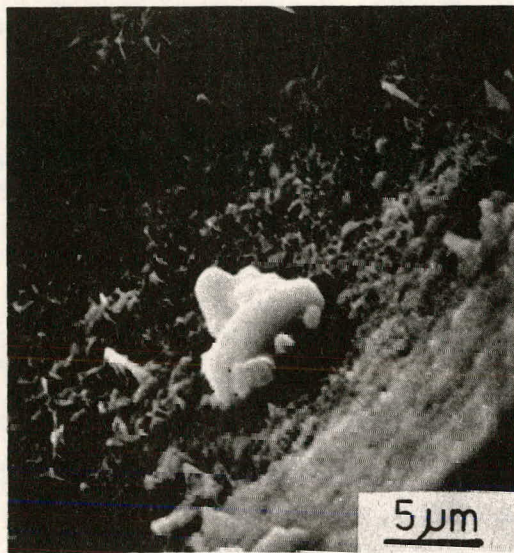
Sample No.	Temp. (°C)	% Saturation Condensed Liquid	MOR (MPa)	Compounds, Weight Percent, as Determined by TGA			Compounds Detected by XRD		
				%Wt. Loss	% Boehmite	% C ₄ A ₃ H ₃	α-Al ₂ O ₃	AH	C ₄ A ₃ H ₃
1	268		25.5	20.7	53	17.8	tr	M	m
2	281	100	26.2	13.5	50.2	37.5	tr	M	m
3	285	98	20.7	13.8	50	38	tr	M	m
4	297	85	19.3	13.6	49	38.5	tr	M	m
5	304	74	20.5	13.5	50.8	38	tr	M	m
6	314	65	17.9	13	49	39	tr	M	m
7	318	58	12.4	13	45	43	tr	M ₁	M ₂
8	327	55	11.4	16.4	32	49	tr	M ₂	M ₁
9	331	52	5.5	10	30	40	m ₂	m ₁	M
10	333	51	3.4	8.6	20.7	40	m ₁	m ₂	M
11	340	46	2.8	4.7	20	42	m ₁	m ₂	M
12	350	41	3.0	4.5	18	43	M ₁	m	M ₂
13	354	39	2.7	4.5	15	41	M	m ₂	m ₁

* M = major, m = minor, tr = trace

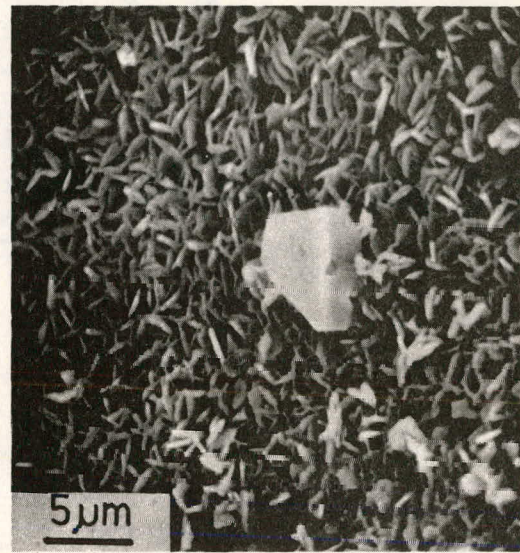
Table XVI. MOR and Compounds Present in C-1 Hydrated Cement Exposed to DOE Atmosphere at 6.9 MPa and Various Degrees of Saturation

Sample No.	Temp. (°C)	% Saturation	MOR (MPa)	Compounds, Weight Percent, as Determined by TGA				Compounds Detected by XRD			
				%wt. loss	% Boehmite	% CaCO ₃	% C ₄ A ₃ H ₃	α-Al ₂ O ₃	AH	CaCO ₃	C ₄ A ₃ H ₃
1	177	condensed liquid	37.9	19	53	23	18	tr	M	m	tr
2	230	100	34.5	14	28	10	13	m ₂	M	m ₁	tr
3	242	80	36.9	14	25	12	17	m ₂	M	m ₁	tr
4	243	79	31.4	13	23	10	12	m ₂	M	m ₁	tr
5	265	54	19.7	12	20	8	17	m ₂	M	m ₁	tr
6	277	45	22.1	13	20	14	15	m	M ₁	M ₂	tr
7	299	32	11.1	13	12	16	16	m	M ₂	M ₁	tr
8	339	19	10.0	11	11	17	18	m ₁	m ₂	M	tr
9	371	13	8.5	10	5	15	18	M ₂	m	M ₁	tr
10	382	11	10.0	10	2	15	20	M ₁	tr	M ₂	tr
11	406	9	9.1	10	--	17	30	M ₁	ud	M ₂	tr
12	458	5.5	9.0	9.5	--	19	38	M	ud	m ₁	m ₂
13	465	5	8.3	9.5	--	20	39	M	ud	m ₁	m ₂

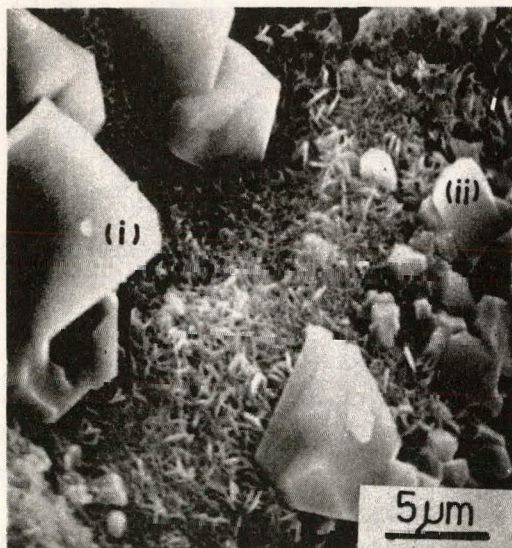
* M = major, m = minor, tr = trace, ud = undetected



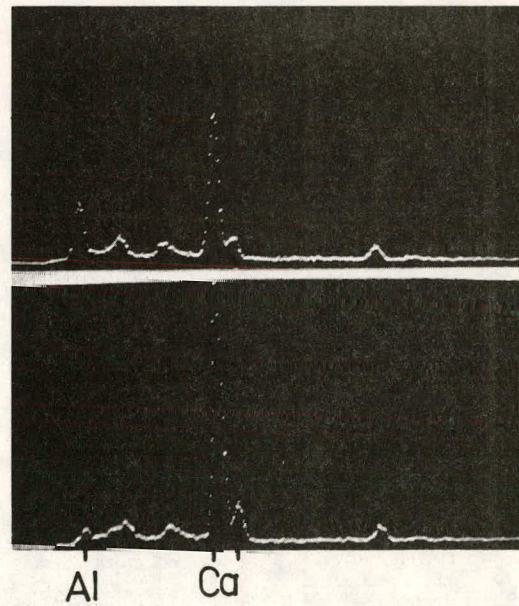
a



b



c



Al Ca

Fig. 10. Microstructure of C-1 cement exposed to DOE atmosphere for 10 days at 6.9 MPa.

- (a) General area around an internal void showing the beginning of boehmite formation, ~20% saturation. (b) Surface of a void showing boehmite crystals (matrix), ~65% saturation. (c) Inside surface of a void showing boehmite (matrix), calcite and $C_4A_3H_3$ crystals, ~100% saturation. (d) EDAX for crystal (i). (e) EDAX for crystal (ii).

the microstructure in the C-1 cement after exposure to the DOE atmosphere showing the development of boehmite, $C_4A_3H_3$, and $CaCO_3$ crystals is given in Fig. 10.

These results show that boehmite can form at ~10 to 30% saturation depending upon the gas composition, but there is no significant increase in MOR below ~40% saturation. Between 50 and 70% saturation, the MOR increases substantially (a 5 to 10 fold increase for neat C-1 cement). A minimum saturation of ~70% is needed to realize the full increase in MOR due to the additional bonding provided by boehmite, but there is no increase in MOR at higher saturations. Interestingly, the minimum saturation for maximum MOR does not appear to vary significantly with gas composition, being ~70% in both pure steam and the DOE atmosphere. From a practical standpoint, therefore, an increase in MOR can be anticipated for a cement-bonded refractory lining in a coal gasifier when the percent saturation of the atmosphere exceeds 40 to 50%.

F. Task VI- Liquid versus Vapor Contact

The results of previous Tasks showed that the calcium aluminate cement phases in refractory castables readily react with CO , CO_2 , or steam to form compounds such as boehmite, calcite, and $C_4A_3H_3$. In most instances the formation of these compounds was accompanied by a reduction in porosity and a substantial increase in flexural strength. In addition to these chemical reactions, some portion of the CaO was leached from the castable, particularly in saturated atmospheres. However, the dissolution of CaO did not appear to reduce the mechanical strength of

the castables. Nevertheless, in some instances, the loss of CaO was higher for specimens immersed in liquid compared to those in contact with vapor.

The objective of this task, therefore, was to determine the relative severity of liquid versus vapor corrosion of cement-bonded castables. The light-weight insulating castables, which because of their high porosity could be more susceptible to chemical attack, were of particular interest. Such refractory castables in coal gasifiers could be in contact with condensed liquids if the temperature at some point in the lining is below the dew point temperature of the gasifier atmosphere.

In addition to previous exposures where specimens immersed in liquid in the bottom of the steam vessel (see Table II), exposures 19, 20, and 36-39 were also conducted using seven cement-bonded castables and three calcium aluminate cements (initially dry powders and hydrated neat cement cubes). All the refractories were exposed simultaneously for 10 days to either saturated steam or the saturated DOE atmosphere. During exposure, one group of specimens (10 bars of each castable and four cubes of each hydrated cement) was totally immersed in the liquid (H_2O) in the bottom of the steam vessel. A second group (same number of specimens along with the initially dry cement powder samples) was in contact with the saturated vapor. The exposure procedure described previously was followed.

The dimensional changes ($<1\%$), density, and porosity of the castables after exposure to saturated steam or saturated DOE atmosphere were basically the same as found previously. There was no significant difference in properties of specimens exposed to either saturated vapor or immersed in liquid.

The MOR of the castables after exposure to saturated steam and the saturated DOE atmosphere was essentially independent of whether the samples were immersed in liquid or in contact with saturated vapor, Table XVII and Fig. 11. As in previous exposures, all the dense castables had a higher MOR after exposure compared to their controls, while the insulating castables showed no major change in MOR. The increase in MOR for the dense castables is attributed to the additional bonding provided primarily by boehmite which formed during exposure. As shown in Table XVIII, samples immersed in liquid or in contact with saturated vapor had essentially the same boehmite content as is consistent with their similar MOR's.

In addition to the formation of boehmite, the change in pH of the water in the exposure vessel suggests that some undetermined amount of CaO was leached from the castables during exposure. For example, for the 10-day exposure in the DOE atmosphere, the pH of the distilled water was initially 7, but within the first 24 hours of exposure increased to ~11. Over a period of ~3 days, the pH then decreased to ~5 and remained constant for the remaining 7 days of the test. This change in pH could be explained by an initial dissolution of some portion of the CaO from the cement phases (water goes basic) and the subsequent precipitation of the CaO in solution as CaCO_3 in the castables, see Fig. 12. Based upon the amount of CaCO_3 they contained, the loss of CaO was not significantly different for immersed samples from those in contact with the vapor.

A plausible sequence of reactions is as follows. Initially, some portion of the CaO dissolves from the castables immersed in water at

Table XVII. Modulus of Rupture of Specimens After Exposure to Saturated Vapor or Immersed in Liquid (number in parentheses)

Refractory	18h in air at 260°C	Saturated Steam		Saturated DOE with 1 Vol% H ₂ S			CO/Steam Mixtures, 6.9 MPa		
		2.8MPa/231°C 10 days	6.9MPa/285°C 10 days	10 days	44 days	60 days*	CO/H ₂ O = 0.1 278°C 20 days*	CO/H ₂ O = 1.0 241°C 20 days*	CO/H ₂ O = 3.0 204°C 20 days*
CC-1	13.4±0.9	nt	nt	nt	nt	19.2±3.4(22.1)	nt	nt	nt
UMR-1	15.2±1.2	29.8±2.3(26.9±2.6)	24.1±1.5(33.7±1.7)	29.5±1.8(23.3±1.6)	27.0±3.1(42.5±2.6)	31.8±6.1(35.8)	32.1±2.2(31.8)	20.1±2.1(32.5)	22.9±2.6(24.8)
UMR-2	8.4±1.1	nt	nt	nt	nt	24.8±3.8(16.7)	15.8±3.9(32.5)	13.8±0.5(26.0)	13.3±3.9(14.0)
UMR-3	11.7±2.1	nt	nt	nt	nt	11.5±2.5(13.9)	nt	nt	nt
UMR-4	11.2±1.2	16.9±1.9(14.4±1.1)	14.8±1.0(17.8±1.1)	21.9±2.9(21.8±4.2)	20.4±2.2 (nt)	nt	16.9±2.3(12.1)	21.5±4.1(24.6)	9.7±2.7(21.4)
UMR-6	12.0±0.7	nt	nt	nt	nt	nt	nt	22.8±2.2(23.0)	27.5±3.0(27.2)
UMR-7	9.9±0.9	nt	nt	nt	nt	nt	nt	24.4±2.5(15.1)	27.4±2.9(29.0)
CC-6	10.8±1.6	nt	nt	nt	nt	24.6±2.9(30.5±1.5)	30.8±4.4(27.3)	31.8±4.3(26.8)	28.0±3.9(24.6)
UMR-5	8.9±0.8	18.7±1.4(18.0±1.1)	17.5±2.0(22.1±2.4)	24.5±1.9(23.2±2.0)	23.0±3.3 (nt)	nt	25.8±2.9(nt)	22.6±4.4(25.5)	27.0±3.2(20.9)
UMR-8	12.2±1.0	29.3±1.9(28.8±5.6)	30.1±1.9(28.8±4.7)	27.7±1.9(23.7±2.4)	32.1±6.5(38.1±3.0)	nt	nt	nt	nt
CC-8	5.4±0.6	4.6±0.3(4.4±0.5)	3.5±0.3(3.3±0.7)	2.6±0.4(3.0±0.2)	5.4±0.8(10.9±0.7)	3.3±1.1(9.2±3.3)	3.4±0.5(1.7)	8.5±1.1(8.2)	7.6±1.2(9.9)
CC-9	1.3±0.2	2.6±0.4(3.0±0.3)	3.7±0.2(4.5±0.7)	5.8±0.7(5.6±0.4)	3.0±0.6 (nt)	nt	3.6±1.2(3.6)	6.9±1.9(16.1)	5.4±0.6(7.0)
CC-10	0.8±0.1	0.4±0.3(0.6±0.1)	0.7±0.2(1.3±0.1)	2.4±0.4(1.4±0.7)	1.5±0.5(4.0±0.2)	nt	0.8±0.2(1.2)	2.1±0.1(2.9)	1.9±0.3(2.7)
CPRM-1	27.0±2.5**	nt	nt	nt	nt	nt	6.3±1.5(7.4)	13.2±5.0(13.1)	12.1±1.6(10.7)

*Two immersed specimens only.

**Fired in air 18h at 538°C.

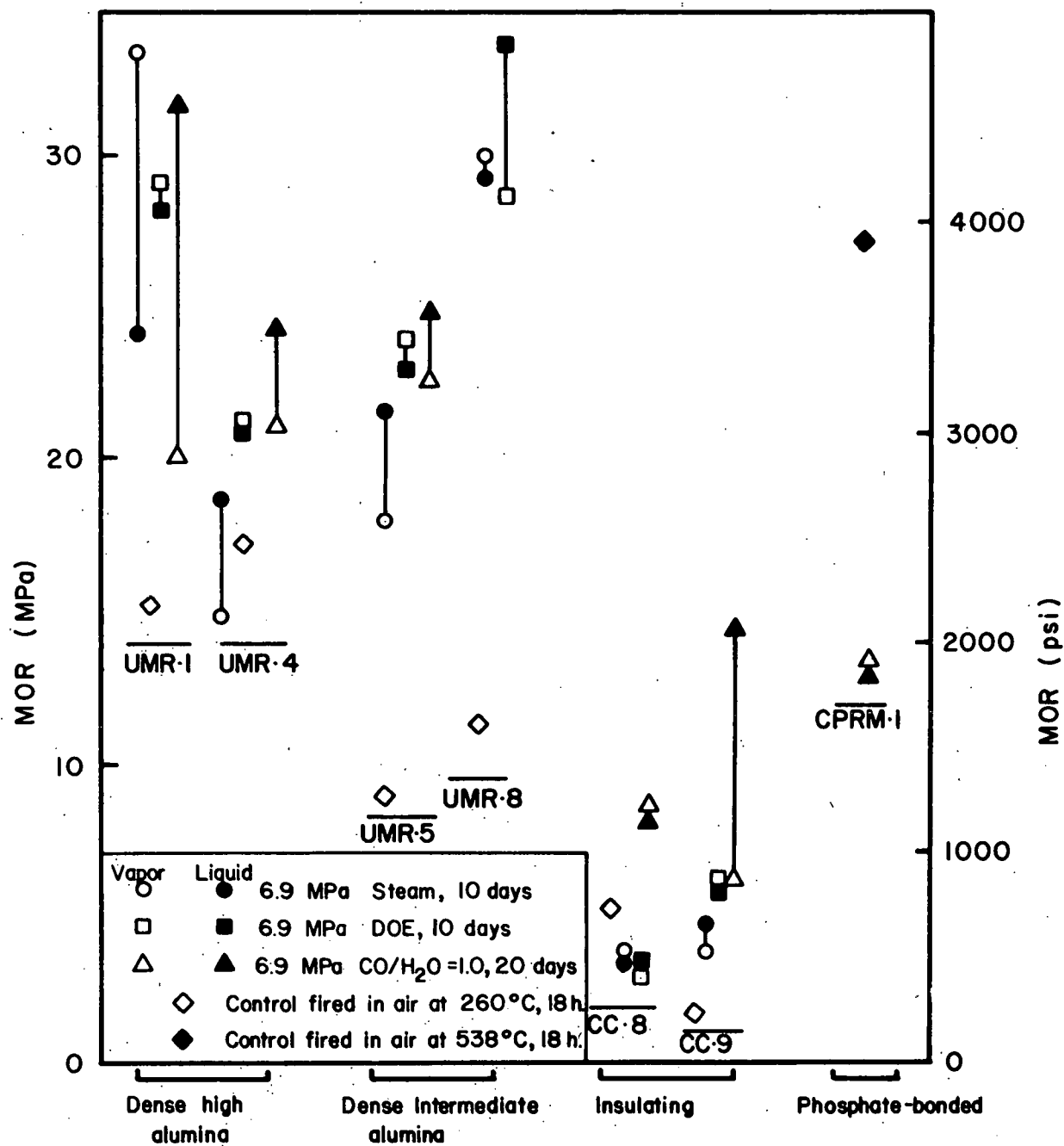


Fig. 11. Comparison of the MOR of refractories exposed to saturated vapor with those immersed in liquid.

Table XVIII. Weight Percent Boehmite After Exposure to Saturated Vapor or Immersed in Liquid (numbers in parentheses)

Refractory	Saturated Steam		Saturated DOE With 1 Vol% H ₂ S			CO/Steam Atmosphere, 6.9 MPa		
	2.83 MPa/231°C	6.9 MPa/285°C	6.9 MPa/231°C			CO/H ₂ O = 0.1	CO/H ₂ O = 1.0	CO/H ₂ O = 3.0
	10 days	10 days	10 days	44 days	60 days	278°C 20 days	241°C 20 days	204°C 20 days
CC-1	nt*	nt	nt	nt	25.0(23.8)	nt	nt	nt
UMR-1	20.2(22)	22.5(23.5)	22.3(21.8)	24.9(25.5)	32.0(29.1)	30.0(25.3)	18.6(26.1)	23.3(21.6)
UMR-2	nt	nt	nt	nt	34.5(27.3)	28.8(28.9)	25.7(27.1)	19.2(25.8)
UMR-3	nt	nt	nt	nt	26.5(26.7)	nt	nt	nt
UMR-4	15.1(14.9)	20.0(18.3)	18.4(19.6)	18.9(nt*)	nt	23.9(23.5)	16.6(18.2)	15.6(21.6)
UMR-6	nt	nt	nt	nt	nt(13.9)	nt	12.1 (nt)	9.2(16.1)
UMR-7	nt	nt	nt	nt	nt(12.7)	nt	10.8 (nt)	8.6(15.1)
CC-6	nt	nt	nt	nt	18.1(22.9)	13.6(18.2)	14.7(18.8)	nt(25.0)
UMR-5	8.7(10.1)	11.3(10.3)	14.6(13.2)	18.9(nt)	14.3(nt)	14.1(15.7)	10.0(23.1)	13.3(10.3)
UMR-8	9.5(11.0)	11.4(10.8)	nt	10.1(14.0)	nt	nt	nt	nt
CC-8	4.0(4.0)	3.6(6.1)	6.4(6.0)	nt	3.1(3.3)	8.3(8.7)	6.7(6.8)	5.6(8.2)
CC-9	13.5(10.1)	nt	nt	17.6(nt)	nt	21.8(nt)	14.9(17.7)	17.6(16.0)
CC-10	5.4(5.5)	8.2(9.5)	9.5(10.8)	nt	nt	10.8(nt)	nt(15.5)	14.1(nt)
CPRM-1	nb**	nb	nb	nb	nb	nb	nb	nb

*nt = not tested

**nb = no boehmite detected

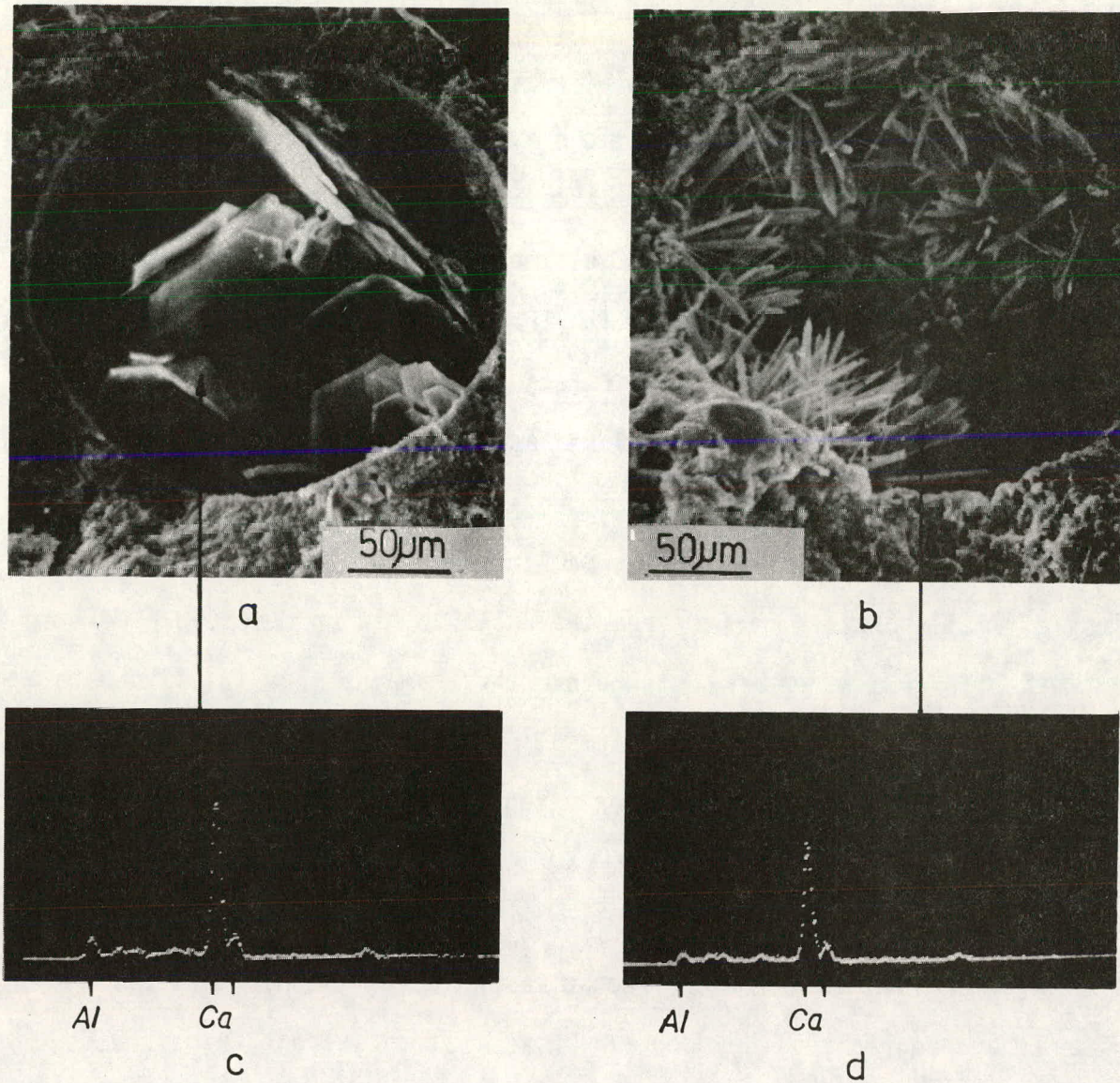


Fig. 12. Microstructure at pores in UMR-1 and UMR-4 after exposure for 10 days to DOE atmosphere at 6.9 MPa/231°C.
 (a) UMR-1 (immersed in liquid) showing the formation of calcite crystals.
 (b) UMR-4 (immersed in liquid) showing an internal void which is almost filled with newly grown crystals high in Ca.
 (c) EDAX for crystals in (a).
 (d) EDAX for crystals in (b).

the start of the exposure test (during heating the vessel) as indicated by both the calcium found in the liquid and by the increase in pH. Eventually the water becomes saturated with CaO (~50 refractory bars in 5 liters water) and, in the presence of CO or CO₂, CaCO₃ is formed and is redeposited on and within the immersed specimens. Thus, the reduction in dissolved CaO along with the dissolution of CO and CO₂ in the water causes the pH to decrease (acidic) and become constant.

Under conditions where the liquid is constantly replenished and may not become saturated with lime, the leaching of the CaO could conceivably continue until all the CaO in the castable is removed. The loss of small portions of CaO from the castable had no detectable effect upon the flexural strength, but whether this remains true if all the CaO is removed is unknown. In a coal gasifier, a major portion of the CaO in the cement bond phases can be expected to react with CO or CO₂ to form CaCO₃ and the extent to which CaO is lost from a castable will depend upon whether any condensed liquids are present.

A comparison of the MOR of dense castables on the basis of the cements and aggregates they contain shows that those containing a high purity cement (UMR-1 and UMR-8 in Fig. 11) generally have a higher MOR than those containing a less chemically pure cement (UMR-4 and UMR-5 in Fig. 11). On the other hand, the type of aggregate seems to have no important effect upon the MOR of the castables. Castables made with the same cement but different aggregates had close to the same MOR, as shown in Fig. 11.

In summary, no major difference in properties was found for castables, even highly porous insulating castables, either immersed in liquid or

exposed to saturated vapor. The presence of liquids seems less important to properties, such as MOR and porosity, than the degree of saturation of the atmosphere. However, the loss of CaO which occurs under saturated conditions, vapor or liquid, is a factor to be considered in the long term service performance of castables exposed to such conditions. No detrimental change in properties, such as loss in strength, was attributable to the leaching of CaO from the castable, but the effect of complete removal of CaO over a much longer time period is unknown. It might be suspected to destroy the structural integrity of a castable if the bonding is destroyed and not replaced by another bond phase of some type (such as boehmite).

G. Task VII-Pressure/Temperature Cycling

As already described, boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is a principal reaction product formed in cement bonded castables exposed to atmospheres >50% saturated. The work in this Task was concerned with two questions. First, whether the additional bonding boehmite provides would be retained when it is subsequently decomposed due to changes in the operating conditions (e.g., start up, shut down, gas composition) of a coal gasifier. Second, whether the volume changes associated with repeated boehmite formation/decomposition might produce internal microcracks and, thereby, eventually weaken the castable. In this task selected castables were exposed for 5-day periods so as to form boehmite and then by changing the temperature, the boehmite was decomposed (dehydrated) as might occur in a coal gasifier lining. This procedure was repeated for a total of 5 boehmite formation/decomposition cycles, with properties measured after each cycle.

Exposures were performed in the DOE atmosphere containing 1 vol% H_2S at 6.9 MPa pressure. Initially, three pressure vessels were connected in series so that the same atmosphere flowed through all three vessels. The steam vessel operated at 231°C while the two vessels containing the samples were at 240°C so as to prevent water condensation in these vessels. The atmosphere in these vessels was only 85% saturated, but this was adequate for boehmite formation as shown in Task V.

The procedure used was as follows. After a 5-day exposure at 240°C one of the vessels was shut down and 16 samples, which now contained boehmite, were removed and divided into two groups. The first group (8 samples) was tested, their properties being given in column 1 of Tables XIX and XX. The second group of 8 samples were heated to 538°C in air for 18 h to decompose the boehmite and then tested, their properties being given in column 2 of Tables XIX and XX. The presence or absence of boehmite in these control specimens was confirmed by XRD and DTA/TGA.

Fifty samples of each castable in the second vessel were exposed to the DOE atmosphere (6.9 MPa/240°C) for 5-day periods to form boehmite. The vessel was then heated to 538°C in the DOE atmosphere, maintaining 6.9 MPa, for 18 h to decompose the boehmite and cooled to room temperature where 10 samples of each castable were removed for testing. This procedure was repeated for 5 boehmite formation/decomposition cycles. The properties are given in column 3 of Tables XIX and XX.

The dimensional and weight changes were small, $\leq 1\%$, and did not vary significantly with the number of boehmite formation/decomposition cycles. All castables generally expanded slightly during boehmite formation and

Table XIX. Percent Weight Change and Percent Porosity (in parentheses) of Castables Exposed to the DOE Atmosphere With 1% H₂S for Repeated Boehmite Formation/Decomposition

		(1)	(2)	(3)				
Materials	Fired 18h at 260°C in air	DOE Atm., 6.9 MPa 5 days @ 240°C (Boehmite Formation)	As column 1, then heated 18h in <u>Air</u> 538°C (Boehmite Decompose)	DOE Atm., 6.9MPa, 5 days @ 240°C, (Boehmite Formation), then heated 18h in the DOE atm., 6.9 MPa @ 538°C (Boehmite Decomposition) for 1, 2, 3, 4, and 5 cycles.				
				1 Cycle	2 Cycle	3 Cycle	4 Cycle	5 Cycle
UMR-1	(20.1)	+0.3(20.3)	+0.4(24.7)	-0.1(25.7)	-0.1(25.3)	Nil(25.7)	Nil(26.2)	+0.2(25.1)
UMR-4	(23.8)	Nil(13.1)	Nil(20.3)	Nil(24.8)	-0.1(24.5)	-0.2(24.5)	-0.2(24.4)	-0.1(24.6)
UMR-5	(16.3)	Nil(12.4)	-0.1(16.1)	-0.1(17.9)	-0.1(17.9)	-0.1(17.7)	-0.2(17.9)	-0.1(17.7)
UMR-8	(16.5)	+0.1(11.7)	-0.2(16.1)	-0.3(18.3)	-0.2(19.0)	-0.1(17.6)	-0.1(18.7)	Nil(19.4)
CC-8	(41.0)	+0.4(44.3)	nt(46.7)	+0.4(48.5)	+0.4(48.0)	+0.1(48.1)	+0.1(49.3)	+0.3(51.0)
CC-9	(52.8)	+0.2(51.9)	nt(53.9)	+0.1(56.4)	+0.2(55.7)	Nil(54.1)	-0.1(56.0)	Nil(56.9)
CC-10	(61.8)	nt(59.5)	nt(64.5)	+1.0(64.3)	+1.0(64.5)	+0.5(62.7)	+0.4(63.8)	+1.0(63.7)

Table XX. Modulus of Rupture (MPa) of Castables Exposed to the DOE Atmosphere
With 1% H₂S for Repeated Boehmite Formation/Decomposition

Materials	(1)		(2)		(3)				
	Controls fired in air 18h		DOE, 6.9MPa 5 days @ 240°C (Boehmite Form)	As (1), then heated 18 h in air @ 538°C (Boehmite Decomp.)	DOE, 6.9 MPa, 5 days @ 240°C (Boehmite Formation) then heated 18h in the DOE at 6.9 MPa @ 538°C (Boehmite Decomposition) for 1, 2, 3, 4, and 5 cycles				
	260°C	538°C			1 Cycle	2 Cycle	3 Cycle	4 Cycle	5 Cycle
UMR-1	15.2±1.2	15.2±1.0	12.8±4.5	11.9±0.6	8.2±0.9	7.1±1.7	9.8±1.2	8.7±1.1	9.4±5.0
UMR-4	11.2±1.2	10.3±0.5	20.4±2.2	26.9±1.0	27.4±1.9	26.4±1.8	24.6±2.4	28.0±5.2	24.2±2.8
UMR-5	8.9±0.8	8.9±0.5	20.9±1.2	18.8±1.2	23.7±2.5	23.8±2.1	21.0±2.1	18.2±1.9	23.6±2.4
UMR-8	12.2±1.0	13.7±1.2	16.9±1.2	14.7±1.8	29.1±4.2	27.7±1.4	26.8±1.9	22.5±1.8	27.1±2.0
CC-8	5.4±0.6	6.5±0.3	5.4±0.4	6.7±0.9	6.8±0.3	6.6±0.9	6.9±0.6	6.8±0.6	6.5±0.3
CC-9	1.3±0.2	1.4±0.3	7.3±0.9	7.3±1.0	6.6±0.9	6.7±0.3	3.3±0.5	5.2±0.6	6.8±0.5
CC-10	0.8±0.1	0.7±0.1	1.3±0.3	0.9±0.3	1.1±0.1	1.0±0.2	0.9±0.2	0.9±0.1	1.1±0.2

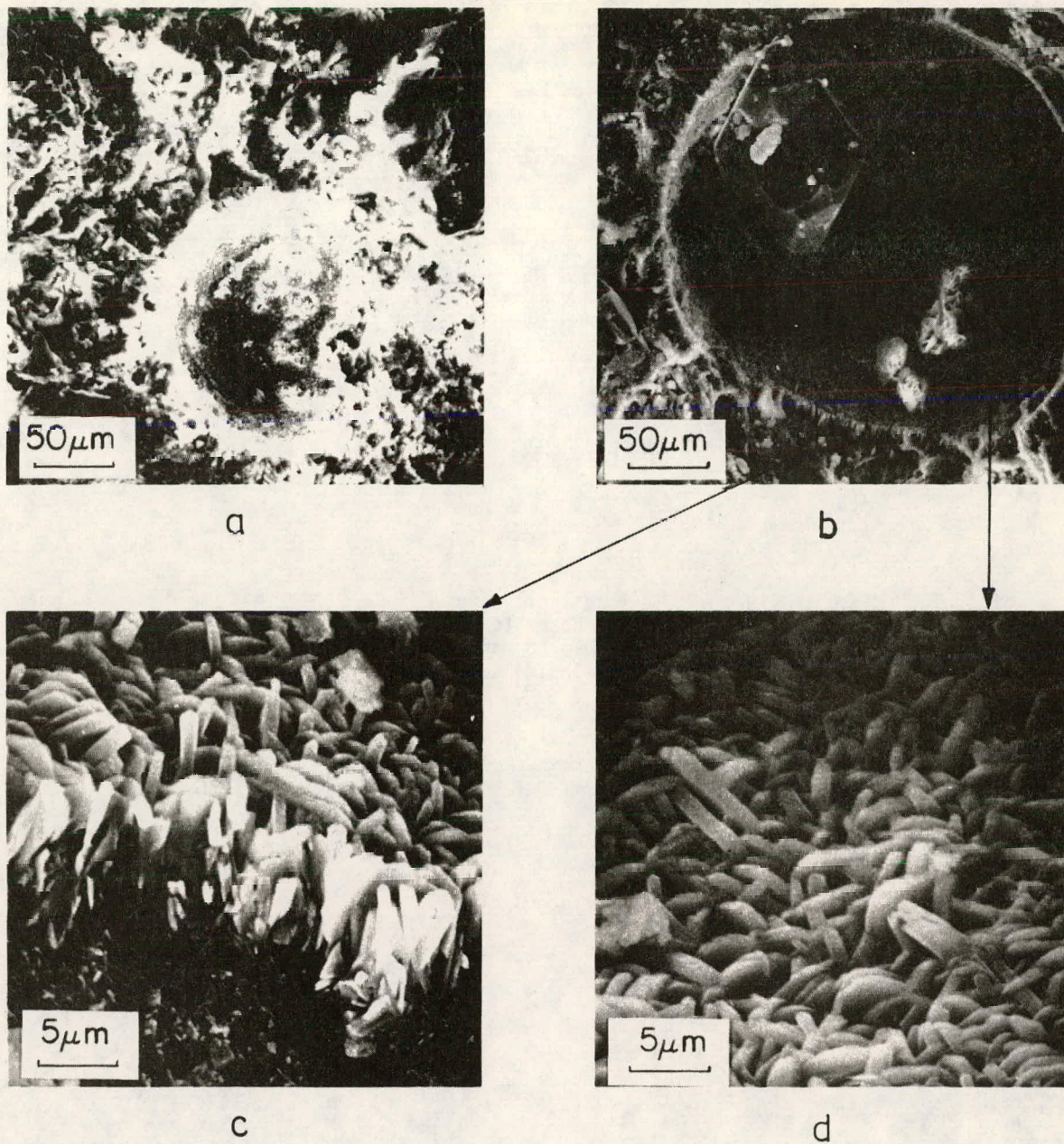


Fig. 13. Microstructure of UMR-1 castable. (a) As-cast and dried; (b) After 44-day exposure to 6.9 MPa/231°C (saturated vapor) DOE atmosphere with 1% H₂S; (c) Structure (boehmite) near the edge of void b; (d) Structure (boehmite) of matrix of void in b.

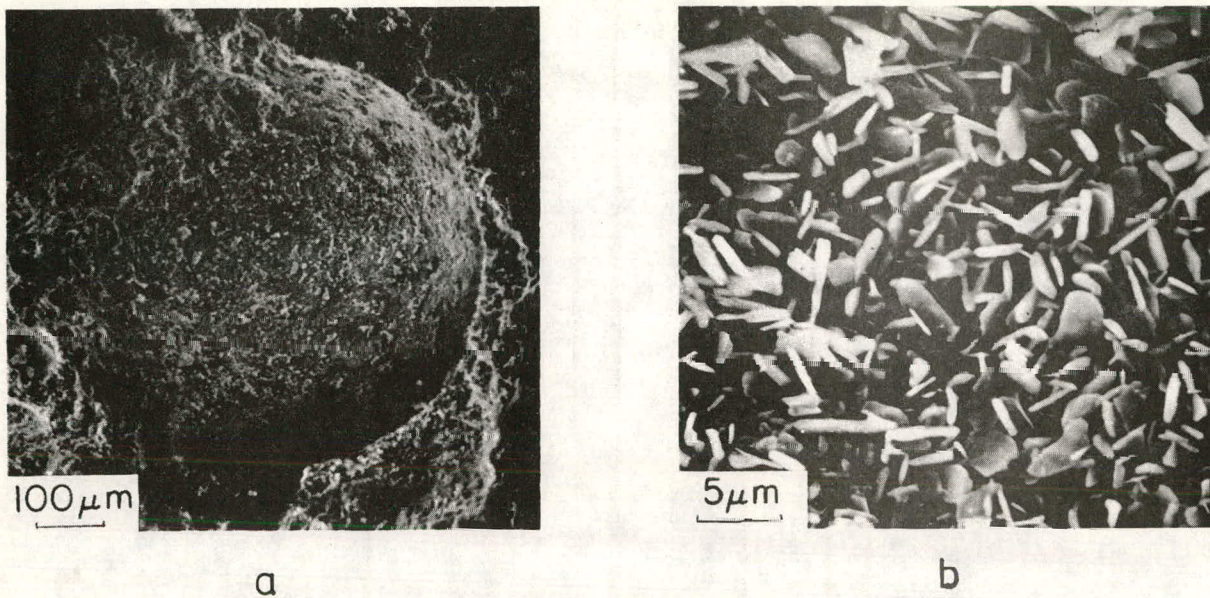


Fig. 14. Microstructure of UMR-1 castable exposed 5 days at 6.9 MPa/240°C in DOE atmosphere to form boehmite and then 18 hours at 6.9 MPa/538°C in the same atmosphere (DOE) to decompose boehmite. (a) General area around internal void; (b) Inside surface of the void in a, crystals are Al_2O_3 .

