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Stability of Refractory Castables to Steam-N_2 and Steam-CO Atmospheres

by

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ABSTRACT

The properties of three refractory castables, designated as High, Intermediate, and Low Al_2O_3, were investigated after the castables had been exposed to steam-N_2 and steam-CO atmospheres at 199°C and 450 psi for 6, 12, and 18 days. Four general chemical reactions were identified. First, the residual unreacted calcium aluminate cement compounds in the castables reacted with the steam to form additional cementitous material. This reaction was considered primarily responsible for the observed increase in mechanical strength of the castables. Second, a portion of the cement bond in the castables was destroyed by the CO, CO_2, and H_2O in the test atmospheres, as evidenced by the reaction of CaO to form $CaCO_3$ and $Ca(HCO_2)_2$. Third, the free Al_2O_3 in the castables hydrated to form boehmite. A volume expansion accompanied this reaction. Fourth, a portion of the free SiO_2 was removed from the SiO_2-containing castables by reacting with the steam.

I. INTRODUCTION

Refractory castables have been used extensively in petrochemical processing applications as protective and thermal linings in reactors, regenerators, coolers, cyclones, and catalyst feed lines.[1] This extensive use is principally due to the lower permeability of castables, compared to refractory brick of similar composition, which makes them more resistant to penetration by liquids and gases,[2] their generally lower thermal conductivity,[3] and ease of installation.

Limited information is available on the effect of high temperature-pressure gases on refractories. At elevated temperatures where CO and H_2 are present, disintegration due to carbon deposition (CO disintegration) and SiO_2 volatilization have been reported.[4,5,6,7,8] When high pressure steam is present, SiO_2 is removed as a result of SiO_2 hydration.[9] High pressure steam poses other problems in that its percolating action can leach out important constituents of refractory castables, such as CaO.[10]

This investigation was undertaken to determine the effect of steam-N_2 and steam-CO atmospheres at 199°C and 450 psi on three general types of commercial refractory castables. These conditions were chosen for two reasons. First, they simulate those at the cold face of castable linings in NH_3 plant transfer lines, where degradation of the linings has been reported.[11] Second, they are relevant

to the conditions found in coal gasification units, where such castables are candidates for use.

The durability of each castable to the test conditions was monitored by modulus of rupture (M.O.R.) measurements, and weight and dimensional changes. Chemical reactions were evaluated by x-ray diffraction, gas chromatography, and atomic absorption.

II. EXPERIMENTAL PROCEDURE

A. Materials

Three refractory castables, designated as High, Intermediate, and Low (insulating) Al_2O_3, with the composition and physical properties shown in Table I were examined.

Specimens were cast as 38.1 x 38.1 x 152.4 mm (1½ x 1½ x 6 in.) bars, cured for 24 hours in air, and dried at 104°C for 24 hours. Additional 12.70 x 12.70 x 31.75 mm (½ x ½ x 1¼ in.) specimens were cut from randomly selected large bars, cleaned and dried, and used for x-ray diffraction analysis. After drying, the weight and dimensions of the large bars and small specimens were recorded.

The raw materials used in each castable were also studied. A sample of each material, except the cements, was placed in an aluminum metal container, dried, and weighed. The cements were mixed with 21-23 wt.% distilled water, cast as 12.70 x 12.70 x 31.75 mm bars, and weighed.

B. Test Conditions and Procedures

The refractory specimens were exposed to steam-N_2 and steam-CO atmospheres in a reaction vessel constructed from 300# ASA carbon steel. Resistance heating elements on the outer surface of the vessel heated the vessel and contents to the desired temperature. Additional information concerning the construction of the vessel is given in Appendix 1.

At the start of each test, excess distilled water was placed in the vessel in sufficient quantities to insure that saturated steam was present during testing. The specimens were positioned in the vessel above the water. The experimental conditions and materials studied in each test are summarized in Table II. The overall composition of the test atmosphere was maintained by controlling the temperature of the vessel, so as to produce a specific steam pressure, and then adding the necessary CO or N_2 (certified standard grade) to produce the desired total pressure. During testing, the test atmosphere was essentially static, but small quantities of CO or N_2 were added periodically, because of small leaks in the system.

C. Analysis Procedures

After exposure to the test atmosphere, the specimens were removed, examined visually, dried at 104°C, weighed and the dimensions measured. Samples were taken for photographic documentation, scanning electron microscope (SEM) analysis, and x-ray diffraction analysis. The SEM and x-ray diffraction analysis procedures are described in Appendices 2 and 3, respectively. The M.O.R. was determined according to ASTM C268-70, with the exception that the bars were tested with a 101.6 mm (4 in.) span. The M.O.R. reported is the average for ten specimens.

