

CHEMICAL AND PHYSICAL STABILITY OF REFRACTORIES
FOR USE IN COAL GASIFICATION

Fourteenth Quarterly Progress Report

August 1, 1979 - October 31, 1979

Prepared by

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Abbas Fakhr and Delbert E. Day
Ceramic Engineering Department and Materials Research Center
University of Missouri-Rolla
Rolla, Missouri 65401
(314) 341-4352

MASTER

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I. INTRODUCTION

The objectives of this investigation are:

(1) to achieve an understanding of the general types of chemical reactions occurring in refractories when exposed to conditions representative of those at the cold face of the refractory lining in coal gasification vessels; (2) to assess the relative importance of these reactions to physical/chemical properties required for long-service life; and (3) to identify those refractory systems providing optimum service performance, particularly in regard to the bond phases.

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

The present work (1 May 1978 - 30 April 1980) is divided into four tasks given in Figure 1:

TASK I - Degree of Saturation

The aim of Task I is to determine the dependence of the chemical reactions occurring in dense and lightweight castables upon the degree of saturation of the atmosphere and to correlate these reactions to changes in physical and mechanical properties.

TASK II - Liquid versus Vapor Corrosion

The objective of Task II is to determine the corrosion resistance of refractory castables to gas-saturated liquids and vapors and to determine the relative severity of liquid versus vapor corrosion, particularly for lightweight insulating castables, which because of their high porosity, may be most susceptible to chemical attack.

TASK III - Pressure/Temperature Cycling

The aim of Task III is to determine the effect of repeated pressure/temperature cycling upon the mechanical strength of alumina castables containing boehmite; especially the effect upon the mechanical strength and structural integrity of a refractory in which boehmite is formed, but is then subsequently decomposed due to a change in temperature or gas composition. This task is completed and the results have been reported in the Third Annual Report.

TASK IV - Hydrothermal Reactions of CA Compounds

The objective of Task IV is to determine the time, temperature, and pressure dependence for the hydrothermal reactions occurring in calcium aluminate refractory cements and to investigate the reaction of CA, CA₂ and CA₃ individually in hydrothermal atmospheres relevant to coal gasification.

The present report summarizes the experimental and analytical work completed from August 1, 1979 to October 31, 1979.

II. WORK COMPLETED

A. TASK I - Degree of Saturation

Several exposures in pure steam and the DOE atmosphere* were planned at pressures up to 1000 psia and for 10 days. Three exposures have been completed as shown in Table I. The data from Test #1 (410 psia) and Test #2 (1000 psia) in pure steam were reported in the Third Annual report and in the Thirteenth Quarterly report, respectively. This report describes the results of Test #3 performed in the DOE atmosphere

*See Table I for composition

at 1000 psia. The purpose of these experiments is to evaluate the dependence of boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) formation upon the degree of saturation.

A rectangular bar (18"X1/4"X1/4") of neat CA-25 cement (water/cement ratio = 0.3) was used for this test. The chemical composition of CA-25 cement is given in Table II. The experimental test procedures are given in the 11th Quarterly progress report. The DOE atmosphere was continuously exhausted, the steam condensed, and the liquid collected every 24 hours for PH measurements.

The PH of the condensed liquid at the end of the first day was ~8.7. It then decreased gradually every day and reached 7.2 on the tenth day. The PH of the distilled water used to generate steam was 7.

The 18" long rectangular specimen was broken in 3-point bending, using a 2 inch span so that two fracture loads were measured for every inch corresponding to a different percent saturation. The MOR was then calculated from the fracture loads. The change in the average flexural strength with the degree of saturation is shown in Fig. 2. Those parts of the hydrated CA-25 cement bar where the atmosphere was >40% saturated were appreciably stronger than those parts exposed to <40% saturation. Specimens exposed to <40% saturation had a MOR similar to that of the as cast and dried (110°F) specimens. The hydrated CA-25 cement bar exposed to the DOE atmosphere at 1000 psia showed a higher overall MOR compared with the MOR of the similar bar exposed to pure steam at 1000 psia.

The compounds present in the 18" bar after exposure, as determined by XRD and TGA, are given in Table III. As in the previous tests in 410 and 1000 psia steam, the amount of boehmite varied with the percent

saturation of the atmosphere as shown in Fig. 3. Similar to the previous tests, a linear relationship exists between the percent saturation and the amount of boehmite below ~70% saturation. The minimum percent saturation required to form boehmite in DOE atmosphere at 1000 psia is ~10% which is slightly less than that in pure steam at 1000 (~20%) and 410 (~30%). As shown in Table III, boehmite was not detected by TGA & XRD in sections of the bar which were above 720°F during exposure. However, scanning electron micrographs of these sections (Fig. 4-a) show small quantities of boehmite formed which are not detected by XRD and TGA. The calcite and $C_4A_3H_3$ detected by XRD and TGA are also shown in the SEM of Fig. 4-C.

B. TASK II - Liquid versus Vapor Corrosion

Several 10-day exposures have been conducted to evaluate liquid versus vapor corrosion. The results of the previous exposures in pure steam/water at 410 and 1000 psia were described in the Third Annual and the Thirteenth Quarterly Reports, respectively. This report summarizes data for the third exposure in the DOE atmosphere at 1000 psia.

The seven commercial and laboratory-prepared cement-bonded castables and three calcium aluminate cements (initially dry powders as well as hydrated neat cement cubes) listed in Table II are being investigated. The experimental procedures are the same as reported previously.

The PH of the water collected every 24 hours from the bottom of the vessel was ~11 on the first day and decreased to ~4 on the second day and then remained essentially constant for the duration of the exposure (10 days). The initial PH of the distilled water used in this test was 7. The high initial PH and its subsequent decrease is consistent

with the dissolution of some portion of the CaO from the cement-bond phases and its precipitation as CaCO_3 within the castables.

1. Cement-Bonded Castables

Table IV gives the properties measured for the castables after exposure to the DOE atmosphere at 1000 psia. Most of the castables showed weight increases after exposure, though the immersed UMR-8 and the vapor exposed VSL-50 had weight losses. The dimensions of the castables did not change appreciably during exposure. Similarly, there was no significant difference in the density or porosity of the specimens exposed to vapor compared with those immersed in the liquid.

The formation of boehmite in the dense castables was confirmed by XRD (Table V) and measured by TGA (see Table VI). As in steam, larger amounts of boehmite were found in the dense high alumina than in the dense intermediate alumina castables after exposure to the DOE atmosphere. There was no significant difference in the quantity of boehmite formed in specimens exposed to vapor compared with those immersed in liquid. The same result was obtained in previous exposures using pure steam. Calcite was also formed in fairly large quantities in all dense castables. Larger amounts of calcite were mostly present in the dense castables exposed to vapor than immersed in liquid. Figs. 5 and 6 show some features of the microstructure of dense castables after being exposed to 1000 psia/447°F DOE atmosphere for 10 days.

With the exception of Litecast 60-25, less boehmite was formed in the insulating castables compared with the dense castables during exposure to DOE atmosphere. The same results were obtained in the previous

exposures in steam atmosphere. The amounts of boehmite contained in immersed insulating castables were almost the same as those exposed to vapor. There was less calcite than boehmite in all the insulating castables.