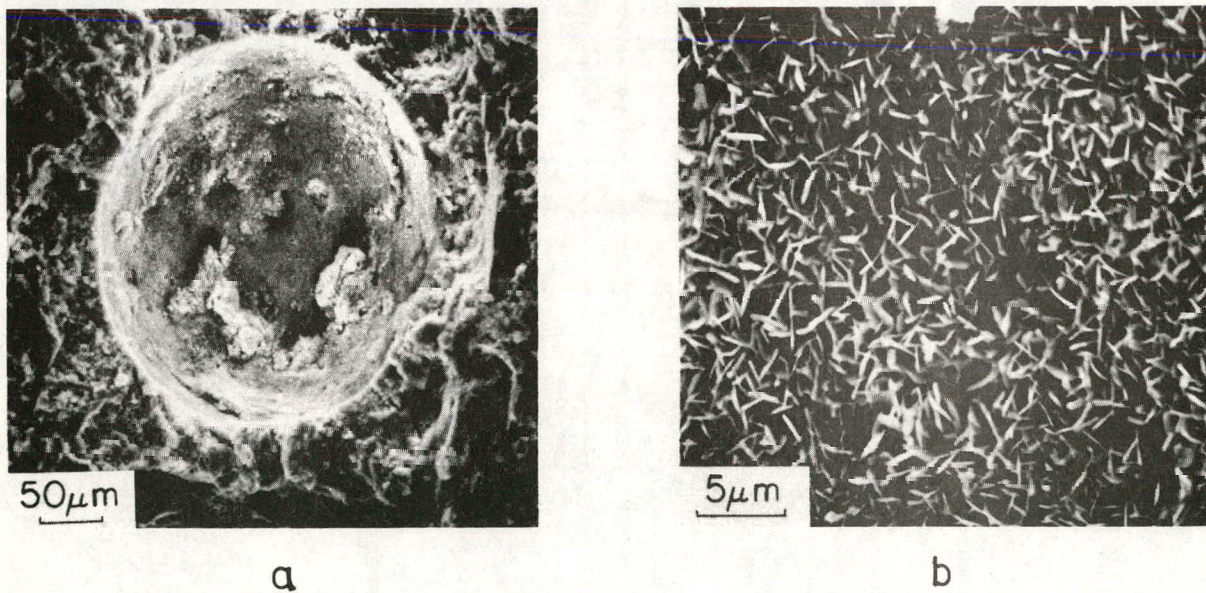


Fig. 15. Microstructure of UMR-1 castable exposed 5 days at 6.9 MPa/240°C in DOE atmosphere to form boehmite and then 18 hours at 538°C in air to decompose boehmite. (a) General area around internal void; (b) Inside surface of the void in b, crystals are Al_2O_3 .

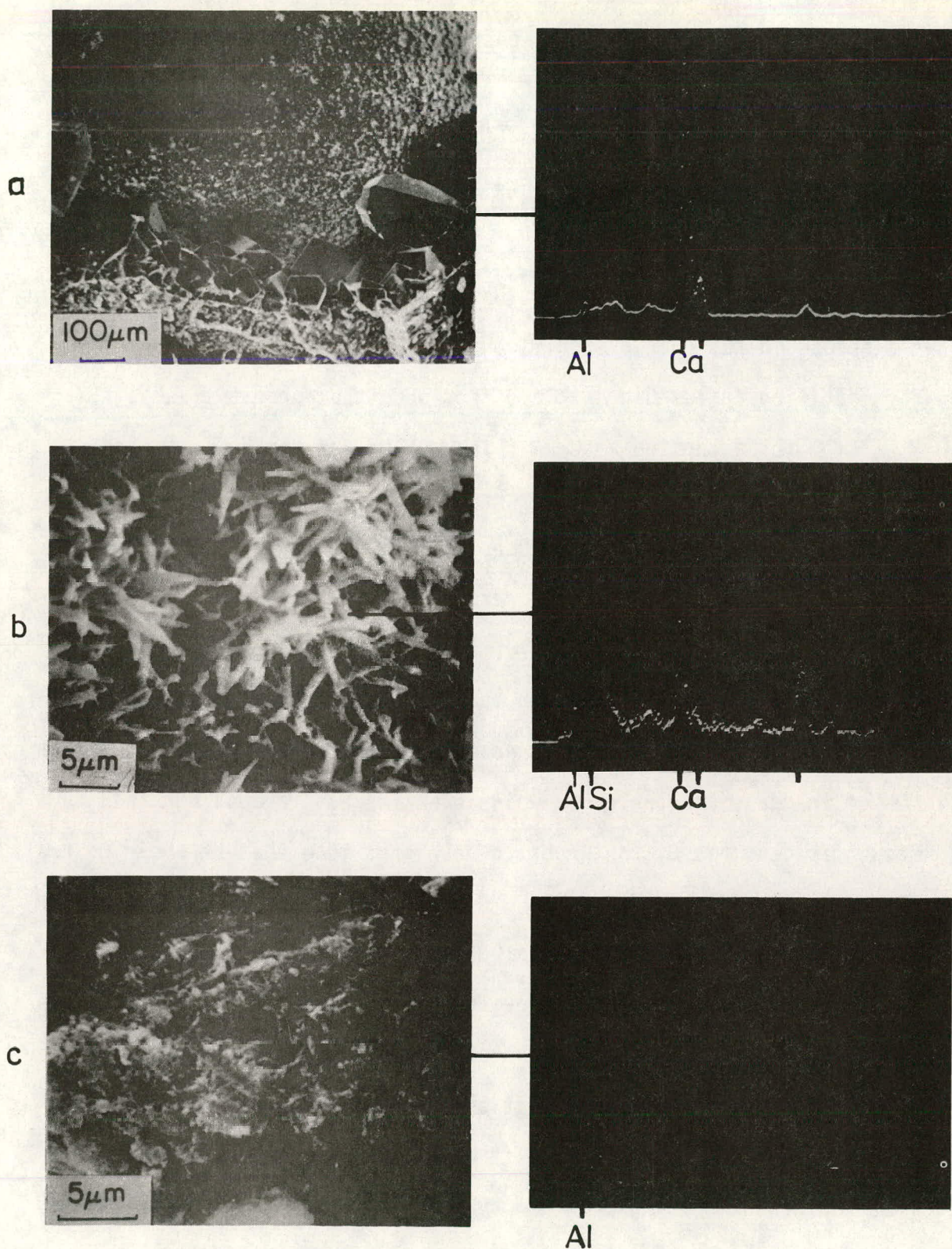


Fig. 16. Microstructure of UMR-8 exposed 44 days to saturated DOE atmosphere with 1 Vol% H_2S at 6.9 MPa/231°C. (a) General area around an internal void, (b) Inside surface of the void in a; (c) General area on the fracture surface of specimen.

decomposition, except the dense castables which shrunk slightly after boehmite decomposition.

The changes in density were small and showed no dependence upon the number of cycles. The porosity of the dense castables after boehmite formation, column 1 in Table XIX, were generally lower than controls fired in air as expected (except UMR-1). The porosity of the insulating castables did not change significantly. Repeated boehmite formation/decomposition cycles had little effect upon the porosity, Table XIX.

With the exception of UMR-1, the MOR of all the dense castables was significantly higher both after boehmite formation, column 1 in Table XX and decomposition, columns 2 and 3, in comparison to controls fired in air to comparable temperatures. No significant loss in MOR is evident with repeated boehmite formation/decomposition for any of the castables investigated, although the MOR of UMR-1 is consistently lower than expected for some unknown reason. As is evident from Table XX, the MOR of the dense castables in which boehmite was formed, but then subsequently decomposed, continues to be higher than that of their controls fired in air, except UMR-1. In UMR-5 and UMR-8, the MOR of the cycled samples is even higher than when boehmite is present. Apparently, the additional bonding initially provided by the boehmite is not lost when the castable is heated to a temperature where boehmite decomposes.

In another recent investigation⁽¹⁴⁾ where boehmite was the only bond phase present (no cement), it was also found that a significant fraction of the bonding provided by boehmite was retained even at temperatures of $>1000^{\circ}\text{C}$ (boehmite decomposes at 500 to 550°C). A general explanation for this is that the crystal habit of boehmite does

not change significantly after its decomposition to Al_2O_3 and the interlocking network of pattern of boehmite crystals is retained.

Examples of the microstructure in the general area of internal voids in specimens from this Task are shown in Figs. 13-16. The interlocking network of boehmite crystals is clearly evident in Fig. 13 and this microstructure for UMR-1 showed very little change in specimens where no boehmite was detected by XRD, Figs. 14 and 15. Fig. 16B shows a network of small crystals on the inside surface of a void in UMR-8 exposed to the saturated DOE atmosphere. EDAX analysis of these crystals show that they contain Al, Si, and Ca. This suggests that the crystals in UMR-8 are a calcium aluminosilicate compound, although no such compound was detectable by XRD. Similar to boehmite, the interlocking network of calcium aluminosilicate crystals formed in the SiO_2 -containing castables during exposure could explain the increase in MOR.

Based upon the conditions of these tests, which do not duplicate in every respect the conditions in an actual coal gasifier, there appears to be no reason to suspect that repeated boehmite formation/decomposition will adversely affect the mechanical properties of a refractory castable lining.

H. Task VIII- Hydrothermal Reaction of CA Compounds and Neat Cements

The results of early tests⁽²⁰⁻²¹⁾ showed that the changes in properties of the cement bonded refractories after exposure were primarily due to chemical reactions occurring between the cement bond phases and steam and CO . To gain a better understanding of these reactions in terms of their dependence upon exposure time, pressure, and gas composition and their relevance to refractory

performance, an investigation was undertaken of the pure cements as well as the compounds CA and CA₂ which are the major constituents of such cements. Data from the individual cementitious compounds CA and CA₂ is more readily interpreted and has been shown to be applicable to the interpretations of the more chemically complex refractory cements, thereby, minimizing the need to test each specific product.

Pelletized samples of CA and CA₂, along with the neat cements, C-1 and C-2, were reacted in saturated steam at 0.69, 3.45, and 6.89 MPa pressures for 5, 10, 20 and 60 hours. The DOE atmosphere was used at 6.89 MPa only, for 5, 10, 20, and 60 hours. The reactions occurring in the samples were determined by analyzing the reaction products by XRD and TGA.⁽¹⁹⁾

1. Phase Compatibility Considerations

Steam-cement systems can be treated ideally as a three component system; Al₂O₃ - CaO - H₂O. The Gibb's phase rule indicates that for saturated conditions only two solid phases can coexist stably at a fixed temperature. Thus, in the saturated steam exposures where three solid hydrated phases are observed, at least one solid is unstable and should react so as to reduce the number of solid phases to two.

When the DOE atmosphere is used, the system can be expressed in additional components if one (or more) of the gaseous species is reactive. Each new component will permit an additional solid phase to be stable.

The reactions observed in saturated steam were discussed in previous reports, but the phases observed (C₃AH₆, C₄A₃H₃, AH and AH₃) are given in Table XXI. The data indicate that product phases form more slowly at 0.69 MPa than at either 3.45 or 6.89 MPa. Not all of the CA and CA₂ reacted completely at 0.69 MPa in 20 h. At 3.45 and 6.89 MPa, CA,

Table XXI. Summary of Phases Observed in Reaction Products

Phases Observed *

		C_3AH_6	$C_4A_3H_3$	$C_4AH_{11}\bar{C}$	AH	AH_3	$C\bar{C}$	Unreacted Material
		1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4	1 2 3 4
STEAM ONLY	0.69 MPa (100 psi)							
	5 h	X X	X X		X X	X X		X X
	10	X	X		X	X		X
	20	X X	X X		X X	X X		X X
	3.45 MPa (500 psi)							
	5 h	X X X X	X X X X		X X X X	X		$\frac{A}{CA}$
	10	X X X X	X X X X		X X X X	X		$\frac{A}{CA}$
	20	X X X X	X X X X		X X X X	X		$\frac{A}{CA}$
	6.9 MPa (1000 psi)							
	5 h	X X X	X X X X		X X X X	X		$\frac{A}{CA}$
	10	X X X	X X X X		X X X X	X		$\frac{A}{CA}$
	20	X X X	X X X X		X X X X	X		$\frac{A}{CA}$
	60	X X X	X X X X		X X X X	X		$\frac{A}{CA}$
DOE	6.9 MPa (1000 psi)							
	5 h		X X X X	X X X X	X X X X			X X A X
	10		X X X X	X X X X	X X X X		X	X X A
	20		X X X X	X X X X	X X X X		X	X X A
	60		X X X X	X X X X	X X X X		X	X X A

1 = CA
 2 = CA_2
 3 = C-1 (CA-25 cement)
 4 = C-2 (Secar 250 cement)

*Cement terminology used.

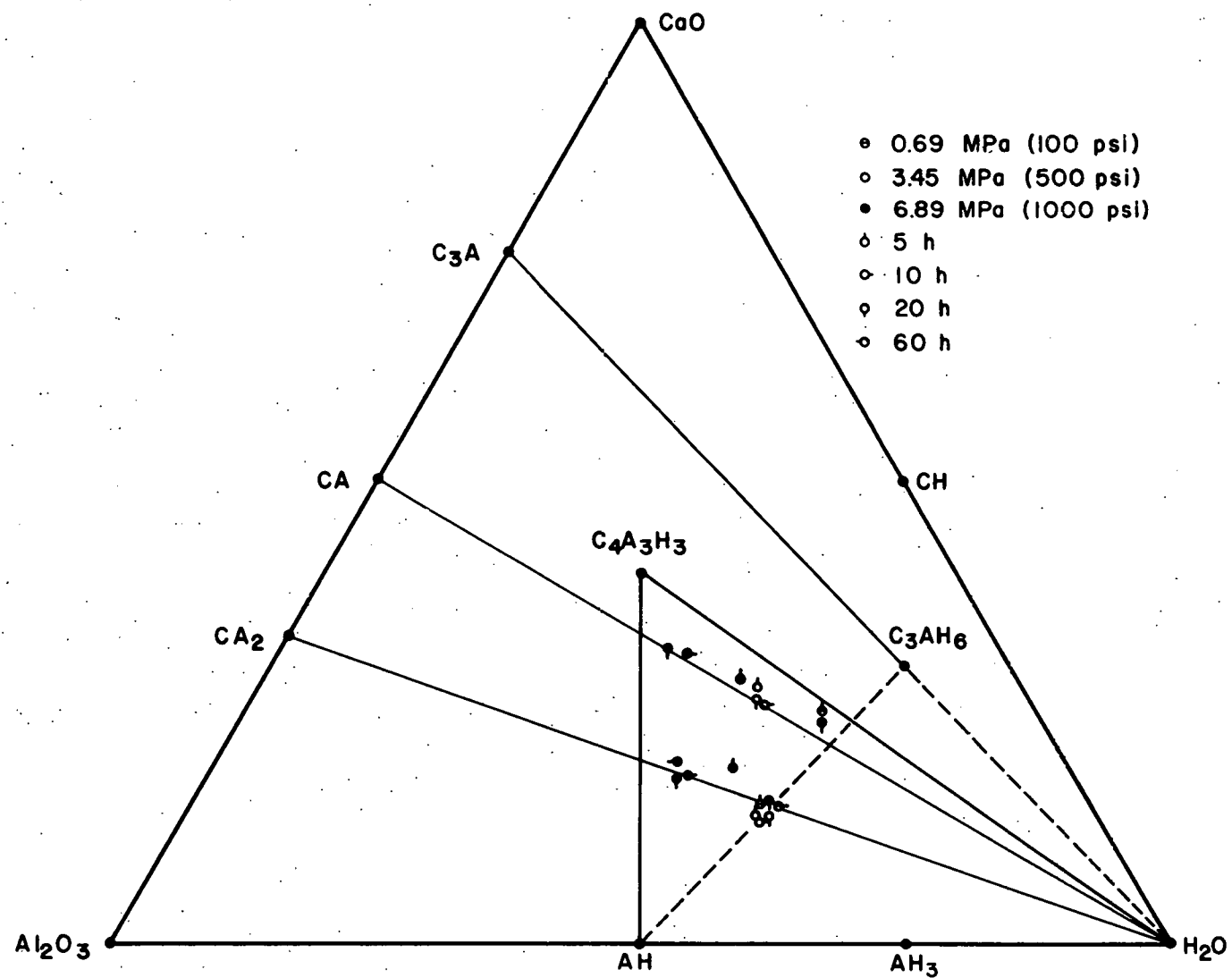


Fig. 17. Ternary composition points for CA and CA_2 for high pressure runs in steam. Diagram plotted in mol percent.

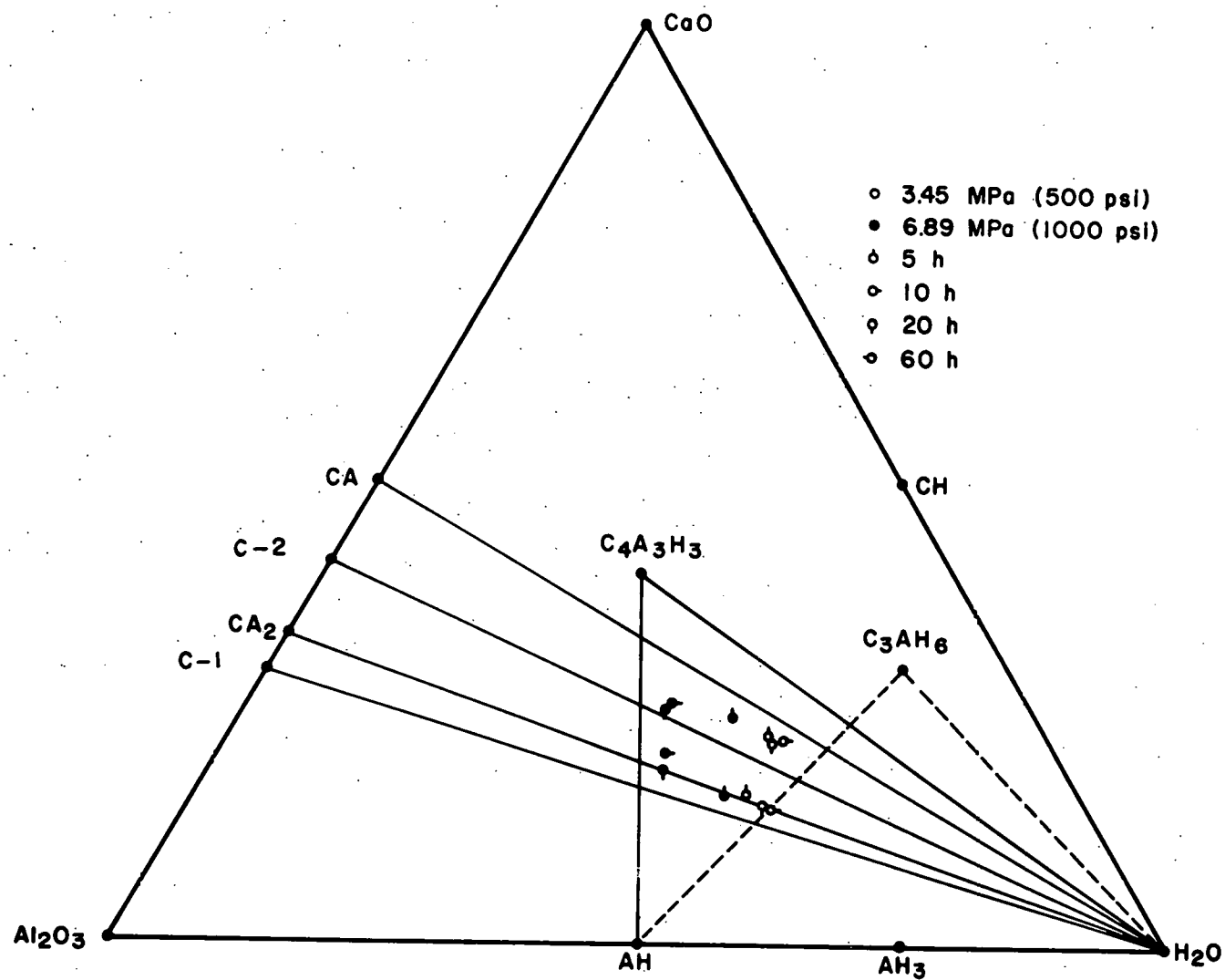


Fig. 18. Ternary composition points for C-1 and C-2 neat cements for high pressure runs in steam. Diagram plotted in mol percent.

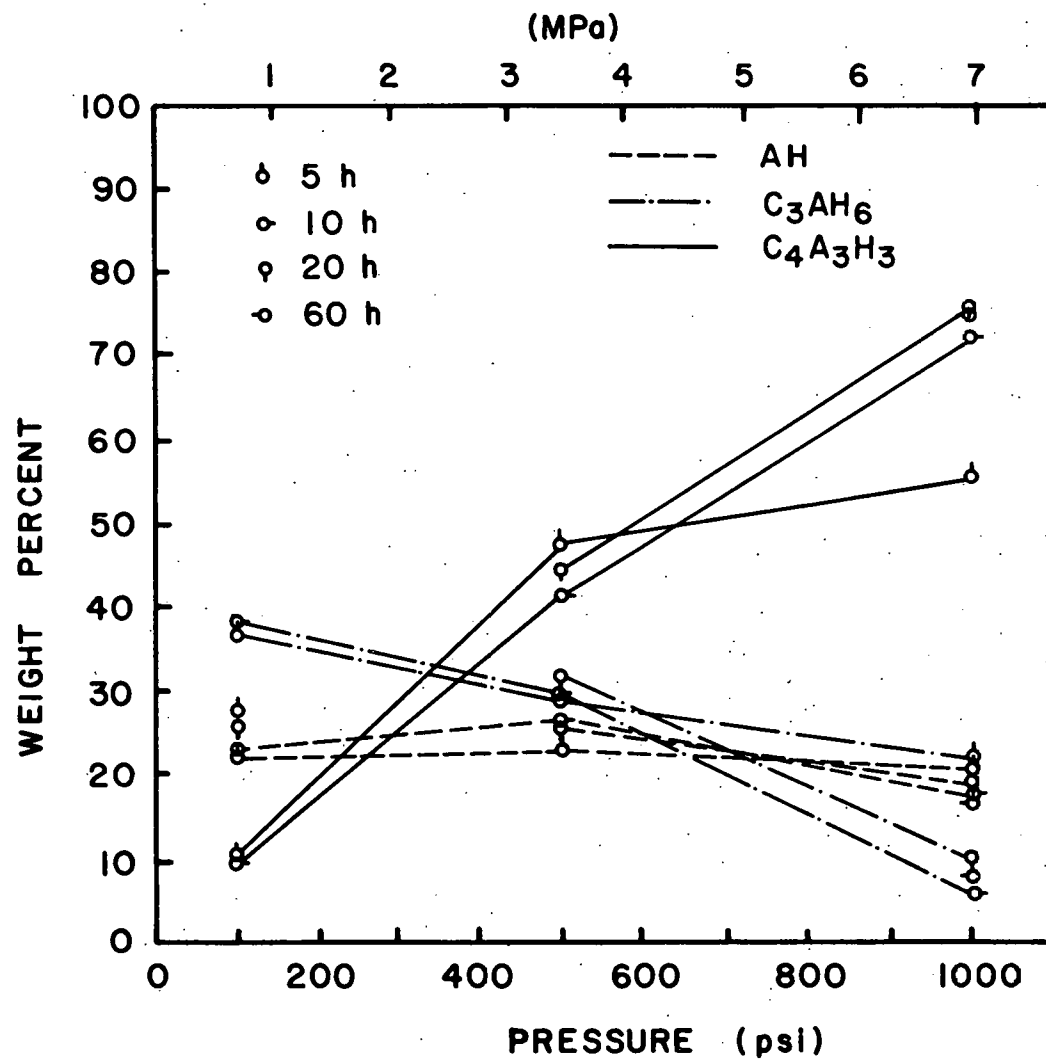


Fig. 19. Weight percentages of hydrated product phases from CA as a function of steam pressure.

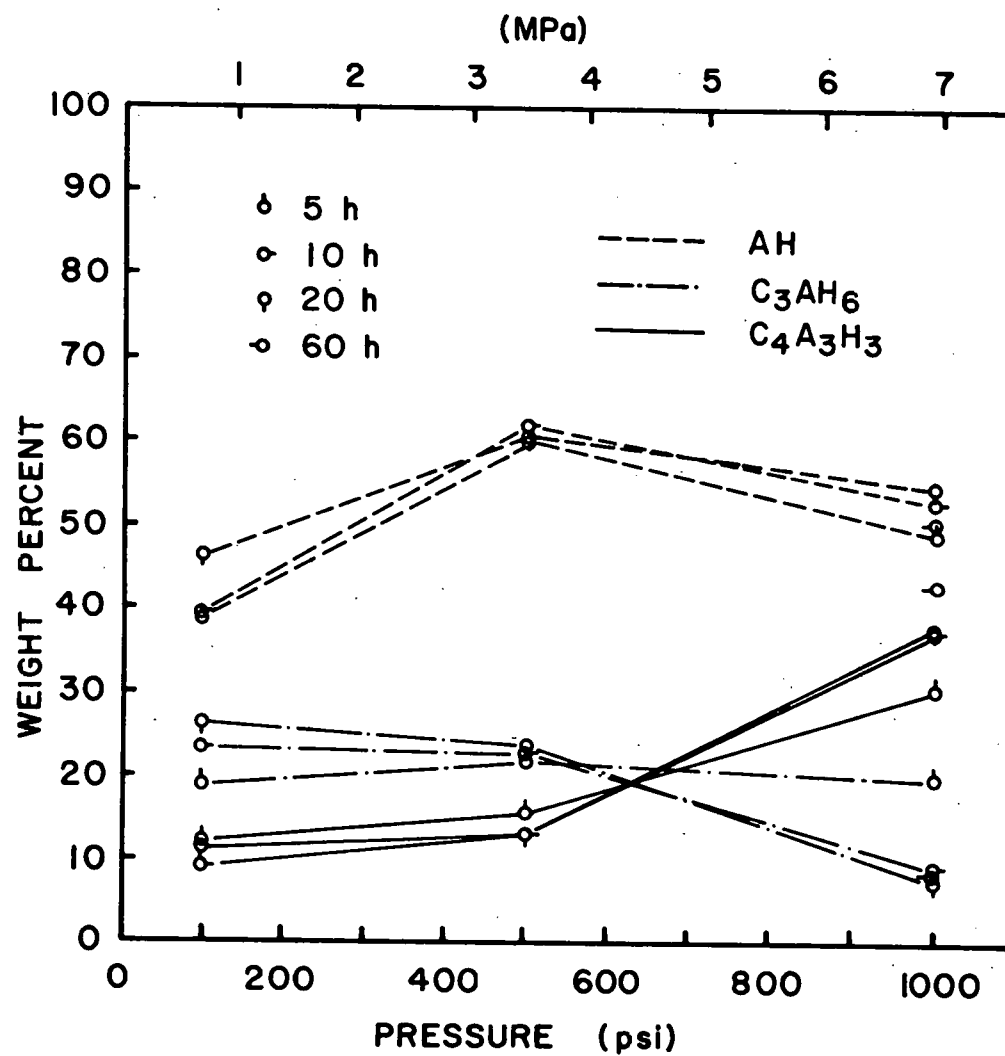


Fig. 20. Weight percentages of hydrated product phases from CA₂ as a function of steam pressure.

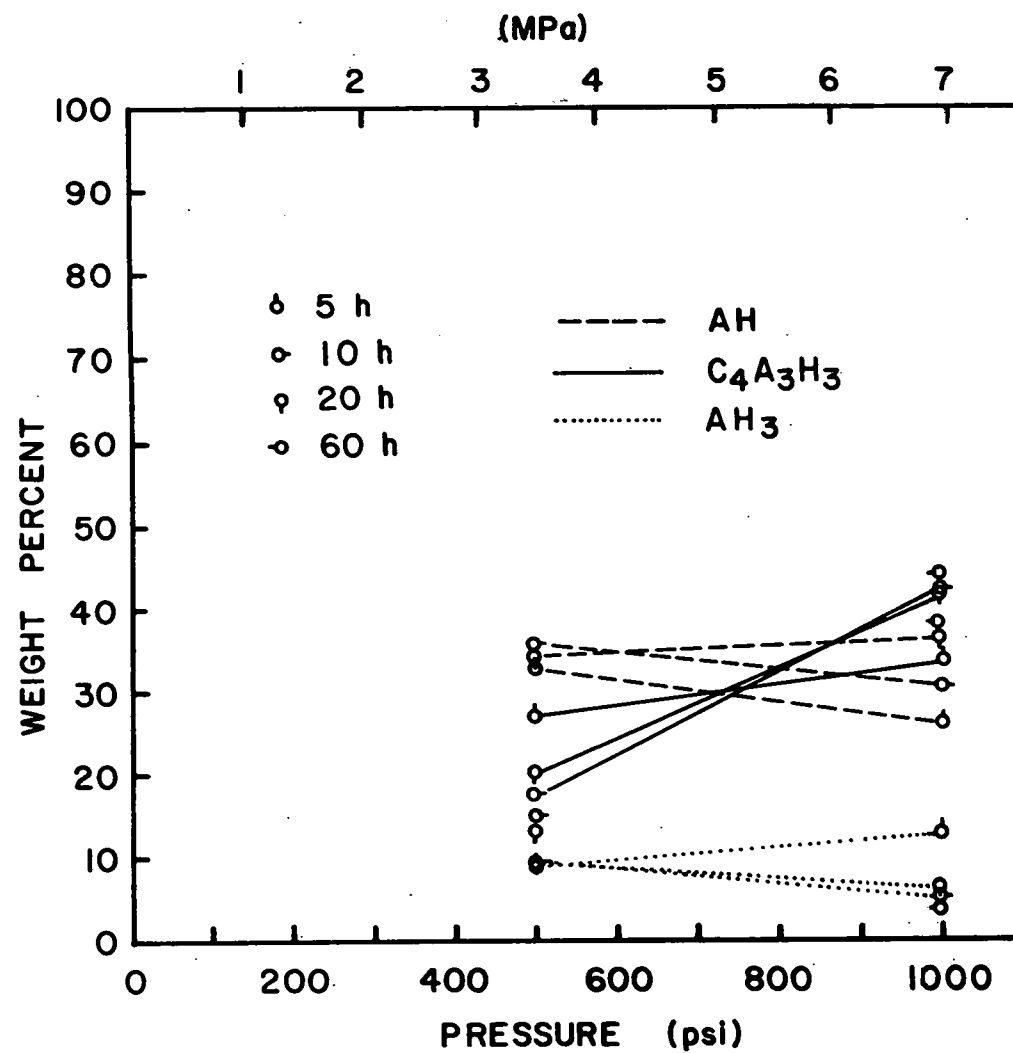


Fig. 21. Weight percentages of hydrated product phases from C-1 cement as a function of steam pressure.

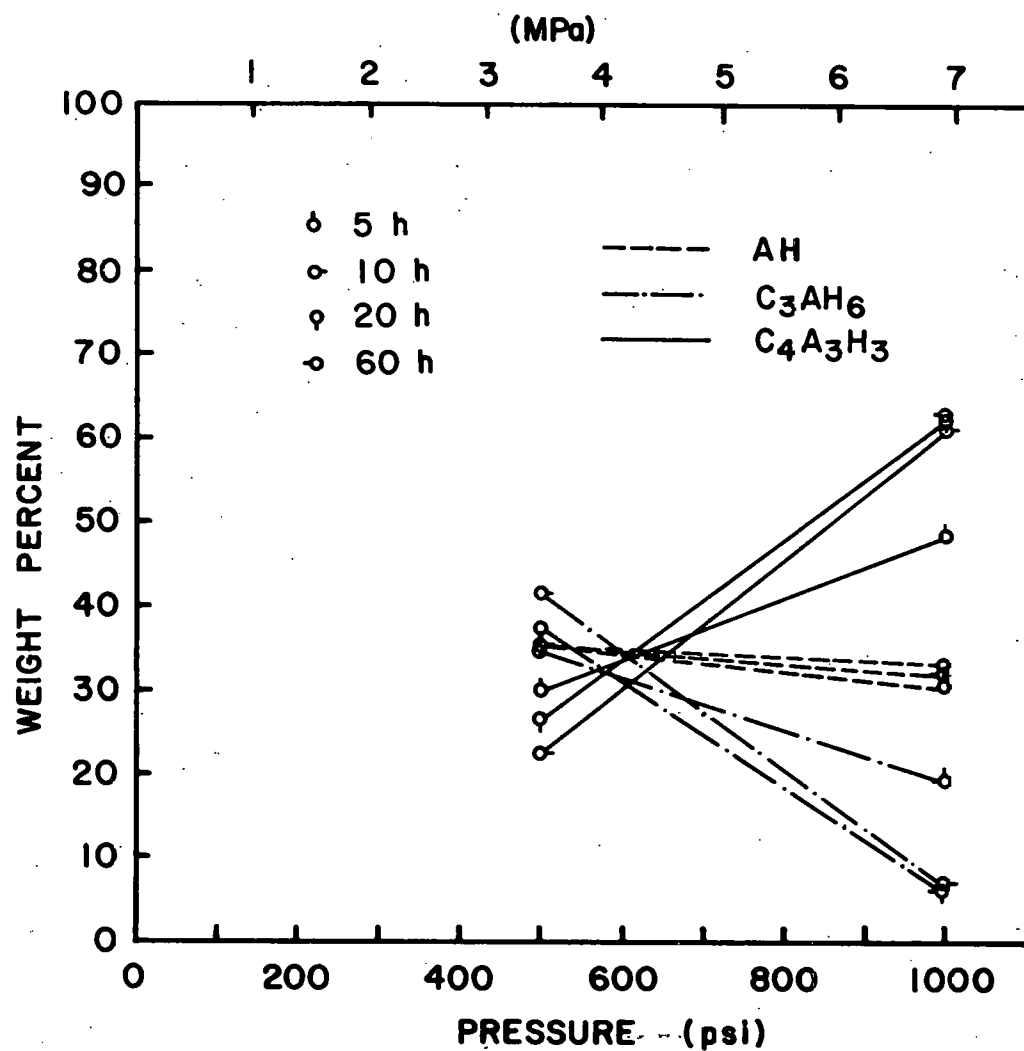


Fig. 22. Weight percentages of hydrated product phases from C-2 cement as a function of steam pressure.

CA₂, and C-2 contained no unhydrated material, even though the phase makeup was changing. The results for C-1 indicated that unreacted material remained at all reaction times at both 3.45 and 6.89 MPa. When the data in Table XXI are combined with the data shown in Fig. 17 and 18, it can be concluded that C₃AH₆ is not a stable phase at the higher pressures. C₃AH₆ appears to form metastably in the initial reaction and then slowly reacts to form the stable phases, which appear to be AH and C₄A₃H₃. The pressure dependence of the reactions can be observed clearly in Figs. 19-22, where the weight percentages of each phase in CA (Fig. 19), CA₂ (Fig. 20), C-1 (Fig. 21), and C-2 (Fig. 22) are shown as a function of pressure.

The reactions observed in the DOE atmosphere were discussed previously in terms of available TGA data, but further analysis indicated that the tentative conclusions reached previously need modification. Table XXI summarizes the phase analyses of samples reacted in the DOE atmosphere. The main conclusion is that C₃AH₆ does not appear, but a new phase, C₄AH₁₁ $\bar{C}$ forms ($\bar{C}$ designates CO₂). In addition, the reactions appear to occur more slowly than in steam because unreacted material is present in all samples except C-2 reacted for ≥ 10 h. The time behavior of the materials is summarized in Fig. 23. Because the system has a larger number of components, the three solids phases observed can coexist in stable equilibrium and the time trends observed for the individual phases reacted in saturated steam are absent in the DOE atmosphere.

In the 6.89 MPa DOE atmosphere, the amounts of the product phases formed from CA and CA₂ do not appear to correlate with the reaction time as was observed in saturated steam. That is, when the amount of

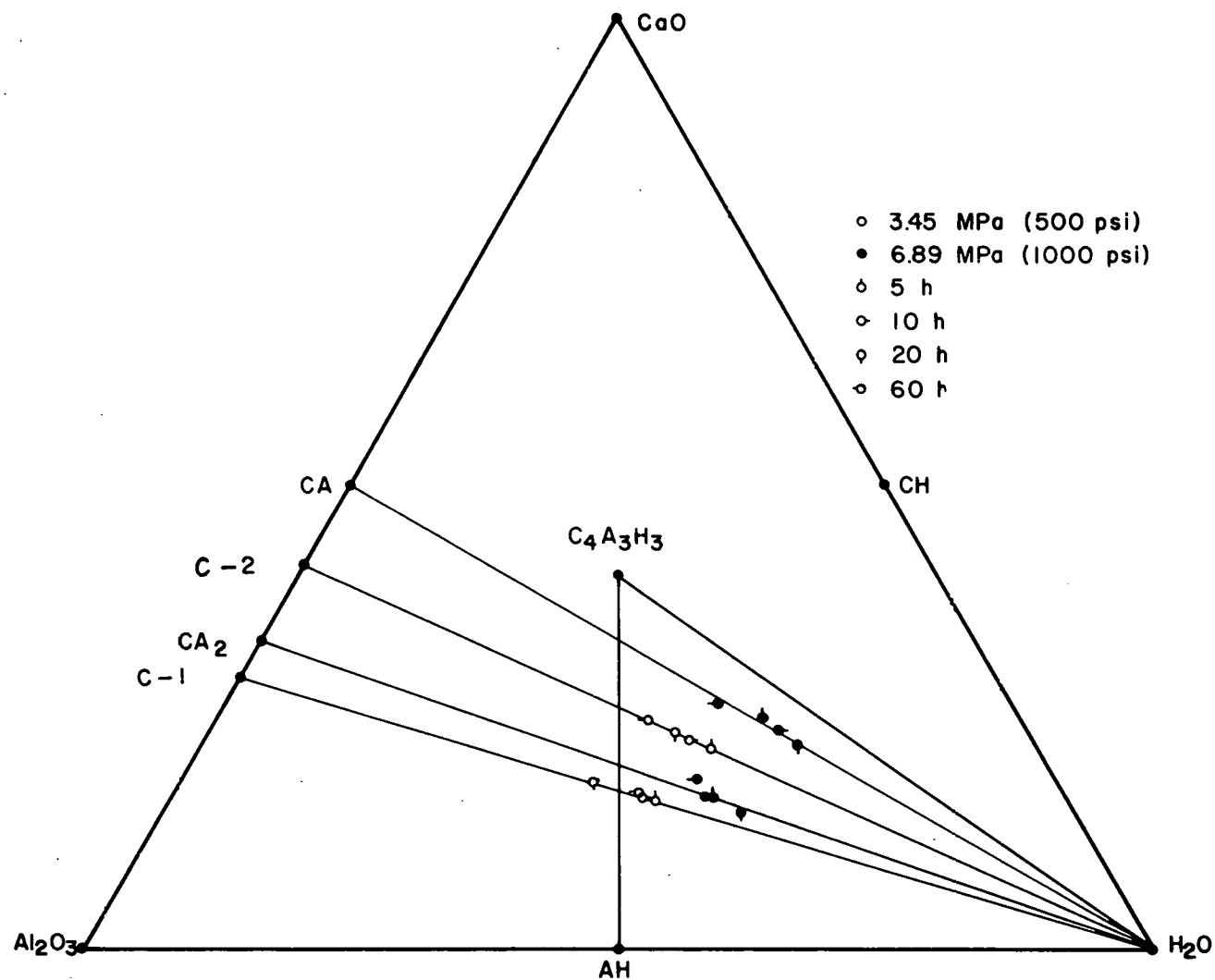


Fig. 23. Ternary composition points for CA, CA_2 , C-1 and C-2 for high pressure runs in DOE atmosphere. Diagram plotted in mol percent.