At the completion of each test, the interior walls of the vessel were closely inspected for atmosphere-metal

and/or refractory-atmosphere-metal reactions, and when feasible, samples were taken for x-ray diffraction analysis.

The water remaining in the vessel at the completion of each test was removed, its volume and pH measured, and any particulate material removed by filtering through No. 40 filter paper. The solid residue was dried and the compounds present determined by x-ray diffraction. In test 6, the Ca content of the remaining water was determined by atomic absorption spectroscopy (see Appendix 4 for the procedures used).

During the steam-CO tests, the atmosphere was sampled periodically and analyzed by gas chromatography to determine any changes in its composition (see Appendix 5 for the procedures used).

D. Compounds Present in the As-prepared Castables

The compounds, identified by x-ray diffraction, in the untested (as-prepared) castables and the associated raw materials are presented in Tables III-V. The relative amounts of each compound were estimated from the overall peak intensities. Comparisons between diffraction patterns were made using peak ratios.

An important difference between the castables is the manner in which the Al_2O_3 is present. In the High and Low Al_2O_3 castables, Al_2O_3 is present both as free Al_2O_3 (corundum) and combined in the cement compounds. However, the Intermediate Al_2O_3 castable contains practically no free

Al_2O_3.

The manner in which the SiO_2 is present in the Intermediate and Low Al_2O_3 castables also differs significantly. The majority of the SiO_2 in the Intermediate Al_2O_3 castable is present as mullite (3 $Al_2O_3 \cdot 2$ SiO_2) and C_2AS, only a minor amount being present as free SiO_2 (α-quartz). In the Low Al_2O_3 castable, free SiO_2 (α-quartz) is the major phase with all the remaining SiO_2 being present as C_2AS and perlite.

III. RESULTS and DISCUSSION

Four general reactions, consisting of cement hydration, the dissolution of CaO from the cement bond phases, boehmite formation, and SiO_2 dissolution were identified from x-ray diffraction analyses of the castables and the associated raw materials exposed to the test conditions. The extent and effect of these reactions upon physical properties differed among the castables, primarily because of the different chemical and mineralogical composition of the castables. A summary of the reactions and their overall effects is given in Table VI.

A. Cement Hydration

The residual unreacted calcium aluminate compounds in the castables, primarily CA and CA_2, reacted with the steam in both atmospheres to form additional CAH_{10}, a metastable compound which has been termed the most common product of normal hydration.[10] The amount of CAH_{10} formed in the castables increased with increasing testing time. Accompanying this reaction was a weight increase, exhibited by the neat cement samples exposed to the test conditions, and more importantly, a strength increase, as shown in Figure 1. After 18 days in the steam-N_2 atmosphere, the N_2 being inert, the strength of the High Al_2O_3 castable increased by a factor of two. Such results clearly show that the mechanical stability of a hydraulic castable can be enhanced

by hydrothermal conditions.

For additional information concerning the effect of the test conditions on cement hydration, refer to Appendix 6.

B. Reaction of the Cement Bond Phases

Although mechanical strength increases accompanied cement hydration, the test atmospheres also adversely affected the CaO in the cements.

As shown in Figure 1, the High Al_2O_3 castable decreased in strength after 18 days in the steam-CO atmosphere. This decrease is attributed primarily to attack of the cement bond phases by the CO. This attack consisted of three simultaneous reactions. The CO reacted to form CO_2, probably as shown in equation (1).

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \qquad (1)$$

This assumption was determined from gas chromatography analyses of the steam-CO atmospheres. The CO_2 content of the steam-CO atmosphere as a function of time at 199°C and 450 psi is shown in Figure 2. CO_2 formation according to equation (2) is not believed to have occurred, since no carbon or carbon compounds were detected in the refractories, in the residues recovered from the water after testing, or on the vessel interior.

$$2\ CO_{(g)} \rightleftharpoons C_{(s)} + CO_{2(g)} \qquad (2)$$

The CO_2 then reacted with the CaO in the cements to form $CaCO_3$, aragonite. In addition, the steam and CO reacted with the CaO to form $Ca(HCO_2)_2$, calcium formate. Calcium carbonate formation is a commonly reported, well understood reaction, but $Ca(HCO_2)_2$ formation has not previously been reported in refractory literature.

The $Ca(HCO_2)_2$ formed probably as the result of the reaction:

$$CaO_{(s)} + 2\ CO_{(g)} + H_2O_{(g)} \longrightarrow \longrightarrow | Ca(HCO_2)_{2(s)} \qquad (3)$$

Two arrows are shown in equation (3) because this reaction may involve more than one step, but only the reactants and subsequent product were identified. Similar formate reactions have been reported at pressures and temperatures above 100 psi and 200°C,[12] which encompass the conditions used in this study.