Comparison of liquid versus vapor exposure, for the DOE atmosphere, in terms of MOR, for various castables is given in Fig. 7. As previously observed for castables exposed to pure steam, all the dense alumina castables had a higher strength after exposure to either the saturated vapor or immersed in liquid, compared with their controls (fired at 500°F in air for 18 h). The large increase in MOR is attributed to the formation of additional bonding phases, such as boehmite and calcite as shown in Fig. 5 and 6. With the exception of UMR-8, which showed a higher flexural strength for immersed specimens, all the castables immersed in liquid or exposed to saturated vapor had similar MOR's, Fig. 8. The higher MOR of the immersed UMR-8 specimens may be explained by its slightly higher boehmite content compared with that of specimens in vapor, Table VI.

Comparison of the flexural strength of dense castables on the basis of the cements and aggregate they contain show that castables containing CA-25 cement (UMR-1 and UMR-8) had a generally higher strength than those containing refcon (UMR-4 and UMR-5), see Fig. 8. On the other hand, the aggregates (tabular alumina versus calcined kaolin) seem to have no significant effect on the flexural strength of dense castables. Samples made with the same cement, but different aggregates had close to the same MOR.

The insulating castables, generally, showed no large change in MOR after exposure to the DOE atmosphere at 1000 psia. The same results were found in the previous tests in pure steam at 410 and 1000 psia.

2. Calcium Aluminate Cements

Table IV summarizes the weight and dimensional changes of hydrated cement cubes. All hydrated cement cubes showed weight and dimensional increases after exposure compared with their dry (230°F) weights and dimensions. Unlike the previous results in 1000 psia pure steam/water, there was no significant difference between the cubes exposed to vapor or immersed in liquid. Both weight and dimensional increases are expected due to the formation of boehmite and calcite.

The XRD data (Table V) show that boehmite is the major component in the hydrated specimens after exposure and both calcite and boehmite are the major components in the initially unhydrated cements (powders) after exposure to the DOE atmosphere. The TGA results showed similar weight losses for cement specimens exposed to vapor compared with those immersed in water, but less boehmite and calcite was found in the immersed specimens.

3. Summary - Task II

The relative severity of the corrosion of several refractory castables by either liquids or saturated vapor has now been determined for pure steam (500 and 1000 psia, 10 days), the DOE atmosphere (1000 psia and 10, 44 and 60 days and CO-steam atmospheres of CO/steam ratio = 0.1, 1.0 and 3.0 (1000 psia, 20 days). In all instances, the properties of a given castable were basically similar after exposure, regardless of whether the specimens had been immersed in liquid or in contact with saturated vapor. In a few instances some small differences in properties (dimensional changes, porosity, and flexural strength) were observed, but

an overall conclusion at this time is that there is no major difference in the corrosion resistance of refractory castables to either saturated vapor or to liquids condensed from the atmospheres investigated to date.

C. TASK III - Pressure/Temperature Cycling

Work on this task is completed and no further work is planned.

D. TASK IV - Hydrothermal Reaction of CA compounds

During the last quarter, the prepared samples of CA and CA₂, along with CA-25 and Secar 250, have been run at 1000 psia in the DOE atmosphere for 5 and 10 hours. The XRD and TGA data for these samples are being collected.

Preliminary analysis indicates that neither calcium carbonate nor calcium formate have been formed in the samples. There appears to be gibbsite (Al₂O₃·3H₂O), C₃AH₆ and C₄A₃H₃ as in previous steam only runs.

III. FUTURE WORK

TASK I - Degree of Saturation

In the past experiment at 1000 psia steam, the temperature gradient between 50 to 100% saturation occurred within a short length and, therefore, only limited data could be obtained for this interesting region. Furthermore, in the previous experiments, steam was supplied from a vessel in which the Task II experiment on refractories was in progress. The second experiment at 1000 psia steam with the temperature gradient for 40-100% saturation covering the entire length of the specimen is recently completed. In this experiment a separate stainless steel vessel was used to produce and continuously supply the required

pure steam. From the results of the past three tests in steam and DOE atmospheres and the data from the recent experiment, it will be decided whether or not any further test is required.

TASK II - Liquid versus Vapor Corrosion

Major experiments on this task are completed and only some detailed XRD analysis is required. This work will be completed during the next quarter.

TASK III - Pressure/Temperature Cycling

Work on this task is completed and no further work is planned.

TASK IV - Hydrothermal Reactions of CA Compounds

Only a small amount of further data analysis is required for samples exposed to the DOE atmosphere at 1000 psia for 5 and 10 hours, which will be completed during the next quarter. The 20 and 60 hours runs in the DOE atmosphere will also be made during the next quarter.

IV. PERSONNEL

During this quarter the following personnel worked on this project.

1. Delbert E. Day, Principal Investigator
2. Gordon Lewis, Co-Investigator
3. Abbas Fakhr, Postdoctoral Fellow (Full time)

Table I - Tests Conditions and Status for Task I

Test #	Atmosphere	Steam Vessel Temp. (°F)	Pressure (psia)	Duration (Days)	Status
1	steam	447	410	10	complete
2	steam	545	1000	10	Complete, temp. gradient 540-900°F
3	DOE*	447	1000	10	complete
4	steam	545	1000	10	Exposure complete, sample characterization in progress

* DOE composition is 18 CO, 12 CO₂, 5 CH₄, 24 H₂, 41 H₂O (Vol %)
plus 1% H₂S

Table II. Refractory Materials Used in Task II Exposure Test

<u>Trade Name or Identification</u>	<u>Manufacturer</u>	<u>Composition and Remarks</u>
Dense, High Alumina Castables		
UMR-1	Univ. of Missouri	93.4% Al ₂ O ₃ , 5.4% CaO (70% Tabular Al ₂ O ₃ * + 30% CA-25 Cement**)
UMR-4	Univ. of Missouri	87.4% Al ₂ O ₃ , 10% CaO, 1.7% SiO ₂ (70% Tabular Al ₂ O ₃ * + 30% Refcon Cement**)
Dense, Intermediate Alumina		
UMR-8	Univ. of Missouri	63.8% Al ₂ O ₃ , 4.8% CaO, 28.3% SiO ₂ (75% Calcined Kaolin Aggregate*** + 25% CA-25 Cement**)
UMR-5	Univ. of Missouri	58.6% Al ₂ O ₃ , 8.6% CaO, 29.6% SiO ₂ (75% Calcined Kaolin Aggregate*** + 25% Refcon Cement**)
Insulating Castables		
Cerlite #75	C. E. Refractories	53.8% Al ₂ O ₃ , 2.9% CaO, 40.5% SiO ₂
Litecast 60-25	General Refract.	46.7% Al ₂ O ₃ , 9.1% CaO, 40.2% SiO ₂
VSL-50	A. P. Green Ref.	34.5% Al ₂ O ₃ , 9.3% CaO, 52.5% SiO ₂
Calcium Aluminate Cements		
CA-25	ALCOA	79% Al ₂ O ₃ , 18% CaO, 0.2% SiO ₂
Secar 250	Lone-Star Lafarge	72% Al ₂ O ₃ , 26% CaO, 0.2% SiO ₂
Refcon	Universal Atlas	58% Al ₂ O ₃ , 33.5% CaO, 5.6% SiO ₂

*Aluminum Company of America, Bauxite, Arkansas. Tabular alumina T-61, used as grog in the high alumina castables, contained the following size fraction (wt%):

-8 to 14 mesh = 20%
 -14 to 28 mesh = 18%
 -28 to 48 mesh = 16%
 -48 mesh = 46%

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

***C. E. Minerals, King of Prussia, Pennsylvania. Mulcoa 60 (4 and 8 mesh sizes) and Mulgrain M47 (20 mesh size) calcined Kaolin aggregate used as grog contained the following size fraction (wt%):

-4 to 8 mesh = 27%
 -8 to 20 mesh = 36%
 -20 to 60 mesh = 13%
 -60 mesh = 24%

Table III. MOR and compounds present in CA-25 hydrated cement exposed to DOE atmosphere at 1000 psia and various degrees of saturation.