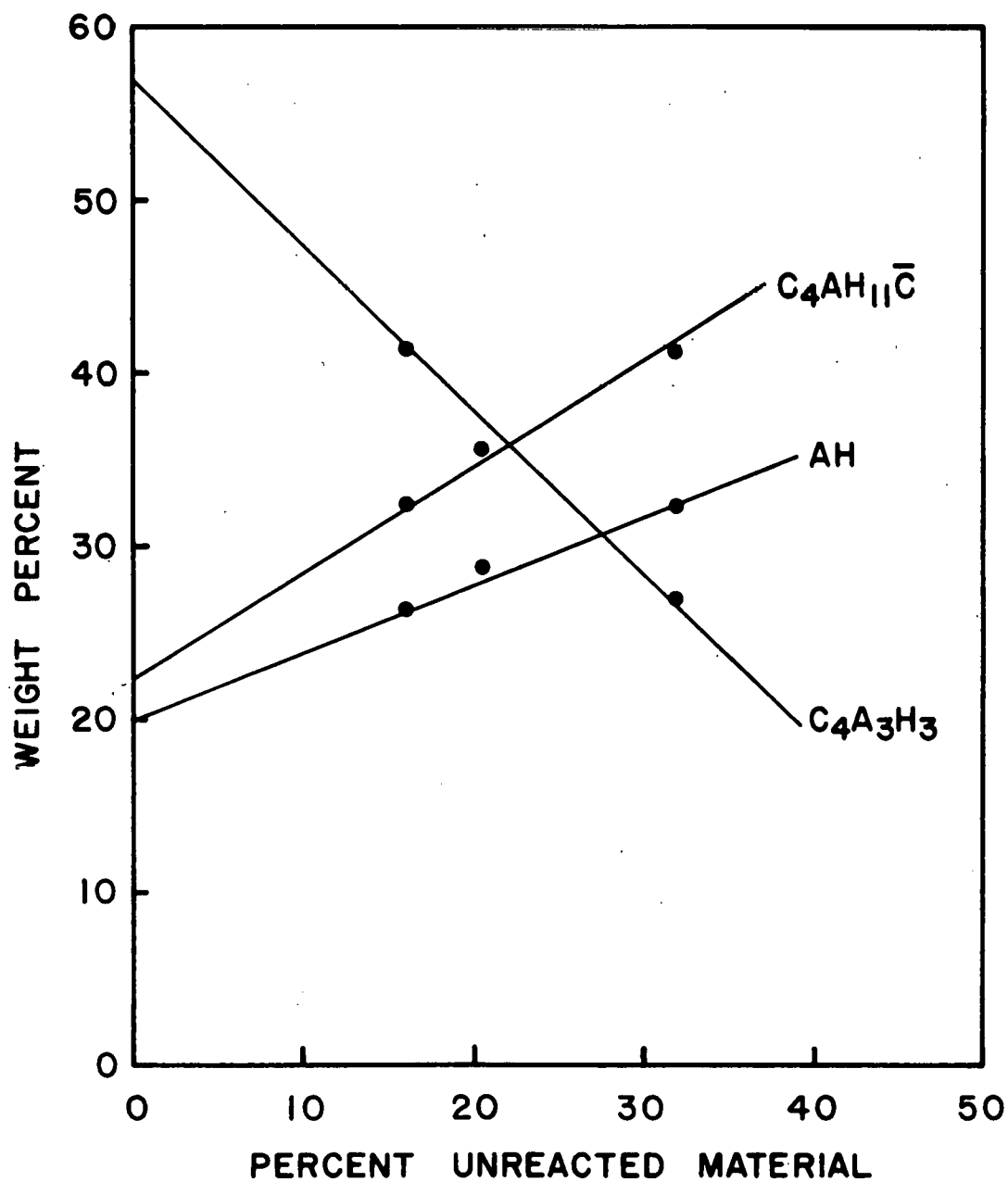


Fig. 24. Weight percentages of product phases from CA as a function of reactant unused (6.89 MPa DOE atmosphere).

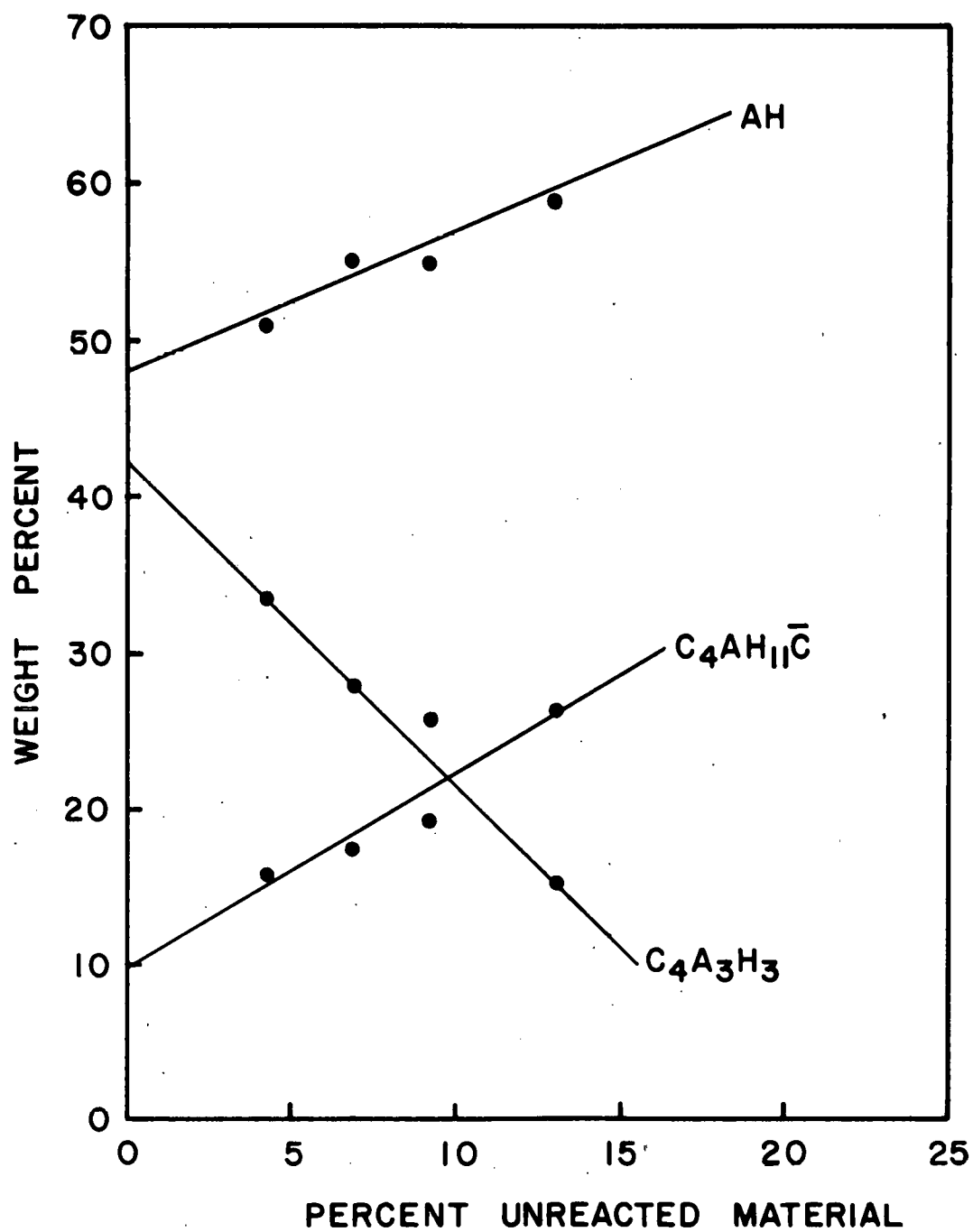


Fig. 25. Weight percentages of product phases from CA_2 as a function of reactant unused (6.89 MPa DOE atmosphere).

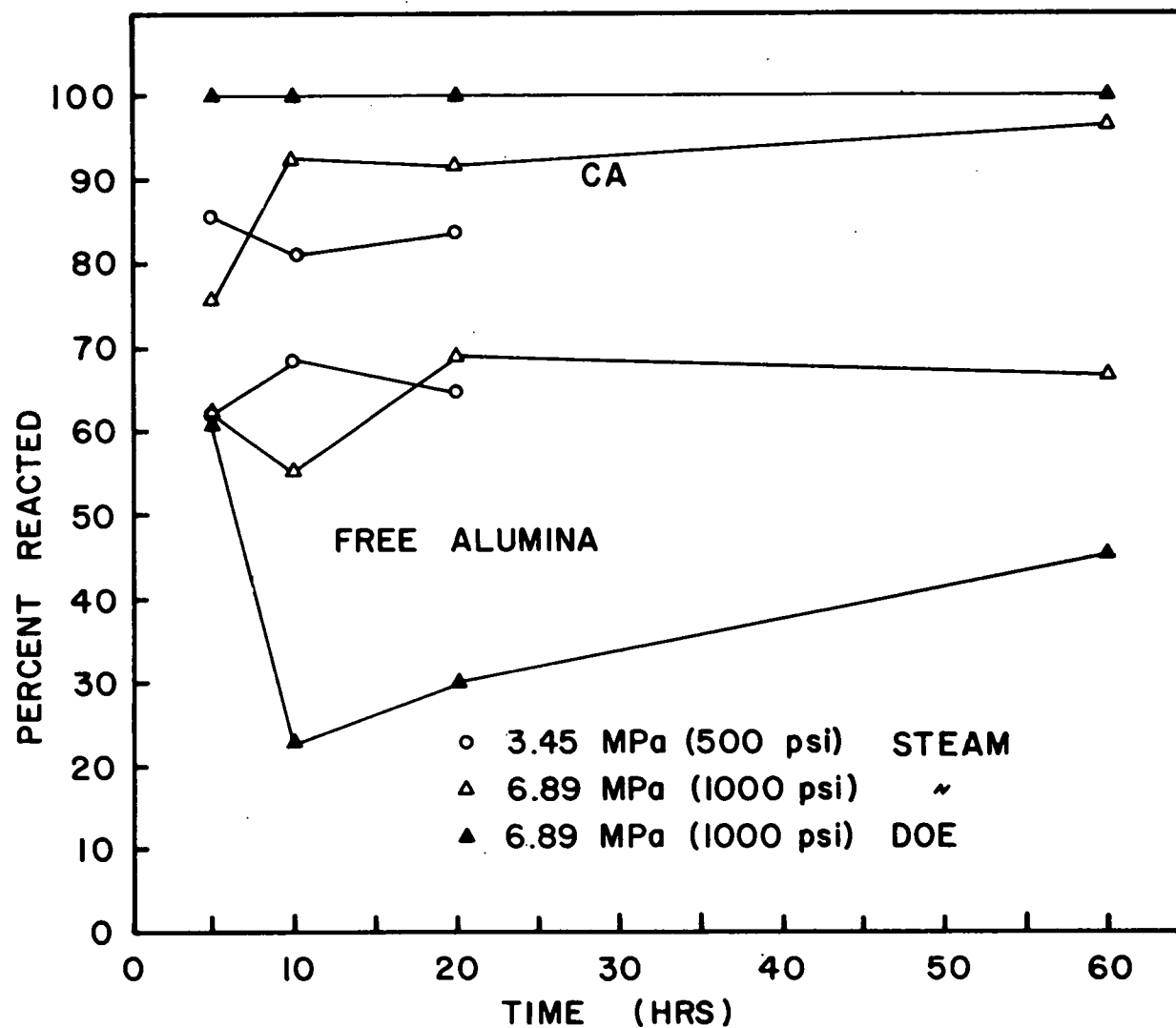


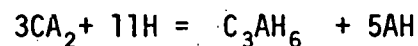
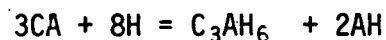
Fig. 26. The time dependence of the amount of the components of C-1 in steam and DOE atmospheres.

Table XXII. Possible Reaction Schemes in Steam and DOE Atmospheres

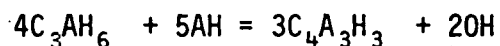
Prepared
Compounds

STEAM

Formation of C_3AH_6



Formation of $C_4A_3H_3$ /Decomposition of C_3AH_6



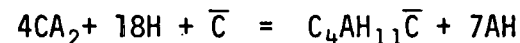
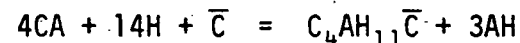
Neat
Cements

C-2 cement appears to follow above reaction scheme.

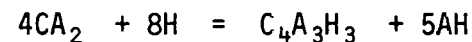
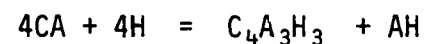
C-1 cement appears to follow above reaction scheme; however, in addition, the active alumina present in the cement forms some AH_3 .

DOE

Formation of $C_4AH_{11}\bar{C}$



Formation of $C_4A_3H_3$



C-2 cement appears to follow above reaction scheme.

C-1 cement appears to follow above reaction scheme; however, in addition small amounts of $\bar{C}\bar{C}$ are formed.

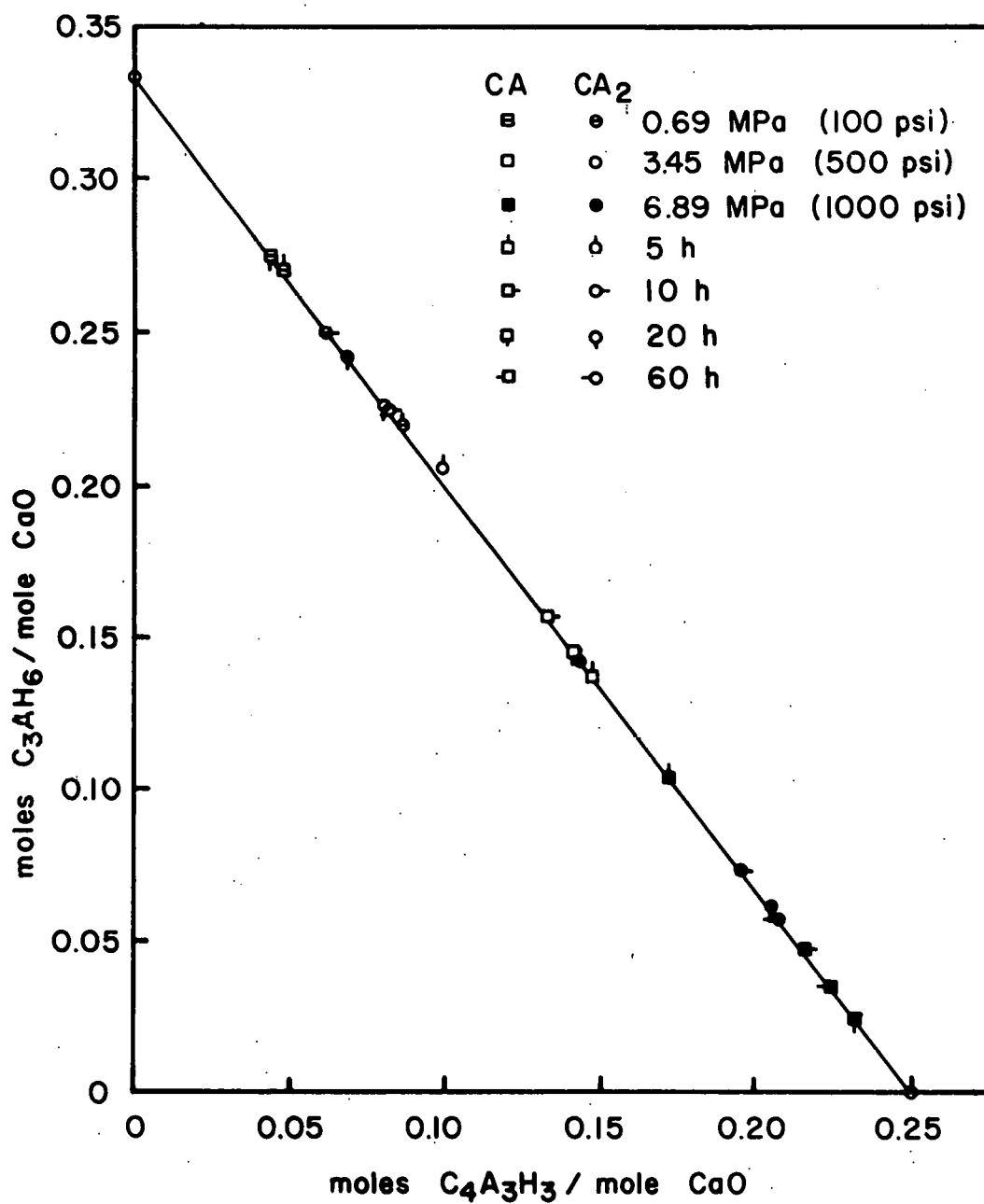


Fig. 27. Data demonstrating the conversion relationship for C_3AH_6 reacting with AH to form $C_4A_3H_3$ in pure steam.

a phase is plotted against reaction time, the amount does not increase or decrease monotonically as was observed in saturated steam. However, when the phase amounts are plotted against the amount of unreacted material, a good correlation appears to result. The data for CA and CA_2 are shown in Figs. 24 and 25, respectively.

Figure 26 summarizes the reactivity of C-1 in both saturated steam and DOE atmosphere at 6.89 MPa. In steam, the two components of C-1, both CA and the active alumina phase, are partially unreacted even after 60 h. However, in the DOE atmosphere, the CA component appears to be completely reacted, whereas, the active alumina component appears to be much less reactive than in pure steam.

The data from the runs can be condensed into a set of possible reaction schemes that summarize the reactions most likely to be followed. A possible set, that explains the phases formed, is presented in Table XXII.

If as proposed, C_3AH_6 forms metastably at the higher pressures and then decomposes by reaction to $C_4A_3H_3$, there should be a relationship between C_3AH_6 and $C_4A_3H_3$ such that when one decreases, the other must increase in amount.

The amount of C_3AH_6 versus the amount of $C_4A_3H_3$ is shown in Fig. 27. Both amounts have been normalized by conversion to a per mole CaO basis so that the data can be plotted on a single line. The data shows that at the lower pressures, C_3AH_6 forms in preference to $C_4A_3H_3$; however, there appears to be no clear time pattern. At 6.89 MPa, both CA and CA_2 show much more $C_4A_3H_3$ and a clear time pattern that indicates the longer the sample is held at pressure, $C_4A_3H_3$ forms at the expense of C_3AH_6 .

2. Summary

These results substantiate the chemical reactions found in the cement bonded castables after exposure to similar conditions. The reaction of CA or CA₂ individually is essentially the same as in commercial refractory cements which contain major proportions of these two compounds. Although metastable compounds initially form in some cases, the reactivity of CA, CA₂, and the commercial cements is relatively high; a major portion of the reactions being completed in only a few hours (e.g., ~20) as opposed to several days. The composition of the atmosphere is an important factor in the reaction products formed and carbonated phases such as CaCO₃ and C₄AH₁₁C̄ can be anticipated after exposure to CO and CO₂ containing atmospheres such as the DOE. For an atmosphere whose composition is similar to that of the DOE, the cement bond phases in refractory castables should be expected to react in only a few hours to form C₄A₃H₃, C₄AH₁₁C̄, AH (boehmite) and CaCO₃ when the atmosphere is close to saturation.

IV. SUMMARY

A. Chemical Reactions

1. The major chemical reactions occurring during exposure were the reaction of the calcium aluminate cement or AlPO₄ bond phases with steam and CO or CO₂ and were essentially dependent upon the degree of saturation of the atmosphere.

2. The chemical reactions were relatively rapid and the major changes occurred within a few days, ≤10 days. No chemical reactions were found at longer exposure times which had not already been detected at 10 days.

3. Boehmite and CaCO_3 were the major compounds formed in the cement-bonded castables during exposure. The amount of boehmite increased significantly with increasing saturation of the atmosphere.

4. The minimum percent saturation required to form boehmite varied from 10 to 30% depending upon the atmosphere and pressure.

5. The principal chemical reaction occurring in phosphate-bonded refractories during exposure was the transformation of orthorhombic AlPO_4 to trigonal AlPO_4 , especially in unsaturated atmospheres.

6. During exposure some portion of the cement and phosphate bond phases are dissolved from the refractories, especially in saturated atmospheres. The mechanical strength of the phosphate-bonded refractories were substantially lower after exposure to saturated atmospheres.

B. Properties

1. Of all variables investigated, exposure time, gas pressure or composition, presence or absence of H_2S , and liquid versus vapor contact, the degree of saturation was found to be the most important factor affecting the properties of refractories exposed to conditions like those expected near the cold face of a coal gasifier lining.

2. The flexural strength of high and intermediate alumina castables, generally, increased by a factor of 2 or 3 with the degree of saturation (due to the formation of new compounds, mainly boehmite), while there was a decrease in the strength of the phosphate-bonded refractories in the saturated atmospheres. No significant change was observed in the strength of insulating castables after exposure.

3. The thermal expansion curves of cement bonded castables exposed to the saturated atmospheres showed a sudden expansion between 500°C and 600°C due to the dehydration of boehmite. The magnitude of this expansion increased with the quantity of boehmite, being largest in the high purity alumina castables and smaller in the intermediate alumina and insulating castables. The thermal expansion of castables exposed to unsaturated atmospheres showed either no or a very small expansion between 500°C and 600°C, but a larger expansion above 800°C due to the decomposition of CaCO_3 .

4. The major changes in properties occurred within the first 10 days of the exposure, thereafter the properties were essentially independent of time at least up to the 60-day maximum used in this study.

5. In atmospheres of varying $\text{CO}/\text{H}_2\text{O}$ ratio, the dissolution of CaO increases with the increasing CO content, particularly for samples immersed in liquid. In the alumina castables containing a high purity calcium aluminate cement, UMR-1 and UMR-2, the strength tends to decrease with increasing $\text{CO}/\text{H}_2\text{O}$ ratio. The strength of castables containing silica tend not to show as large a dependence upon $\text{CO}/\text{H}_2\text{O}$ ratio.

6. The properties of a given refractory were basically similar after exposure regardless of whether they were immersed in liquid or in contact with saturated vapor. In a few instances some small differences in properties were observed, but in general condensed liquids were not particularly chemically corrosive.

7. Five boehmite formation/decomposition cycles, did not produce any detectable deterioration in properties, mainly MOR, of any of the castables investigated. SiO_2 -containing refractories and those made with less pure cement were affected less by these cyclic exposures than the high purity, high alumina castables.

C. Refractory Composition

1. While substantial reductions in mechanical strength were found for phosphate bonded refractories, in no case was total mechanical failure or loss of structural integrity observed for the refractories investigated.

2. Generally, cement-bonded castables of the same type, but made by different manufacturers, showed essentially the same behavior, but larger differences were found for similar phosphate bonded refractory products made by different manufacturers.

3. The properties of all refractories after exposure to various conditions changed to some degree, but the intermediate alumina and insulating castables showed the least evidence of any substantial deterioration in physical or mechanical properties.

4. In terms of overall behavior there was no significant difference between castables made with a high purity alumina aggregate or those made with an aluminosilicate aggregate. The type of cement was more important to the properties after exposure since all of the chemical reactions observed occur between the cement bond phases and steam, CO, CO_2 . No evidence was found of any chemical reaction with the refractory aggregate.

5. Castables containing a high purity cement generally had strengths comparable to those containing a less pure alumina cement, but the latter were somewhat less susceptible to the gas composition. The presence of SiO_2 in the castables, present either as SiO_2 additions, in the cement, or aluminosilicate aggregate, is tentatively concluded to be beneficial in that the flexural strengths were often somewhat higher and less dependent upon the exposure conditions.

V. REFERENCES

1. National Science Foundation and the Office of Coal Research: Materials Problem and Research Opportunities in Coal Conversion, Workshop held at Ohio State Univ., Columbus, OH, April 16-18, 1975. (Available from Corrosion Center, OSU, Columbus, Ohio).
2. Office of Coal Research, U.S. Dept. of Interior, Washington, D.C.: Ind. Heat., Nov. 1974, Vol. XLI, pp. 73-81.
3. N. S. Raymon and L. Y. Sadler, "Refractory Lining Materials for Coal Gasifiers, A Literature Review of Reactions Involving High-Temperature Gas and Alkali Metal Vapors" Bu Mines Info. Circular No. 8721, 1976.
4. W. T. Bakker, "Refractories for Coal Conversion Process: An Engineering Approach, Twelfth Annual Sym. on Refractories, St. Louis Section of Am. Ceram. Soc., St. Louis, MO, March 1976.
5. M. S. Crowley, Am. Ceram. Soc. Bull., 1975, 54, 1072-74.
6. R. E. Dial, Am. Ceram. Soc. Bull., 1975, 54, 640-43.
7. C. R. Venable, Jr., Am. Ceram. Soc. Bull., 1959, 38, 363-68; *ibid* 1969, 48, 1114-17.
8. L. Y. Sadler, N. S. Raymon, K. H. Ivey, et al., Am. Ceram. Soc. Bull., 1979, 58, (7), 705-09.
9. S. M. Weiderhorn, et al., J. Eng. Mater. Tech., 1977, 99, 143-46.
10. D. E. Day and F. D. Gac, Am. Ceram. Soc. Bull., 1977, 56, 644-48.
11. W. V. Ballard and D. E. Day, Am. Ceram. Soc. Bull., 1978, 57, 438-43; *ibid* 1978, 57, 660-65.
12. K. W. Wistrom and D. E. Day, Am. Ceram. Soc. Bull., 1978, 57, 680-84.

13. K. S. E. Forssberg, *Ceramurgia Int.*, 1976, 2, 135-40.
14. G. Schiroky and D. E. Day, *Am. Ceram. Soc. Bull.*, (scheduled for publication in 1980).
15. S. J. Schneider, *Materials Research for Clean Utilization of Coal*, Nat. Bur. of Standards, Washington, D.C. DOE Contract EA-77-A-01-6010, Quarterly Progress Report, 1 Jan-31 Mar 1978.
16. M. S. Crowley, *Am. Ceram. Soc. Bull.*, 1967, 46, 674-82; *ibid* 1970, 49, 527-30.
17. S. F. Rahman and D. E. Day, *J. Materials for Energy Systems* 1979, 1, 34-44.
18. S. F. Rahman and D. E. Day, *J. Materials for Energy Systems* (scheduled for 1980 publication).
19. D. E. Day and G. Lewis, *Am. Ceram. Soc. Bull.*, 1979, 58, 441-443.
20. A. Fakhr, G. L. Lewis and D. E. Day, "Chemical and Physical Stability of Refractories for Use in Coal Gasification", Thirteenth Quarterly Progress Report, Mat. Res. Ctr., Univ. of Missouri-Rolla, MO 65401.
21. A. Fakhr, G. L. Lewis and D. E. Day, "Chemical and Physical Stability of Refractories for Use in Coal Gasification", Sixteenth Quarterly Report, Mat. Res. Ctr., Univ. of Missouri-Rolla, MO 65401.

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CHEMICAL AND PHYSICAL STABILITY OF REFRACTORIES
FOR USE IN COAL GASIFICATION

Final Report

May 1, 1976 - July 31, 1980

Prepared by

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September 1, 1980

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EXECUTIVE SUMMARY

The dimensional stability, density, porosity, flexural strength and thermal expansion of eighteen cement-bonded, dense and lightweight refractory castables and three phosphate bonded refractories were determined before and after exposure to conditions chosen to simulate those at the cold face ($\sim 250^{\circ}\text{C}$) of a refractory lining in a coal gasification vessel. Chemical reactions occurring in the refractories during exposure were determined by XRD, DTA/TGA and SEM and correlated with the above properties. The variables investigated were (1) exposure time, 60 days maximum, (2) temperature, up to 538°C , (3) pressure, 6.9 MPa maximum, (4) gas composition, particularly CO/steam ratio (0.1, 1, and 3.0) and presence of 1 Vol% H_2S , (5) degree of saturation and (6) liquid versus vapor contact.

Of all the variables investigated, the degree of saturation of the test atmosphere was the single most important factor affecting the properties after exposure. In dry atmospheres, the properties were close to those for specimens heated to the same temperature in air. In 100% saturated atmospheres, however, the dense cement bonded castables typically had a flexural strength two to three times higher than that before exposure and a significantly lower porosity. Conversely, the flexural strength of the phosphate bonded refractories was only 1/2 to 1/5 of that before exposure. The exposure time was not particularly important since the chemical reactions occurring in the refractories during exposure, which are responsible for these changes in properties, are relatively rapid and appear to be nearing completion within a few days, ≤ 10 . All of the refractories were structurally intact after the 60-day maximum exposure to both dry or saturated conditions.

The principal chemical reactions in the cement bonded castables were between the cement bond phases and steam, CO, and CO_2 . No evidence was found of any reaction involving the various refractory aggregates. In dry atmospheres, the principal reaction was the formation of CaCO_3 which had no discernible effect upon the properties investigated. More extensive chemical reactions occur in 100% saturated atmospheres where the calcium aluminate cement phases reacted to form CaCO_3 and boehmite

($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and some portion of the CaO was leached from the refractory. The increase in flexural strength of the dense castables correlated well with the additional bonding expected from the interlocking network of boehmite crystals as observed by SEM. The minimum percent saturation needed for boehmite formation varied from ~10 to 20%, depending upon the gas composition, but no increase in flexural strength was observed below ~40% saturation. No specific chemical reactions were found in the phosphate bonded refractories after exposure to either dry or saturated conditions, but attack of the phosphate bond phase(s) by saturated steam is considered the likely reason for their lower flexural strength after exposure to saturated atmospheres.

These results indicate that the degree of saturation of a coal gasifier atmosphere is a more important process design parameter in selecting refractories for use in coal gasification than gas composition (within limits), or pressure. If the gasifier design or operational requirements (including start up or shut down) are such that saturated conditions (dew point temperature) will exist for an extended period (few days) at some point in the refractory lining, then cement bonded castables appear preferable to phosphate bonded refractories. High alumina, cement-bonded castables had no decided advantage over intermediate alumina castables at cold face temperatures, the performance of these two classes of refractories being comparable. In certain cases, a small amount of silica in the refractories, either from the aggregate, cement, or as free silica, was beneficial to high flexural strength under saturated conditions.

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I. INTRODUCTION

Commercialization of the numerous, high-pressure coal gasification processes currently under study is dependent upon the availability of refractory materials which can provide long term thermal, mechanical, and chemical protection for the metal pressure-confinement vessel; i.e., prevent overheating and chemical attack of the metal gasifier vessel. There are many excellent reviews of existing and proposed gasification processes^(1,2) and the potential problems associated with the use of refractories in these processes⁽³⁻⁶⁾ where the temperature, pressure, and gas composition may vary considerably. Generally, temperatures of 100-2000°C, pressures of 100 kPa to 10 MPa, and atmospheres containing CO, CO₂, CH₄, H₂, steam, and small amounts of H₂S, NH₃, alkali vapors and organic compounds may be encountered.

The refractories used in some related petrochemical applications provide a rough guide to the design engineer for refractory selection and use in coal gasification since some of the process parameters are similar. However, there are important differences in the process parameters which make it difficult to reliably predict the service performance and life-time of refractories that might be used for coal gasification. Knowledge of the behavior of refractories under conditions simulating those encountered in coal gasification is important to the reliability of operation since premature failure of the refractory lining will usually require gasifier shut down.

A. Objectives

This investigation was commenced on 1 May 1976 with the following objectives:

- a. to achieve an understanding of the general types of chemical reactions occurring in monolithic refractories when exposed to conditions representative of those at the cold face of the refractory lining in coal gasification vessels,
- b. to assess the relative importance of these reactions to those physical/chemical properties required for long-service life, and
- c. to identify those refractory systems providing optimum service performance.

The evaluation of the corrosion resistance, especially the bond phases used in monolithic refractories, to the high pressure/temperature gases and liquids found in coal gasification was of particular importance.

B. Tasks

The investigation consisted of the following tasks, some of which depended upon the results of previous tasks.

Task I. Exposure System Design and Construction: The first task was to design and construct an experimental exposure system capable of duplicating the conditions at the cold face of a refractory lining in a coal gasifier and sufficiently versatile to operate with a wide variety of gas compositions, pressures, and temperatures.

Task II. Screening of Commercial Refractories: The objective was to survey the performance and properties of a large number of commercial and experimental refractory compositions considered candidates for use as refractory linings in coal gasifiers. Particular emphasis was placed on identifying any classes of refractories which might be totally unsatisfactory.

Task III. Exposure Time: This task consisted of investigating the durability of selected refractories (based upon results from Task II) to atmospheres representative of those at the cold face of a lining in coal gasifiers for ≤ 60 days.

Task IV. CO/Steam Ratio: The purpose of this task was to determine the effect of CO/steam ratio upon the reactions found in cement and phosphate bonded castables, steam and CO being major constituents in gasifier atmospheres.

Task V. Degree of Saturation: This task consisted of determining the dependence of the chemical reactions occurring in dense and light-weight (insulating) castables upon the degree of saturation of the atmosphere and to correlate these reactions with changes in the physical and mechanical properties of the refractories.

Task VI. Liquid versus Vapor Corrosion: In this task, the corrosion resistance of castables to condensed liquids and saturated vapors and the relative severity of liquid versus vapor corrosion was determined. Light-weight insulating castables were of particular interest because of their higher porosity (internal surface area) which could make them more susceptible to chemical attack.

Task VII. Pressure/Temperature Cycling: The aim of this task was to determine the effect of repeated boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) formation and decomposition (by repeated pressure/temperature cycling) upon the mechanical strength of selected cement-bonded castables. The boehmite formation/decomposition reaction is accompanied by volume changes which might be detrimental to the mechanical strength and structural integrity. Changes in the operating temperature or gas composition in a gasifier,

as during start up or shut down, or temperature upset, could decompose previously formed boehmite so it was of interest to know whether the strength of the refractory was affected.

Task VIII. Hydrothermal Reactions of Calcium Aluminate Compounds and Commercial Cements: The objective of this task was to determine the time, temperature, and pressure dependence for the reactions found in calcium aluminate cements (formation of CaCO_3 , boehmite and CaO dissolution) and to investigate the reaction of CA^* and CA_2 individually in hydrothermal atmospheres relevant to coal gasification.

II. EXPERIMENTAL PROCEDURES

A. Raw Materials

Based upon the experience acquired from monolithic refractory linings used in related process vessels⁽⁵⁻⁸⁾, cement and phosphate-bonded refractories were investigated. Eighteen calcium aluminate cement-bonded refractory castables (dense high alumina, dense intermediate alumina, and insulating), three dense, high alumina phosphate-bonded ramming mixes, and five neat calcium aluminate cements were tested. These refractories cover the spectrum of commercially available products currently available for use as lining materials in coal gasifiers. Their overall chemical composition is listed in Table I where CC denotes a Commercial Cement-Bonded Castable, CPRM denotes a Commercial Phosphate-Bonded Ramming Mix,

*Cement terminology used where C = CaO , A = Al_2O_3 , S = SiO_2 , $\bar{\text{C}}$ = CO_2 , etc.

and C denotes a Commercial Refractory Cement. The compositions designated as UMR were prepared in our laboratory and contained 70 to 75% aggregate and 25 to 30% of one of the commercial refractory cements.

B. Specimen Preparation

The castables were cast into slabs 30.5 by 7.6 by 1.3 cm, cured for 24h in air at 100% relative humidity at 20-25°C, and dried at 110°C for 24h. These slabs were cut (diamond saw) into 7.6 by 1.3 by 1.3 cm rectangular bars. The phosphate-bonded refractories were hand rammed into 7.6 by 1.9 by 1.9 cm bars, dried in the molds at 110°C for 24h, and fired in air at 538°C for 18h prior to exposure.

C. Pre- and Post-Exposure Analysis

The weight and length of each specimen were measured before exposure. After exposure, the specimens were inspected visually for any surface deterioration, dried at 110°C for 24h, and the weight and length remeasured. The modulus of rupture (MOR) was measured in three point bending (ASTM C268-70) using a span of 5.08 cm and a crosshead speed of 0.5 cm/min. Parts of fractured specimens were used to measure the bulk density and apparent porosity according to ASTM C20-74 except that the samples were saturated with kerosene under vacuum. The MOR, bulk density, apparent porosity, and weight and length changes were also measured for control specimens of each refractory as-cast and dried at 110°C and fired in air at 260 and 538°C. The properties reported herein are the average of at least seven specimens. The crystalline phases in the refractories before and after exposure were identified by XRD*. The exposed specimens

*X-ray diffraction, Siemens Diffractometer, Karlsruhe, Germany.

Table I. Chemical Analysis of As-Received Refractories and Cements

No.	Identification	Al ₂ O ₃	CaO	Weight Percent					Total	Remarks	
				SiO ₂	Fe ₂ O ₃	TiO ₂	P ₂ O ₅	MgO			
<u>Dense, High Alumina Castables</u>											
1	CC-1	95.0	4.5	0.1	0.2	--	--	--	99.8	Greencast 94, A. P. Green Refractories	
2	CC-2	93.0	6.0	0.5	0.1	0.1	--	--	99.7	KAOTAB, Babcock & Wilcox	
3	CC-3	93.7	5.6	0.1	0.3	--	--	--	99.7	CASTOLAST G, Harbison-Walker	
4	CC-4	93.6	5.4	0.03	0.3	trace	--	0.1	99.43	PURO-TAB, Kaiser Refractories	
5	UMR-1	93.4	5.4	0.1	0.13	--	--	0.1	99.13	70% Tabular Al ₂ O ₃ * + 30% CA-25** cement	
6	UMR-2	91.3	7.8	0.1	0.1	--	--	--	99.3	70% Tabular Al ₂ O ₃ * + 30% Secar***250	
7	UMR-3	91.3	7.4	0.3	0.13	trace	--	0.1	99.23	70% Tabular Al ₂ O ₃ * + 30% C-3**	
8	UMR-4	87.1	10.1	1.7	0.5	--	--	--	99.4	70% Tabular Al ₂ O ₃ * + 30% Refcon**	
9	UMR-6	88.7	5.1	5.1	0.1	--	--	0.1	99.1	95% UMR-1 + 5% SiO ₂ ⁵	
10	UMR-7	84.0	4.9	10.1	0.1	--	--	0.1	99.2	90% UMR-1 + 10% SiO ₂	
<u>Dense Intermediate Alumina Castables</u>											
11	CC-5	55.0	5.0	36.0	1.2	1.5	--	--	98.7	LO-ABRADE, A. P. Green Refractories	
12	CC-6	57.4	5.5	33.5	1.3	1.7	--	--	99.4	RC-3, General Refractories	
13	UMR-5	58.6	8.4	29.6	1.3	--	--	--	97.9	75% Mulcoa and Mulgrain*** + 25% Refcon Cement	
14	UMR-8	63.8	4.8	28.3	1.0	--	--	0.1	98.0	75% Mulcoa and Mulgrain*** + 25% CA-25	

Table I. Chemical Analysis of As-Received Refractories and Cements (Continued).

No.	Identification	Al ₂ O ₃	CaO	SiO ₂	Weight Percent				Total	Remarks
					Fe ₂ O ₃	TiO ₂	P ₂ O ₅	MgO		
<u>Insulating Castables</u>										
15	CC-7	59.0	4.5	33.0	0.8	0.7	--	--	98.0	KAST-O-LITE 30, A. P. Green Refractories
16	CC-8	53.8	2.9	40.5	0.9	0.63	--	--	98.73	CERLITE 75, C. E. Refractories
17	CC-9	46.7	9.1	40.2	1.6	1.0	--	0.1	98.7	LITECAST 60-25, General Refractories
18	CC-10	34.5	9.3	52.5	--	--	--	--	96.3	VSL-50, A. P. Green Refractories
<u>Phosphate-Bonded Ramming Mixes</u>										
19	CPRM-1	96.0	0.1	3.0	0.3	0.1	--	0.1	99.6	Greenpak 90-P, A. P. Green Refractories
20	CPRM-2	96.5	0.04	2.7	0.5	--	--	--	99.74	90 RAM HS, C. E. Refractories
21	CPRM-3	89.5	--	6.0	--	--	3.7	--	99.2	BRIKRAM 90-R, General Refractories Co.
<u>Calcium Aluminate Cements</u>										
22	C-1	79.0	18.0	0.2	0.3	--	--	0.4	98.9	CA-25 Cement, Aluminum Co. of America
23	C-2	72.0	26.0	0.2	0.1	--	--	0.1	98.4	Secar 250, Lane Star Lafarge Co.
24	C-3	72.0	24.5	0.7	0.3	--	--	0.4	97.9	C-3, Babcock and Wilcox
25	C-4	58.0	33.5	5.6	1.5	--	--	--	98.6	Refcon, Universal Atlas Cement
26	C-5	44.0	36.0	8.6	8.5	--	--	0.7	97.8	Lumnite, Universal Atlas Cement

*The Tabular T-61 alumina aggregate (Alumina Co. of America) contained the following fraction (wt% of aggregate): -8 to +14 mesh = 20, -14 to +28 mesh = 18.6, -28 to +48 mesh = 15.7 and -48 mesh = 45.7.