The $Ca(HCO_2)_2$ was observed as white fibrous and flaky material only on the castable surfaces as shown in Figures 3(a) and (b), the top samples. The dark regions on the lower samples are areas where Fe_3O_4 and/or Fe_2O_3 were deposited as a result of "iron-staining" by rust-laden steam. This rust resulted from the reaction of the steam in the test atmospheres with the carbon steel vessel.

$CaCO_3$, calcite, was also detected in the castables exposed to the steam-N_2 atmosphere, but only in small amounts. This $CaCO_3$ is attributed to the reaction of the CaO with trace CO_2 (air), apparently arising from inadequate purging

of the vessel. The amount of $CaCO_3$ detected on the surface of the castables exposed to both test atmospheres decreased with increasing testing time.

The greatest amounts of $Ca(HCO_2)_2$ were observed on the Intermediate Al_2O_3 castable. Generally, such large amounts of $Ca(HCO_2)_2$ formed within 6 days on all of the castables exposed to the steam-CO atmosphere, that it was difficult to visually determine any change with increasing testing time. Weight change data was obtained, but it was complicated by other reactions. Dissolution and dissociation of the calcium-containing compounds were verified, however, by three factors.

The first was the change in pH of the water recovered after testing, as shown in Table VII. In the steam-N_2 atmosphere, the water was basic, which is consistent with the dissolution of CaO. CaO and $CaCO_3$ are soluble in acidic liquids,[13] and the distilled water initially added was slightly acidic. Therefore, it is believed that CaO and $CaCO_3$ were leached from the castables by the percolating steam. In the steam-CO atmosphere, the water recovered after testing was acidic. $Ca(HCO_2)_2$ is soluble in water and tends to dissociate under high temperature and pressure conditions to form formic acid,[12,13] according to the equation:

$$Ca(HCO_2)_2 + 2\ H^+ \rightleftharpoons 2\ H_2CO_2 + Ca^{2+} \qquad (4)$$

If equilibrium conditions were achieved, the CO_2 (resulting

from the reaction shown in equation (1)) would also dissolve in the water to form carbonic acid,[14] as shown in equation (5).

$$CO_{2(g)} + H_2O_{(1)} \rightleftharpoons H_2CO_3\ (1) \qquad (5)$$

Such acid formation explains the acidic condition of the water recovered from the steam-CO tests, and the dissolution of the CaO and $CaCO_3$.

Second, atomic absorption analysis of the water recovered after testing showed that it contained >> 1000 ppm Ca. The Ca content of the distilled water added before testing was << 1 ppm Ca.

Third, the solid residues, filtered from the water recovered after testing, contained $CaCO_3$ and $Ca(HCO_2)_2$, as indicated by x-ray diffraction.

It could not be determined which cement compounds were most readily attacked by the test atmospheres, nor were any differences in cement compound reactivity noted between the CA-25 and Refcon cements. However, the overall test results demonstrate the corrosiveness of CO, even on a high purity castable, such as the High Al_2O_3 castable, which would be expected to exhibit excellent resistance to "conventional" CO disintegration.[5]

Additional information concerning the reaction of the CaO in the cement bond phases is given in Appendix 7.

C. Boehmite Formation

In addition to reactions involving the cement bond phases, the free Al_2O_3 (corundum) in the castables reacted with the steam in the test atmospheres to form boehmite, α-$Al_2O_3 \cdot H_2O$.

In the High Al_2O_3 castable, the boehmite formed is attributed to the hydration of the α-Al_2O_3 in the CA-25 cement, since no boehmite was found on the T-61 Tabular Al_2O_3 aggregate present in this castable. In the Intermediate Al_2O_3 castable, the trace amount of boehmite detected is attributed to the hydration of the trace α-Al_2O_3 in the Refcon cement. Both the trace α-Al_2O_3 in the Refcon cement and the calcined Al_2O_3, introduced as refractory aggregate, were responsible for boehmite formation in the Low Al_2O_3 castable. The Al_2O_3 combined in the cement compounds might also be expected to have reacted to form boehmite, especially under those conditions where the CaO was removed, leaving a reactive, free Al_2O_3. However, no evidence for this was found.

The amount of boehmite detected in all three castables increased with increasing testing time. In general, the lower the bulk density (Table I), or the more permeable the castable, the deeper the location at which boehmite was detected, as shown by the data in Table VIII. It is also evident that boehmite formed at greater depths in the steam -CO atmosphere than in the steam-N_2 atmosphere. This data was obtained from x-ray diffraction analyses of progressive

depth sections removed from the castables. If this reaction proceeds to a sufficient degree, expansion cracks or spalling might occur. This was occasionally observed when boehmite formed in the interior of the castables, as shown in Figures 4(a) and (b). Each photograph shows expansion cracks on the left side of the center samples. The areas adjacent to these cracks contained substantial amounts of boehmite. The dimension change data in Table IX also verify the occurence of the α-Al_2O_3 - boehmite transformation. The High and Low Al_2O_3 castables, which on the basis of the amount of boehmite formed, contain the most reactive free Al_2O_3 (Table III - the CA-25 cement, Table V - the calcined Al_2O_3, respectively) available for reaction, exhibited the largest expansion. The Intermediate Al_2O_3 castable, which contains the least amount of reactive free Al_2O_3 (Table IV), had the lowest expansion. These data also suggest that for the test atmospheres investigated, the CA-25 cement is more reactive than the Refcon cement, because of the large amount of free Al_2O_3 available to form boehmite.