(TASK I)

Sample No.	Temp. (°F)	% Saturation	MOR (PSI)	TGA Data			X-Ray Data*			
				%W.L.	Wt.%AH	Wt.%CaCO ₃	α-Al ₂ O ₃	AH	CaCO ₃	C ₄ A ₃ H ₃
1	350	condensed liquid	5500	19	53	23	tr	M	m	tr
2	447	100	5000	14	28	10	m ₂	M	m ₁	tr
3	468	80	5350	14	25	12	m ₂	M	m ₁	tr
4	470	79	4550	13	23	10	m ₂	M	m ₁	tr
5	510	54	2860	12	20	8	m ₂	M	m ₁	tr
6	530	45	3200	13	20	14	m	M ₁	M ₂	tr
7	570	32	1610	13	12	16	m	M ₂	M ₁	tr
8	642	19	1450	11	11	17	m ₁	m ₂	M	tr
9	700	13	1230	10	5	15	M ₂	m	M ₁	tr
10	720	11	1450	10	2	15	M ₁	tr	M ₂	tr
11	763	9	1320	10	--	17	M ₁	ud	M ₂	tr
12	857	5.5	1300	9.5	--	19	M	ud	m ₁	m ₂
13	870	5	1200	9.5	--	20	M	ud	m ₁	m ₂

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

Table IV. Properties of castables and pure cements after exposure to DOE atmosphere at 1000 psia.

(TASK II)

Trade name or Identification	% Weight Change		% Dimensional Change		MOR (PSI)		Density (gm/cc)		% Porosity	
	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)
<u>Dense High Alumina</u>										
UMR-1 (Tabular + CA-25)	+1.16	+0.80	+0.05	+0.11	4270± 260	4110± 235	2.78	2.75	12.96	13.19
UMR-4 (Tabular + Refcon)	+3.69	+1.78	+0.09	+0.04	3185± 420	3170± 610	2.62	2.63	19.90	20.18
<u>Dense, Intermediate Alumina</u>										
UMR-5 (Kaolin + Refcon)	+2.06	+1.98	-0.30	-0.09	3560± 270	3365± 290	2.46	2.45	10.28	10.47
UMR-8 (Kaolin + CA-25)	+0.06	-0.66	+0.03	0	4015± 240	4890± 355	2.44	2.41	12.36	12.02
<u>Insulating Castables</u>										
Cerlite #75	+0.43	+0.73	+0.45	+0.58	380± 62	430± 35	1.54	1.54	48.72	48.24
Litecast 60-25	+1.30	+2.45	-0.04	+0.12	845± 103	810±60	1.25	1.25	51.35	51.79
VSL-50	-0.22	+2.39	+0.19	+0.93	345±60	210±95	1.04	0.91	60.29	65.05

Table IV (Continued)

Trade name or Identification	% Weight Change		% Dimensional Change		MOR (PSI)		Density (gm/cc)		% Porosity	
	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)	Vapor	Liquid (Immersed)
<u>Hydrated Cement</u>										
CA-25	+11.60	+11.83	+0.72	+0.73	Not measured		Not measured		Not measured	
Secar 250	+10.88	+10.55	+0.72	+0.72	"	"	"	"	"	"
Refcon	+10.64	+10.71	+0.71	+0.71	"	"	"	"	"	"

Table V. X-ray data for castables and cements after exposure to DOE atmosphere at 1000 psia for ten days.

Trade Name	Dense High Alumina				Dense Inter-mediate Alumina				Insulating Castables					
	UMR-1		UMR-4		UMR-5		UMR-8		Cerlite #75		Litecast 60-25		VSL-50	
Identification	V	L	V	L	V	L	V	L	V	L	V	L	V	L
α -Alumina (Al_2O_3)	M ₁	M ₁	M ₁	M ₁			m ₁	m ₁	m ₁	m ₁	m ₁	m ₁	m ₂	m ₂
Boehmite (AH)	M ₂	M ₂	M ₂	M ₂	m ₁	m ₁	m ₃	m ₂	tr	tr	tr	tr		
Calcite ($CaCO_3$)	m	tr	m	M ₃	m ₂	tr	m ₂	m ₃	m ₃	m ₃	m ₃	m ₃	m ₁	m ₁
Mullite (A_3S_2)					M ₁	M ₁	M ₁	M ₁						
α -Quartz (SiO_2)									M ₁	M ₁	M ₁	M ₁	M ₁	M ₁
Kyanite (AS)									m ₂	m ₂	m ₂	m ₂		
α -Cristobalite (SiO_2)					tr	tr								
β -Cristobalite (SiO_2)							tr	tr						
CA									tr	tr	tr	tr		
C_4AH_6														

Table V. Continued

Trade name & Identification	CA-25 Cement CA		Secar 250 Cement S		Refcon Cement R				
	Hydrated	Unhydrated	Hydrated	Unhydrated	Hydrated	Unhydrated			
Compounds	V	L	V	V	L	V	L	V	
$\alpha\text{-Al}_2\text{O}_3$	tr	m	tr	m ₃	m ₃	m	tr	tr	
Boehmite	M ₁	M ₁	M ₂	M ₁	M	M ₂	M ₁	M ₂	M ₂
Calcite	M ₂	m	M ₁	m ₂	m ₂	M ₁	m ₁	tr	M ₁
C ₃ AH ₆		tr		m ₁	m ₁		m ₂	m ₁	

V = Vapor, L = Liquid, M = major, m = minor, tr = trace, ud = undetected.

Table VI. % Weight lost, boehmite and calcite for castables and cements after exposure at 1000 psia DOE atmosphere for 10 days (Task II) as determined by TGA.