**Information on various cements appears elsewhere in this Table.

***The Mulcoa 60 and Mulgrain M60 aggregate (C-E Minerals) contained the following fractions (wt%): -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, Del Monte Properties Co., La Salle County, IL 60557.

were also analyzed by DTA/TGA* from 25-950°C at a heating rate of 10°C/min using a 400 mg sample. The thermal expansion of a 5 cm specimen randomly selected from each group of exposed samples was measured continuously from 20 to 950°C and during cooling to room temperature.

III. RESULTS AND DISCUSSION

A. Task I- Exposure System Design, Construction, and Operation

A schematic diagram of the exposure test system is shown in Fig. 1. It consisted of two primary pressure vessels 15 cm I.D. by 46 cm long, a steam vessel constructed from 316 stainless steel, and a test-vessel made from 347 stainless steel. Both vessels were rated for a maximum working pressure of 6.9 MPa (1000 psi) at 538°C (1000°F). Resistance heating elements on the external surface of each vessel heated the vessel and contents to the required temperature. At the maximum working temperature and pressure, the temperature within the vessels varied only $\pm 10^{\circ}\text{C}$ from top to bottom and $\pm 5^{\circ}\text{C}$ from side to side. The vessels were connected to the other parts of the system and the control panel (located in a separate room) with 316 SS tubing.

Safety precautions and subsystems consisted of adjustable relief valves which would open in case of excessive pressure and automatically reduce the pressure to safe limits. Also, the gas handling and mixing system was equipped with several pre-set rupture discs and an emergency dump valve. In addition to the primary temperature controller, equipped with thermocouple break protection, a second controller served as a high

*Type TA-1 Thermoanalyzer, Mettler Instrument Corporation, Hightstown, New Jersey.

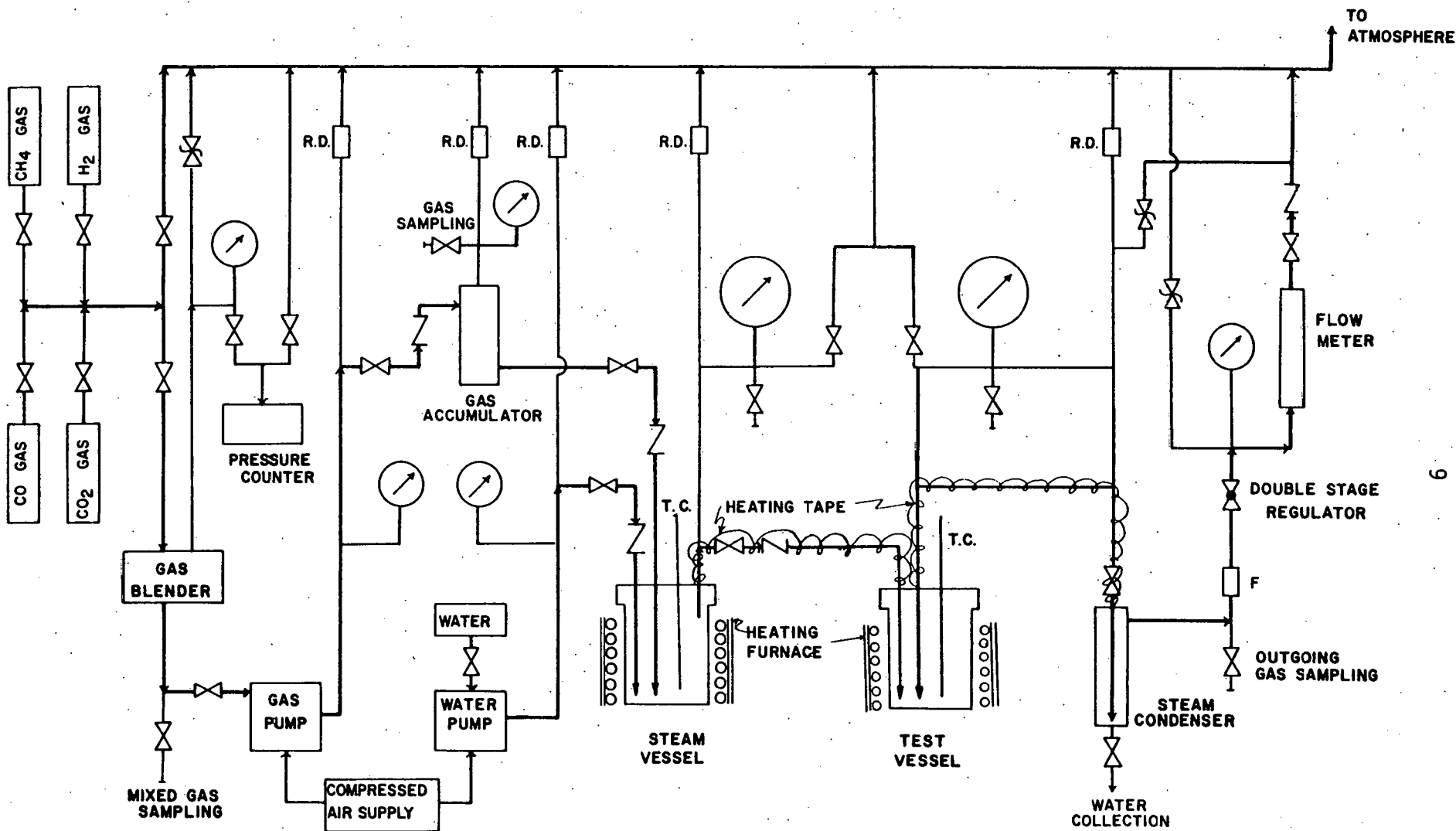
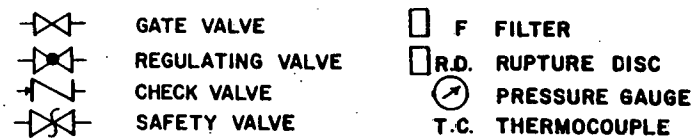


Fig. 1. Schematic diagram of the exposure test system.



temperature limit and would shut down the system totally in case of any failure of the primary controller.

The system can be operated with either a static or flowing gas atmosphere. The usual operating condition was with a flowing gas atmosphere, the flow rate controlled by a flow meter. When the pressure in the vessels dropped slightly below the selected pressure, additional gas was automatically added to the system by a high pressure gas pump operated by compressed air.

This system has been safely and successfully operated during the period of this project and remains in perfect operating condition. The longest period of continuous operation was for 60 days, but there is no apparent limit to the time of continuous operation. The system operated so dependably that direct supervision during evenings and nights was unnecessary. The pressure vessels can each accommodate 150-200 specimens of the size mentioned in section II-B.

At the beginning of an exposure test, specimens were placed in both vessels; those in the steam vessel (above water level or immersed in water) being exposed to a 100% saturated atmosphere, while those in the test vessel were exposed to an unsaturated (dry) atmosphere. Each group of specimens was separated from each other in the vessels by thin alumina plates. Distilled water was placed in the steam vessel, both vessels were purged with N_2 , pressurized, and checked for leaks. The nitrogen was exhausted and the vessels heated $\sim 50^\circ\text{C}/\text{h}$. During heating, the exhaust of the test vessel was open to the atmosphere so the water present in the unfired castables could escape. When the steam pressure in the steam vessel reached the required pressure, the remaining gases

were added from a pre-mixed mixture until the required overall pressure and gas composition was obtained. When the test vessel attained the required temperature, it was pressurized with the steam/gas mixture from the steam vessel. After flowing through both vessels, the gases exited through a steam condenser and then through a flow meter at a rate of ~ 4 l/h (STP) which provided for one complete change of the test atmosphere every 24h. Additional water was pumped into the steam vessel as needed.

Any necessary modifications in the above procedures needed for a particular Task are described at the beginning of the section describing that Task. Table II summarizes the time, temperature, pressure, gas composition, and the refractories employed in each of the 42 exposures used in this study.

B. Task II- Screening of Commercial Refractories

Seven dense high alumina castables (CC-1, 2, 3, 4, and UMR-1, 2, 3), two dense intermediate alumina castables (CC-5, 6), two insulating castables (CC-7, 8), and three phosphate-bonded ramming mixes (CPRM-1, 2, 3) were exposed to the DOE atmosphere, whose composition is given in Table II. The specimens were exposed to a 100% saturated atmosphere at 231°C in the steam vessel and an unsaturated atmosphere at 538°C in test vessel at a pressure of 6.9 MPa. The refractories were exposed to these conditions for a maximum of 30 days with samples removed at 10 and 20 days. Two tests were made, the first in the atmosphere cited above without any H_2S , exposures 4-10 in Table II, while the second used the

Table II. Exposure Test Conditions and Materials

Exposure No.	Atmosphere	Pressure (MPa) _s	Temp. (°C)	Duration (day)	Remarks	Materials Exposed Indicated by x																								
						CC-1	CC-2	CC-3	CC-4	UMR-1	UMR-2	UMR-3	UMR-4	UMR-6	UMR-7	CC-5	CC-6	UMR-5	UMR-8	CC-7	CC-8	CC-9	CC-10	CPRM-1	CPRM-2	CPRM-3	C-1	C-2	C-3	C-4
1	Air	0.1 (atm)	110	1		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x					x	x	x	x	x	
2	"	"	260	3/4		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x										
3	"	"	538	3/4		x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x								
4	DOE*(without H ₂ S)	3.4	260	10	31% Saturated	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x				
5	"	"	"	20	" "	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x	x	x		
6	"	"	"	30	" "	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x				
7	"	6.9	538	10	-10% saturated	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x					
8	"	"	"	20		x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x	x	x		
9	"	"	"	30		x	x	x	x	x	x			x	x		x	x			x	x	x	x	x					
10	"	"	231	30	100% Saturated	x	x		x	x	x			x	x		x	x			x	x	x	x						
11	DOEwith 1 Vol% H ₂ S	"	"	44	Saturated vapor					x		x					x	x		x	x	x								
12	"	"	"	44	Liquid					x								x		x		x								
13	"	"	240	5	85% Saturated					x		x					x	x		x	x	x								
14	DOEwith 1 Vol% H ₂ S cyclic exposure	6.9	240 then 538	Each cycle 5 days	As #13, then heated 18h (538°C) for 5 cycles.					x		x					x	x		x	x	x								
15	DOEwith 1 Vol% H ₂ S	6.9	538	10	-0% Saturated	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x	x	x		
16	"	"	"	20	" "	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x	x	x		
17	"	"	"	30	" "	x	x	x	x	x	x			x	x		x	x			x	x	x	x	x	x	x	x		
18	"	"	371	60	13.3% Saturated	x				x	x	x			x			x			x									

Table II. Exposure Test Conditions and Materials (Continued).

Exposure No.	Atmosphere	Pressure (MPa) ^s	Temp. (°C)	Duration (days)	Remarks	Materials Exposed Indicated by x																								
						CC-1	CC-2	CC-3	CC-4	UMR-1	UMR-2	UMR-3	UMR-4	UMR-6	UMR-7	CC-5	CC-6	UMR-5	UMR-8	CC-7	CC-8	CC-9	CC-10	CPRM-1	CPRM-2	CPRM-3	C-1	C-2	C-3	C-4
19	DOE with 1% H ₂ S	6.9	231	10	100% Saturated vapor					x		x					x	x		x	x	x				x	x	x		
20	"	"	"	10	Liquid					x		x					x	x		x	x	x								
21	"	"	"	30	100% Saturated vapor	x	x	x	x	x	x	x				x	x			x	x			x	x	x			x	x
22	"	"	"	60	100% Saturated vapor	x				x	x	x					x	x			x	x		x		x				
23	"	"	"	60	Liquid	x				x	x	x		x	x		x						x							
24	CO**/H ₂ O = 1.1 (without H ₂ S)	3.2	199	10	100% Saturated vapor	x	x	x	x	x	x	x				x	x			x	x			x	x	x	x	x	x	x
25	"	"	260	10	37.5% Saturated	x	x	x	x	x	x	x				x	x			x	x			x	x	x	x	x	x	x
26	"	"	538	10	~ 0% Saturated	x	x	x	x	x	x	x				x	x			x	x			x	x	x	x	x	x	x
27	CO**/H ₂ O = 0.1 + 1 Vol% H ₂ S	6.9	538	20	~ 0% Saturated vapor					x	x		x				x	x			x	x	x	x						
28	"	"	278	20	100% Saturated vapor					x	x		x				x	x			x	x	x	x						
29	"	"	278	20	Liquid					x	x		x				x	x			x	x	x	x						
30	CO**/H ₂ O = 1.0 + 1 Vol% H ₂ S	6.9	538	20	~0% Saturated					x	x		x	x	x		x	x			x	x	x	x						
31	"	"	241	20	100% Saturated vapor					x	x		x	x	x		x	x			x	x	x	x						
32	"	"	241	20	Liquid					x	x		x	x	x		x	x			x	x	x	x						
33	CO**/H ₂ O = 3.0 + 1 Vol% H ₂ S	6.9	538	20	~0% Saturated					x	x		x	x	x		x	x			x	x	x	x						

Table II. Exposure Test Conditions and Materials (Continued).

Exposure No.	Atmosphere	Pressure (MPa) [§]	Temp. (°C)	Duration (days)	Remarks	Materials Exposed Indicated by x																									
						CC-1	CC-2	CC-3	CC-4	UMR-1	UMR-2	UMR-3	UMR-4	UMR-6	UMR-7	CC-5	CC-6	UMR-5	UMR-8	CC-7	CC-8	CC-9	CC-10	CPRM-1	CPRM-2	CPRM-3	C-1	C-2	C-3	C-4	C-5
34	CO**/H ₂ O = 3.0 + 1 Vol% H ₂ S	6.9	204	20	100% Sat. vapor					x	x		x	x	x		x	x		x	x	x	x								
35	"	"	204	20	Liquid					x	x		x	x	x		x	x		x	x	x	x								
36	Steam	2.8	230	10	100% Sat. vapor					x			x					x	x		x	x	x				x	x	x		
37	"	"	"	10	Liquid					x			x					x	x		x	x	x								
38	Steam	6.9	285	10	100% Sat. vapor					x			x					x	x		x	x	x				x	x	x		
39	"	"	"	10	Liquid					x			x					x	x		x	x	x								
40	"	2.8	varied	10	Various % sat.																						x				
41	"	6.9	"	10	" "																						x				
42	DOE + 1 Vol% H ₂ S	6.9	"	10	" "																						x				

*DOE Composition is 18 CO, 12 CO₂, 5 CH₄, 24 H₂, 41 H₂O (vol.%)

**Vol % Ratio

§1 MPa = 145 psia

same atmosphere to which 1 vol% H_2S was added, exposures 15-17, 19-21 in Table II.

1. Dimensional and Weight Changes

The dimensional changes for all the refractory specimens after exposure was small, <1%. The castables generally showed a slight shrinkage in the unsaturated DOE atmosphere at 538°C, while a slight expansion occurred in the saturated atmospheres at 231°C. The dimensional change for the phosphate-bonded specimens was barely measurable.

The weight loss for the cement bonded castables, Table III, was ~3% and 4-5% when fired in air at 260°C and 538°C, respectively. The weight loss of the high alumina castables after exposure to the unsaturated atmosphere at 538°C was generally smaller than that of the controls fired in the air at 538°C. The presence of 1% H_2S in the atmosphere at 538°C had little effect upon the weight loss.

In the saturated DOE atmosphere (231°C) the weight loss for all the high alumina castables was less than that at 538°C and in some cases a small weight gain occurred. Once again the presence of 1% H_2S had no major effect upon the weight change.

The weight changes for the intermediate and insulating castables after exposure were essentially the same in both the saturated and unsaturated atmosphere and were not much different from their controls fired in air. However, the weight change for these castables was significantly different when the atmosphere contained 1% H_2S , particularly in the saturated atmosphere.

All of the phosphate ramming mixes exposed to the unsaturated atmosphere at 538°C showed small weight changes, CPRM-3 having the

Table III. Percent Weight Change* Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls, fired 18h in air		DOE atmosphere, 30 days	
	<u>260°C</u>	<u>538°C</u>	<u>231°C</u> (100% saturated)	<u>538°C</u>
Dense, High Alumina Castables				
CC-1	-3.1**	-4.5	[§] +0.1/ [§] -0.9	[§] -1.9/ [§] -2.2
CC-2	-2.9	-4.7	-1.6/-2.3	-3.7/-3.8
CC-3	-2.3	-3.9	[#] nt/-0.1	-0.9/-1.8
CC-4	-3.0	-4.1	+2.0/-0.5	-1.4/-1.8
UMR-1	-3.2	-5.0	+0.2/+0.5	-2.0/-1.2
UMR-2	-4.3	-5.0	nt/-2.4	-3.6/-4.0
UMR-3	-3.0	-4.0	-1.7/+0.5	-3.8/-2.8
Dense, Intermediate Alumina Castables				
CC-5	-3.0	-4.7	-4.2/-1.9	-4.2/-4.1
CC-6	-3.2	-5.0	-5.2/-2.7	-4.4/-4.1
Insulating Castables				
CC-7	-3.4	-5.0	-5.0/+0.3	-5.0/-4.7
CC-8	-2.1	-3.5	-1.9/+1.4	-3.2/-2.9
Phosphate-Bonded Ramming Mixes				
CPRM-1	nt	nt	+0.7/+2.0	Nil/-0.3
CPRM-2	nt	nt	+1.0/+2.9	+0.2/Nil
CPRM-3	nt	nt	-3.3/-0.3	-1.2/-0.7

*Referenced to as-dried at 110°C weight for cement-bonded castables and to as-fired at 538°C weight for phosphate-bonded specimens.

**+ = Weight gain; - = Weight loss

§First number is for no H₂S present while the second is for the same atmosphere containing 1 Vol. % H₂S. This procedure also followed in Tables IV, V, VI and VIII.

#nt - not determined. Same for succeeding tables.

Table IV. Bulk Density (gm/cm^3) Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls			DOE atmosphere, 30 days	
	As-Dried	Fired 18h in air			
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>231°C</u>	<u>538°C</u>
	(100% saturated)				
Dense, High Alumina Castables					
CC-1	2.77	2.75	2.67	2.79*/2.77	2.75*/2.77
CC-2	2.62	2.56	2.49	2.53/2.51	2.57/2.55
CC-3	2.85	2.81	2.74	nt/2.79	2.85/2.77
CC-4	2.88	2.84	2.78	2.94/2.87	2.87/2.89
UMR-1	2.75	2.71	2.68	2.75/2.73	2.73/2.78
UMR-2	2.66	2.58	2.52	nt/2.58	2.59/2.60
UMR-3	2.47	2.45	2.35	2.44/2.44	2.44/2.45
Dense, Intermediate Alumina Castables					
CC-5	2.33	2.29	2.26	2.24/2.26	2.25/2.23
CC-6	2.31	2.27	2.21	2.15/2.26	2.25/2.24
Insulating Castables					
CC-7	1.53	1.52	1.46	1.45/1.59	1.49/1.53
CC-8	1.58	1.55	1.54	1.54/1.59	1.53/1.54
Phosphate-Bonded Ramming Mixes					
CPRM-1	nt	nt	2.95	2.96/2.90	2.95/2.87
CPRM-2	nt	nt	2.92	2.94/2.99	2.96/2.91
CPRM-3	nt	nt	2.96	2.93/2.97	3.00/2.95

*First number is for DOE atmosphere without H_2S while second is for DOE with 1% H_2S .

Table V. Percent Apparent Porosity Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls			DOE atmosphere, 30 days	
	As-Dried	Fired 18h in air		(100% saturated)	
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>231°C</u>	<u>538°C</u>
Dense, High Alumina Castables					
CC-1	14.2%	20.0%	23.3%	13.0 [*] /15.5%	24.3/23.7%
CC-2	18.7	25.2	27.6	28.8/28.5	28.0/28.3
CC-3	13.7	16.9	20.1	nt/16.4	21.1/23.9
CC-4	14.4	17.1	21.8	6.2/12.7	21.0/20.7
UMR-1	16.1	20.1	22.9	10.5/15.3	26.1/23.5
UMR-2	15.6	24.1	27.8	nt/17.8	27.0/26.8
UMR-3	23.3	25.1	31.2	28.0/28.2	31.6/30.7
Dense, Intermediate Alumina Castables					
CC-5	13.3	16.6	20.3	11.8/15.8	21.2/21.9
CC-6	16.1	18.7	22.8	22.3/16.7	22.6/22.3
Insulating Castables					
CC-7	42.9	46.0	48.6	53.8/44.9	52.3/50.5
CC-8	38.8	41.0	42.3	52.0/45.4	52.4/51.4
Phosphate-Bonded Ramming Mixes					
CPRM-1	nt	nt	17.3	20.6/20.6	18.2/20.1
CPRM-2	nt	nt	19.8	21.1/18.7	18.6/19.4
CPRM-3	nt	nt	16.3	21.5/18.5	16.2/17.5

*First number is for DOE atmosphere without H₂S while second is for DOE with 1% H₂S.

Table VI. Modulus of Rupture (MPa^{*}) Before and After 30-day Exposure to DOE Atmosphere at 6.9 MPa (1000 psia)

Refractory	Controls			DOE atmosphere, 30 days	
	As-Dried	Fired 18h in air			
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>231°C</u>	<u>538°C</u>
	(100% saturated)				
Dense, High Alumina Castables					
CC-1	19.8±2.0**	13.4±0.9	13.0±0.4	29.2 [§] /24.4±2.6	9.0±0.9/8.2±0.9
CC-2	17.2±1.0	8.2±1.2	9.5±1.0	13.7/11.9±1.0	5.2±0.4/6.5±0.2
CC-3	21.2±1.7	17.3±1.3	18.3±0.6	nt/28.6±3.1	10.8±0.4/11.8±0.7
CC-4	22.8±2.6	16.6±1.8	15.3±2.4	33.5/37.1±1.9	11.9±1.9/12.5±5.6
UMR-1	19.7±1.3	15.3±1.2	15.2±1.0	45.7/33.6±1.4	12.4±1.4/13.9±1.1
UMR-2	20.2±2.3	8.4±1.1	12.5±2.0	nt/27.9±3.9	4.6±0.6/7.1±0.9
UMR-3	16.3±2.1	11.7±2.1	6.7±1.6	18.3/14.6±1.7	8.6±1.0/9.7±0.7
Dense, Intermediate Alumina Castables					
CC-5	19.3±3.9	12.9±2.3	12.1±1.2	24.4/16.2±1.7	17.5±2.3/12.8±1.3
CC-6	15.2±1.7	10.8±1.6	9.6±0.7	23.0/27.0±2.7	16.9±2.2/16.1±1.3
Insulating Castables					
CC-7	4.5±0.7	3.1±3.0	3.3±0.2	6.4/5.4±0.3	4.5±0.4/3.6±0.4
CC-8	6.7±0.8	5.4±0.6	6.5±3.1	6.6/3.9±0.5	7.5±0.6/6.2±0.4
Phosphate-Bonded Ramming Mixes					
CPRM-1	nt	nt	27.0±2.2	11.2/7.6±0.8	24.9±3.9/15.4±2.9
CPRM-2	nt	nt	23.5±1.7	3.2/4.2±0.9	20.8±2.8/16.6±2.2
CPRM-3	nt	nt	18.3±4.1	3.0/6.2±2.2	11.1±4.4/14.6±1.4

*1 MPa = 145 psi.

**The ± limit corresponds to one standard deviation.

[§]Standard deviation is not shown since only two specimens were tested in the DOE atmosphere without H₂S.

largest at ~1%. In the saturated atmosphere, CPRM-1 and 2 had a weight gain of 1 to 3%, while CPRM-3 continued to show a weight loss (-3.3%) which became smaller when 1% H₂S was present (-0.3%).

2. Density

As shown by the data in Table IV, the bulk density after exposure was comparable to that of the controls fired in air at equivalent temperatures. Comparison of the data for 231° and 538°C indicates that the degree of saturation of the atmosphere had no appreciable effect upon the bulk density. Similarly, the presence of 1% H₂S had no significant effect upon the bulk density.

3. Porosity

In comparison to the change in weight or bulk density, a large reduction in porosity occurred in most of the high and intermediate alumina castables after exposure to the saturated (231°C) atmosphere, Table V. On the other hand, the porosity after exposure to the unsaturated atmosphere at 538°C was close to that for the respective controls fired in air at 538°C, the insulating castables CC-7 and CC-8 being the only exception where a moderate increase in porosity was found. The change in porosity of the phosphate-bonded refractories was much less than that of the cement bonded castables and appeared less dependent upon the degree of saturation of the test atmosphere. While the presence of 1% H₂S does not appear of major significance, the porosity of the cement-bonded castables appears to be affected to a greater degree than phosphate-bonded refractories.

4. Flexural Strength

The modulus of rupture (MOR) for controls fired in air and after exposure to the DOE atmosphere at 231° and 538°C is given in Table VI.

In all cases, the MOR of the as-cast and dried (110°C) specimens equalled and generally exceeded the manufacturer's MOR value. The decrease in MOR for the controls fired at higher temperatures is normal for cement-bonded castables.

In general, the MOR of the refractories after exposure to the unsaturated (538°C) atmosphere were not too different from that of their respective controls fired in air at 538°C, the MOR being lower for the high alumina castables (except UMR-3), higher for the intermediate alumina castables, and about the same for the insulating castables and phosphate-bonded refractories (except CPRM-3). The presence of 1% H₂S did not affect the MOR of the cement-bonded castables to a significant degree, but did seem to result in generally lower strengths for the phosphate-bonded refractories.

As is clearly evident from Table VI, the largest and most significant change in MOR occurred after exposure to the saturated (231°C) atmosphere. The MOR of the high and intermediate alumina castables increased significantly, sometimes more than doubling, whereas the phosphate-bonded refractories showed a large decrease in MOR. The MOR of the insulating castables remained relatively unchanged. The presence of 1% H₂S in the saturated atmosphere produced no clearly discernible change in MOR, although more samples showed a decrease in MOR than increase.

This large increase in MOR for cement-bonded castables and decrease in MOR for phosphate-bonded refractories has also been found in other saturated steam⁽⁹⁾ and steam/CO^(8,9-12) atmospheres. As might be expected, a reasonably good correlation is found between the change

in MOR and porosity of the cement-bonded castables after exposure to the saturated atmosphere. Those castables such as CC-1, CC-4, and UMR-1 with the larger increases in MOR, Table VI, also showed large reductions in porosity, Table V, whereas CC-2 and UMR-3 whose porosity changed only slightly showed only a slight increase in MOR.

5. Thermal Expansion

The thermal expansion of high and intermediate alumina castables before and after exposure to the saturated DOE atmosphere (231°C) is shown in Figs. 2 and 3. After exposure, a sudden expansion was observed between 500°C and 600°C which varied in magnitude for different castables, being generally smaller in the intermediate alumina castables than in the high alumina castables.

After exposure to the unsaturated DOE atmosphere (538°C), high and intermediate alumina castables showed similar thermal expansion hysteresis, the expansion being almost linear up to 800°C. Above 800°C, the expansion increased but was less pronounced than in the castables exposed to the saturated atmosphere.

The insulating castables exposed to the saturated DOE atmosphere generally showed very distinct changes in the expansion rate during heating from 25 to 950°C, as illustrated in Fig. 4. Specimens exposed to the unsaturated atmosphere had comparatively smooth expansion curves.

6. Chemical Reactions

a. General

The crystalline compounds identified by XRD in each refractory prior to exposure are summarized in Table VII. Only minor or trace amounts of the calcium aluminate compounds (CA, CA₂) and hydrated

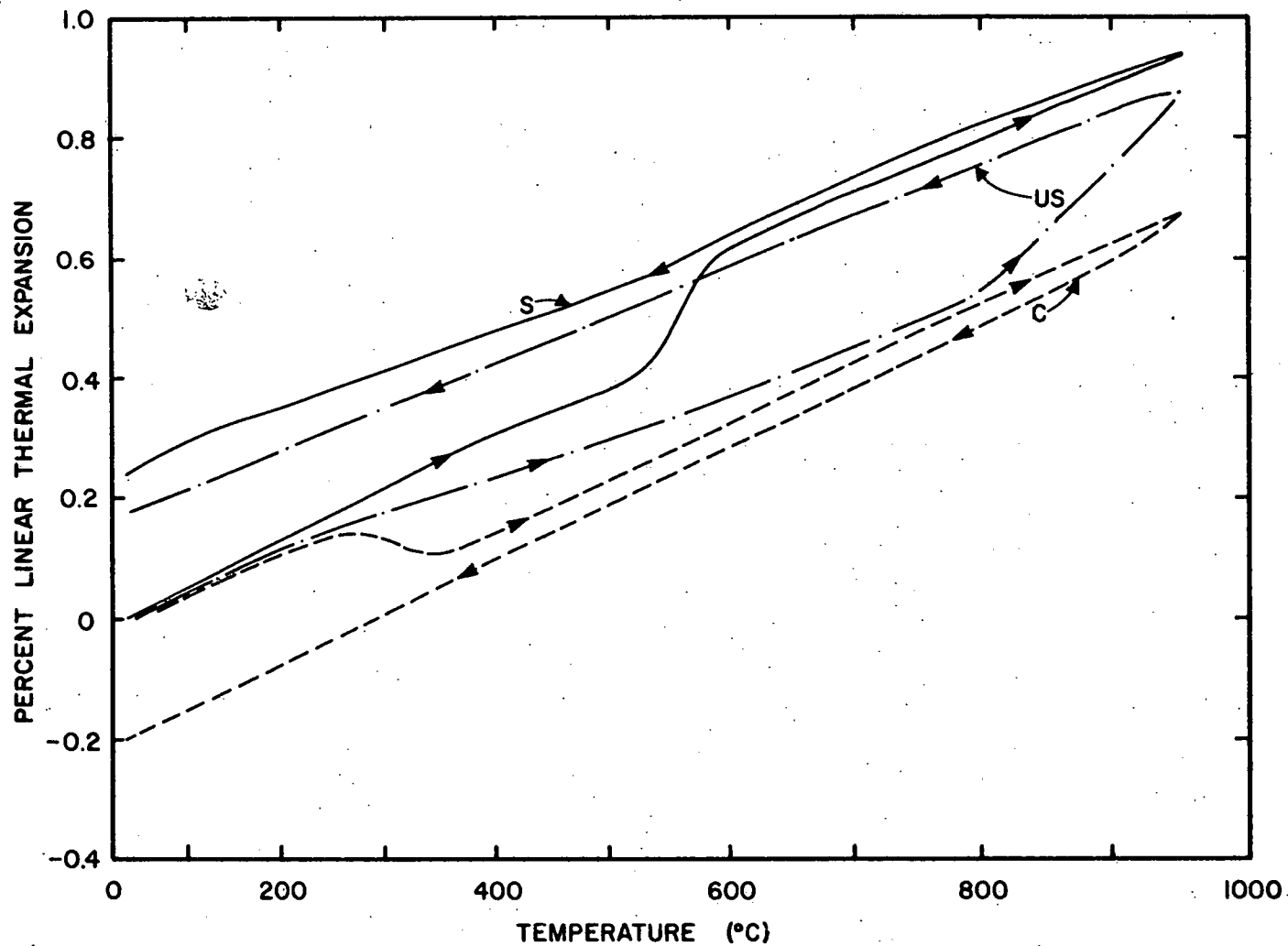


Fig. 2. Typical thermal expansion curves for high alumina castable, UMR-1.
 C -Control (as-cast and dried)
 S -After exposure to saturated DOE atmosphere at 6.9 MPa/ 231°C.
 US -After exposure to unsaturated DOE atmosphere at 6.9 MPa/538°C.

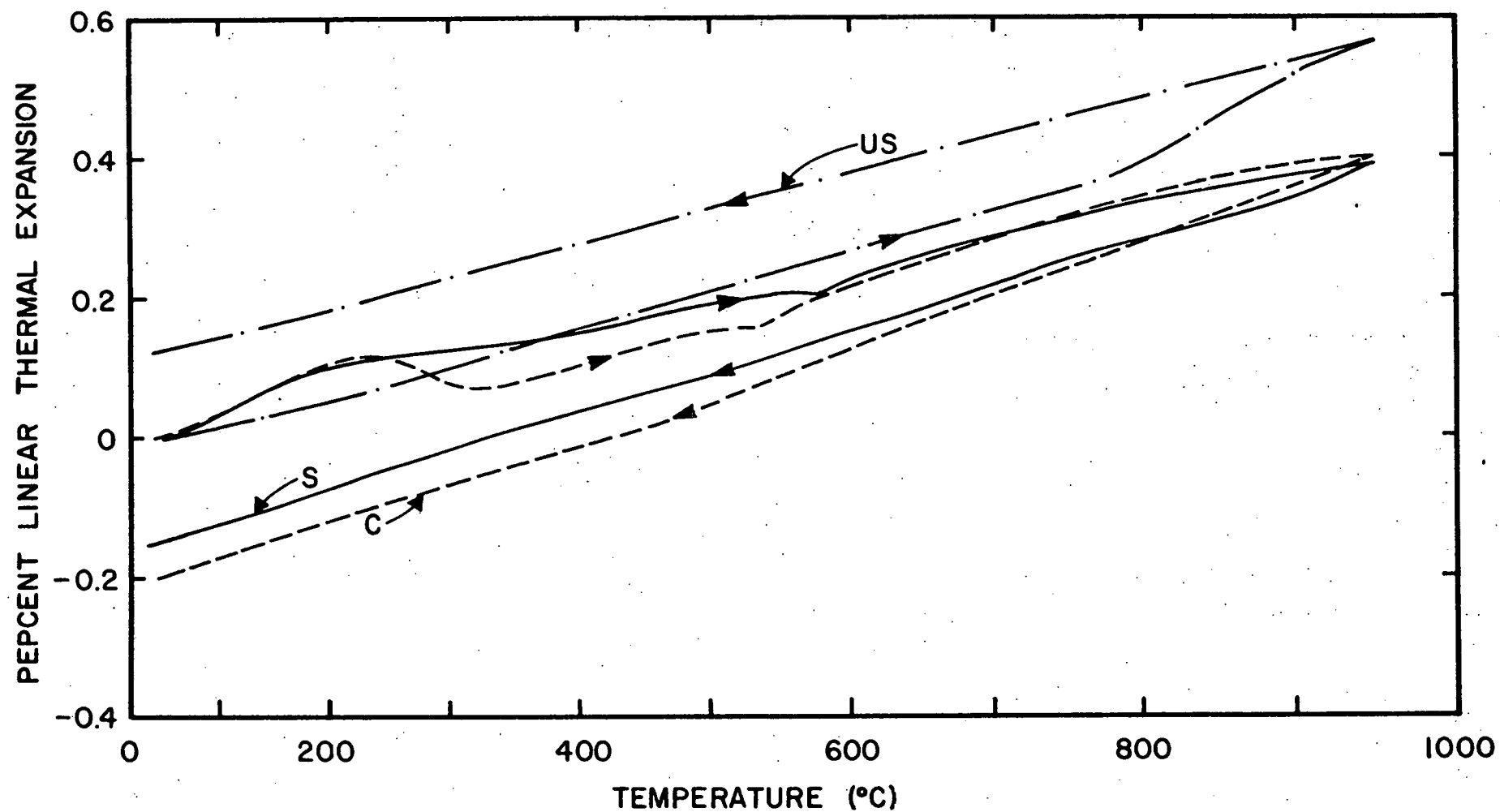


Fig. 3. Typical thermal expansion curves for intermediate alumina castable, CC-6.
 C - Control (as-cast and dried)
 S - After exposure to saturated DOE atmosphere at 6.9 MPa/231°C.
 US- After exposure to unsaturated DOE atmosphere at 6.9 MPa/538°C.

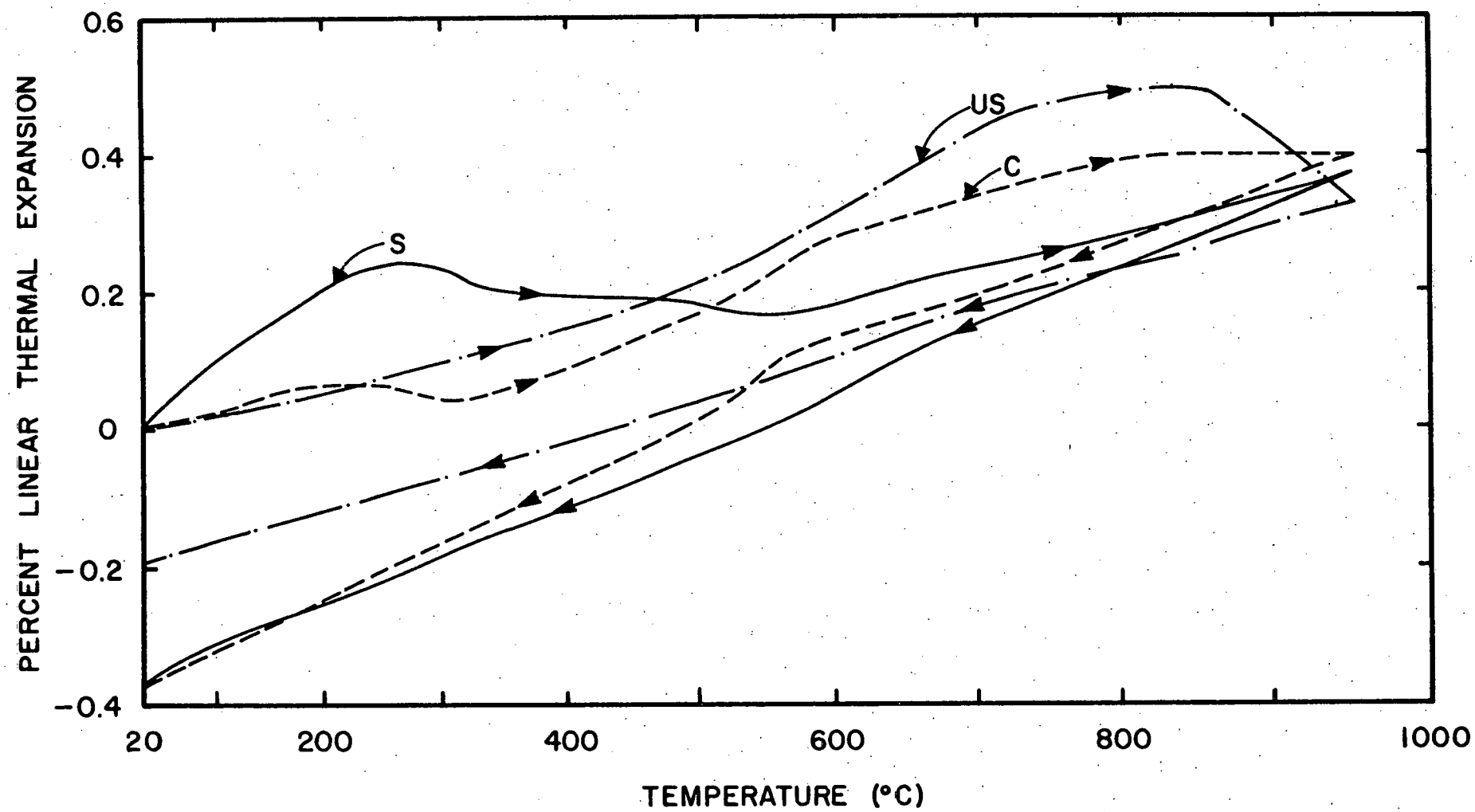


Fig. 4. Typical thermal expansion curves for insulating castable, CC-8.
 C - Control (as-cast and dried)
 S - After exposure to saturated DOE atmosphere at 6.9 MPa/231°C.
 US- After exposure to unsaturated DOE atmosphere at 6.9 MPa/538°C.