The Al_2O_3 - H_2O phase diagram[16] shows boehmite as a stable phase between 15-1500 psi and 150-300°C, so this may be a difficult reaction to prevent, depending upon the quantity and reactivity of the fine grained Al_2O_3 in the castable aggregate or the calcium aluminate cement.

Although volume expansions and cracking accompanied boehmite formation, decreases in the mechanical strength of the castables could not be attributed solely to this

reaction.

Appendix 8 contains additional information on boehmite formation.

D. SiO_2 Dissolution

The steam in the test atmospheres also reacted with the SiO_2 in the Intermediate and Low Al_2O_3 castables, and removed a portion of the SiO_2 from the castables. This reaction was confined to only the free SiO_2, present as α-quartz. No decrease in the amount of C_2AS in the Refcon cement or the mullite in the Intermediate Al_2O_3 castable was detected.

The loss of SiO_2 from the specimens was indicated by three facts. First, in addition to containing substantial amounts of Fe_2O_3, Fe_3O_4, $CaCO_3$, and $Ca(HCO_2)_2$, the solid residue, filtered from the water recovered after testing, contained α-quartz. Second, the samples of the raw materials containing free SiO_2 (flint clay and silica sand - Tables IV and V, respectively) showed a small weight loss upon exposure to the test conditions. Third, the amount of α-quartz detected in the Intermediate and Low Al_2O_3 castables decreased with increasing testing time, as indicated by x-ray diffraction.

The amount of SiO_2 lost from the Intermediate and Low Al_2O_3castables was essentially identical for the steam-N_2 and steam-CO atmospheres. This suggests that steam is principally responsible for SiO_2 removal.

Since SiO_2 is a constituent of many refractory castables, its removal must be considered detrimental to the long term stability of SiO_2-containing castables. However, the strength decreases observed in the Intermediate and Low Al_2O_3 castables, shown in Figures 5 and 6, cannot be attributed solely to this reaction, as will be discussed later.

Additional information for the dissolution of the SiO_2 from the castables is given in Appendix 9.

E. Mechanical Properties of the Low and Intermediate Al_2O_3 Castables

Thus far, primarily the High Al_2O_3 castable has been used to illustrate the effects of the various reactions observed in this study. However, as shown in Table VI, the Intermediate and Low Al_2O_3 castables were also significantly affected.

The mechanical strength data in Figure 5 show that the Intermediate Al_2O_3 castable was similarly affected by both test atmospheres. The castable initially exhibited a strength increase, which is attributed to cement hydration. However, after 18 days, the strength of the specimens exposed to the steam-N_2 atmosphere had decreased to its original value, and the castable exposed to the steam-CO atmosphere appears to be following the same pattern. The strength decrease is believed to be due to the combined effects of boehmite formation, SiO_2 dissolution, and dissolution of the cement bond phases. Based upon the data in

Table IV, which shows ∝-Al_2O_3 and ∝-quartz present in only trace amounts, it can be concluded that the dissolution of the cement bond phases is the principal reaction. The trend of the strength data suggest that with increasing testing time, the strength will continue to decrease. Therefore, the long term stability of this class of castables to atmospheres containing steam and CO is questionable.

The mechanical strength data in Figure 6 shows that the Low Al_2O_3 castable did not exhibit a strength increase, even though cement hydration was considered a principal reaction, as shown in Table VI. Instead, a strength decrease occurred, and the trend of the data suggests that with increasing exposure time, the mechanical strength will continue to decrease.

The deterioration of the Low Al_2O_3 castable is also attributed to the combined effects of boehmite formation, SiO_2 dissolution, and dissolution of the cement bond phases, since substantial amounts of all of the necessary reactants, free ∝-Al_2O_3, free SiO_2, and cement compounds, are present in this castable, as shown in Table V.