Trade name or identification	Vapor			Liquid		
	% W.L.	% AH	%CaCO ₃	% W.L.	% AH	% CaCO ₃
<u>Dense High Alumina</u>						
UMR-1	7.6	22.3	7.6	7.5	21.8	4.7
UMR-4	11.3	18.4	11.0	8.9	19.6	10.5
<u>Dense Intermediate Alumina</u>						
UMR-5	7.5	14.6	7.8	7.2	13.2	8.0
UMR-8	5.2	11.1	5.8	5.	14.	3.2
<u>Insulating Castables</u>						
Cerlite #75	4.5	6.5	3.5	6.7	6.0	2.8
Litecast 60-25	10.8	16.2	6.1	8.4	16.5	6.6
VSL-50	10	9.5	6.5	10.8	10.8	7.3
<u>Hydrated Cements</u>						
CA-25	20.5	60.4	20.8	20.7	61.8	13.4
Secar 250	23.3	57.9	12.3	24.	52.5	14.
Refcon	22.7	41.5	24.7	18.9	36.8	8.3
<u>Unhydrated Cements</u>						
CA-25	23.5	55.3	25.9			
Secar 250	25.6	52.9	33.9			
Refcon	26.7	55.7	28.7			

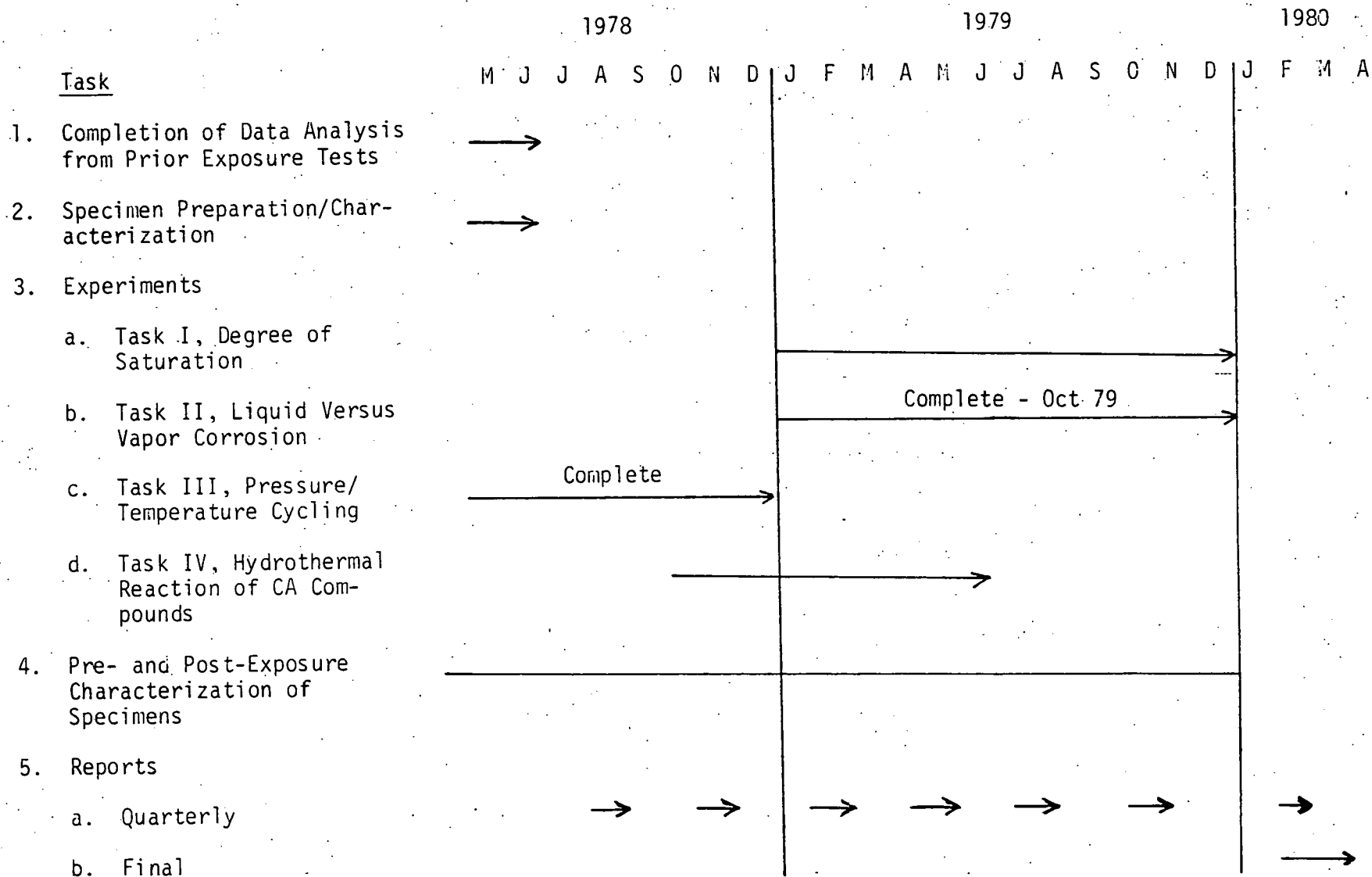


Figure 1. Work Schedule, 1 May 1978 to 30 April 1980

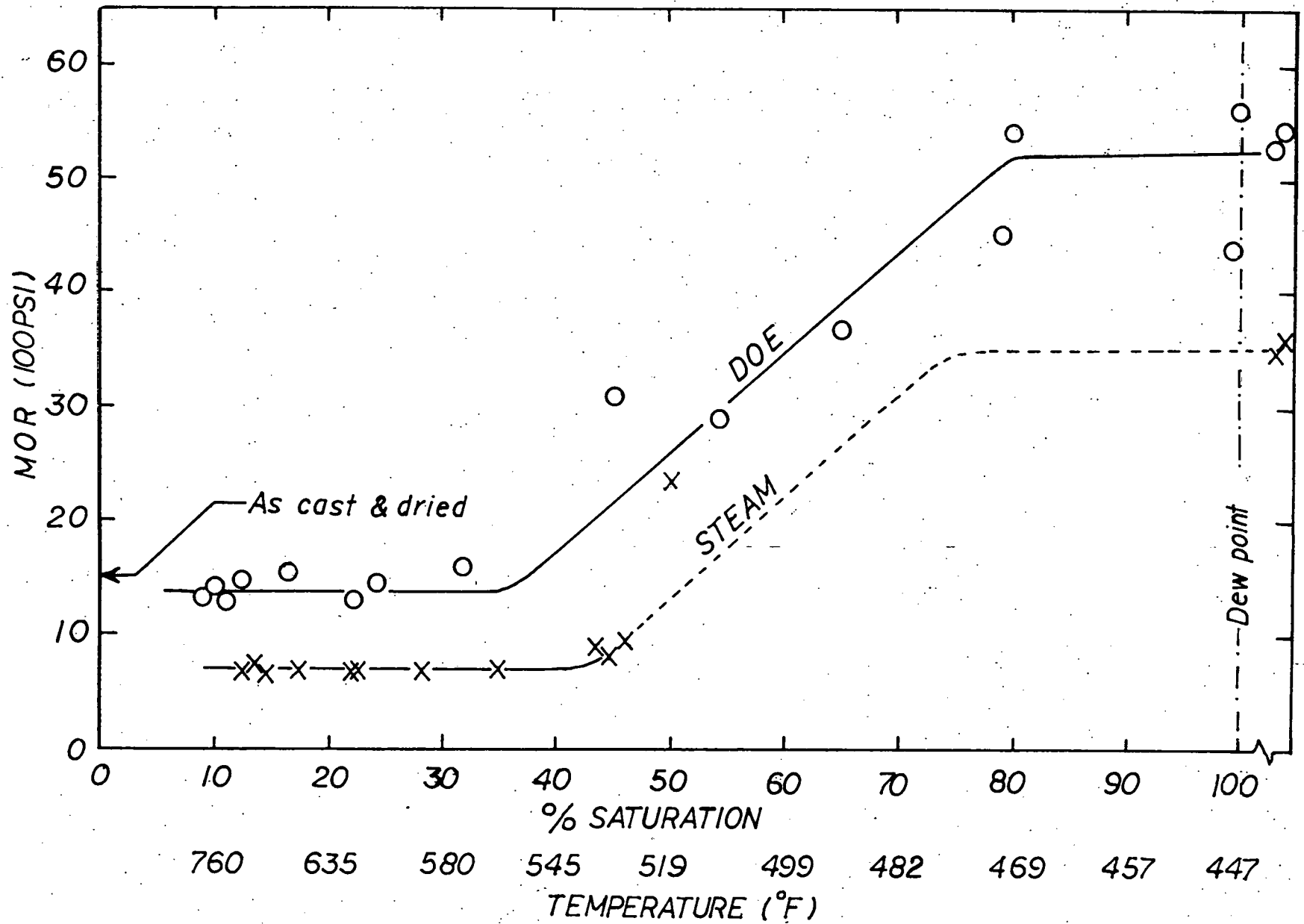


Fig. 2. Variation of MOR of hydrated CA-25 cement exposed to DOE atmosphere and pure steam at 1000 psia with the degree of saturation.