Table VII. Compounds* Initially Present in Castables (As-Cast and Dried at 110°C) and Ramming Mixes (As-fired at 538°C in Air) Prior to Exposure.

<u>Refractory</u>	<u>Compounds</u>
Dense, High Alumina Castables	
CC-1	α -Alumina, $C_3AH_6^{**}(\text{tr}^S)$, $AH_3(\text{tr})$, $CA(\text{tr})$
CC-2	α -Alumina, CA_2
CC-3	α -Alumina, CA
CC-4	α -Alumina, CA
UMR-1	α -Alumina, CA
UMR-2	α -Alumina, CA , $C_3AH_6(\text{tr})$, $AH_3(\text{tr})$
UMR-3	α -Alumina, CA_2
Dense, Intermediate Alumina Castables	
CC-5	Mullite, β -Cristoballite, α -Alumina, CA
CC-6	Mullite, β -Cristoballite, α -Alumina, CA
Insulating Castables	
CC-7	Kyanite, Mullite, α -Quartz, β -Cristoballite, α -Alumina, CA
CC-8	α -Quartz, Kyanite, α -Alumina, CA
Phosphate-Bonded Ramming Mixes	
CPRM-1	α -Alumina, $AlPO_4$ (Orthorhombic and trigonal, tr)
CPRM-2	α -Alumina, $AlPO_4$ (Orthorhombic, tr)
CPRM-3	α -Alumina, $AlPO_4$ (Trigonal, tr)

* Listed in order of decreasing concentration as estimated from XRD peak intensity.

** Cement Chemistry Notation; C = CaO, A = Al_2O_3 , H = H_2O
 str represents trace amount

Table VIII. Weight Percent CaCO_3 and Boehmite Determined by TGA
 After a 30-day Exposure to DOE Atmosphere at 6.9 MPa
 (1000 psia) and 231 or 538°C.

	% CaCO_3		%CaO**		%CaO	% Boehmite***
	231°C	538°C	231°C	538°C	As-Received	231°C
CC-1	5.5*/5.0*	6.8/7.3	3.3/3.0	3.9/4.3	4.5	22.3/22.8
CC-2	5.9/5.4	6.4/6.4	3.3/3.2	3.7/3.7	6.0	20.3/19.2
CC-3	nt/3.8	6.4/6.9	nt/2.3	3.7/4.0	5.6	nt ^{xx} /23.2
CC-4	3.5/3.6	7.6/8.4	2.1/2.2	4.5/4.9	5.4	23.9/32.4
UMR-1	5.2/5.1	8.0/7.8	3.1/3.1	4.7/4.5	5.4	29.1/29.1
UMR-2	nt/5.2	10.1/10.9	nt/3.2	6.0/6.5	7.8	nt/37.3
UMR-3	8.8/4.7	7.7/6.1	5.3/2.8	4.5/3.5	7.4	27.9/27.2
CC-5	2.7/4.3	3.1/2.4	1.6/2.5	1.8/1.4	5.0	8.2/13.3
CC-6	4.1/4.7	4.4/4.4	2.4/2.8	2.6/2.5	5.5	13.5/15.4
CC-7	1.5/2.6	3.4/3.2	0.9/1.5	1.9/1.8	4.5	11.5/11.9
CC-8	2.8/3.3	2.2/1.9	1.7/2.0	1.3/1.1	2.9	9.1/6.4

*First number is for no H_2S present while second number is for DOE atmosphere containing 1 Vol% H_2S .

**Calculated from wt% CaCO_3 as determined from TGA.

***No boehmite present at 538°C.

^{xx}nt = not determined.

phases (C_3AH_6 or AH_3) were found in the cement-bonded castables. The only bond phase identified in the phosphate-bonded refractories was $AlPO_4$, either orthorhombic or trigonal (berlinite).

b. Cement-Bonded Castables

XRD analysis of the cement-bonded castables showed that all of the CA , C_3AH_6 , and AH_3 had disappeared (reacted) in both the saturated ($231^\circ C$) and unsaturated ($538^\circ C$) atmosphere in ~ 10 days, the shortest time investigated. No evidence was found for any significant reaction involving the alumina, aluminosilicate (mullite, kyanite), or silica (quartz, cristobalite) aggregate in the cement-bonded castables, the intensity of the XRD peaks for these compounds being essentially unchanged after exposure.

The major new compounds formed in the cement-bonded castables after exposure to the saturated atmosphere were boehmite (AH) and $CaCO_3$ (calcite or aragonite) as determined by XRD and DTA/TGA. Only $CaCO_3$, mostly present as calcite, but in some cases as aragonite, was detected in the castables exposed at $538^\circ C$. These results agree with other investigations⁽¹⁰⁻¹²⁾ where boehmite and $CaCO_3$ have been found in cement-bonded castables exposed to saturated steam- CO atmospheres.

In addition to the reaction of the calcium aluminate cement-bond phases to form $CaCO_3$ and boehmite, some portion of the CaO is dissolved from the refractories during exposure to the saturated atmosphere particularly. In all cases, the percent CaO in the castables after exposure, as calculated from the quantity of $CaCO_3$ present is less than the amount initially present, Table VIII. This is especially true for the castables exposed to the saturated atmosphere at $231^\circ C$. This

difference could be explained by some of the CaO not reacting to form CaCO_3 , but additional evidence of the removal of CaO from the castables during exposure to the saturated atmosphere was the higher calcium concentration in the water remaining in the vessel at the completion of the exposure. The distilled water used initially contained <1 ppm Ca, but at the completion of the exposure the Ca concentration had increased to 5000 ppm Ca.

c. Phosphate Bonded Ramming Mixes

The main change found by XRD in the phosphate-bonded refractories after exposure to the unsaturated (538°C) atmosphere was an increase in the amount of trigonal AlPO_4 present in CPRM-1 and 3, although trace quantities of orthorhombic AlPO_4 remained after exposure. Only a trace of trigonal AlPO_4 was detected in CPRM-2 after exposure, the AlPO_4 being present in the orthorhombic form as before exposure, Table VII. No new compounds were detected by XRD or DTA/TGA.

After exposure to the saturated atmosphere, the estimated amount of trigonal AlPO_4 was considerably lower in CPRM-1, but about the same in CPRM-3. No AlPO_4 in either form was detected by XRD in CPRM-2. A new compound tentatively identified as $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}^*$ was found in all three refractories. This compound probably results from the phosphate-bonded refractories coming in contact with the CaO dissolved from the cement-bonded castables since both groups of refractories were exposed simultaneously in the same vessel and the CaO content of the phosphate-bonded refractories is quite low, Table I.

*ASTM Index Card #12-27.

The XRD intensity of the $\alpha\text{-Al}_2\text{O}_3$ peaks in the phosphate refractories was essentially unchanged after exposure indicating that the alumina grog did not react to any detectable extent, as found for the cement-bonded castables. However, during exposure to the saturated atmosphere some unknown portion of the phosphate bond appears to have been dissolved from these refractories since fairly large quantities of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ were found in the bottom of the steam vessel at the completion of the exposure and the water recovered contained about $\sim 5\text{ppm } (\text{PO}_4)^{-3}$.

7. Discussion

The 30-day exposure time is only a small fraction of the desired service-life for a refractory lining in a coal gasifier, but it is important to note that none of the refractories disintegrated or were otherwise totally destroyed. The loss of CaO from the cement-bonded castables and the major reduction in strength for the phosphate-bonded refractories in the saturated atmosphere could be potentially detrimental to the long-term (months to years) service performance. Other than the phosphate bonded refractories in saturated atmospheres, no reactions occurring in short times have been found which render these commercial refractories totally unsatisfactory for use in a coal gasifier.

In general, cement-bonded castables of the same type, but made by different manufacturers showed essentially the same behavior after exposure. Similarly, the results for the commercial and laboratory-prepared castables were in good agreement, indicating that investigations utilizing the latter can provide a reliable indication of the performance of commercial products. In the phosphate-bonded refractories larger differences, primarily in MOR, were found for similar products made by different (three) manufacturers.

The most significant change in properties of the cement-bonded castables was the increase in flexural strength and reduction in porosity found for most of the dense high and intermediate alumina castables after exposure to the saturated atmosphere. These changes are consistent with the chemical reactions described previously. The increase in MOR is attributed to the boehmite formed during exposure since, in a general way, the increase in MOR usually corresponded to the quantity of boehmite present. Furthermore, previous work^(13,14) has demonstrated that boehmite formed by autoclaving alumina bodies in steam, without cement, can provide substantial bonding; MOR's of 5-7 MPa were reported. An increase in MOR has also been attributed⁽¹⁵⁾ to the formation of CAS_2 (anorthite) in similar intermediate alumina castables exposed to high pressure steam. However, no XRD evidence of CAS_2 was found in the CC-5 and -6 intermediate alumina castables in the present investigation after exposure, but in Task VII, a calcium aluminosilicate compound was found by EDAX analysis of a similar castable (UMR-8).

The reduction in porosity can also be explained by the formation of CaCO_3 and boehmite within the pores of the castables. Since the specific volume of boehmite is larger than that of alumina and the external dimensional changes of these castables were small, $\leq 1\%$, it appears that the volume increase associated with boehmite formation is accommodated within the original pore volume of the castables, thereby lowering the porosity.

The sudden expansion between 500°C and 600°C in the thermal expansion curves of castables exposed to the saturated atmosphere (231°C) is

due to the dehydration of boehmite which occurs in this temperature range. The magnitude of this expansion generally corresponded to the quantity of boehmite and was absent in specimens exposed to the unsaturated atmosphere (538°C) which did not contain boehmite. The expansion above 800°C appears to be associated with the decomposition of calcite.

The significant reduction in strength of the phosphate-bonded refractories after exposure to the saturated atmosphere is attributed to a general corrosion of the AlPO_4 bond phase by saturated steam. The sensitivity of the phosphate bond phase(s) to saturated steam can be expected to vary widely with the crystallinity and composition of the bond phase, i.e., the temperature to which such a refractory is fired prior to exposure to saturated steam. Well crystallized (high fired) AlPO_4 powder has been reported⁽¹¹⁾ to show no evidence of reaction with steam in a saturated steam (47.5%)-CO (52.5%) atmosphere at 3.2 MPa/199°C.

Finally, it is important to mention all of the chemical reactions identified were between the refractory bond phases, cement or phosphate, and steam, CO, or CO_2 . No evidence was found for any significant reaction with other gases (H_2 , CH_4 , H_2S) or with the pure alumina or siliceous aggregates, such as silica volatilization by H_2 or dissolution by steam. At higher temperatures reactions involving siliceous aggregates become more likely⁽¹⁶⁾ but, for the conditions in this investigation, the chemical reactions were basically confined to the refractory bond phases.

The reader is referred to Ref. 17 for additional details.

C. Task III- Exposure Time

Several of the same commercial and experimental cement and phosphate-bonded refractories used in Task II were investigated at the same conditions

used for the 30-day screening exposure, but for periods of time between 10 and 60 days (Exp. 15-18, 21-23 in Table II). The purpose was to determine how the structural integrity, properties, and the chemical reactions found in these refractories varied with exposure time, up to 60 days.

The dimensional changes for all the refractories were small, $\leq 1\%$, and were essentially independent of exposure time between 10 and 60 days. The weight changes at 60 days were generally similar to those found in Task II at 30 days. The porosity after exposure to the unsaturated DOE atmosphere (538°C) was about the same as that after firing in air at 538°C, was similar to that found previously in Task II for the respective refractories, and was essentially independent of exposure time, Table IX. After exposure to the 100% saturated atmosphere for 30 days at 231°C, the porosity of the castables was generally less than that of the controls fired in air or after exposure at 538°C, except UMR-3. This agreed with similar decreases in porosity reported in Task II for this saturated atmosphere. After 60 days at 231°C, the porosity was consistently higher than at 30 days suggesting an increase in porosity with exposure time when the refractories are exposed to saturated vapor.

The change in porosity of the phosphate-bonded refractories after exposure at 538°C or 231°C was small and independent of exposure time.

Table X gives the MOR values for refractories used in Task III. The MOR after exposure at 538°C was essentially constant between 10-30 days and comparable with the controls, but was generally somewhat larger after 60 days at 371°C, Fig. 5. In the 100% saturated atmosphere, the MOR of the high and intermediate alumina castables more than doubled

Table IX. Percent Apparent Porosity After Firing in Air or Exposure to DOE Atmosphere With 1 Vol% H₂S at 6.9 MPa (1000 psia).

Refractories	Controls fired in air			Exposure Temperature and Time					
	110°C, 24 h	260°C, 18 h	538°C, 18 h	538°C			371°C, 13.3% Sat. 60 days	231°C, 100% Saturated 30 days	231°C, 100% Saturated 60 days
				10 days	20 days	30 days			
<u>Dense High Alumina Castables</u>									
CC-1	14.2	20.0	23.3	23.8	24.1	23.7	25.9	15.5	23.1
UMR-1	16.1	20.1	22.9	26.2	24.8	23.5	26.8	15.3	20.7
UMR-2	15.6	24.1	27.8	26.9	26.3	26.8	28.7	17.8	23.4
UMR-3	23.3	25.1	31.2	30.7	30.8	30.7	31.1	28.2	32.4
<u>Dense, Intermediate Alumina Castable</u>									
CC-6	16.1	18.7	22.8	22.5	22.1	22.3	19.8	16.7	19.3
<u>Insulating Castable</u>									
CC-8	38.8	41.0	42.3	50.9	50.6	51.4	52.0	45.4	50.1
<u>Phosphate-bonded Ramming Mixes</u>									
CPRM-1	nt	nt	17.3	20.4	19.7	20.1	nt	20.6	21.2
CPRM-2	nt	nt	19.8	19.7	19.4	19.4	nt	18.7	nt
CPRM-3	nt	nt	16.3	16.8	16.2	17.5	nt	18.5	22.1

Table X. Modulus of Rupture (MPa*) After Firing in Air or Exposure to DOE Atmosphere
With 1 Vol% H₂S at 6.9 MPa (1000 psia).

Refractories	Controls fired in air			Exposure Temperature and Time					
	110°C, 24 h	260°C, 18 h	538°C, 18 h	538°C			371°C 13.3% Sat. 60 days	231°C, 100% Saturated 30 days	231°C, 100% Saturated 60 days
				10 days	20 days	30 days			
<u>Dense High Alumina Castables</u>									
CC-1	19.8±2.0**	13.4±0.9	13.0±0.4	8.6±0.8	7.6±0.4	8.3±0.9	8.5±0.5	24.4±2.6	19.2±3.4
UMR-1	19.7±1.3	15.3±1.5	15.2±1.0	11.9±0.7	12.1±0.7	13.9±1.1	12.1±1.3	33.6±1.4	31.8±6.1
UMR-2	20.2±2.3	8.4±1.1	12.5±2.0	7.8±1.0	6.1±1.3	7.1±0.9	10.9±0.7	27.9±3.9	24.8±3.8
UMR-3	16.3±2.1	11.7±2.1	6.7±1.6	8.9±1.2	8.9±1.1	9.7±0.7	14.6±1.0	14.6±1.7	11.5±2.5
<u>Dense, Intermediate Alumina Castable</u>									
CC-6	15.2±1.7	10.8±1.6	9.6±0.7	15.5±1.5	14.8±1.0	16.1±1.3	24.5±2.5	27.0±2.7	24.6±2.9
<u>Insulating Castable</u>									
CC-8	6.7±0.8	5.4±0.6	6.5±3.1	6.0±0.3	6.2±0.4	6.2±0.4	7.2±0.8	3.9±0.5	3.3±1.1
<u>Phosphate-bonded Ramming Mixes</u>									
CPRM-1	nt	nt	27.0±2.2	16.2±1.7	15.0±2.1	15.4±2.9	nt	7.6±0.8	11.0±1.8
CPRM-2	nt	nt	23.5±1.7	16.6±3.0	16.8±1.8	16.6±2.2	nt	4.2±0.9	nt
CPRM-3	nt	nt	18.3±4.1	15.1±2.3	15.4±2.8	14.6±1.4	nt	6.2±2.2	10.5±1.1

*1 MPa = 145 psi.

**The ± limit corresponds to one standard deviation.

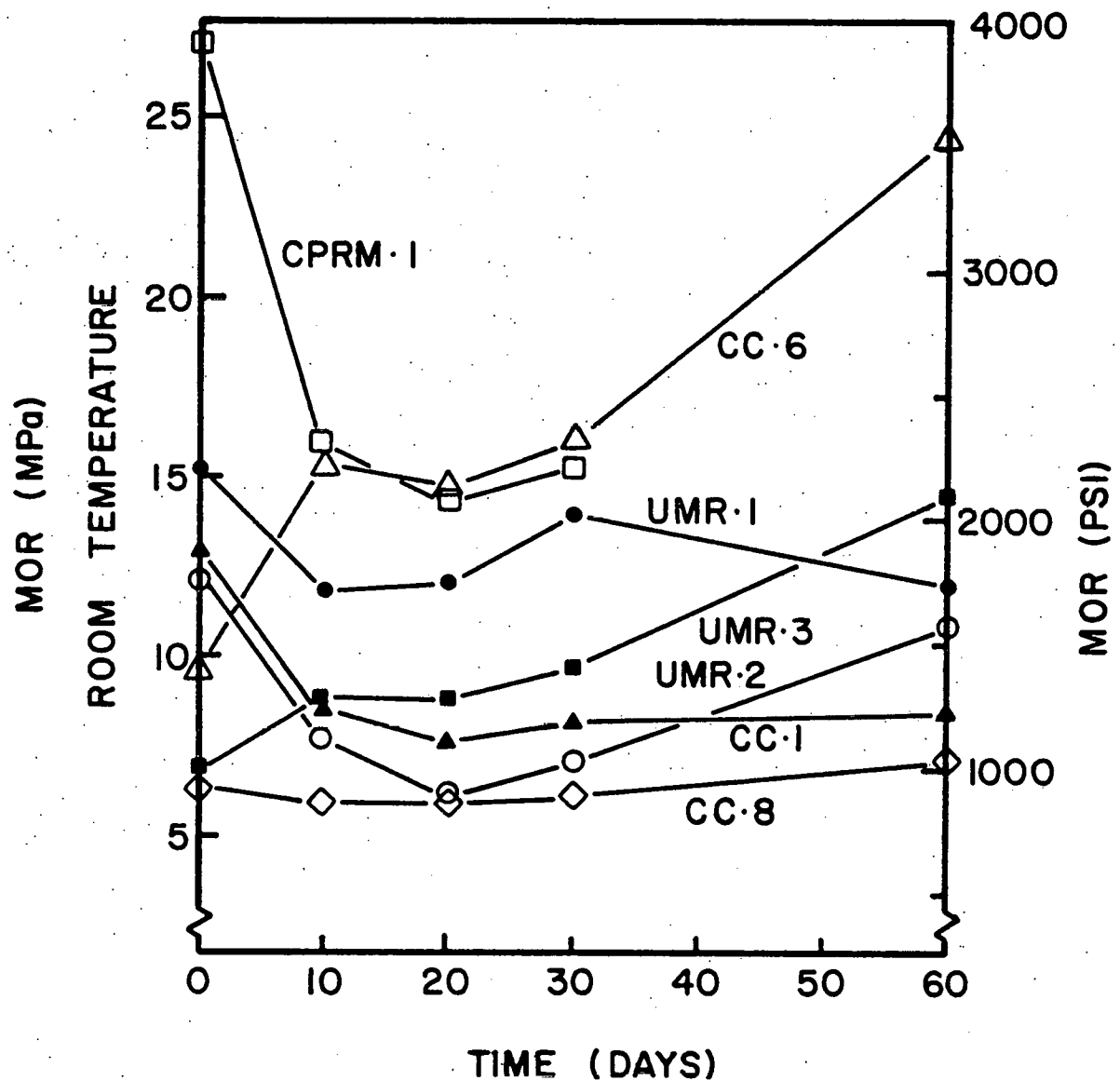


Fig. 5. Room temperature modulus of rupture after exposure. 10-, 20-, and 30-day data are for exposure to DOE (with 1% H₂S) at 6.9 MPa/538°C while 60-day data are for exposure to same atmosphere at 6.9 MPa/371°C (13.3% saturated). MOR for controls (no exposure) is after firing in air at 538°C.

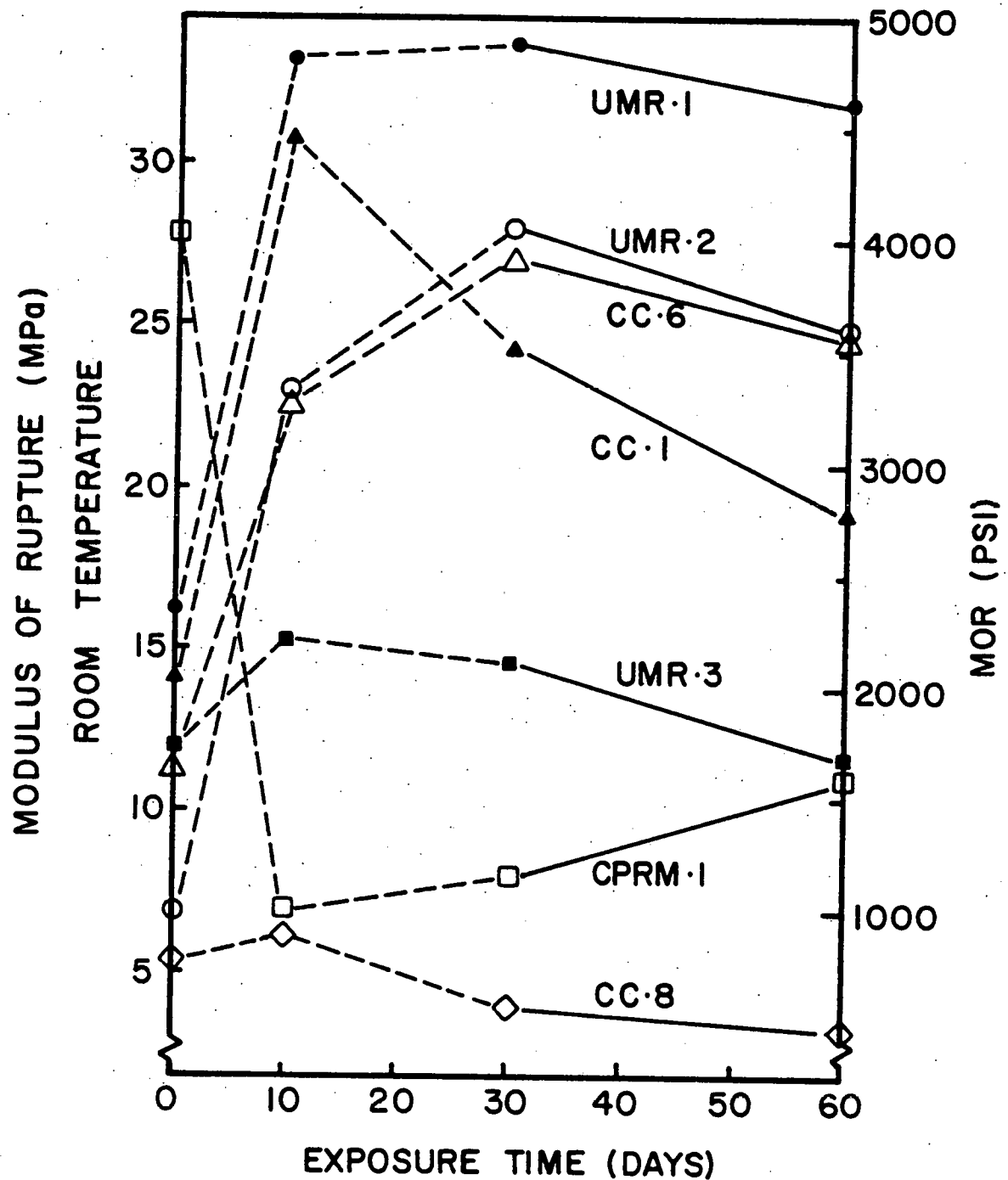


Fig. 6. Room temperature modulus of rupture after exposure. 30- and 60-day data are for exposure to 100% saturated DOE (with 1% H_2S) at 6.9 MPa/231°C while 10-day data are for exposure to 100% saturated $CO/H_2O = 1.1$ atmosphere at 3.2 MPa/199°C (Exp. #24).

Table XI. Weight Percent of CaCO_3 and Boehmite in Castables After Exposure to DOE Atmosphere at 6.9 MPa (1000 psia) - as determined by TGA.

Refractories	Exposure Temperature and Time								
	%CaCO ₃ , 538°C*			371°C, 13.3% saturated		231°C, 100% Saturated			
	10 days	20 days	30 days	60 days		30 days	60 days	30 days	60 days
				%CaCO ₃	%Boehmite				
				%CaCO ₃	%Boehmite				
Dense High Alumina Castables									
CC-1	6.8	6.8	7.3	7.7	0.0	5.0	22.8	5.8	25.0
UMR-1	7.5	9.4	7.8	8.3	0.0	5.1	29.1	5.7	32.0
UMR-2	9.9	10.8	10.9	11.6	4.7	5.2	37.3	9.0	34.5
UMR-3	4.1	5.5	6.1	9.3	5.3	4.7	27.2	9.1	26.5
Dense, Intermediate Alumina Castable									
CC-6	3.9	5.0	4.4	7.1	7.3	4.7	15.4	4.4	18.1
Insulating Castable									
CC-8	1.7	2.2	1.9	3.2	4.9	3.3	6.4	3.8	3.1

*No boehmite present at 538°C.

in some cases, Fig. 6. The MOR of phosphate-bonded specimens (e.g., CPRM-1) was significantly lower than the controls and the MOR of the insulating castables (e.g., CC-8) remained almost unchanged. Increasing the exposure time from 30 to 60 days in the saturated atmosphere did not produce any major change in MOR, excepting CC-1.

The present results, like those of other similar studies^(8,10-12), show the most pronounced changes in properties occur within the first few days of exposure, ~6-10, and the changes thereafter are relatively small for the conditions investigated. This point is illustrated in Figs. 5 and 6 where the MOR at 30 and 60 days is generally similar and about the same as that at 10 days. There are a few exceptions to this generalization such as CC-1 in Fig. 6 where the MOR at 60 days is lower. Similarly CC-6, UMR-2, and UMR-3 in Fig. 5 have a higher MOR at 60 days but this is due to the difference in the 60 day exposure conditions, higher saturation which caused boehmite to form in these samples, but was absent in the 10-30 day samples.

Overall, the results indicate that after a relatively short period of ~10 days, the exposure time is not an important factor affecting the properties measured in this study. This is not unexpected since the chemical reactions which are responsible for the property changes, particularly boehmite formation, are also fairly rapid and appear close to completion after ~10 days; note the small changes in the % CaCO_3 and % boehmite found for the exposure times in Table XI. While the possibility of some slower chemical reactions, that might not become evident until much longer exposure times, cannot be totally excluded,

no reactions were observed at 60 days which were different or had not already been detected at 10 or 30 days.

The reader is referred to Ref. 18 for more detailed information on the effect of exposure time.

D. Task IV- CO/Steam Ratio

The results of Tasks II and III as well as other investigations⁽¹⁰⁻¹²⁾ indicate that CO and steam are the most important chemically reactive gas species at temperatures and pressures below 538°C and 6.9 MPa, respectively. The purpose of this task, therefore, was to investigate the effect of various CO-steam compositions. Twenty day exposure tests were made at 6.9 MPa for CO/steam ratios 0.1, 1, and 3 containing 1 vol% H₂S in both the 100% saturated and unsaturated atmosphere (exposures 27-35, Table II). These ratios basically cover those for low to high BTU gasification processes. The results were compared with those of previous exposures in the DOE atmosphere and also with the results of another exposure in CO/H₂O = 1.1 atmosphere with no H₂S at 3.2 MPa pressure and 199°C (saturated), 260°C and 538°C (unsaturated) temperatures (exposures 24-26).

Two new refractory compositions containing 5 and 10% SiO₂ additions were investigated. They are designated UMR-6 and UMR-7 and were basically 95% UMR-1 + 5% SiO₂ and 90% UMR-1 + 10% SiO₂, respectively.

The dimensional changes were similar to those observed in previous exposures, generally being $\leq 1\%$. The weight changes of the cement-bonded castables at 538°C (unsaturated vapor) were also similar to those for previous exposures in the DOE atmosphere at 538°C with no significant

difference between CO/steam ratio (Table XII). In 100% saturated vapor, all samples either showed smaller weight losses or weight increases. The weight loss of the phosphate bonded refractory in the three CO/steam atmospheres was <1%.

In the three unsaturated (dry) CO/steam mixtures at 538°C, the density of the dense castables usually decreased and the porosity increased, Table XIII. These results are similar to those observed in previous exposures in the DOE atmosphere and CO-steam with no H₂S at 6.9 MPa.

Table XIV and Fig. 7 show the MOR of the refractories after exposure to the CO/steam mixtures. As found in previous DOE exposures, the strength of the high and intermediate alumina castables was usually higher after exposure to saturated atmospheres. This is attributed to the formation of boehmite during exposure. None of the refractories showed any direct dependence of strength upon the CO/steam ratio, but there were some differences in the MOR of castables depending upon composition.

Comparison of the MOR data in Table XIV and Fig. 7 for the saturated atmospheres shows that the strength of the high alumina castables containing pure calcium aluminate cements (UMR-1 and UMR-2) was lowest in the CO/steam = 3 atmosphere. This loss of strength is attributed to the removal of some portion of CaO from the cement bond phase(s) which became progressively higher with increasing CO/steam ratio. The UMR-2 samples in the saturated CO/steam = 3 vapor also contained ~5% calcium formate, Ca(HCO₂)₂.

The UMR-4 samples in the saturated CO/steam = 3 vapor showed a significant loss of strength compared to those in the saturated CO/Steam =

Table XII. Percent Weight Change* After Firing in Air or Exposure in CO/Steam Mixtures at 6.9 MPa (1000 psia) for 20 Days.

<u>Refractories</u>	<u>Controls fired in air for 18h</u>		<u>CO/H₂O = 0.1 + 1 Vol % H₂S</u>		<u>CO/H₂O = 1.0 + 1 Vol % H₂S</u>		<u>CO/H₂O = 3.0 + 1 Vol % H₂S</u>	
	<u>260°C</u>	<u>583°C</u>	<u>538°C</u>	<u>278°C Saturated</u>	<u>538°C</u>	<u>241°C Saturated</u>	<u>538°C</u>	<u>204°C Saturated</u>
<u>Dense High Alumina Castables</u>								
UMR-1	-3.2**	-5.0	-2.1	+1.9	-2.3	-2.9	-2.0	-1.0
UMR-2	-4.3	-5.0	-3.6	+2.4	-3.8	+0.7	-4.0	+1.7
UMR-4	-4.6	-5.8	-2.4	+3.0	-3.5	-0.3	-3.3	+3.8
UMR-6	-4.0	-4.4	nt	nt	-4.2	-3.2	-3.4	-0.6
UMR-7	-3.7	-4.1	nt	nt	-4.1	-0.9	-3.6	-0.5
<u>Dense Intermediate Alumina Castables</u>								
UMR-5	-4.2	-4.7	-5.0	-1.1	-4.0	-0.4	-2.7	+0.8
CC-6	-3.2	-5.0	-5.1	-2.8	-3.8	-1.3	-3.5	-0.3
<u>Insulating Castables</u>								
CC-8	-2.1	-3.5	-3.2	-0.6	-2.7	+0.5	-2.6	-0.1
CC-9	-5.4	-6.4	-6.7	-1.6	-6.2	+0.4	-6.2	+1.4
CC-10	-4.5	-5.6	-7.0	-7.7	-6.1	-6.2	-6.5	-6.6
<u>Phosphate-Bonded Ramming Mix</u>								
CPRM-1	nt	nt	-0.2	-0.7	-0.2	-0.4	-0.2	-0.4

*Referenced to as-cast and fired at 110°C weight for castables and to as-fired at 538°C weight for the ramming mix.

**Weight gain = + and weight loss = -.

Table XIII. Percent Apparent Porosity After Firing in Air or Exposure in CO/Steam Mixtures at 6.9 MPa (1000 psia) for 20 Days

<u>Refractories</u>	<u>Controls fired in air</u>			<u>CO/H₂O = 0.1 + 1 Vol% H₂S</u>		<u>CO/H₂O = 1.0 + 1 Vol% H₂S</u>		<u>CO/H₂O = 3.0 + 1 Vol% H₂S</u>	
	<u>110°C 24h</u>	<u>260°C 18h</u>	<u>538°C 18h</u>	<u>538°C</u>	<u>278°C Saturated</u>	<u>538°C</u>	<u>241°C Saturated</u>	<u>538°C</u>	<u>204°C Saturated</u>
<u>Dense High Alumina Castables</u>									
UMR-1	16.1	20.1	22.9	26.3	13.4	25.1	25.7	24.8	22.0
UMR-2	15.6	24.1	27.8	27.7	14.8	26.8	22.0	24.8	21.6
UMR-4	17.8	23.8	27.0	24.3	19.4	25.3	26.0	26.2	22.8
UMR-6	17.2	22.0	26.8	nt	nt	25.4	23.3	25.0	8.0
UMR-7	19.1	23.6	26.9	nt	nt	25.9	18.3	25.3	5.8
<u>Dense Intermediate Alumina Castables</u>									
UMR-5	11.0	16.3	18.8	22.0	15.8	18.6	17.2	18.1	13.1
CC-6	16.1	18.7	22.8	22.2	16.9	20.3	18.0	22.7	8.7
<u>Insulating Castables</u>									
CC-8	38.8	41.0	42.3	52.4	52.1	48.8	51.0	46.9	51.0
CC-9	47.8	52.8	54.4	61.0	56.0	57.9	57.0	54.8	56.2
CC-10	56.0	61.8	62.9	67.7	67.9	66.8	70.2	65.4	67.4
<u>Phosphate-Bonded Ramming Mix</u>									
CPRM-1	nt	nt	17.3	20.1	22.7	19.1	21.3	20.3	21.8

Table XIV. Room Temperature Modulus of Rupture (MPa*) After Firing in Air or Exposure to CO/Steam Mixtures at 6.9 MPa (1000 psia) for 20 Days

Refractories	<u>Controls fired in air</u>			<u>CO/H₂O = 0.1 + 1 Vol% H₂S</u>		<u>CO/H₂O = 1.0 + 1 Vol% H₂S</u>		<u>CO/H₂O = 3.0 + 1 Vol% H₂S</u>	
	<u>110°C</u>	<u>260°C</u>	<u>538°C</u>	<u>538°C</u>	<u>278°C Saturated</u>	<u>538°C</u>	<u>241°C Saturated</u>	<u>538°C</u>	<u>204°C Saturated</u>
<u>Dense High Alumina Castables</u>									
UMR-1	19.7±1.3**	15.3±1.5	15.2±1.0	10.5±0.5	32.1±2.2	12.3±0.6	20.1±2.1	11.6±1.4	22.9±2.6
UMR-2	20.2±2.3	8.4±1.1	12.5±2.0	5.7±0.6	15.8±3.9	7.2±0.7	13.8±0.5	8.2±0.9	13.3±3.9
UMR-4	15.6±1.2	11.2±1.2	10.3±0.5	15.0±1.6	16.9±2.3	12.3±1.0	21.5±4.1	14.9±1.2	9.7±2.7
UMR-6	18.2±2.3	12.0±0.7	11.2±0.6	nt	nt	17.6±2.6	22.8±2.2	18.5±1.1	27.5±3.0
UMR-7	16.9±2.4	9.9±0.9	9.2±1.1	nt	nt	17.2±2.3	24.4±2.5	15.9±1.2	27.4±2.9
<u>Dense Intermediate Alumina Castables</u>									
UMR-5	16.3±1.4	8.9±0.6	8.9±0.5	17.0±2.3	25.8±2.9	13.2±1.5	22.6±4.4	10.7±1.7	27.0±3.2
CC-6	15.2±1.7	10.8±1.6	9.6±0.7	22.5±1.7	30.8±4.4	17.0±2.8	31.8±4.3	12.2±0.8	28.0±3.9
<u>Insulating Castables</u>									
CC-8	6.7±0.8	5.4±0.6	6.5±3.1	6.8±0.6	3.4±0.5	7.0±0.3	8.5±1.1	5.5±0.3	7.6±1.2
CC-9	3.0±0.6	1.3±0.2	1.4±0.3	3.2±0.6	3.6±1.2	2.3±0.6	6.9±1.9	2.6±0.3	5.4±0.6
CC-10	1.0±0.1	0.8±0.1	0.7±0.1	0.3±0.1	0.8±0.2	0.8±0.1	2.1±0.1	0.8±0.1	1.9±0.3
<u>Phosphate-Bonded Ramming Mix</u>									
CPRM-1	nt	nt	27.0±2.5	17.0±2.5	6.3±1.5	20.1±1.3	13.2±5.0	16.8±2.7	12.1±1.6

*1 MPa = 145.04 psi.

**The ± limit corresponds to one standard deviation.

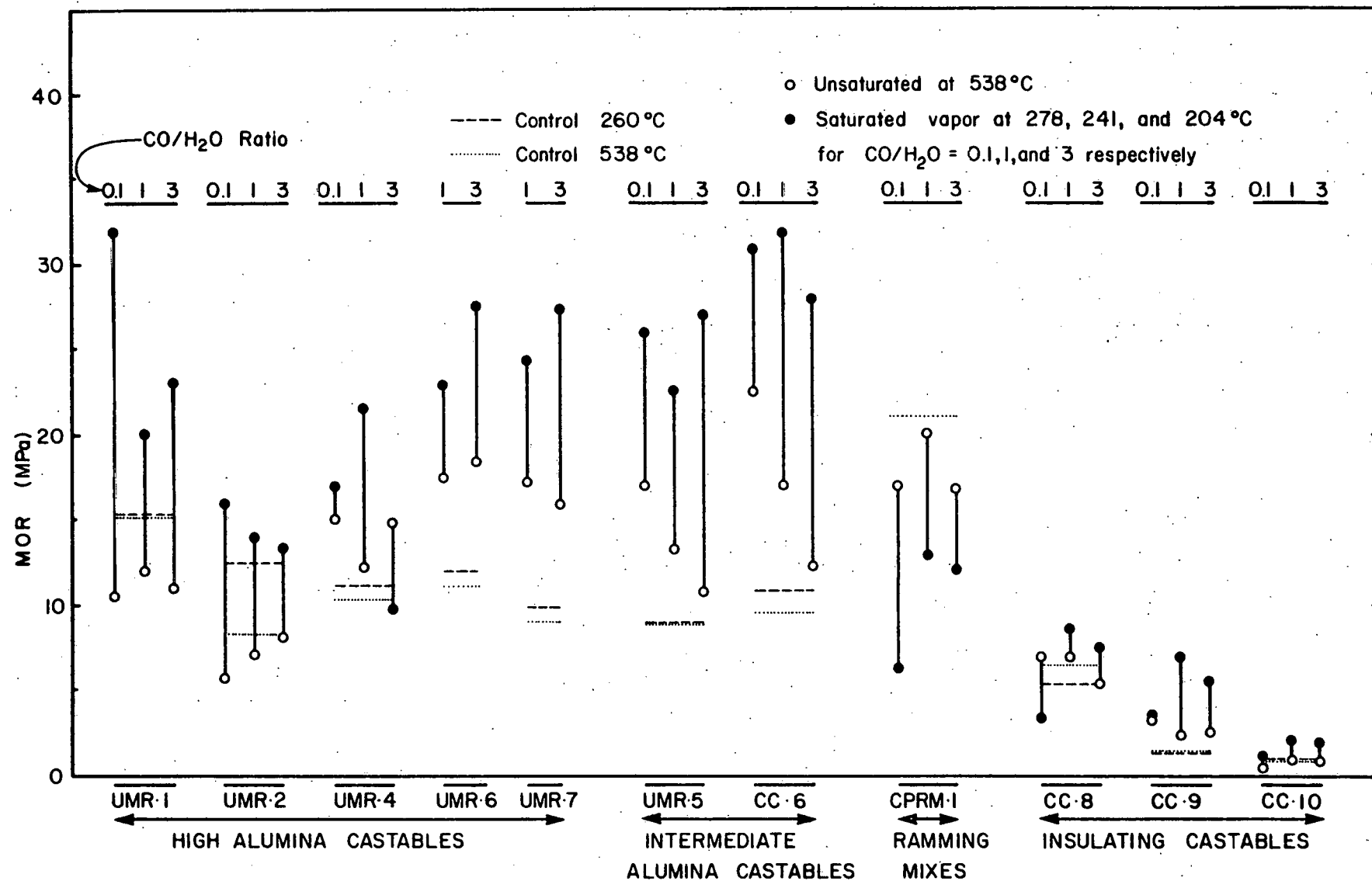


Fig. 7. Room temperature modulus of rupture of refractories after exposure to CO/H₂O = 0.1, 1 and 3 atmospheres with 1 Vol% H₂S at 6.9 MPa pressure for 20 days. Controls are for samples fired in air for 18 hours at 260 (---) and 538°C (.....).