Examples of the type of visible deterioration observed in the Low Al_2O_3 castable are shown in Figures 7 and 8. In Figure 7(a),large cracks are evident in the center sample. Upon moving the sample, it fell apart, as shown in Figure 7(b). The material adjacent to the crumbled areas contained large amounts of boehmite and $Ca(HCO_2)_2$, and only

trace amounts of free SiO_2 and cement bonding material. The sample shown in Figure 8 was very "spongy" when removed from the steam-N_2 atmosphere, and the ends of the sample were somewhat bloated and decomposed. X-ray analysis of these areas showed that they contained substantial amounts of boehmite, and only trace amounts of cement bonding material and free SiO_2.

Even though the strength data for the Low Al_2O_3 castable do not show decreases in strength of the magnitude observed in the High Al_2O_3 castable, the overall data for the Low Al_2O_3 castable does suggest that steam-CO atmospheres are detrimental to the stability of this class of castables.

F. Additional Information

The weight change data for the castables verifies the occurrence of all the chemical reactions. However, the data is somewhat unclear, and explanation of it tends to be complicated. Therefore, this data is in Appendix 10.

To aid in comparison of the results obtained in future investigations, Appendix 11 contains the strength data used in Figures 1, 5, and 6.

Investigations were also conducted at higher temperatures and pressures, and under different atmospheres. A discussion of these tests is presented in Appendix 12.

IV. CONCLUSIONS

Four general chemical reactions were observed in steam-N_2 and steam-CO atmospheres at 450 psi and 199°C.

First, the residual unreacted calcium aluminate cement compounds in the castables reacted with the steam in the test atmospheres to form additional cementitous material. This reaction is considered to be responsible for the higher mechanical strengths observed in the steam-N_2 atmosphere.

Second, the CaO in the cement bond phases reacted with the CO, steam, and CO_2 (resulting from the reaction of the CO and H_2O) to form $CaCO_3$ and $Ca(HCO_2)_2$. This reaction is believed to have the most significant effect on the structural integrity of the castables, since it indicates destruction of the cement bond phases.

Third, the free Al_2O_3 in the castables hydrated to form boehmite. Although associated with this reaction were a volume expansion and cracks, decreases in the mechanical strength could not be attributed solely to this reaction.

Fourth, the steam in the test atmospheres reacted with the free SiO_2 (α-quartz), and removed a portion of the SiO_2 from the castables.

It could not be determined from the data obtained which cement compounds were most readily attacked by the test atmospheres, but the data does suggest that the CA-25 cement was more reactive than the Refcon cement, due to the

large amount of reactive free Al_2O_3 available to form boehmite.

In general, the steam-CO atmosphere was the more corrosive of the two atmospheres. In all cases, except for the High Al_2O_3 castable exposed to the steam-N_2 atmosphere, the strength data suggest that with increasing exposure time the mechanical stability of the castables will decrease.

The tests in this study were performed for only 18 days, a very short time compared to the expected service life of commercial castables. Longer duration tests are desirable to determine the eventual effect of the chemical reactions observed on physical and mechanical properties.