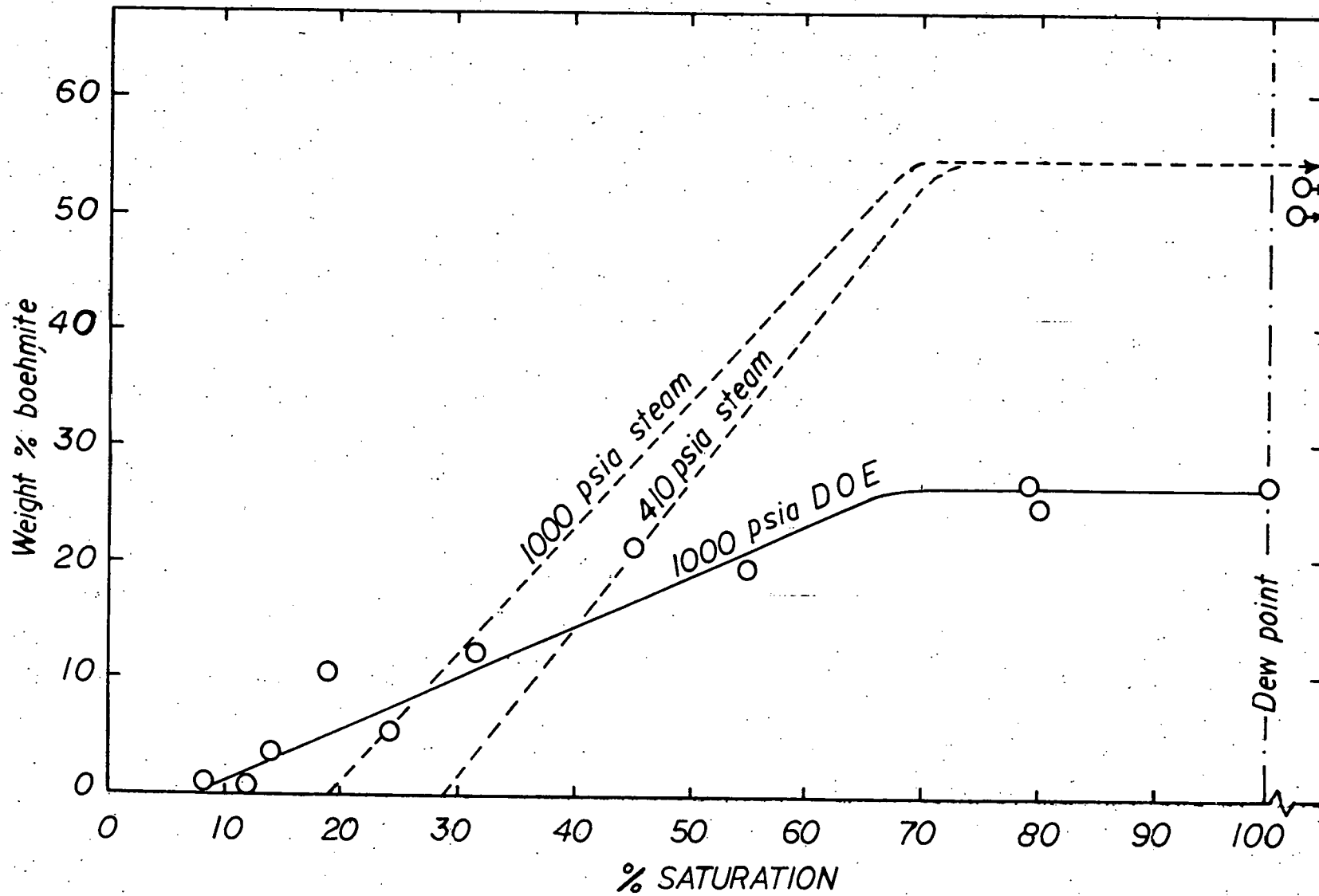


Fig. 3. Weight % boehmite as a function of the degree of saturation for CA-25 cement exposed to DOE atmosphere and pure steam.