1 and 0.1. These samples, containing Refcon cement, were severely cracked during exposure. Neat Refcon cement cubes exposed to the saturated CO/steam = 3 vapor were also heavily cracked. UMR-4 also contained trace amounts of calcium formate. These results and the higher iron content of Refcon cement (Table I) are suggestive of a CO disintegration mechanism.

A comparison of the MOR data for the UMR-6 and UMR-7 samples in Fig. 7 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/steam atmospheres (at 538°C) was always lower than the unexposed control specimens (fired to either 260 or 538°C), the addition of 5% (UMR-6) or 10% SiO_2 (UMR-7) to the silica-free UMR-1 composition resulted in the exposed specimens having a higher strength than the controls. Similarly, this same behavior where the strength of specimens exposed to the unsaturated (538°C) CO/steam mixtures is higher than controls fired in air is also observed for the other silica-containing refractories, CC-6 and UMR-5.

The presence of SiO_2 in the refractory (introduced either as a component of the refractory grain or refractory cement) is suspected as having a beneficial effect in terms of strength retention in unsaturated gases. The MOR data for UMR-6 and UMR-7, which were prepared specifically to test this suspicion, provides additional evidence that the mechanical properties of silica-containing compositions are less adversely affected by exposure to unsaturated gases than the high-purity, silica-free compositions.

The chemical reactions identified in the cement-bonded castables after exposure to CO/steam mixtures were basically the same as those in the DOE atmosphere, i.e., the formation of boehmite and calcite as the major new compounds and the solution of some portion of CaO. The CO/steam ratio does not appear to be of major importance to the refractory properties, although there is some evidence indicating that the CO disintegration reaction is favored by a high CO content as would be expected. For the CO/steam ratios likely to be present in a typical gasifier, however, there is no reason to suspect that slight to moderate changes in this ratio will have any major effect upon refractories such as those investigated.

E. Task V- Degree of Saturation

The percent saturation of the gases in a coal gasifier will vary across the refractory lining due to the temperature gradient across the lining. At the hot face, the percent saturation will be low and may approach zero depending upon the temperature, pressure, and gas composition. Closer to the cold face the degree of saturation will increase and, depending upon such factors as the thermal conductivity and thickness of the refractory, gas composition, and pressure, may approach 100% saturation. If the gasifier operating parameters and refractory design are such that the temperature at some point in the refractory lining or at the cold face is below the dew point temperature, then the refractory will be in contact with condensed liquids as well as saturated vapors.

Significant changes in properties, primarily in flexural strength, were found in the initial screening of the commercial refractories, Task II, when exposed to 100% saturated or nonsaturated (dry) gases. In dense cement bonded castables, the MOR doubled or tripled after exposure to saturated gases while the MOR of the phosphate bonded refractories decreased by a factor of 3 to 5, Tables VI and X. In the cement bonded castables this increase in MOR was attributed to the formation of boehmite (AH) which has been shown^(13,14) to provide additional bonding. Since the strength of a castable is an important factor in its erosion/abrasion resistance and ability to withstand thermal and mechanical stresses, the formation of boehmite could have practical importance to the use of such castables in coal gasifiers.

The purpose of the work in Task V, therefore, was to determine (a) the dependence of boehmite formation upon the degree of saturation, (b) the minimum saturation required for boehmite formation, and (c) the dependence of other chemical reactions upon the degree of saturation. Exposure tests 40, 41, and 42 in Table II were conducted for this purpose. Since the major chemical reactions were known to occur between the calcium aluminate cement bond phases and steam, CO, or CO₂, hydrated C-1 neat cement specimens were used for this task. Bars, 10 by 10 by 400 mm, of the hydrated neat cement (water/cement ratio of ~0.3) were cast, cured in air at 100% humidity for 24h, dried at 110°C for 24h and exposed to either the DOE atmosphere or pure steam at 6.9 MPa for 10 days using the test system and procedures described previously. The bar was contained in a horizontal pressure vessel, 450 mm long and 15 mm in

diameter, which was located in a temperature gradient furnace. The temperature gradient was controlled such that the atmosphere was 100% saturated at the ends of the pressure vessel and close to zero in the middle. After exposure, the MOR of the bar was measured at 25 mm intervals and the compounds present in every piece were determined by XRD and DTA/TGA. The results are summarized in Figs. 8 and 9 and Tables XV and XVI.

As shown in Fig. 8, the minimum percent saturation at which boehmite was detected depended primarily upon the gas composition, being ~10% saturation in the DOE atmosphere and ~20 to 30% saturation in pure steam. The maximum amount of boehmite formed also varied with the gas atmosphere, being largest in pure steam, but in both atmospheres (DOE and pure steam) the quantity of boehmite was essentially constant above ~70% saturation. The quantity of other major compounds formed in the DOE atmosphere, namely CaCO_3 and $\text{C}_4\text{A}_3\text{H}_3$, did not vary appreciably with the degree of saturation.

A general correlation exists between the MOR and the quantity of boehmite, but it is apparent from Fig. 9 that a minimum saturation of ~40% was required before any increase in MOR occurred even though boehmite forms at lower saturations. At >70% saturation, the MOR became essentially constant, as did the boehmite content. A dependence of the MOR upon the gas atmosphere is again evident from Fig. 9, the MOR being higher in the DOE atmosphere than in pure steam. The reason for the higher MOR in the DOE is not completely known, since the boehmite content is lower, but it is possible that some amount of bonding may also be provided by the CaCO_3 which forms in the DOE atmosphere. An example of

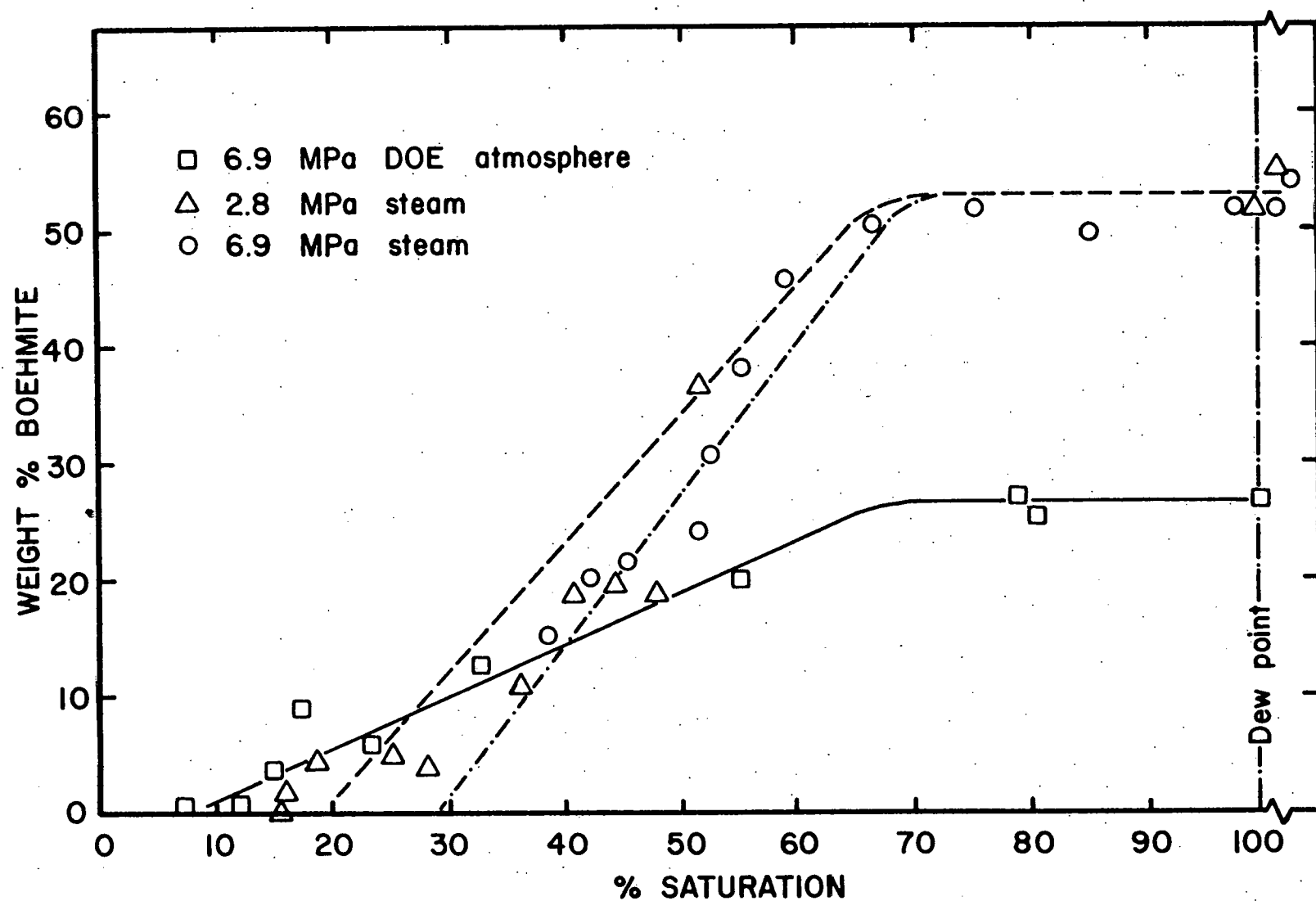


Fig. 8. Weight % boehmite as a function of the degree of saturation for C-1 neat cement exposed to DOE atmosphere and steam for 10 days.

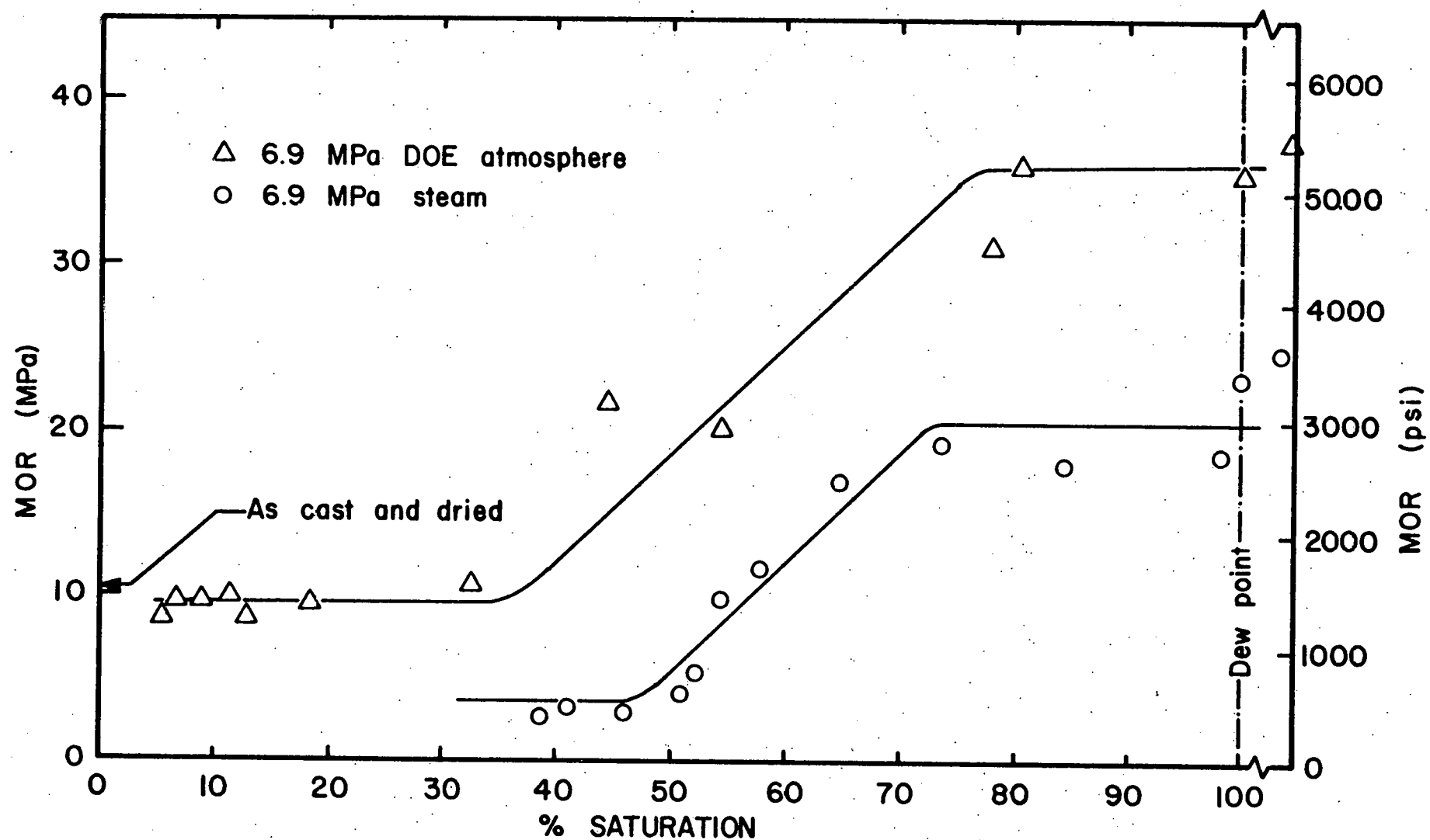


Fig. 9. Variation of modulus of rupture of hydrated C-1 neat cement exposed to DOE atmosphere and steam at 6.9 MPa for 10 days.

Table XV. MOR and Compounds Present in C-1 Cement Bar After Exposure to Steam at 6.9 MPa for 10 Days

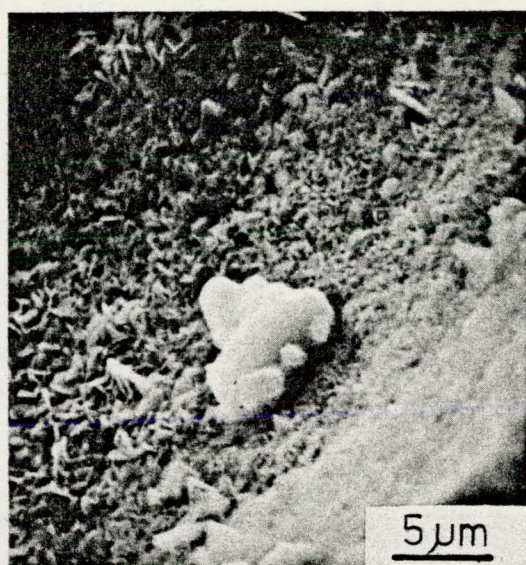
Sample No.	Temp. (°C)	% Saturation	MOR (MPa)	Compounds, Weight Percent, as Determined by TGA			Compounds Detected by XRD		
				%Wt. Loss	% Boehmite	% $C_4A_3H_3$	α - Al_2O_3	AH	$C_4A_3H_3$
1	268	Condensed Liquid	25.5	20.7	53	17.8	tr	M	m
2	281	100	26.2	13.5	50.2	37.5	tr	M	m
3	285	98	20.7	13.8	50	38	tr	M	m
4	297	85	19.3	13.6	49	38.5	tr	M	m
5	304	74	20.5	13.5	50.8	38	tr	M	m
6	314	65	17.9	13	49	39	tr	M	m
7	318	58	12.4	13	45	43	tr	M ₁	M ₂
8	327	55	11.4	16.4	32	49	tr	M ₂	M ₁
9	331	52	5.5	10	30	40	m ₂	m ₁	M
10	333	51	3.4	8.6	20.7	40	m ₁	m ₂	M
11	340	46	2.8	4.7	20	42	m ₁	m ₂	M
12	350	41	3.0	4.5	18	43	M ₁	m	M ₂
13	354	39	2.7	4.5	15	41	M	m ₂	m ₁

* M = major, m = minor, tr = trace

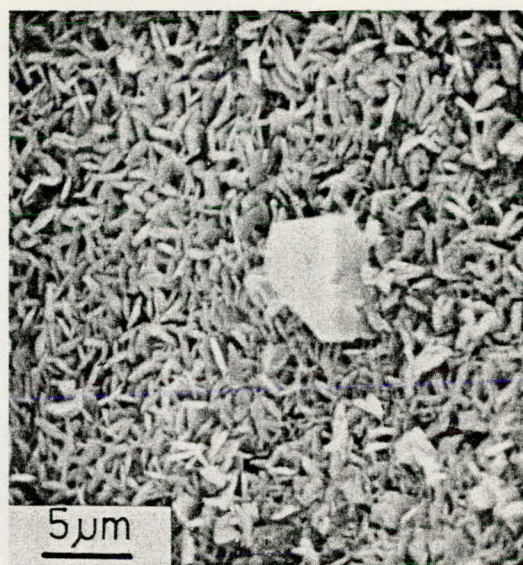
Table XVI. MOR and Compounds Present in C-1 Hydrated Cement Exposed to DOE Atmosphere at 6.9 MPa and Various Degrees of Saturation

Sample No.	Temp. (°C)	% Saturation	MOR (MPa)	Compounds, Weight Percent, as Determined by TGA				Compounds Detected by XRD			
				%wt. loss	% Boehmite	% CaCO ₃	% C ₄ A ₃ H ₃	α-Al ₂ O ₃	AH	CaCO ₃	C ₄ A ₃ H ₃
1	177	condensed liquid	37.9	19	53	23	18	tr	M	m	tr
2	230	100	34.5	14	28	10	13	m ₂	M	m ₁	tr
3	242	80	36.9	14	25	12	17	m ₂	M	m ₁	tr
4	243	79	31.4	13	23	10	12	m ₂	M	m ₁	tr
5	265	54	19.7	12	20	8	17	m ₂	M	m ₁	tr
6	277	45	22.1	13	20	14	15	m	M ₁	M ₂	tr
7	299	32	11.1	13	12	16	16	m	M ₂	M ₁	tr
8	339	19	10.0	11	11	17	18	m ₁	m ₂	M	tr
9	371	13	8.5	10	5	15	18	M ₂	m	M ₁	tr
10	382	11	10.0	10	2	15	20	M ₁	tr	M ₂	tr
11	406	9	9.1	10	--	17	30	M ₁	ud	M ₂	tr
12	458	5.5	9.0	9.5	--	19	38	M	ud	m ₁	m ₂
13	465	5	8.3	9.5	--	20	39	M	ud	m ₁	m ₂

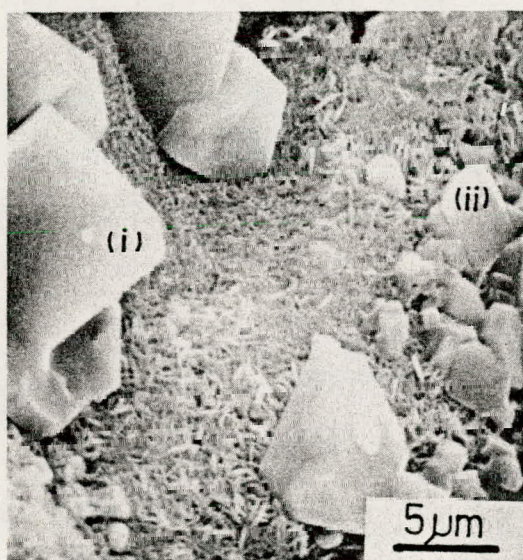
* M = major, m = minor, tr = trace, ud = undetected



a



b



c

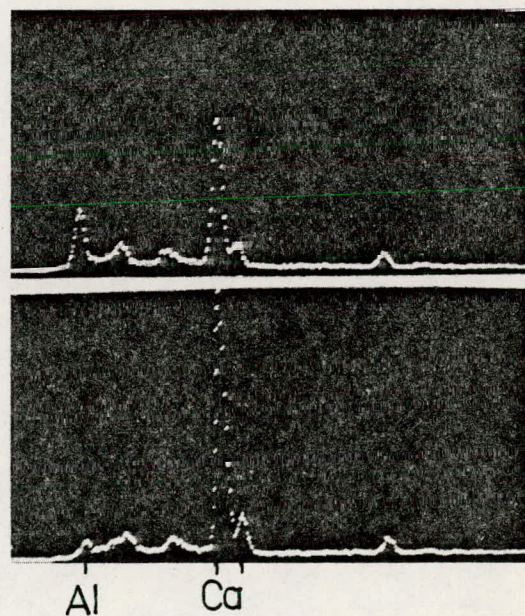


Fig. 10. Microstructure of C-1 cement exposed to DOE atmosphere for 10 days at 6.9 MPa.
 (a) General area around an internal void showing the beginning of boehmite formation, ~20% saturation. (b) Surface of a void showing boehmite crystals (matrix), ~65% saturation. (c) Inside surface of a void showing boehmite (matrix), calcite and $C_4A_3H_3$ crystals, ~100% saturation. (d) EDAX for crystal (i). (e) EDAX for crystal (ii).

the microstructure in the C-1 cement after exposure to the DOE atmosphere showing the development of boehmite, $C_4A_3H_3$, and $CaCO_3$ crystals is given in Fig. 10.

These results show that boehmite can form at ~10 to 30% saturation depending upon the gas composition, but there is no significant increase in MOR below ~40% saturation. Between 50 and 70% saturation, the MOR increases substantially (a 5 to 10 fold increase for neat C-1 cement). A minimum saturation of ~70% is needed to realize the full increase in MOR due to the additional bonding provided by boehmite, but there is no increase in MOR at higher saturations. Interestingly, the minimum saturation for maximum MOR does not appear to vary significantly with gas composition, being ~70% in both pure steam and the DOE atmosphere. From a practical standpoint, therefore, an increase in MOR can be anticipated for a cement-bonded refractory lining in a coal gasifier when the percent saturation of the atmosphere exceeds 40 to 50%.

F. Task VI- Liquid versus Vapor Contact

The results of previous Tasks showed that the calcium aluminate cement phases in refractory castables readily react with CO , CO_2 , or steam to form compounds such as boehmite, calcite, and $C_4A_3H_3$. In most instances the formation of these compounds was accompanied by a reduction in porosity and a substantial increase in flexural strength. In addition to these chemical reactions, some portion of the CaO was leached from the castable, particularly in saturated atmospheres. However, the dissolution of CaO did not appear to reduce the mechanical strength of

the castables. Nevertheless, in some instances, the loss of CaO was higher for specimens immersed in liquid compared to those in contact with vapor.

The objective of this task, therefore, was to determine the relative severity of liquid versus vapor corrosion of cement-bonded castables. The light-weight insulating castables, which because of their high porosity could be more susceptible to chemical attack, were of particular interest. Such refractory castables in coal gasifiers could be in contact with condensed liquids if the temperature at some point in the lining is below the dew point temperature of the gasifier atmosphere.

In addition to previous exposures where specimens immersed in liquid in the bottom of the steam vessel (see Table II), exposures 19, 20, and 36-39 were also conducted using seven cement-bonded castables and three calcium aluminate cements (initially dry powders and hydrated neat cement cubes). All the refractories were exposed simultaneously for 10 days to either saturated steam or the saturated DOE atmosphere. During exposure, one group of specimens (10 bars of each castable and four cubes of each hydrated cement) was totally immersed in the liquid (H_2O) in the bottom of the steam vessel. A second group (same number of specimens along with the initially dry cement powder samples) was in contact with the saturated vapor. The exposure procedure described previously was followed.

The dimensional changes ($<1\%$), density, and porosity of the castables after exposure to saturated steam or saturated DOE atmosphere were basically the same as found previously. There was no significant difference in properties of specimens exposed to either saturated vapor or immersed in liquid.

The MOR of the castables after exposure to saturated steam and the saturated DOE atmosphere was essentially independent of whether the samples were immersed in liquid or in contact with saturated vapor, Table XVII and Fig. 11. As in previous exposures, all the dense castables had a higher MOR after exposure compared to their controls, while the insulating castables showed no major change in MOR. The increase in MOR for the dense castables is attributed to the additional bonding provided primarily by boehmite which formed during exposure. As shown in Table XVIII, samples immersed in liquid or in contact with saturated vapor had essentially the same boehmite content as is consistent with their similar MOR's.

In addition to the formation of boehmite, the change in pH of the water in the exposure vessel suggests that some undetermined amount of CaO was leached from the castables during exposure. For example, for the 10-day exposure in the DOE atmosphere, the pH of the distilled water was initially 7, but within the first 24 hours of exposure increased to ~11. Over a period of ~3 days, the pH then decreased to ~5 and remained constant for the remaining 7 days of the test. This change in pH could be explained by an initial dissolution of some portion of the CaO from the cement phases (water goes basic) and the subsequent precipitation of the CaO in solution as CaCO_3 in the castables, see Fig. 12. Based upon the amount of CaCO_3 they contained, the loss of CaO was not significantly different for immersed samples from those in contact with the vapor.

A plausible sequence of reactions is as follows. Initially, some portion of the CaO dissolves from the castables immersed in water at

Table XVII. Modulus of Rupture of Specimens After Exposure to Saturated Vapor or Immersed in Liquid (number in parentheses)

Refractory	18h in air at 260°C	Saturated Steam		Saturated DOE with 1 Vol% H ₂ S			CO/Steam Mixtures, 6.9 MPa		
		2.8MPa/231°C 10 days	6.9MPa/285°C 10 days	10 days	44 days	60 days*	CO/H ₂ O = 0.1 278°C 20 days*	CO/H ₂ O = 1.0 241°C 20 days*	CO/H ₂ O = 3.0 204°C 20 days*
CC-1	13.4±0.9	nt	nt	nt	nt	19.2±3.4(22.1)	nt	nt	nt
UMR-1	15.2±1.2	29.8±2.3(26.9±2.6)	24.1±1.5(33.7±1.7)	29.5±1.8(28.3±1.6)	27.0±3.1(42.5±2.6)	31.8±6.1(35.8)	32.1±2.2(31.8)	20.1±2.1(32.5)	22.9±2.6(24.8)
UMR-2	8.4±1.1	nt	nt	nt	nt	24.8±3.8(16.7)	15.8±3.9(32.5)	13.8±0.5(26.0)	13.3±3.9(14.0)
UMR-3	11.7±2.1	nt	nt	nt	nt	11.5±2.5(13.9)	nt	nt	nt
UMR-4	11.2±1.2	16.9±1.9(14.4±1.1)	14.8±1.0(17.8±1.1)	21.9±2.9(21.8±4.2)	20.4±2.2 (nt)	nt	16.9±2.3(12.1)	21.5±4.1(24.6)	9.7±2.7(21.4)
UMR-6	12.0±0.7	nt	nt	nt	nt	nt	nt	22.8±2.2(23.0)	27.5±3.0(27.2)
UMR-7	9.9±0.9	nt	nt	nt	nt	nt	nt	24.4±2.5(15.1)	27.4±2.9(29.0)
CC-6	10.8±1.6	nt	nt	nt	nt	24.6±2.9(30.5±1.5)	30.8±4.4(27.3)	31.8±4.3(26.8)	28.0±3.9(24.6)
UMR-5	8.9±0.8	18.7±1.4(18.0±1.1)	17.5±2.0(22.1±2.4)	24.5±1.9(23.2±2.0)	23.0±3.3 (nt)	nt	25.8±2.9(nt)	22.6±4.4(25.5)	27.0±3.2(20.9)
UMR-8	12.2±1.0	29.3±1.9(28.8±5.6)	30.1±1.9(28.8±4.7)	27.7±1.9(33.7±2.4)	32.1±6.5(38.1±3.0)	nt	nt	nt	nt
CC-8	5.4±0.6	4.6±0.3(4.4±0.5)	3.5±0.3(3.3±0.7)	2.6±0.4(3.0±0.2)	5.4±0.8(10.9±0.7)	3.3±1.1(9.2±3.3)	3.4±0.5(1.7)	8.5±1.1(8.2)	7.6±1.2(9.9)
CC-9	1.3±0.2	2.6±0.4(3.0±0.3)	3.7±0.2(4.5±0.7)	5.8±0.7(5.6±0.4)	3.0±0.6 (nt)	nt	3.6±1.2(3.6)	6.9±1.9(16.1)	5.4±0.6(7.0)
CC-10	0.8±0.1	0.4±0.3(0.6±0.1)	0.7±0.2(1.3±0.1)	2.4±0.4(1.4±0.7)	1.5±0.5(4.0±0.2)	nt	0.8±0.2(1.2)	2.1±0.1(2.9)	1.9±0.3(2.7)
CPRM-1	27.0±2.5**	nt	nt	nt	nt	nt	6.3±1.5(7.4)	13.2±5.0(13.1)	12.1±1.6(10.7)

*Two immersed specimens only.

**Fired in air 18h at 538°C.

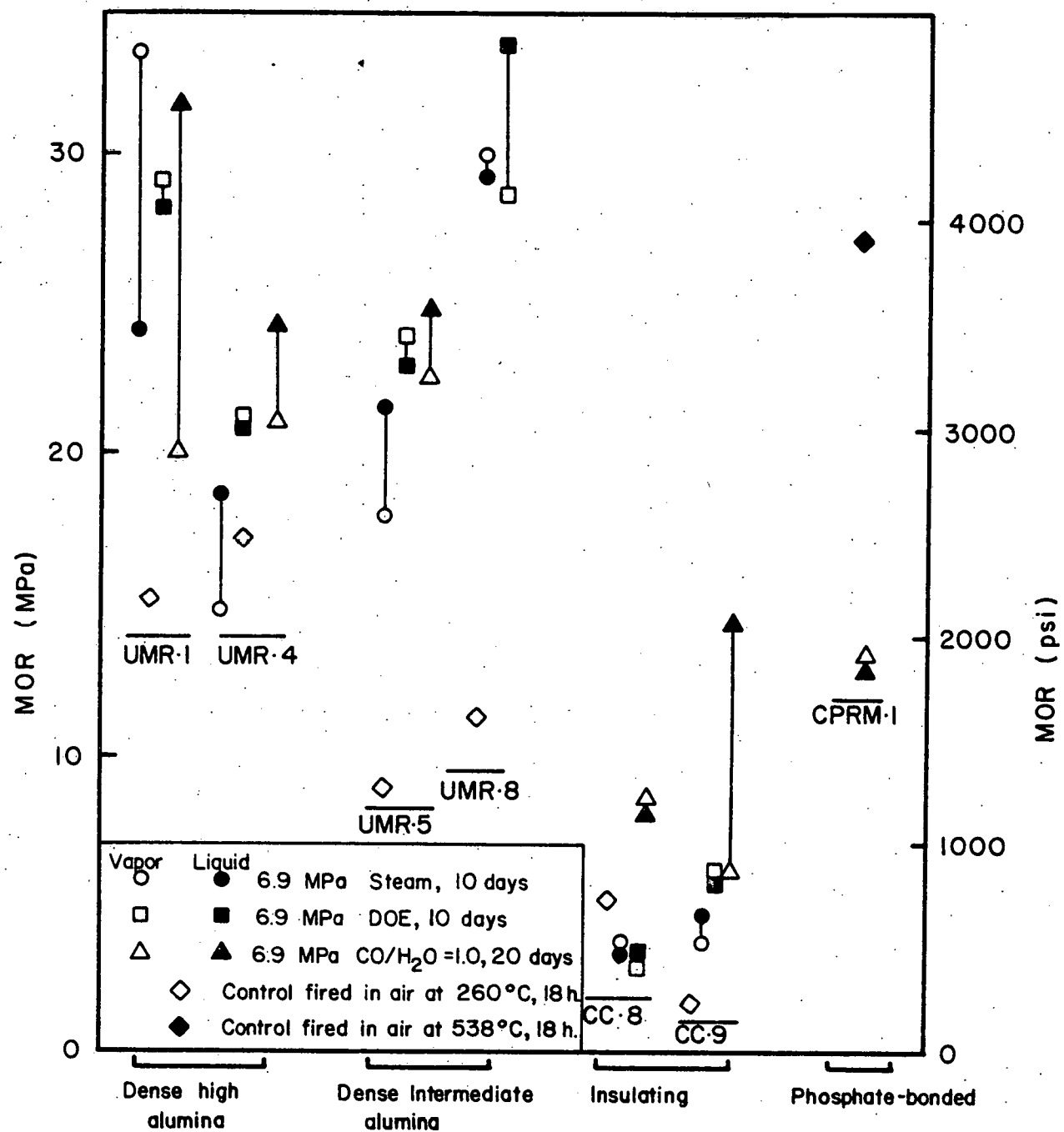


Fig. 11. Comparison of the MOR of refractories exposed to saturated vapor with those immersed in liquid.

Table XVIII. Weight Percent Boehmite After Exposure to Saturated Vapor or Immersed in Liquid (numbers in parentheses)

Refractory	Saturated Steam		Saturated DOE With 1 Vol% H ₂ S			CO/Steam Atmosphere, 6.9 MPa		
	2.83 MPa/231°C	6.9 MPa/285°C	6.9 MPa/231°C		60 days	CO/H ₂ O = 0.1	CO/H ₂ O = 1.0	CO/H ₂ O = 3.0
	10 days	10 days	10 days	44 days		278°C 20 days	241°C 20 days	204°C 20 days
CC-1	nt*	nt	nt	nt	25.0(23.8)	nt	nt	nt
UMR-1	20.2(22)	22.5(23.5)	22.3(21.8)	24.9(25.5)	32.0(29.1)	30.0(25.3)	18.6(26.1)	23.3(21.6)
UMR-2	nt	nt	nt	nt	34.5(27.3)	28.8(28.9)	25.7(27.1)	19.2(25.8)
UMR-3	nt	nt	nt	nt	26.5(26.7)	nt	nt	nt
UMR-4	15.1(14.9)	20.0(18.3)	18.4(19.6)	18.9(nt*)	nt	23.9(23.5)	16.6(18.2)	15.6(21.6)
UMR-6	nt	nt	nt	nt	nt(13.9)	nt	12.1 (nt)	9.2(16.1) 8
UMR-7	nt	nt	nt	nt	nt(12.7)	nt	10.8 (nt)	8.6(15.1)
CC-6	nt	nt	nt	nt	18.1(22.9)	13.6(18.2)	14.7(18.8)	nt(25.0)
UMR-5	8.7(10.1)	11.3(10.3)	14.6(13.2)	18.9(nt)	14.3(nt)	14.1(15.7)	10.0(23.1)	13.3(10.3)
UMR-8	9.5(11.0)	11.4(10.8)	nt	10.1(14.0)	nt	nt	nt	nt
CC-8	4.0(4.0)	3.6(6.1)	6.4(6.0)	nt	3.1(3.3)	8.3(8.7)	6.7(6.8)	5.6(8.2)
CC-9	13.5(10.1)	nt	nt	17.6(nt)	nt	21.8(nt)	14.9(17.7)	17.6(16.0)
CC-10	5.4(5.5)	8.2(9.5)	9.5(10.8)	nt	nt	10.8(nt)	nt(15.5)	14.1(nt)
CPRM-1	nb**	nb	nb	nb	nb	nb	nb	nb

*nt = not tested

**nb = no boehmite detected

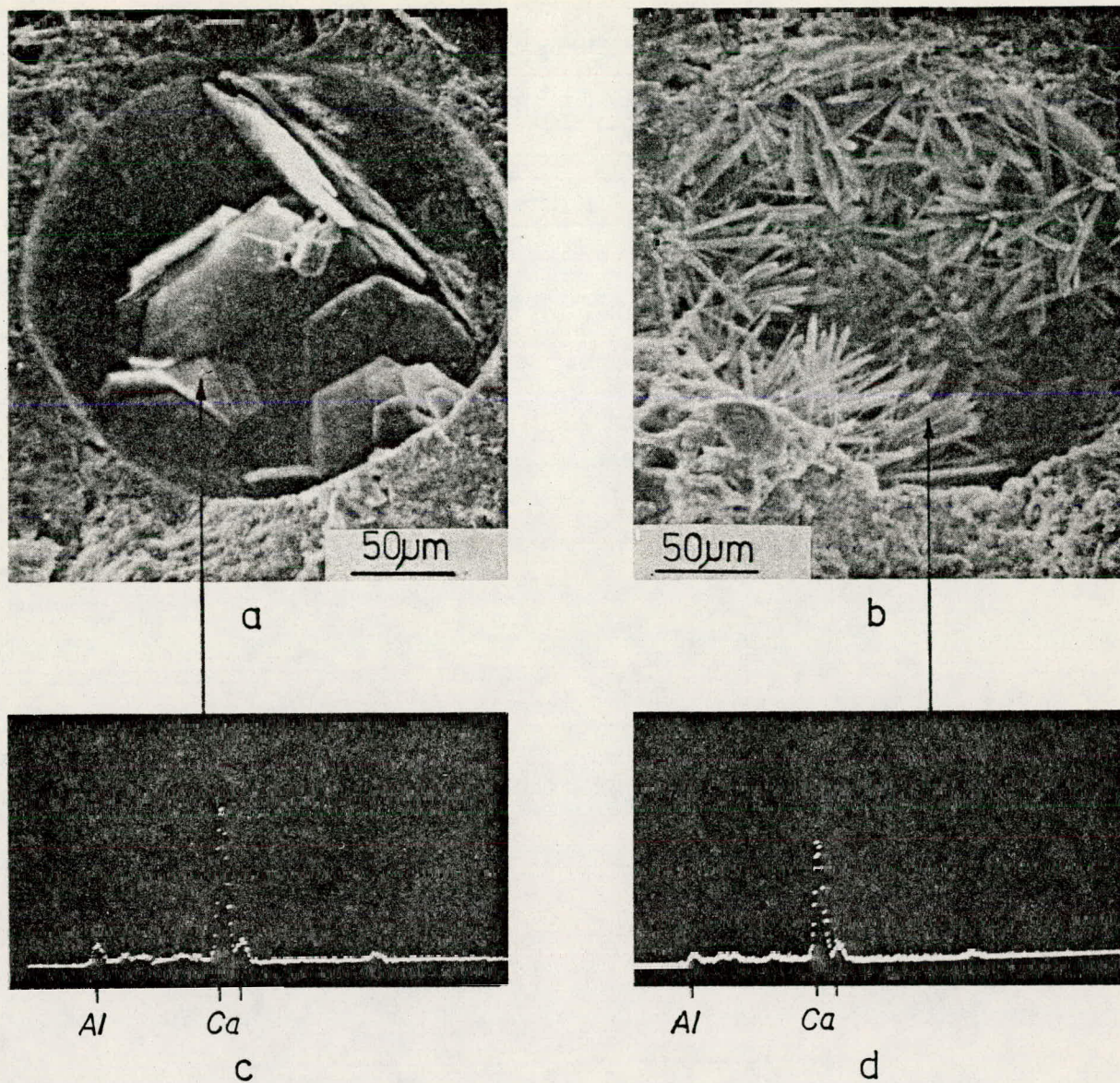


Fig. 12. Microstructure at pores in UMR-1 and UMR-4 after exposure for 10 days to DOE atmosphere at 6.9 MPa/231°C.
 (a) UMR-1 (immersed in liquid) showing the formation of calcite crystals.
 (b) UMR-4 (immersed in liquid) showing an internal void which is almost filled with newly grown crystals high in Ca.
 (c) EDAX for crystals in (a).
 (d) EDAX for crystals in (b).

the start of the exposure test (during heating the vessel) as indicated by both the calcium found in the liquid and by the increase in pH. Eventually the water becomes saturated with CaO (~50 refractory bars in 5 liters water) and, in the presence of CO or CO₂, CaCO₃ is formed and is redeposited on and within the immersed specimens. Thus, the reduction in dissolved CaO along with the dissolution of CO and CO₂ in the water causes the pH to decrease (acidic) and become constant.