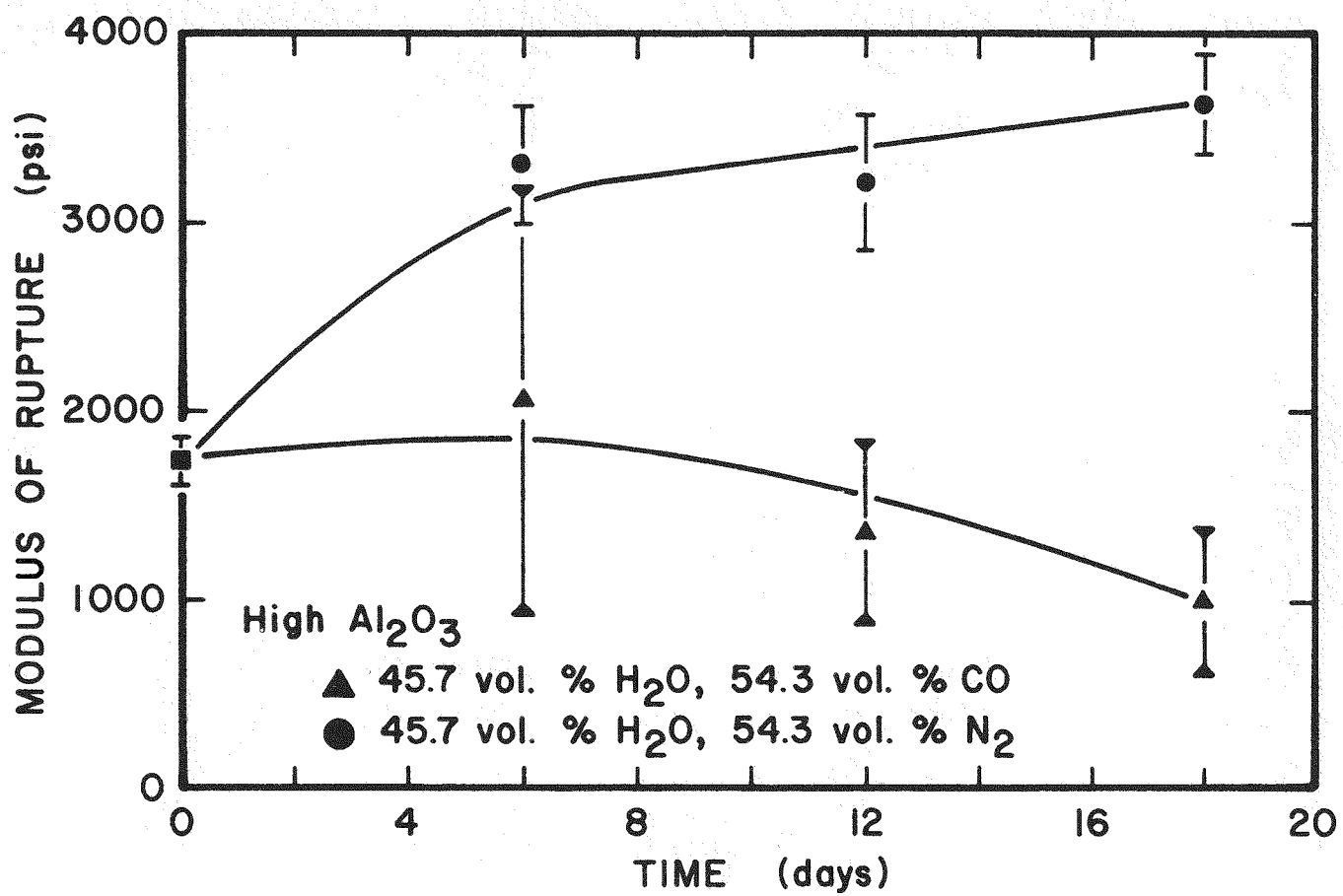


Figure 1. Modulus of Rupture of the High Al_2O_3 Castable After Exposure to the Atmospheres Shown at 199°C and 450 psi.