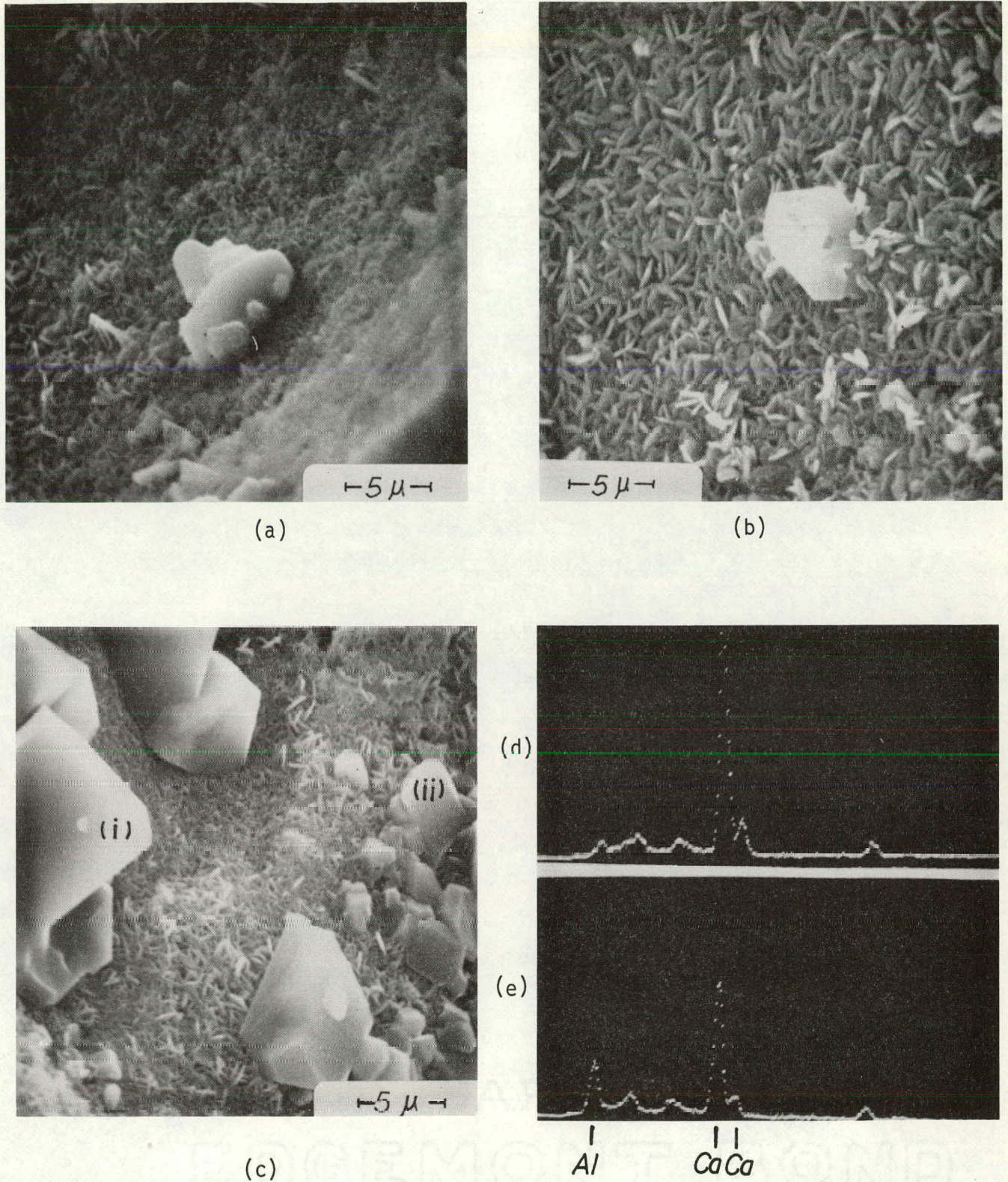
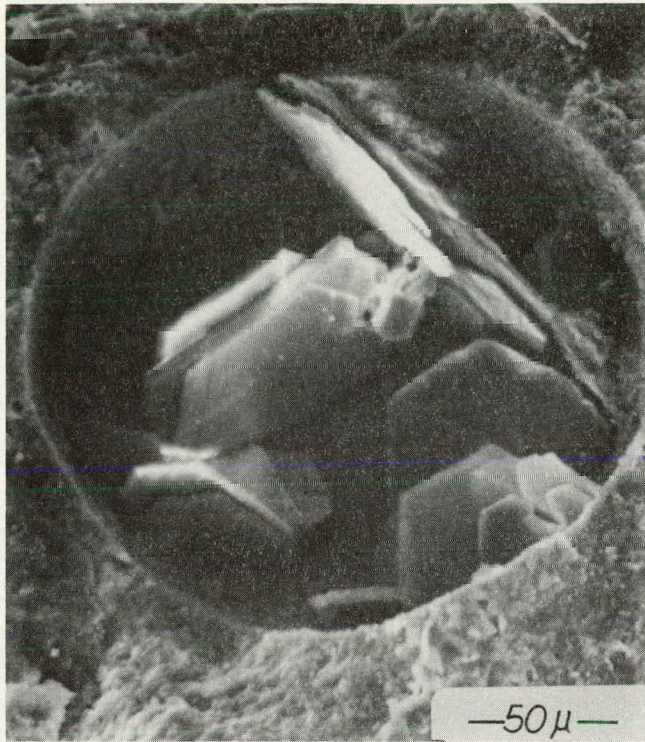
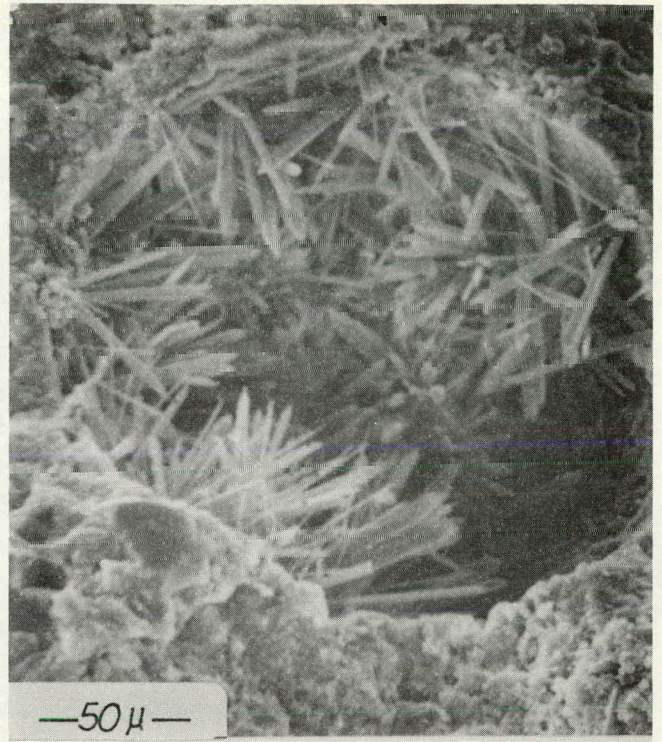


Fig. 4. Microstructure of CA-25 cement exposed to DOE atmosphere for 10 days.

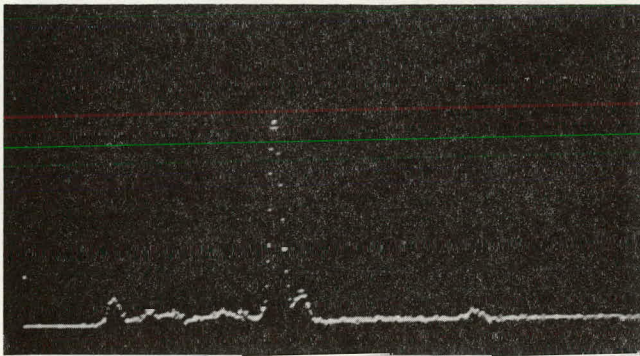
- (a) General area around an internal void showing the beginning of boehmite formation, <10% saturation. (b) Surface of a void showing boehmite crystals (matrix), $\approx 65\%$ saturation. (c) Inside surface of a void showing boehmite (matrix), calcite and $C_4A_3H_3$ crystals, $\sim 100\%$ saturation. (d) EDAX for crystal (i). (e) EDAX for crystal (ii).



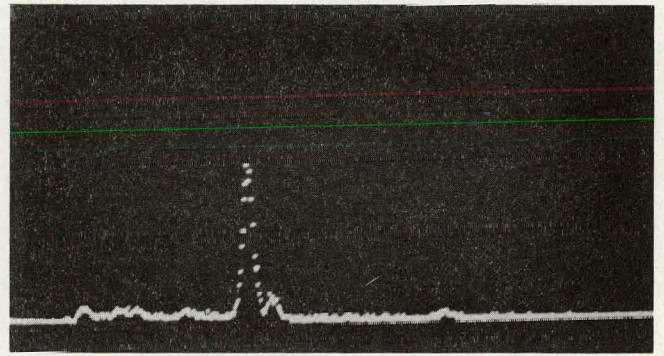
(A)



(B)