Under conditions where the liquid is constantly replenished and may not become saturated with lime, the leaching of the CaO could conceivably continue until all the CaO in the castable is removed. The loss of small portions of CaO from the castable had no detectable effect upon the flexural strength, but whether this remains true if all the CaO is removed is unknown. In a coal gasifier, a major portion of the CaO in the cement bond phases can be expected to react with CO or CO₂ to form CaCO₃ and the extent to which CaO is lost from a castable will depend upon whether any condensed liquids are present.

A comparison of the MOR of dense castables on the basis of the cements and aggregates they contain shows that those containing a high purity cement (UMR-1 and UMR-8 in Fig. 11) generally have a higher MOR than those containing a less chemically pure cement (UMR-4 and UMR-5 in Fig. 11). On the other hand, the type of aggregate seems to have no important effect upon the MOR of the castables. Castables made with the same cement but different aggregates had close to the same MOR, as shown in Fig. 11.

In summary, no major difference in properties was found for castables, even highly porous insulating castables, either immersed in liquid or

exposed to saturated vapor. The presence of liquids seems less important to properties, such as MOR and porosity, than the degree of saturation of the atmosphere. However, the loss of CaO which occurs under saturated conditions, vapor or liquid, is a factor to be considered in the long term service performance of castables exposed to such conditions. No detrimental change in properties, such as loss in strength, was attributable to the leaching of CaO from the castable, but the effect of complete removal of CaO over a much longer time period is unknown. It might be suspected to destroy the structural integrity of a castable if the bonding is destroyed and not replaced by another bond phase of some type (such as boehmite).

G. Task VII-Pressure/Temperature Cycling

As already described, boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is a principal reaction product formed in cement bonded castables exposed to atmospheres >50% saturated. The work in this Task was concerned with two questions. First, whether the additional bonding boehmite provides would be retained when it is subsequently decomposed due to changes in the operating conditions (e.g., start up, shut down, gas composition) of a coal gasifier. Second, whether the volume changes associated with repeated boehmite formation/decomposition might produce internal microcracks and, thereby, eventually weaken the castable. In this task selected castables were exposed for 5-day periods so as to form boehmite and then by changing the temperature, the boehmite was decomposed (dehydrated) as might occur in a coal gasifier lining. This procedure was repeated for a total of 5 boehmite formation/decomposition cycles, with properties measured after each cycle.

Exposures were performed in the DOE atmosphere containing 1 vol% H_2S at 6.9 MPa pressure. Initially, three pressure vessels were connected in series so that the same atmosphere flowed through all three vessels. The steam vessel operated at 231°C while the two vessels containing the samples were at 240°C so as to prevent water condensation in these vessels. The atmosphere in these vessels was only 85% saturated, but this was adequate for boehmite formation as shown in Task V.

The procedure used was as follows. After a 5-day exposure at 240°C one of the vessels was shut down and 16 samples, which now contained boehmite, were removed and divided into two groups. The first group (8 samples) was tested, their properties being given in column 1 of Tables XIX and XX. The second group of 8 samples were heated to 538°C in air for 18 h to decompose the boehmite and then tested, their properties being given in column 2 of Tables XIX and XX. The presence or absence of boehmite in these control specimens was confirmed by XRD and DTA/TGA.

Fifty samples of each castable in the second vessel were exposed to the DOE atmosphere (6.9 MPa/ 240°C) for 5-day periods to form boehmite. The vessel was then heated to 538°C in the DOE atmosphere, maintaining 6.9 MPa, for 18 h to decompose the boehmite and cooled to room temperature where 10 samples of each castable were removed for testing. This procedure was repeated for 5 boehmite formation/decomposition cycles. The properties are given in column 3 of Tables XIX and XX.

The dimensional and weight changes were small, $\leq 1\%$, and did not vary significantly with the number of boehmite formation/decomposition cycles. All castables generally expanded slightly during boehmite formation and

Table XIX. Percent Weight Change and Percent Porosity (in parentheses) of Castables
Exposed to the DOE Atmosphere With 1% H₂S for Repeated Boehmite
Formation/Decomposition

Materials	(1) Fired 18h at 260°C in air	(2) DOE Atm., 6.9 MPa 5 days @ 240°C (Boehmite Formation)	(3) As column 1, then heated 18h in Air 538°C (Boehmite Decompose)	(3) DOE Atm., 6.9MPa, 5 days @ 240°C, (Boehmite Formation), then heated 18h in the DOE atm., 6.9 MPa @ 538°C (Boehmite Decomposition) for 1, 2, 3, 4, and 5 cycles.				
				1 Cycle	2 Cycle	3 Cycle	4 Cycle	5 Cycle
UMR-1	(20.1)	+0.3(20.3)	+0.4(24.7)	-0.1(25.7)	-0.1(25.3)	Nil(25.7)	Nil(26.2)	+0.2(25.1)
UMR-4	(23.8)	Nil(13.1)	Nil(20.3)	Nil(24.8)	-0.1(24.5)	-0.2(24.5)	-0.2(24.4)	-0.1(24.6)
UMR-5	(16.3)	Nil(12.4)	-0.1(16.1)	-0.1(17.9)	-0.1(17.9)	-0.1(17.7)	-0.2(17.9)	-0.1(17.7)
UMR-8	(16.5)	+0.1(11.7)	-0.2(16.1)	-0.3(18.3)	-0.2(19.0)	-0.1(17.6)	-0.1(18.7)	Nil(19.4)
CC-8	(41.0)	+0.4(44.3)	nt(46.7)	+0.4(48.5)	+0.4(48.0)	+0.1(48.1)	+0.1(49.3)	+0.3(51.0)
CC-9	(52.8)	+0.2(51.9)	nt(53.9)	+0.1(56.4)	+0.2(55.7)	Nil(54.1)	-0.1(56.0)	Nil(56.9)
CC-10	(61.8)	nt(59.5)	nt(64.5)	+1.0(64.3)	+1.0(64.5)	+0.5(62.7)	+0.4(63.8)	+1.0(63.7)

Table XX. Modulus of Rupture (MPa) of Castables Exposed to the DOE Atmosphere
With 1% H₂S for Repeated Boehmite Formation/Decomposition

Materials	(1)		(2)	(3)					
	Controls fired in air 18h 260°C 538°C		DOE, 6.9MPa 5 days @ 240°C (Boehmite Form)	As (1), then heated 18 h in air @ 538°C (Boehmite Decomp.)	DOE, 6.9 MPa, 5 days @ 240°C (Boehmite Formation) then heated 18h in the DOE at 6.9 MPa @ 538°C (Boehmite Decomposition) for 1, 2, 3, 4, and 5 cycles				
					1 Cycle	2 Cycle	3 Cycle	4 Cycle	5 Cycle
UMR-1	15.2±1.2	15.2±1.0	12.8±4.5	11.9±0.6	8.2±0.9	7.1±1.7	9.8±1.2	8.7±1.1	9.4±5.0
UMR-4	11.2±1.2	10.3±0.5	20.4±2.2	26.9±1.0	27.4±1.9	26.4±1.8	24.6±2.4	28.0±5.2	24.2±2.8
UMR-5	8.9±0.8	8.9±0.5	20.9±1.2	18.8±1.2	23.7±2.5	23.8±2.1	21.0±2.1	18.2±1.9	23.6±2.4
UMR-8	12.2±1.0	13.7±1.2	16.9±1.2	14.7±1.8	29.1±4.2	27.7±1.4	26.8±1.9	22.5±1.8	27.1±2.0
CC-8	5.4±0.6	6.5±0.3	5.4±0.4	6.7±0.9	6.8±0.3	6.6±0.9	6.9±0.6	6.8±0.6	6.5±0.3
CC-9	1.3±0.2	1.4±0.3	7.3±0.9	7.3±1.0	6.6±0.9	6.7±0.3	3.3±0.5	5.2±0.6	6.8±0.5
CC-10	0.8±0.1	0.7±0.1	1.3±0.3	0.9±0.3	1.1±0.1	1.0±0.2	0.9±0.2	0.9±0.1	1.1±0.2

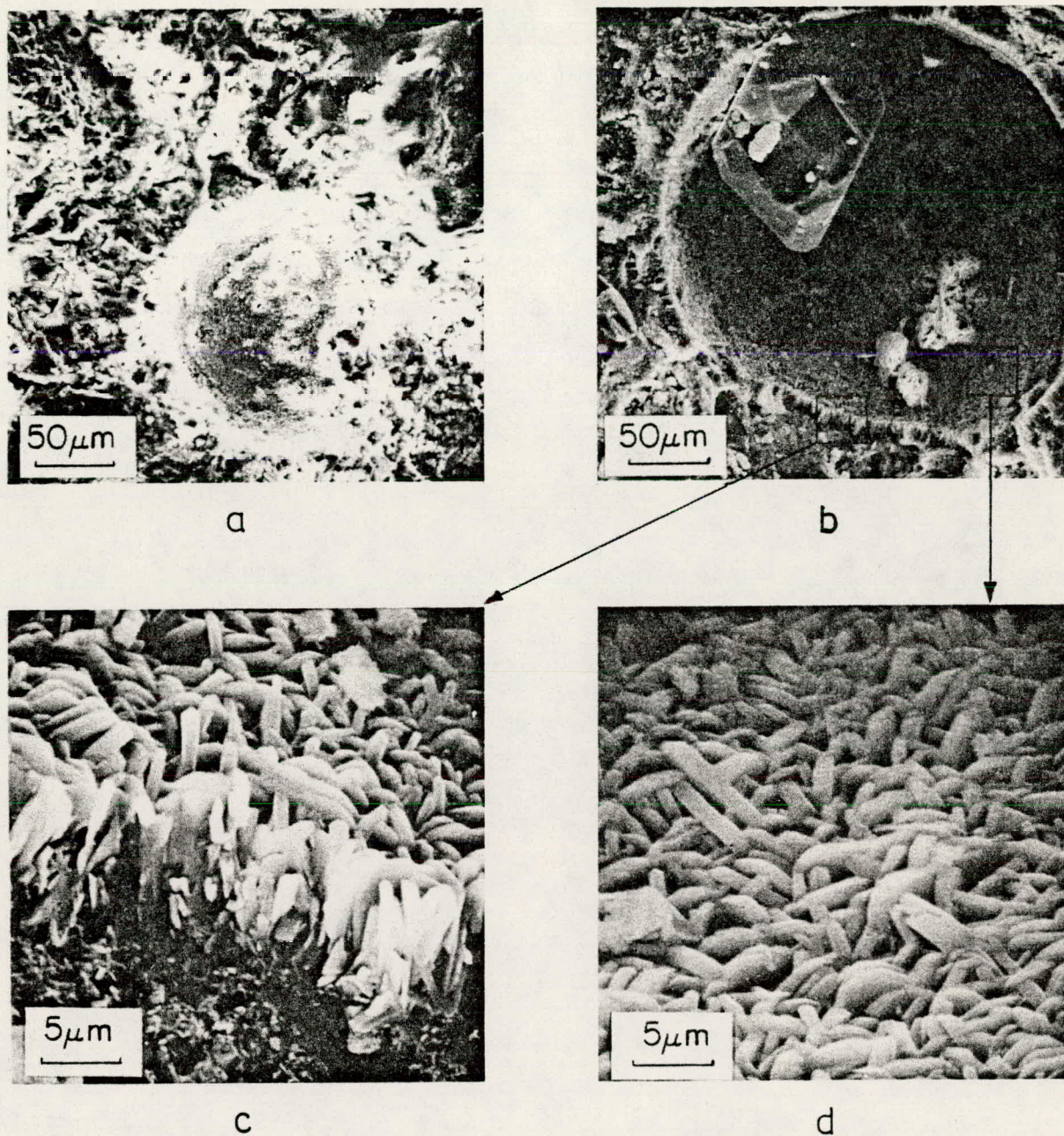
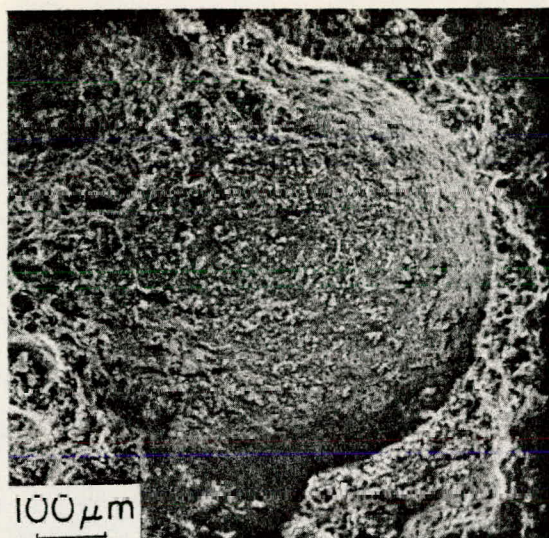
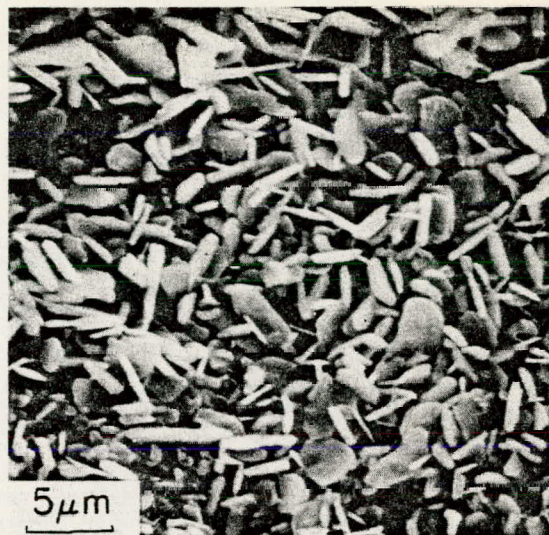


Fig. 13. Microstructure of UMR-1 castable. (a) As-cast and dried; (b) After 44-day exposure to 6.9 MPa/231°C (saturated vapor) DOE atmosphere with 1% H_2S ; (c) Structure (boehmite) near the edge of void b; (d) Structure (boehmite) of matrix of void in b.

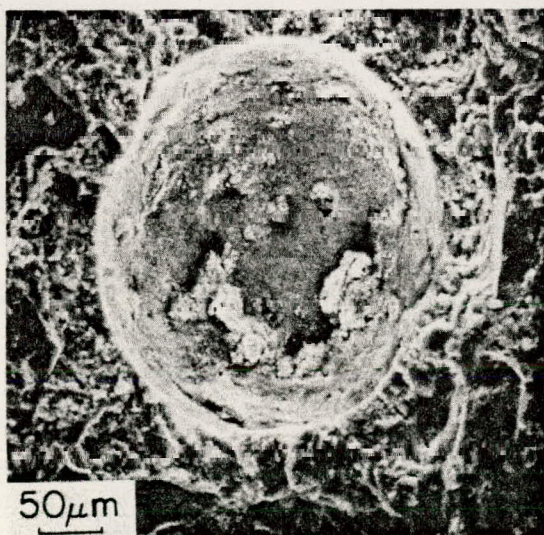


a

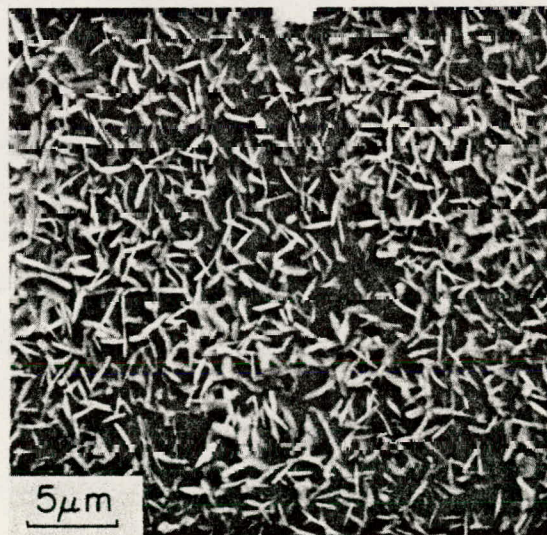


b

Fig. 14. Microstructure of UMR-1 castable exposed 5 days at 6.9 MPa/240°C in DOE atmosphere to form boehmite and then 18 hours at 6.9 MPa/538°C in the same atmosphere (DOE) to decompose boehmite. (a) General area around internal void; (b) Inside surface of the void in a, crystals are Al_2O_3 .



a



b

Fig. 15. Microstructure of UMR-1 castable exposed 5 days at 6.9 MPa/240°C in DOE atmosphere to form boehmite and then 18 hours at 538°C in air to decompose boehmite. (a) General area around internal void; (b) Inside surface of the void in b, crystals are Al_2O_3 .

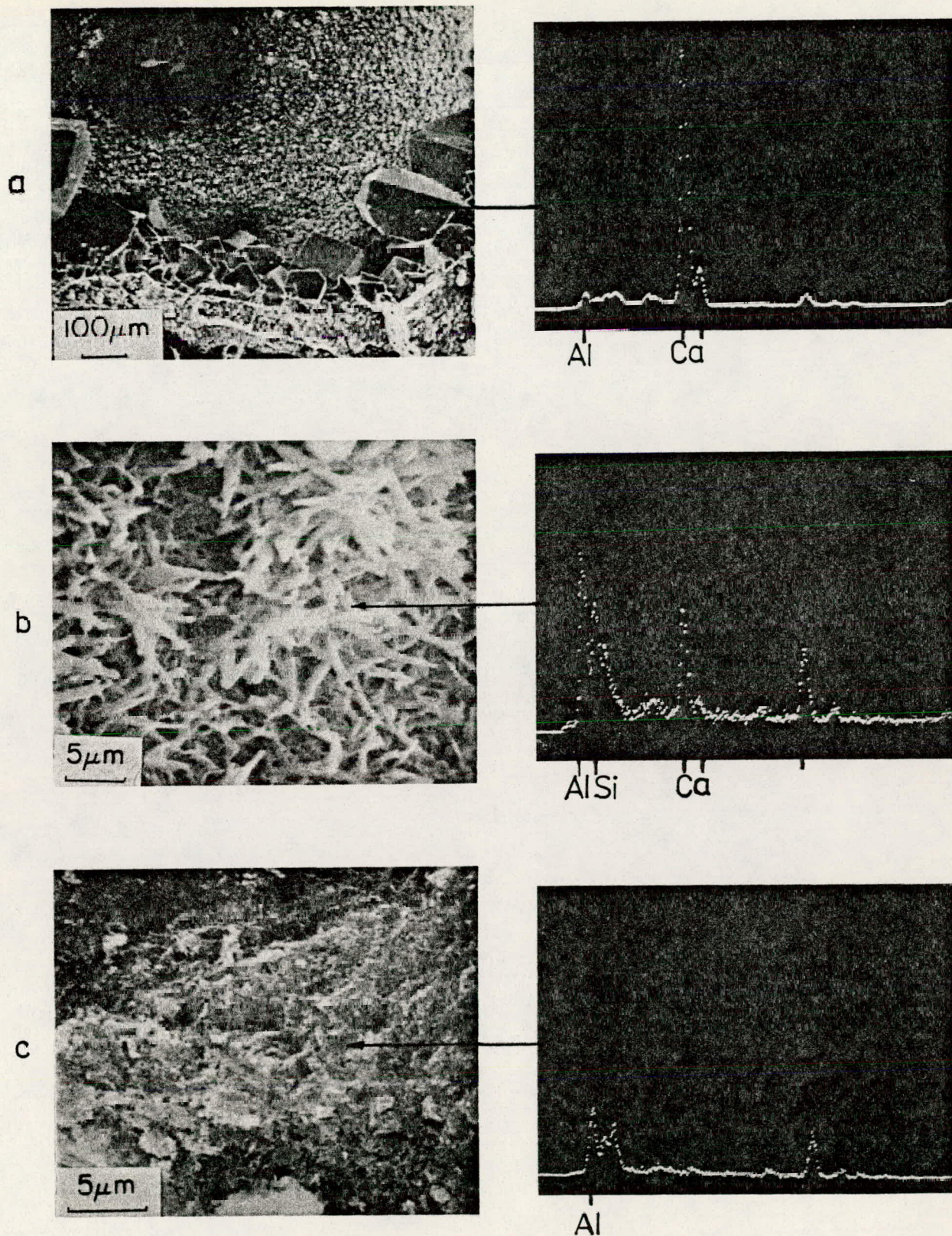


Fig. 16. Microstructure of UMR-8 exposed 44 days to saturated DOE atmosphere with 1 Vol% H_2S at 6.9 MPa/231°C. (a) General area around an internal void, (b) Inside surface of the void in a; (c) General area on the fracture surface of specimen.

decomposition, except the dense castables which shrunk slightly after boehmite decomposition.

The changes in density were small and showed no dependence upon the number of cycles. The porosity of the dense castables after boehmite formation, column 1 in Table XIX, were generally lower than controls fired in air as expected (except UMR-1). The porosity of the insulating castables did not change significantly. Repeated boehmite formation/decomposition cycles had little effect upon the porosity, Table XIX.

With the exception of UMR-1, the MOR of all the dense castables was significantly higher both after boehmite formation, column 1 in Table XX and decomposition, columns 2 and 3, in comparison to controls fired in air to comparable temperatures. No significant loss in MOR is evident with repeated boehmite formation/decomposition for any of the castables investigated, although the MOR of UMR-1 is consistently lower than expected for some unknown reason. As is evident from Table XX, the MOR of the dense castables in which boehmite was formed, but then subsequently decomposed, continues to be higher than that of their controls fired in air, except UMR-1. In UMR-5 and UMR-8, the MOR of the cycled samples is even higher than when boehmite is present. Apparently, the additional bonding initially provided by the boehmite is not lost when the castable is heated to a temperature where boehmite decomposes.

In another recent investigation⁽¹⁴⁾ where boehmite was the only bond phase present (no cement), it was also found that a significant fraction of the bonding provided by boehmite was retained even at temperatures of $>1000^{\circ}\text{C}$ (boehmite decomposes at 500 to 550°C). A general explanation for this is that the crystal habit of boehmite does

not change significantly after its decomposition to Al_2O_3 and the interlocking network of pattern of boehmite crystals is retained.

Examples of the microstructure in the general area of internal voids in specimens from this Task are shown in Figs. 13-16. The interlocking network of boehmite crystals is clearly evident in Fig. 13 and this microstructure for UMR-1 showed very little change in specimens where no boehmite was detected by XRD, Figs. 14 and 15. Fig. 16B shows a network of small crystals on the inside surface of a void in UMR-8 exposed to the saturated DOE atmosphere. EDAX analysis of these crystals show that they contain Al, Si, and Ca. This suggests that the crystals in UMR-8 are a calcium aluminosilicate compound, although no such compound was detectable by XRD. Similar to boehmite, the interlocking network of calcium aluminosilicate crystals formed in the SiO_2 -containing castables during exposure could explain the increase in MOR.

Based upon the conditions of these tests, which do not duplicate in every respect the conditions in an actual coal gasifier, there appears to be no reason to suspect that repeated boehmite formation/decomposition will adversely affect the mechanical properties of a refractory castable lining.

H. Task VIII- Hydrothermal Reaction of CA Compounds and Neat Cements

The results of early tests⁽²⁰⁻²¹⁾ showed that the changes in properties of the cement bonded refractories after exposure were primarily due to chemical reactions occurring between the cement bond phases and steam and CO . To gain a better understanding of these reactions in terms of their dependence upon exposure time, pressure, and gas composition and their relevance to refractory

performance, an investigation was undertaken of the pure cements as well as the compounds CA and CA₂ which are the major constituents of such cements. Data from the individual cementitious compounds CA and CA₂ is more readily interpreted and has been shown to be applicable to the interpretations of the more chemically complex refractory cements, thereby, minimizing the need to test each specific product.

Pelletized samples of CA and CA₂, along with the neat cements, C-1 and C-2, were reacted in saturated steam at 0.69, 3.45, and 6.89 MPa pressures for 5, 10, 20 and 60 hours. The DOE atmosphere was used at 6.89 MPa only, for 5, 10, 20, and 60 hours. The reactions occurring in the samples were determined by analyzing the reaction products by XRD and TGA. (19)

1. Phase Compatibility Considerations

Steam-cement systems can be treated ideally as a three component system; Al₂O₃ - CaO - H₂O. The Gibb's phase rule indicates that for saturated conditions only two solid phases can coexist stably at a fixed temperature. Thus, in the saturated steam exposures where three solid hydrated phases are observed, at least one solid is unstable and should react so as to reduce the number of solid phases to two.

When the DOE atmosphere is used, the system can be expressed in additional components if one (or more) of the gaseous species is reactive. Each new component will permit an additional solid phase to be stable.

The reactions observed in saturated steam were discussed in previous reports, but the phases observed (C₃AH₆, C₄A₃H₃, AH and AH₃) are given in Table XXI. The data indicate that product phases form more slowly at 0.69 MPa than at either 3.45 or 6.89 MPa. Not all of the CA and CA₂ reacted completely at 0.69 MPa in 20 h. At 3.45 and 6.89 MPa, CA,

[illegible]

1 = CA
2 = CA₂
3 = C-1 (CA-25 cement)
4 = C-2 (Secar 250 cement)

*Cement terminology used.

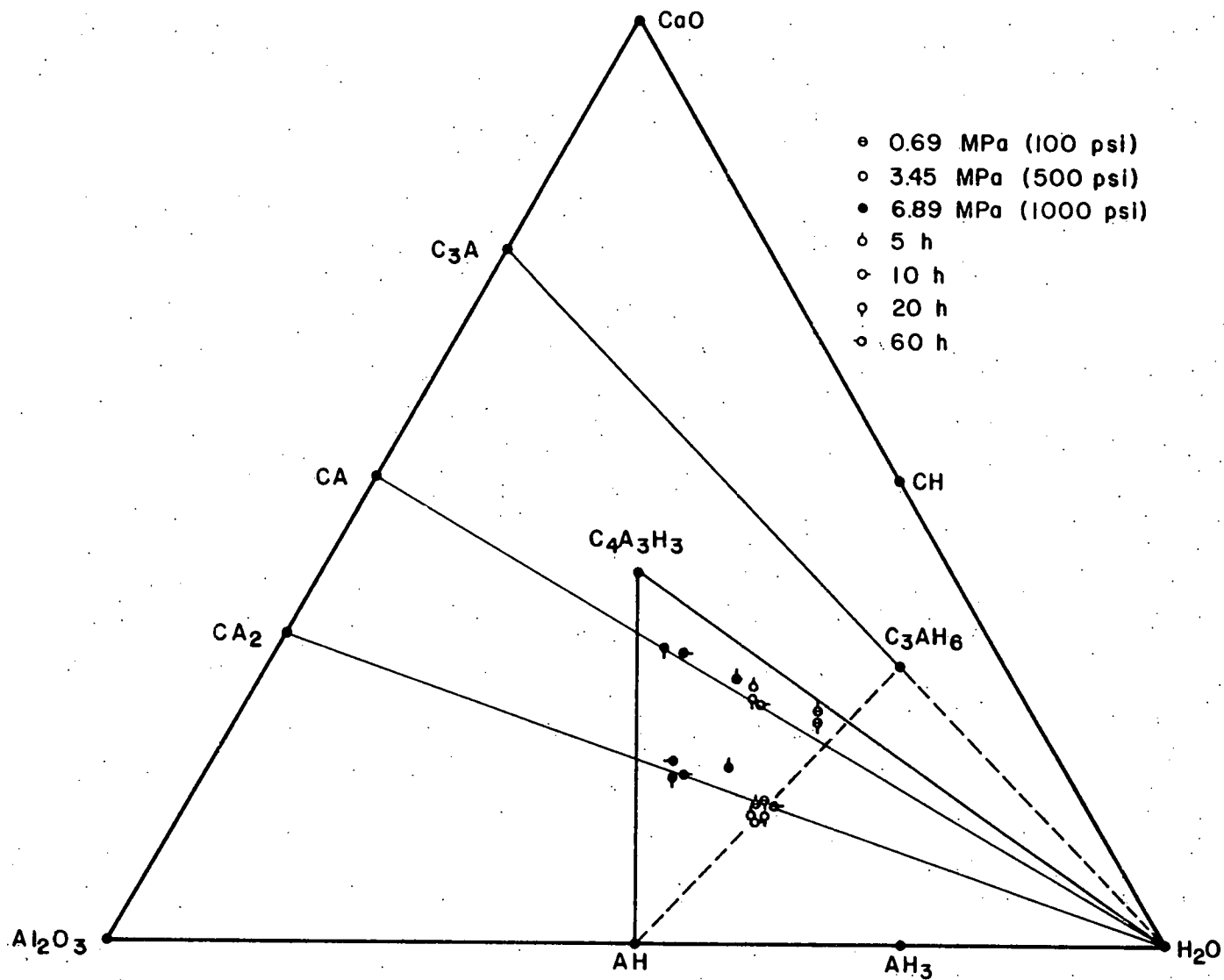


Fig. 17. Ternary composition points for CA and CA_2 for high pressure runs in steam. Diagram plotted in mol percent.

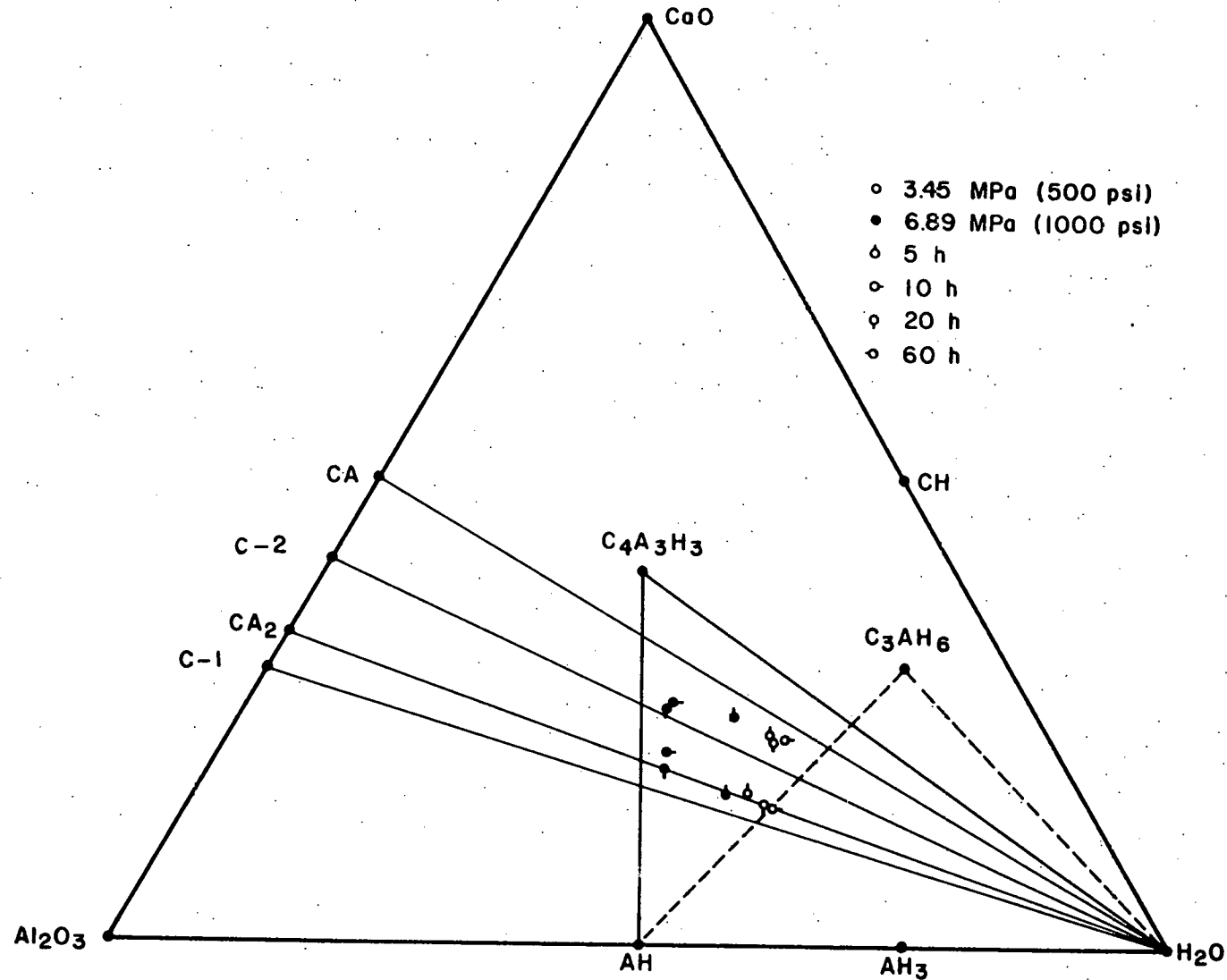


Fig. 18. Ternary composition points for C-1 and C-2 neat cements for high pressure runs in steam. Diagram plotted in mol percent.

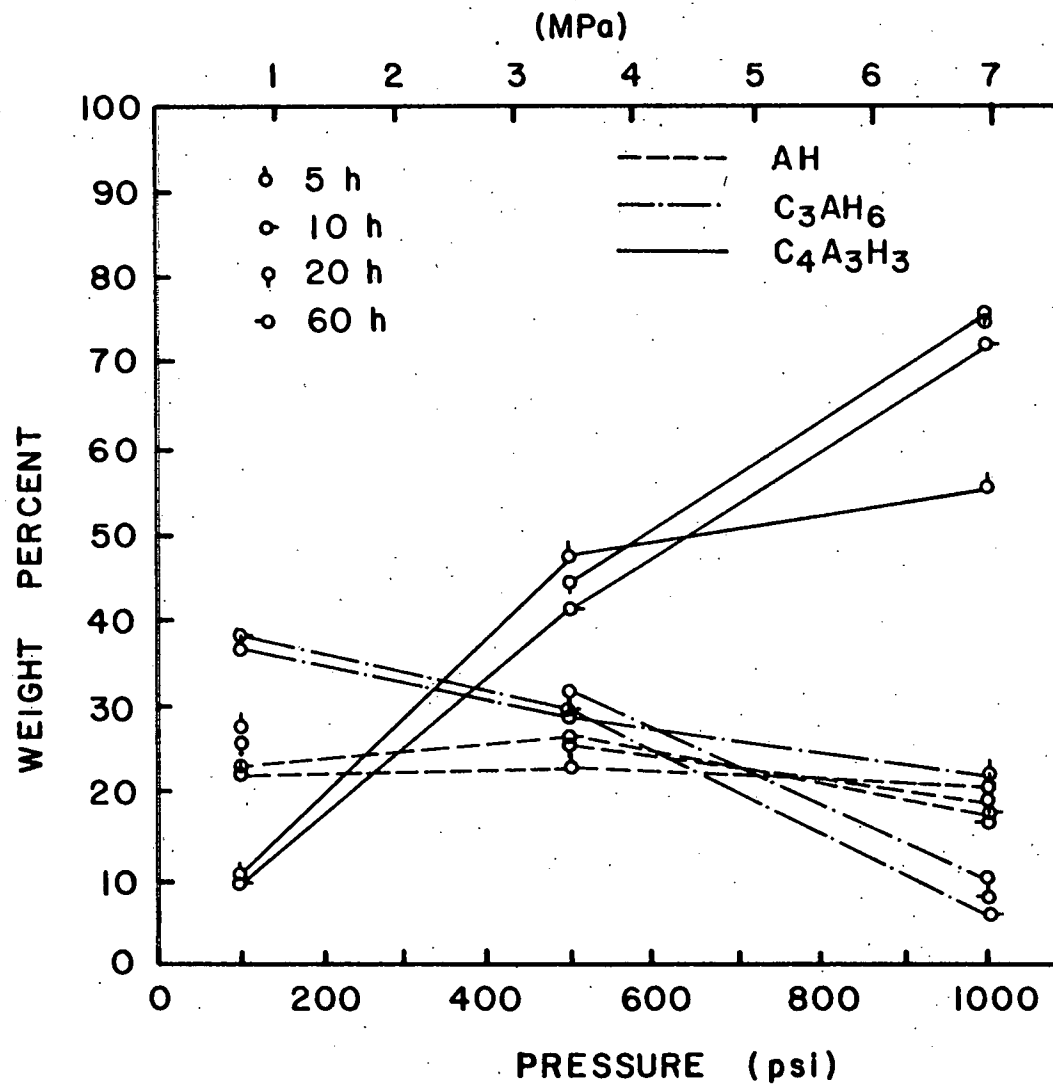


Fig. 19. Weight percentages of hydrated product phases from CA as a function of steam pressure.

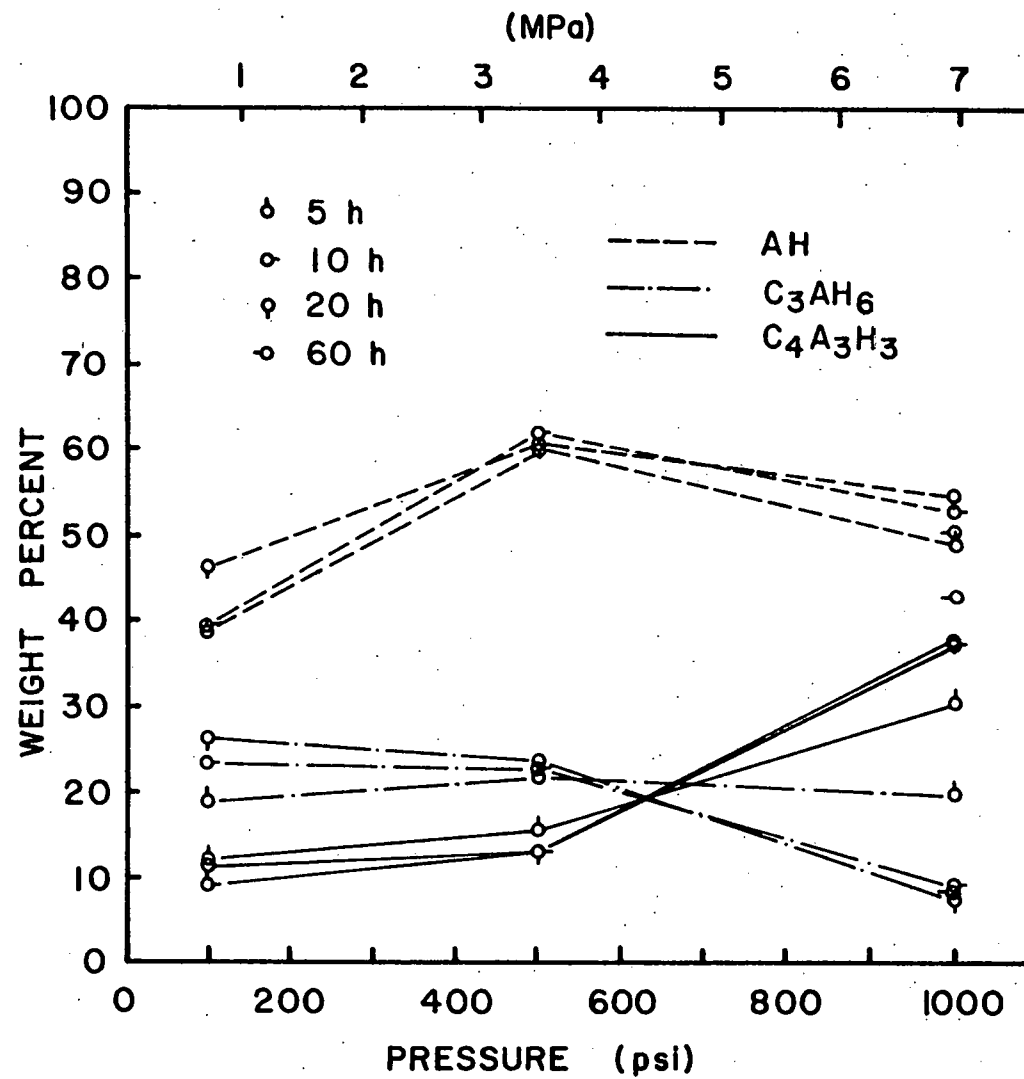


Fig. 20. Weight percentages of hydrated product phases from CA_2 as a function of steam pressure.