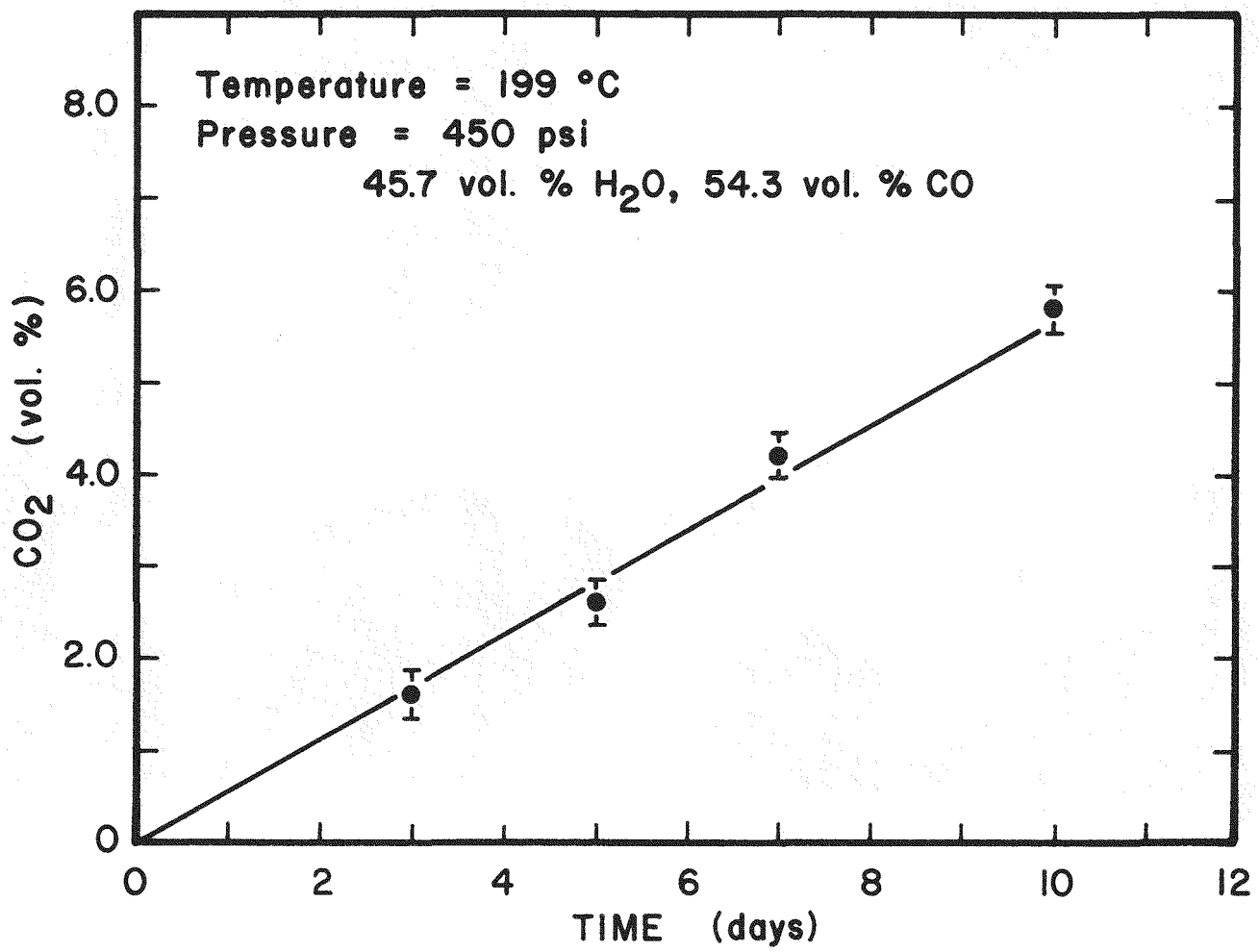
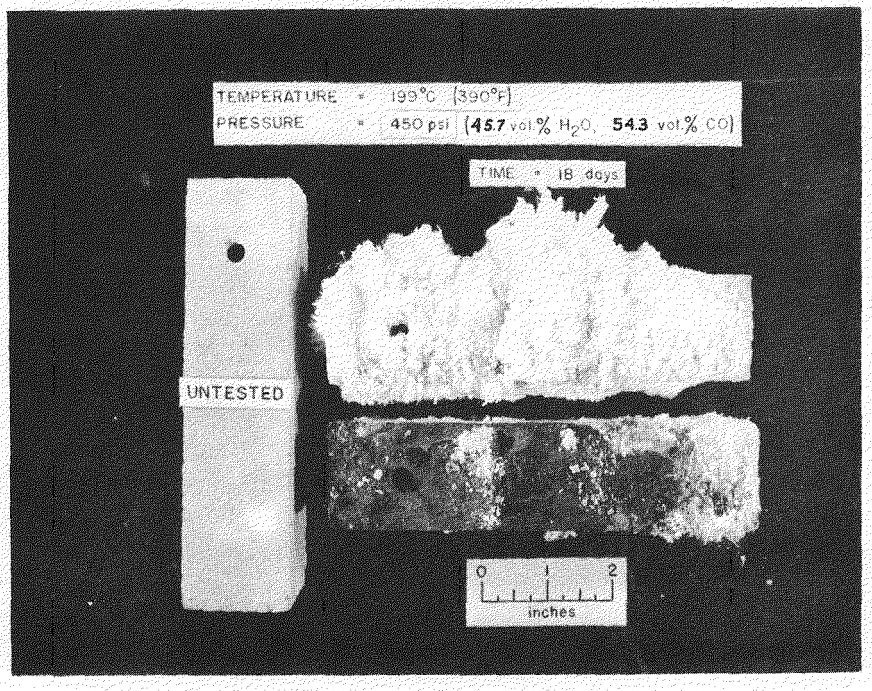
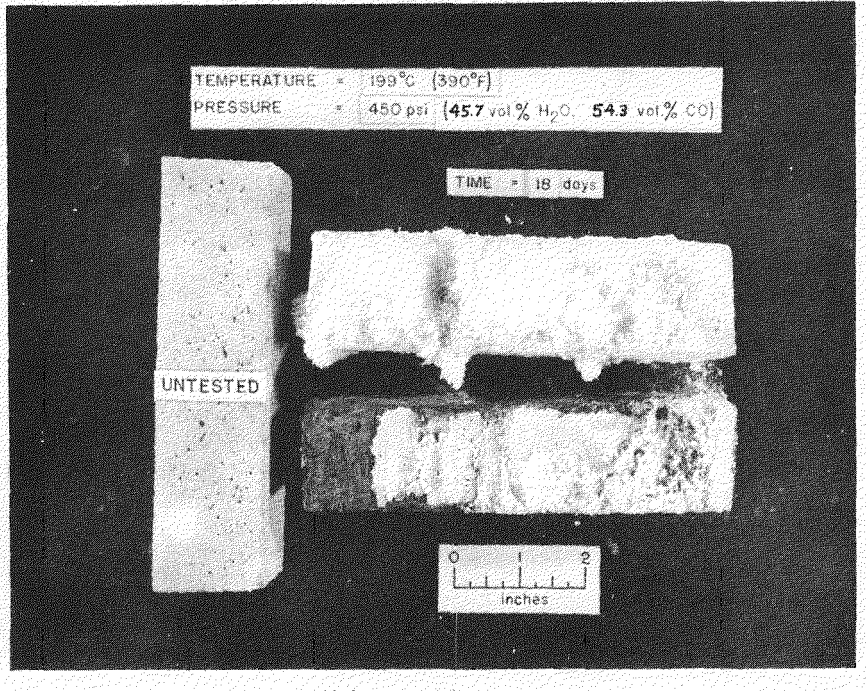


Figure 2. CO_2 Content of the Steam-CO Atmosphere as a Function of the Test Duration.