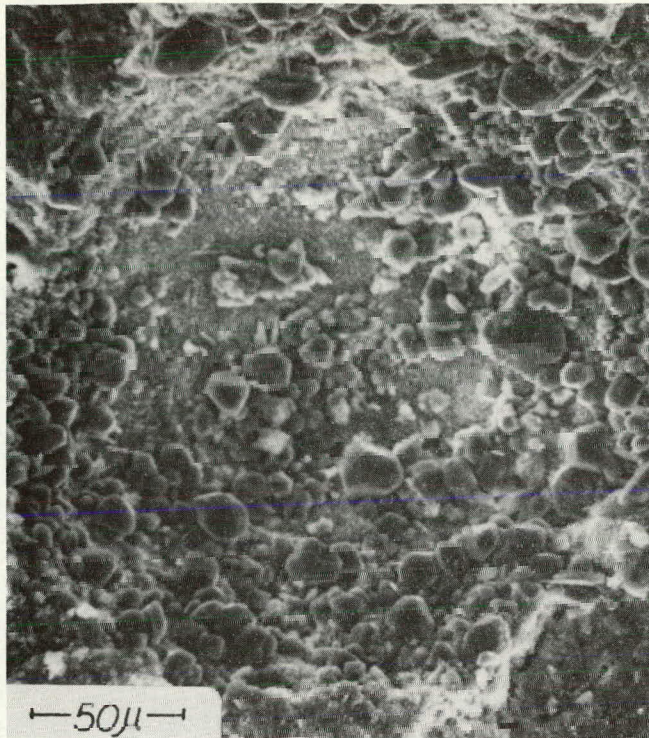
Al Ca Ca
(C)



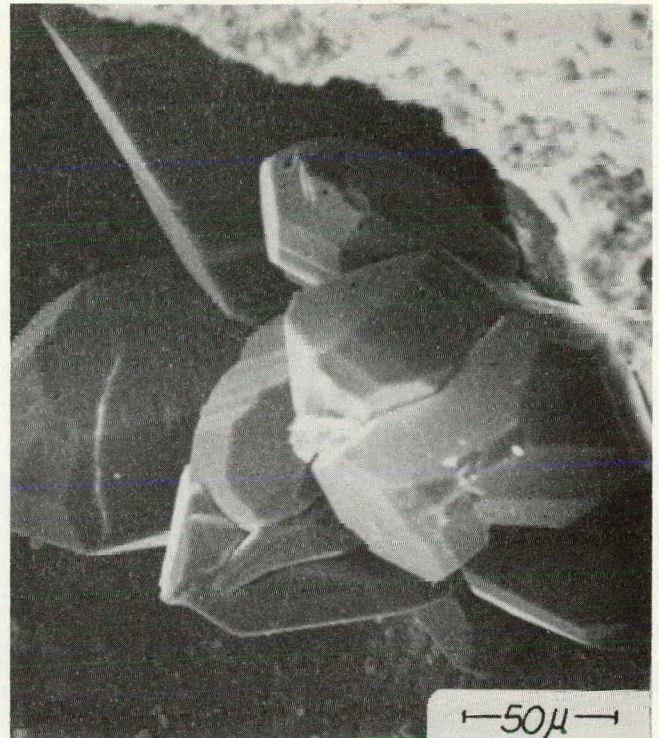
Ca Ca
(D)

Fig. 5. Microstructure of UMR-1 and UMR-4 after exposure to 1000 psia/447°F DOE atmosphere.

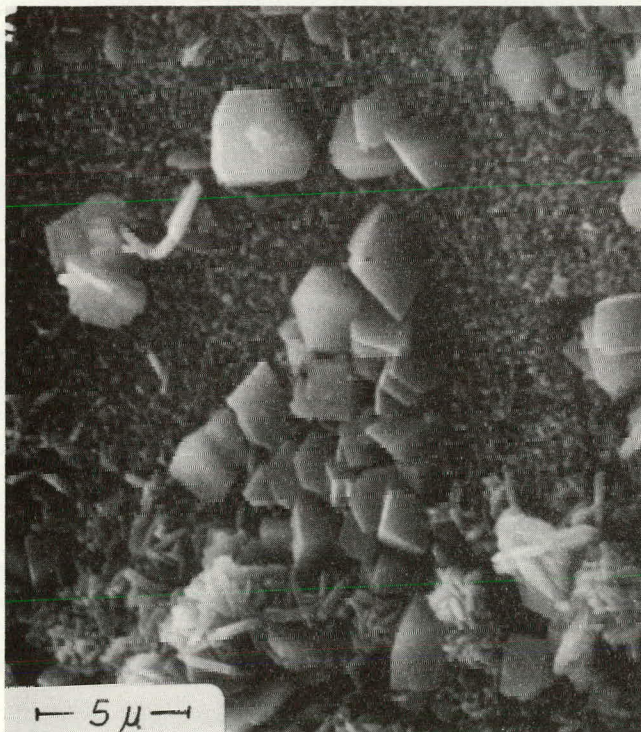
- (A) UMR-1 (Saturated liquid), showing the formation of calcite crystals.
- (B) EDAX for crystals in (A).
- (C) UMR-4 (Saturated liquid). An internal void is almost filled with newly grown crystals.
- (D) EDAX for crystals in (B).



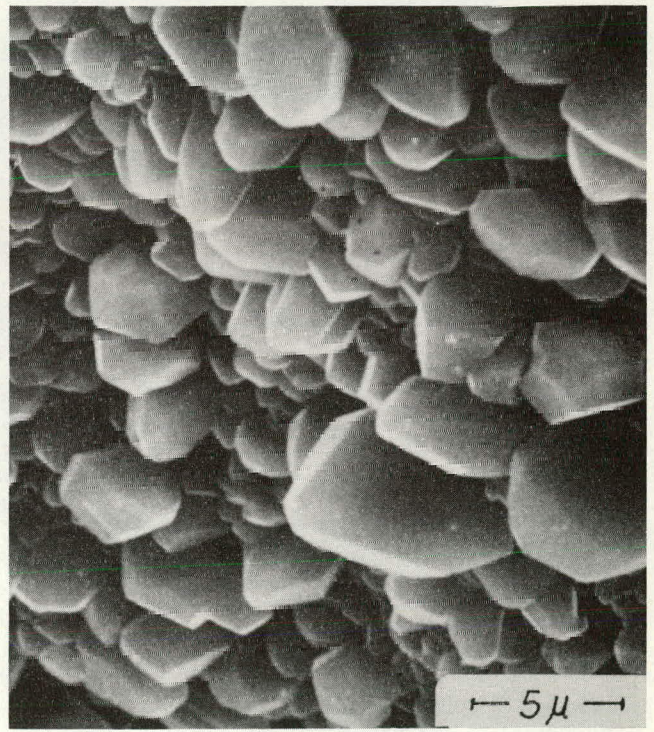
(A)



(B)



(C)



(D)

Fig. 6. Microstructure of dense castables after exposure to 1000 psia/447°F DOE atmosphere showing large calcite crystals.