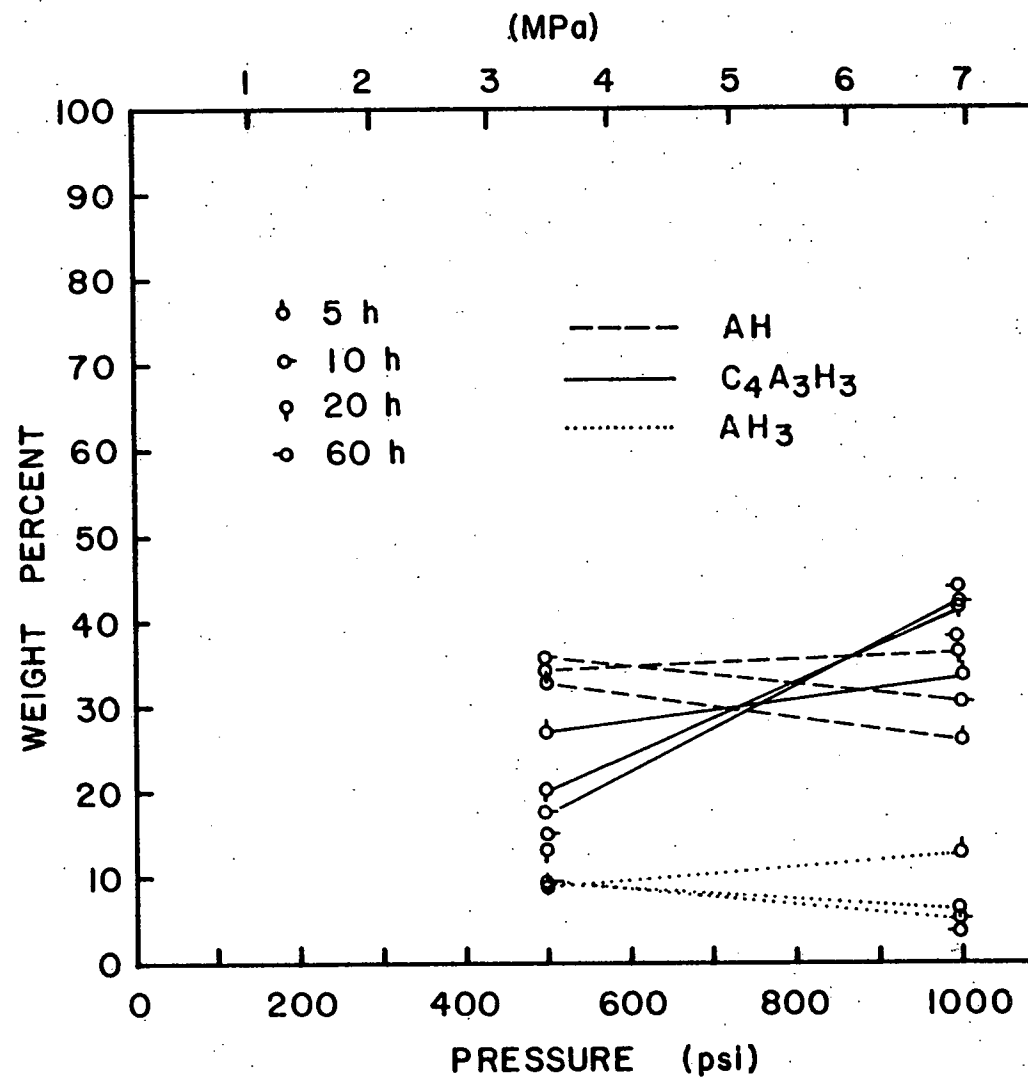


Fig. 21. Weight percentages of hydrated product phases from C-1 cement as a function of steam pressure.

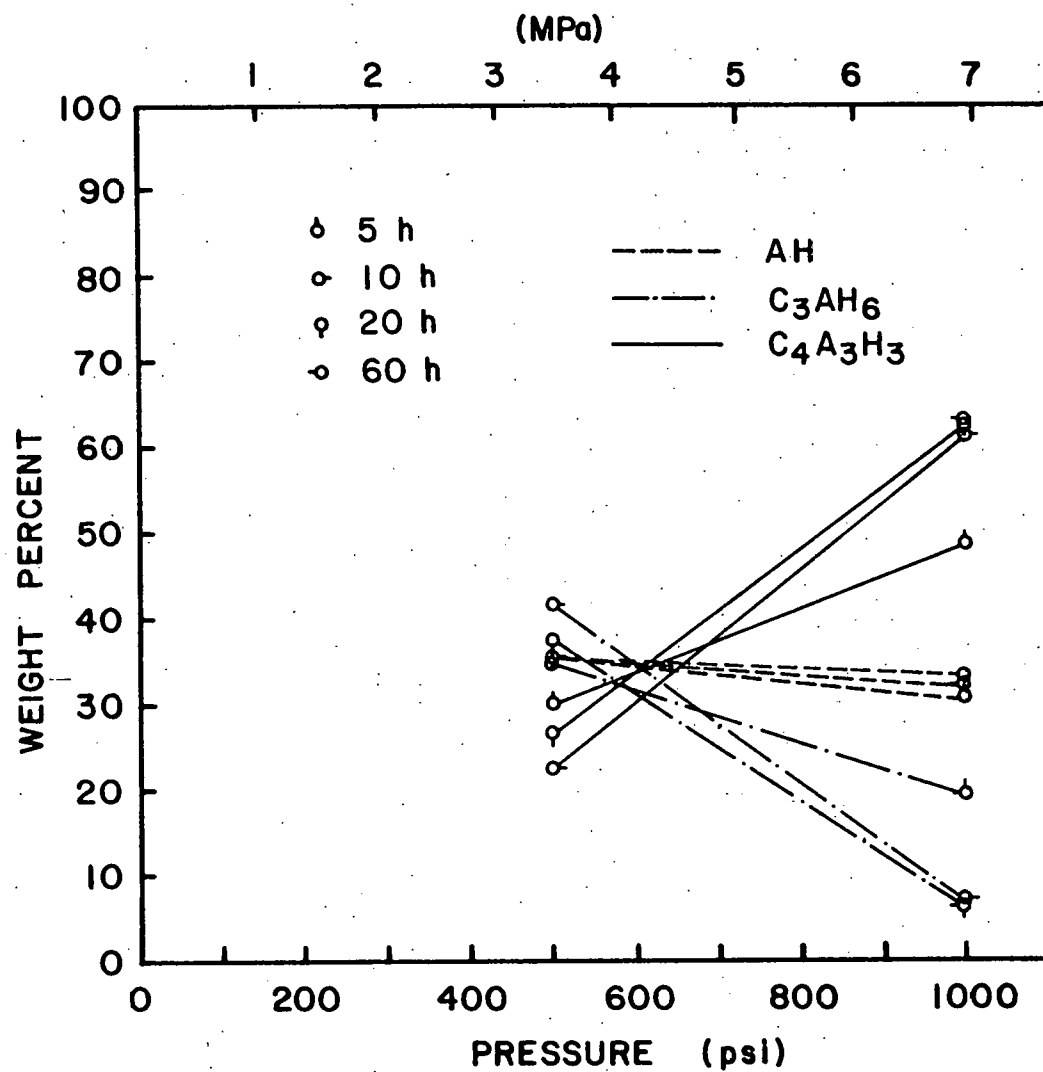


Fig. 22. Weight percentages of hydrated product phases from C-2 cement as a function of steam pressure.

CA₂, and C-2 contained no unhydrated material, even though the phase makeup was changing. The results for C-1 indicated that unreacted material remained at all reaction times at both 3.45 and 6.89 MPa. When the data in Table XXI are combined with the data shown in Fig. 17 and 18, it can be concluded that C₃AH₆ is not a stable phase at the higher pressures. C₃AH₆ appears to form metastably in the initial reaction and then slowly reacts to form the stable phases, which appear to be AH and C₄A₃H₃. The pressure dependence of the reactions can be observed clearly in Figs. 19-22, where the weight percentages of each phase in CA (Fig. 19), CA₂ (Fig. 20), C-1 (Fig. 21), and C-2 (Fig. 22) are shown as a function of pressure.

The reactions observed in the DOE atmosphere were discussed previously in terms of available TGA data, but further analysis indicated that the tentative conclusions reached previously need modification. Table XXI summarizes the phase analyses of samples reacted in the DOE atmosphere. The main conclusion is that C₃AH₆ does not appear, but a new phase, C₄AH₁₁ $\bar{C}$ forms ($\bar{C}$ designates CO₂). In addition, the reactions appear to occur more slowly than in steam because unreacted material is present in all samples except C-2 reacted for ≥ 10 h. The time behavior of the materials is summarized in Fig. 23. Because the system has a larger number of components, the three solids phases observed can coexist in stable equilibrium and the time trends observed for the individual phases reacted in saturated steam are absent in the DOE atmosphere.

In the 6.89 MPa DOE atmosphere, the amounts of the product phases formed from CA and CA₂ do not appear to correlate with the reaction time as was observed in saturated steam. That is, when the amount of

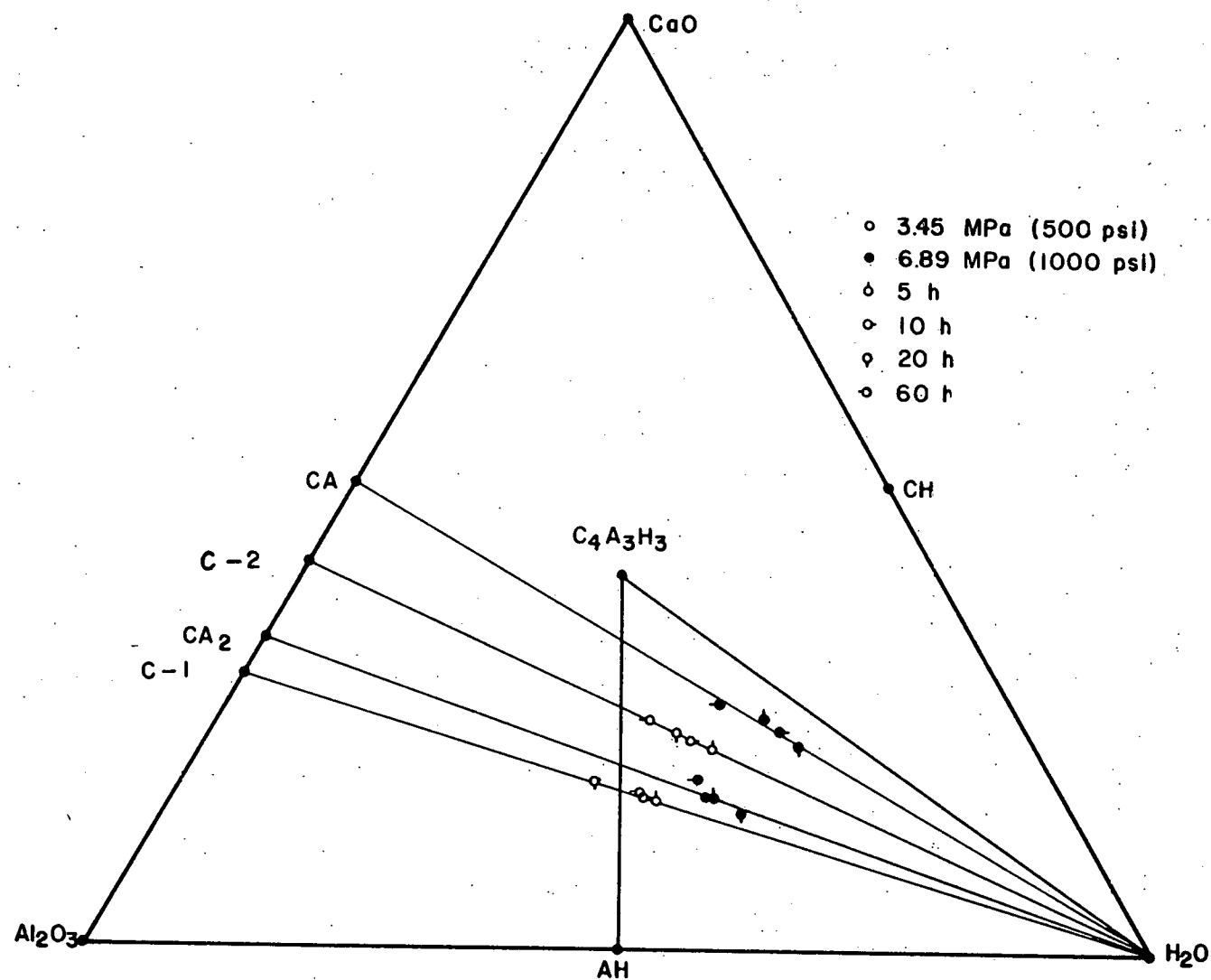


Fig. 23. Ternary composition points for CA , CA_2 , C-1 and C-2 for high pressure runs in DOE atmosphere. Diagram plotted in mol percent.

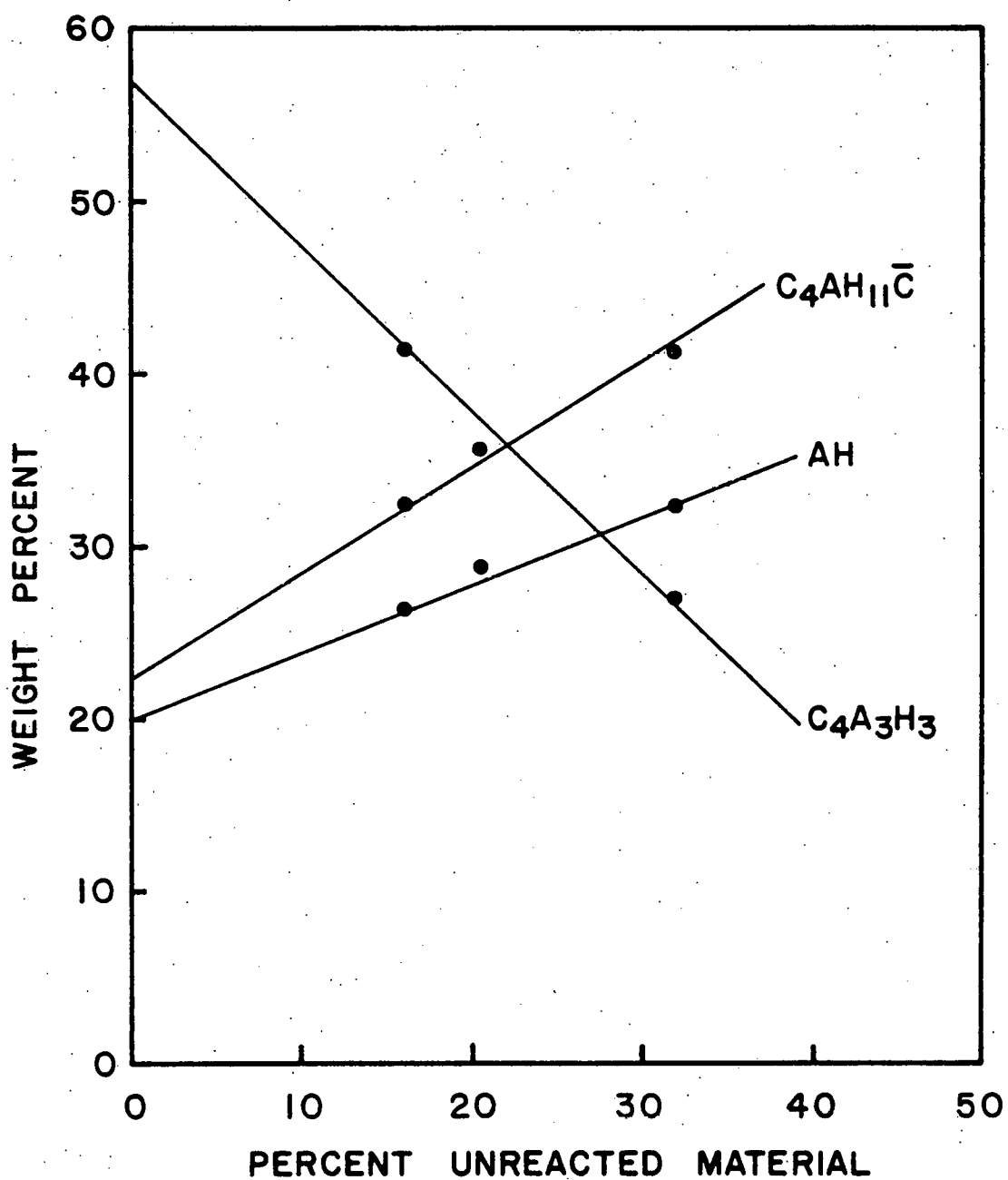


Fig. 24. Weight percentages of product phases from CA as a function of reactant unused (6.89 MPa DOE atmosphere).

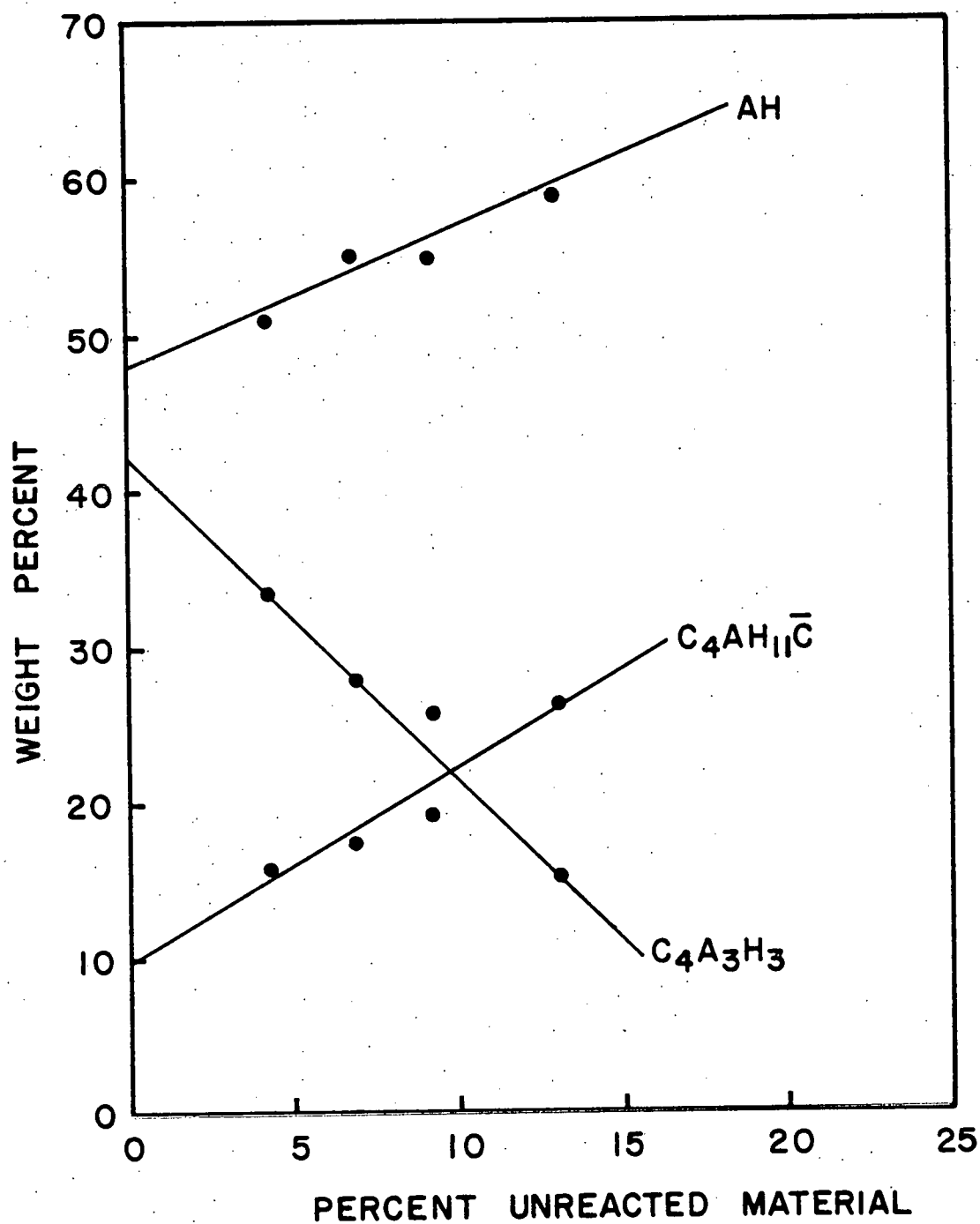


Fig. 25. Weight percentages of product phases from CA_2 as a function of reactant unused (6.89 MPa DOE atmosphere).

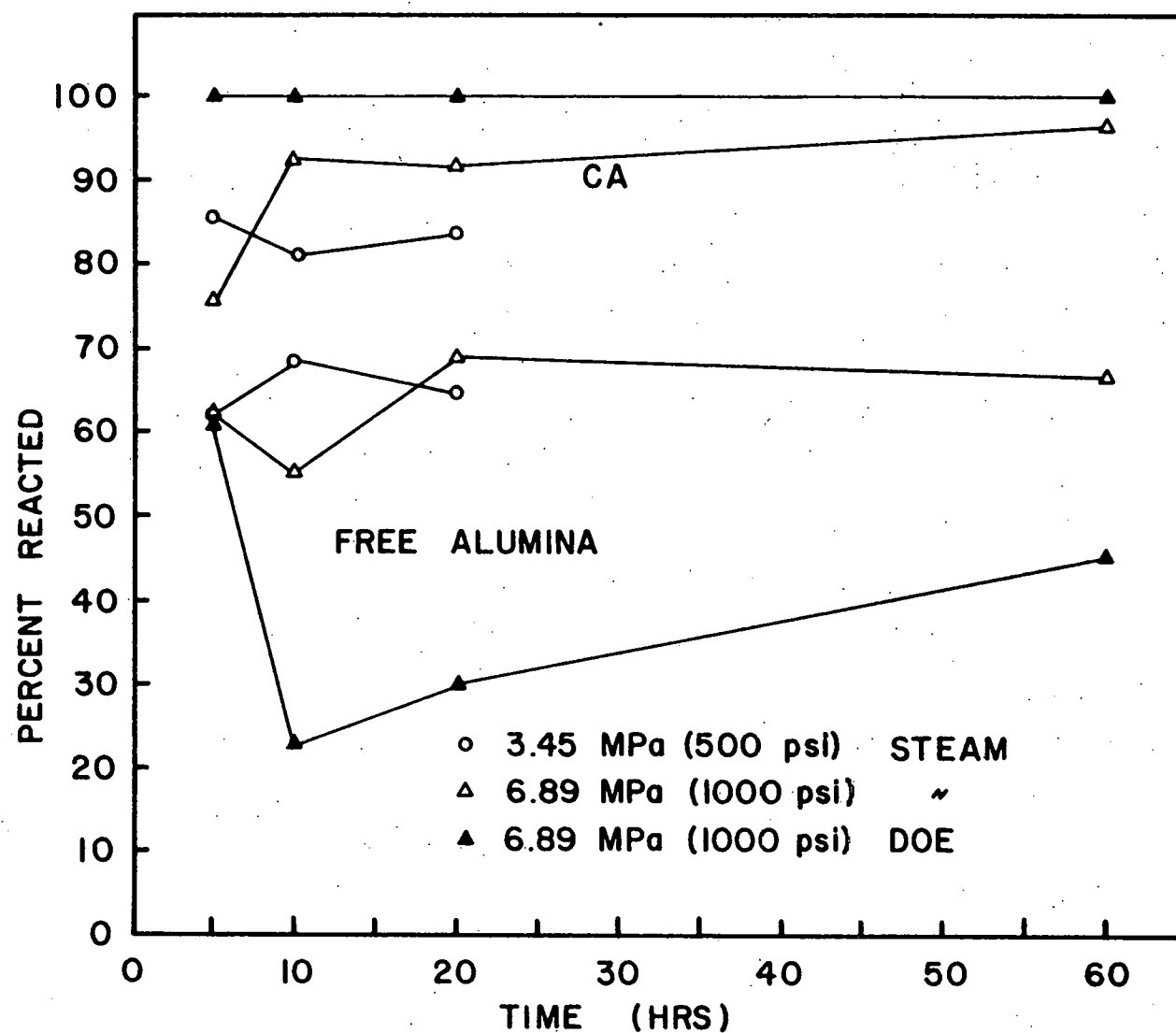


Fig. 26. The time dependence of the amount of the components of C-1 in steam and DOE atmospheres.

Table XXII. Possible Reaction Schemes in Steam and DOE Atmospheres

	STEAM	DOE
<u>Prepared Compounds</u>	Formation of C_3AH_6	Formation of $C_4AH_{11}\bar{C}$
	$3CA + 8H = C_3AH_6 + 2AH$	$4CA + 14H + \bar{C} = C_4AH_{11}\bar{C} + 3AH$
	$3CA_2 + 11H = C_3AH_6 + 5AH$	$4CA_2 + 18H + \bar{C} = C_4AH_{11}\bar{C} + 7AH$
	Formation of $C_4A_3H_3$ /Decomposition of C_3AH_6	Formation of $C_4A_3H_3$
<u>Neat Cements</u>	$4C_3AH_6 + 5AH = 3C_4A_3H_3 + 20H$	$4CA + 4H = C_4A_3H_3 + AH$
		$4CA_2 + 8H = C_4A_3H_3 + 5AH$
	C-2 cement appears to follow above reaction scheme.	C-2 cement appears to follow above reaction scheme.
	C-1 cement appears to follow above reaction scheme; however, in addition, the active alumina present in the cement forms some AH_3 .	C-1 cement appears to follow above reaction scheme; however, in addition small amounts of $\bar{C}\bar{C}$ are formed.

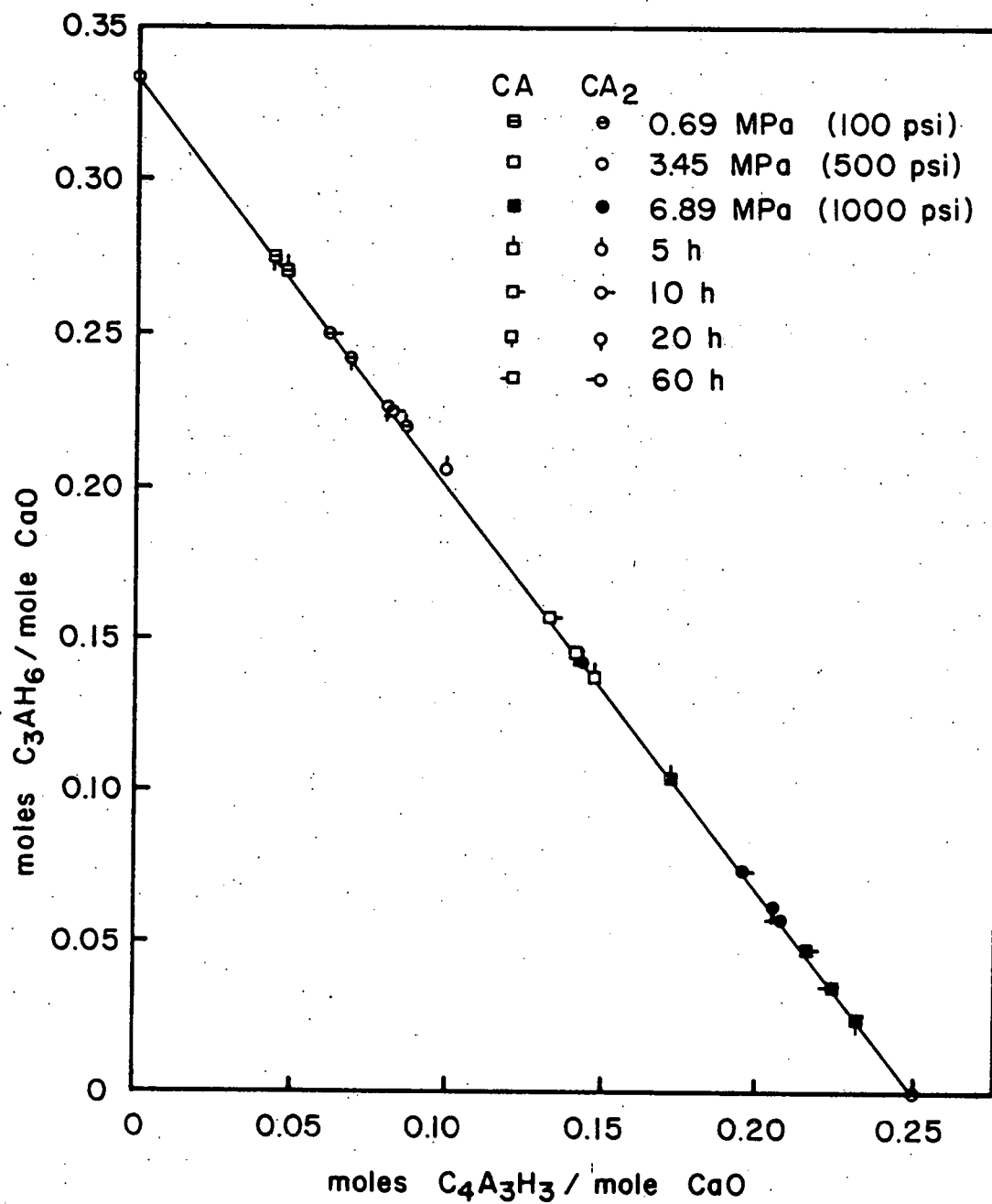


Fig. 27. Data demonstrating the conversion relationship for C_3AH_6 reacting with AH to form $C_4A_3H_3$ in pure steam.

a phase is plotted against reaction time, the amount does not increase or decrease monotonically as was observed in saturated steam. However, when the phase amounts are plotted against the amount of unreacted material, a good correlation appears to result. The data for CA and CA_2 are shown in Figs. 24 and 25, respectively.

Figure 26 summarizes the reactivity of C-1 in both saturated steam and DOE atmosphere at 6.89 MPa. In steam, the two components of C-1, both CA and the active alumina phase, are partially unreacted even after 60 h. However, in the DOE atmosphere, the CA component appears to be completely reacted, whereas, the active alumina component appears to be much less reactive than in pure steam.

The data from the runs can be condensed into a set of possible reaction schemes that summarize the reactions most likely to be followed. A possible set, that explains the phases formed, is presented in Table XXII.

If as proposed, C_3AH_6 forms metastably at the higher pressures and then decomposes by reaction to $C_4A_3H_3$, there should be a relationship between C_3AH_6 and $C_4A_3H_3$ such that when one decreases, the other must increase in amount.

The amount of C_3AH_6 versus the amount of $C_4A_3H_3$ is shown in Fig. 27. Both amounts have been normalized by conversion to a per mole CaO basis so that the data can be plotted on a single line. The data shows that at the lower pressures, C_3AH_6 forms in preference to $C_4A_3H_3$; however, there appears to be no clear time pattern. At 6.89 MPa, both CA and CA_2 show much more $C_4A_3H_3$ and a clear time pattern that indicates the longer the sample is held at pressure, $C_4A_3H_3$ forms at the expense of C_3AH_6 .

2. Summary

These results substantiate the chemical reactions found in the cement bonded castables after exposure to similar conditions. The reaction of CA or CA_2 individually is essentially the same as in commercial refractory cements which contain major proportions of these two compounds. Although metastable compounds initially form in some cases, the reactivity of CA, CA_2 , and the commercial cements is relatively high; a major portion of the reactions being completed in only a few hours (e.g., ~20) as opposed to several days. The composition of the atmosphere is an important factor in the reaction products formed and carbonated phases such as $CaCO_3$ and $C_4AH_{11}\bar{C}$ can be anticipated after exposure to CO and CO_2 containing atmospheres such as the DOE. For an atmosphere whose composition is similar to that of the DOE, the cement bond phases in refractory castables should be expected to react in only a few hours to form $C_4A_3H_3$, $C_4AH_{11}\bar{C}$, AH (boehmite) and $CaCO_3$ when the atmosphere is close to saturation.

IV. SUMMARY

A. Chemical Reactions

1. The major chemical reactions occurring during exposure were the reaction of the calcium aluminate cement or $AlPO_4$ bond phases with steam and CO or CO_2 and were essentially dependent upon the degree of saturation of the atmosphere.

2. The chemical reactions were relatively rapid and the major changes occurred within a few days, ≤ 10 days. No chemical reactions were found at longer exposure times which had not already been detected at 10 days.

3. Boehmite and CaCO_3 were the major compounds formed in the cement-bonded castables during exposure. The amount of boehmite increased significantly with increasing saturation of the atmosphere.

4. The minimum percent saturation required to form boehmite varied from 10 to 30% depending upon the atmosphere and pressure.

5. The principal chemical reaction occurring in phosphate-bonded refractories during exposure was the transformation of orthorhombic AlPO_4 to trigonal AlPO_4 , especially in unsaturated atmospheres.

6. During exposure some portion of the cement and phosphate bond phases are dissolved from the refractories, especially in saturated atmospheres. The mechanical strength of the phosphate-bonded refractories were substantially lower after exposure to saturated atmospheres.

B. Properties

1. Of all variables investigated, exposure time, gas pressure or composition, presence or absence of H_2S , and liquid versus vapor contact, the degree of saturation was found to be the most important factor affecting the properties of refractories exposed to conditions like those expected near the cold face of a coal gasifier lining.

2. The flexural strength of high and intermediate alumina castables, generally, increased by a factor of 2 or 3 with the degree of saturation (due to the formation of new compounds, mainly boehmite), while there was a decrease in the strength of the phosphate-bonded refractories in the saturated atmospheres. No significant change was observed in the strength of insulating castables after exposure.

3. The thermal expansion curves of cement bonded castables exposed to the saturated atmospheres showed a sudden expansion between 500°C and 600°C due to the dehydration of boehmite. The magnitude of this expansion increased with the quantity of boehmite, being largest in the high purity alumina castables and smaller in the intermediate alumina and insulating castables. The thermal expansion of castables exposed to unsaturated atmospheres showed either no or a very small expansion between 500°C and 600°C, but a larger expansion above 800°C due to the decomposition of CaCO_3 .

4. The major changes in properties occurred within the first 10 days of the exposure, thereafter the properties were essentially independent of time at least up to the 60-day maximum used in this study.

5. In atmospheres of varying $\text{CO}/\text{H}_2\text{O}$ ratio, the dissolution of CaO increases with the increasing CO content, particularly for samples immersed in liquid. In the alumina castables containing a high purity calcium aluminate cement, UMR-1 and UMR-2, the strength tends to decrease with increasing $\text{CO}/\text{H}_2\text{O}$ ratio. The strength of castables containing silica tend not to show as large a dependence upon $\text{CO}/\text{H}_2\text{O}$ ratio.

6. The properties of a given refractory were basically similar after exposure regardless of whether they were immersed in liquid or in contact with saturated vapor. In a few instances some small differences in properties were observed, but in general condensed liquids were not particularly chemically corrosive.

7. Five boehmite formation/decomposition cycles, did not produce any detectable deterioration in properties, mainly MOR, of any of the castables investigated. SiO_2 -containing refractories and those made with less pure cement were affected less by these cyclic exposures than the high purity, high alumina castables.

C. Refractory Composition

1. While substantial reductions in mechanical strength were found for phosphate bonded refractories, in no case was total mechanical failure or loss of structural integrity observed for the refractories investigated.

2. Generally, cement-bonded castables of the same type, but made by different manufacturers, showed essentially the same behavior, but larger differences were found for similar phosphate bonded refractory products made by different manufacturers.

3. The properties of all refractories after exposure to various conditions changed to some degree, but the intermediate alumina and insulating castables showed the least evidence of any substantial deterioration in physical or mechanical properties.

4. In terms of overall behavior there was no significant difference between castables made with a high purity alumina aggregate or those made with an aluminosilicate aggregate. The type of cement was more important to the properties after exposure since all of the chemical reactions observed occur between the cement bond phases and steam, CO , CO_2 . No evidence was found of any chemical reaction with the refractory aggregate.

5. Castables containing a high purity cement generally had strengths comparable to those containing a less pure alumina cement, but the latter were somewhat less susceptible to the gas composition. The presence of SiO_2 in the castables, present either as SiO_2 additions, in the cement, or aluminosilicate aggregate, is tentatively concluded to be beneficial in that the flexural strengths were often somewhat higher and less dependent upon the exposure conditions.

V. REFERENCES

1. National Science Foundation and the Office of Coal Research:
Materials Problem and Research Opportunities in Coal Conversion,
Workshop held at Ohio State Univ., Columbus, OH, April 16-18,
1975. (Available from Corrosion Center, OSU, Columbus, Ohio).
2. Office of Coal Research, U.S. Dept. of Interior, Washington, D.C.:
Ind. Heat., Nov. 1974, Vol. XLI, pp. 73-81.
3. N. S. Raymon and L. Y. Sadler, "Refractory Lining Materials for
Coal Gasifiers, A Literature Review of Reactions Involving High-
Temperature Gas and Alkali Metal Vapors" Bu Mines Info. Circular
No. 8721, 1976.
4. W. T. Bakker, "Refractories for Coal Conversion Process: An
Engineering Approach, Twelfth Annual Sym. on Refractories, St.
Louis Section of Am. Ceram. Soc., St. Louis, MO, March 1976.
5. M. S. Crowley, Am. Ceram. Soc. Bull., 1975, 54, 1072-74.
6. R. E. Dial, Am. Ceram. Soc. Bull., 1975, 54, 640-43.
7. C. R. Venable, Jr., Am. Ceram. Soc. Bull., 1959, 38, 363-68; *ibid*
1969, 48, 1114-17.
8. L. Y. Sadler, N. S. Raymon, K. H. Ivey, et al., Am. Ceram. Soc.
Bull., 1979, 58, (7), 705-09.
9. S. M. Weiderhorn, et al., J. Eng. Mater. Tech., 1977, 99, 143-46.
10. D. E. Day and F. D. Gac, Am. Ceram. Soc. Bull., 1977, 56, 644-48.
11. W. V. Ballard and D. E. Day, Am. Ceram. Soc. Bull., 1978, 57,
438-43; *ibid* 1978, 57, 660-65.
12. K. W. Wistrom and D. E. Day, Am. Ceram. Soc. Bull., 1978, 57
680-84.

13. K. S. E. Forssberg, *Ceramurgia Int.*, 1976, 2, 135-40.
14. G. Schiroky and D. E. Day, *Am. Ceram. Soc. Bull.*, (scheduled for publication in 1980).
15. S. J. Schneider, *Materials Research for Clean Utilization of Coal*, Nat. Bur. of Standards, Washington, D.C. DOE Contract EA-77-A-01-6010, Quarterly Progress Report, 1 Jan-31 Mar 1978.
16. M. S. Crowley, *Am. Ceram. Soc. Bull.*, 1967, 46, 674-82; *ibid* 1970, 49, 527-30.
17. S. F. Rahman and D. E. Day, *J. Materials for Energy Systems* 1979, 1, 34-44.
18. S. F. Rahman and D. E. Day, *J. Materials for Energy Systems* (scheduled for 1980 publication).
19. D. E. Day and G. Lewis, *Am. Ceram. Soc. Bull.*, 1979, 58, 441-443.
20. A. Fakhr, G. L. Lewis and D. E. Day, "Chemical and Physical Stability of Refractories for Use in Coal Gasification", Thirteenth Quarterly Progress Report, Mat. Res. Ctr., Univ. of Missouri-Rolla, MO 65401.
21. A. Fakhr, G. L. Lewis and D. E. Day, "Chemical and Physical Stability of Refractories for Use in Coal Gasification", Sixteenth Quarterly Report, Mat. Res. Ctr., Univ. of Missouri-Rolla, MO 65401.