- (A) UMR-5 (saturated liquid)
- (B) UMR-8 (saturated liquid)
- (C) UMR-1 (saturated liquid)
- (D) UMR-8 (saturated vapor)

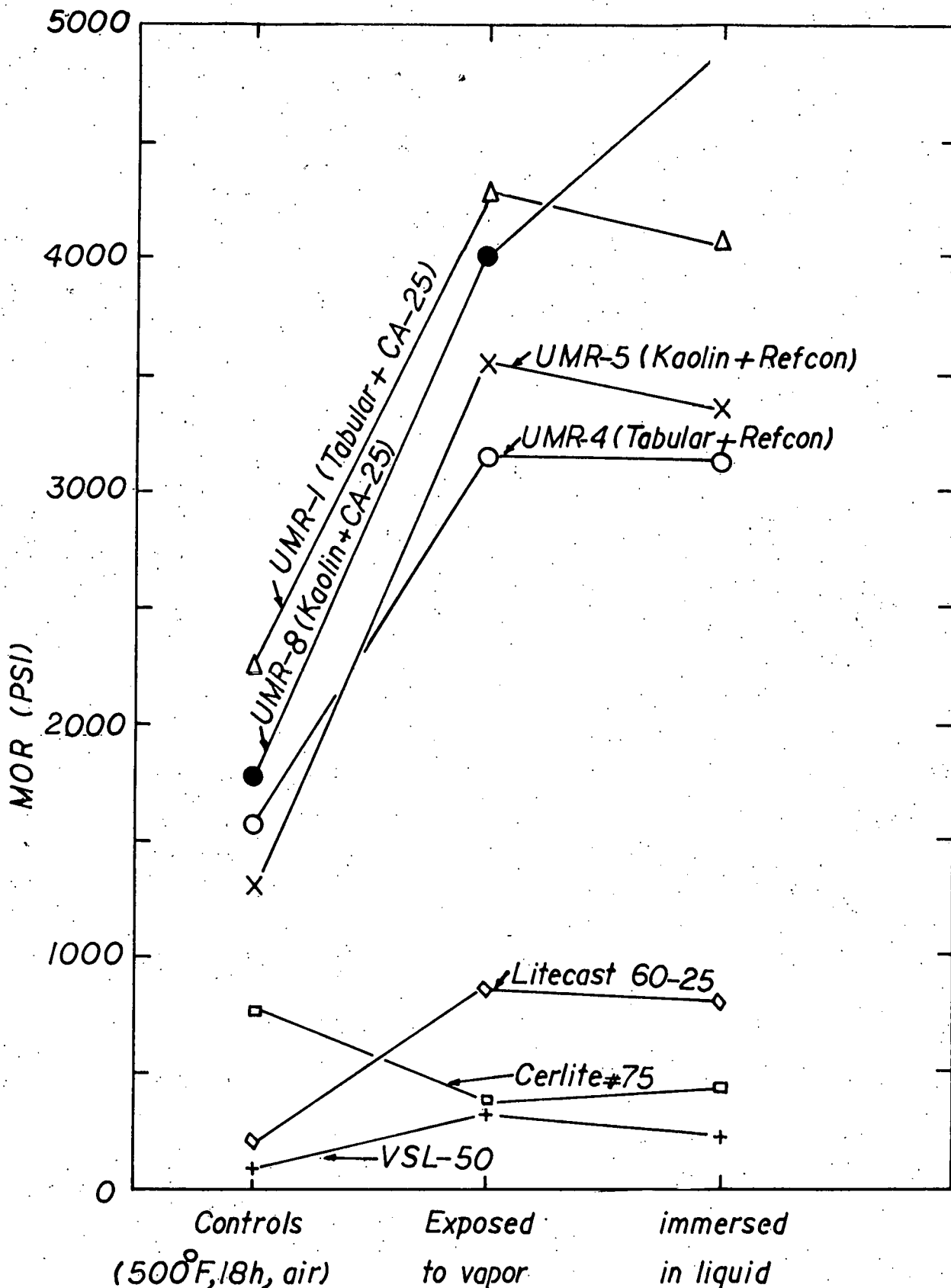


Fig. 7. Room temperature Modulus of Rupture of Castables after a 10-day Exposure to DOE atmosphere at 1000 psia/447°F.

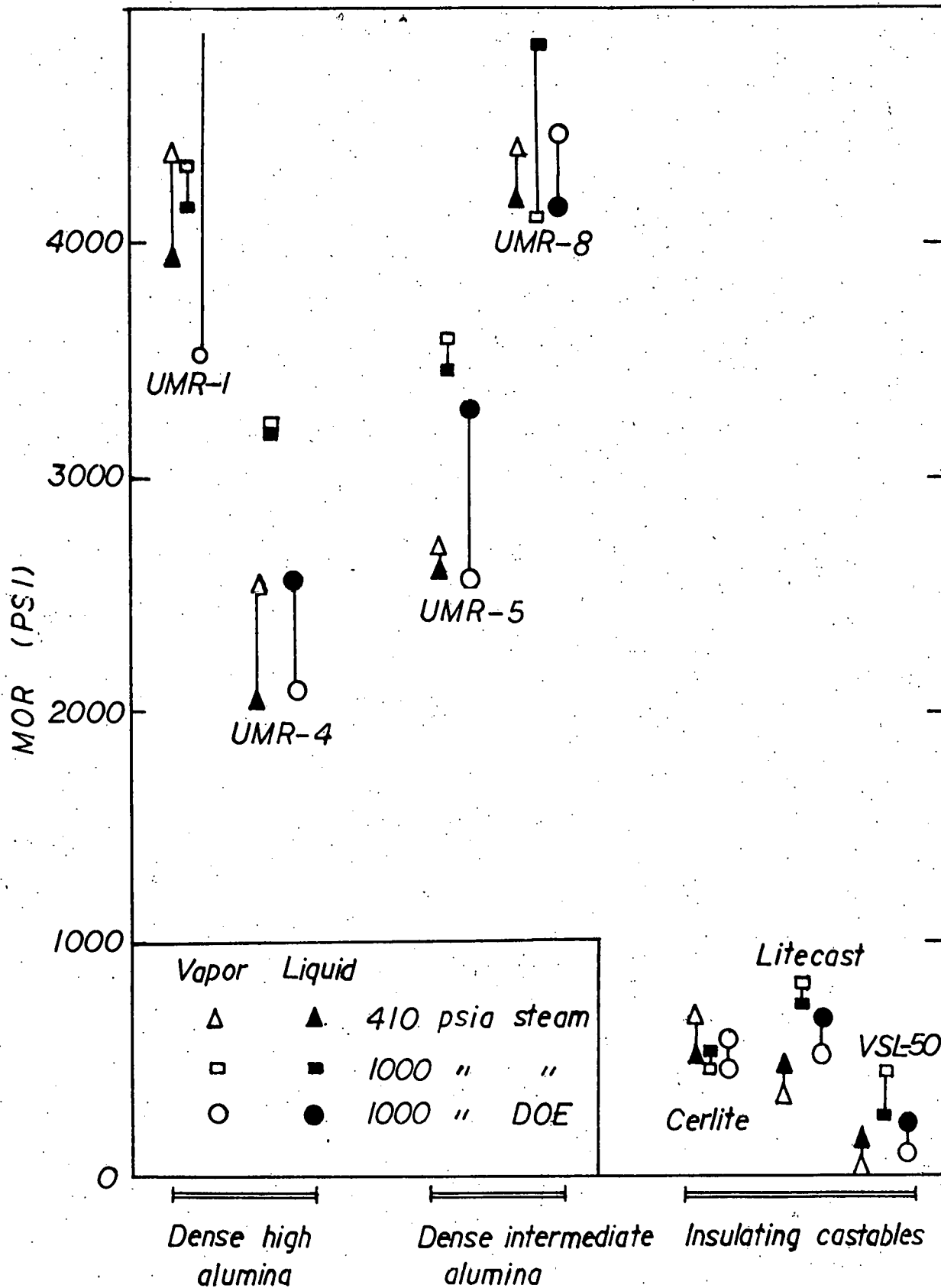


Fig. 8. Comparison of the MOR of castables exposed in liquid and vapor at different pressures and atmospheres.