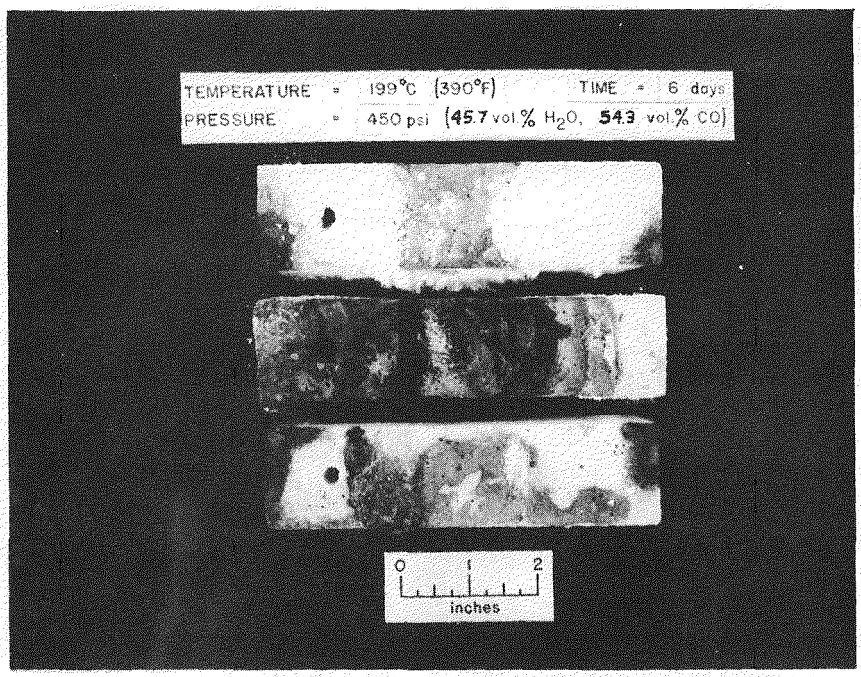


(a). Top

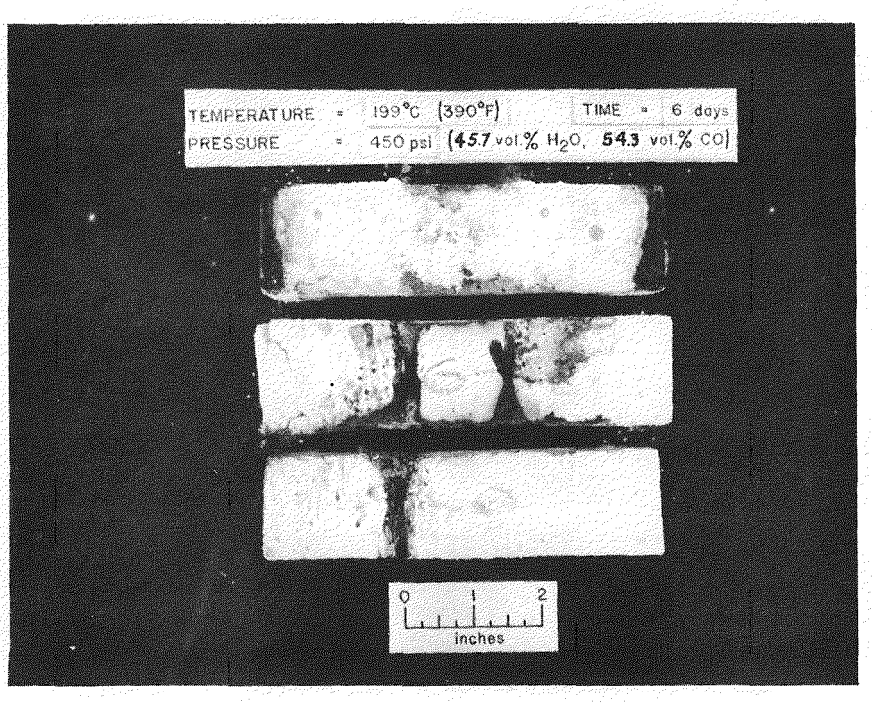


(b). Side

Figure 3. Appearance of an Intermediate Al_2O_3 Castable After Exposure to the Test Conditions Shown.



(a). Top



(b). Side

Figure 4. Appearance of a High Al_2O_3 Castable After Exposure to the Test Conditions Shown.

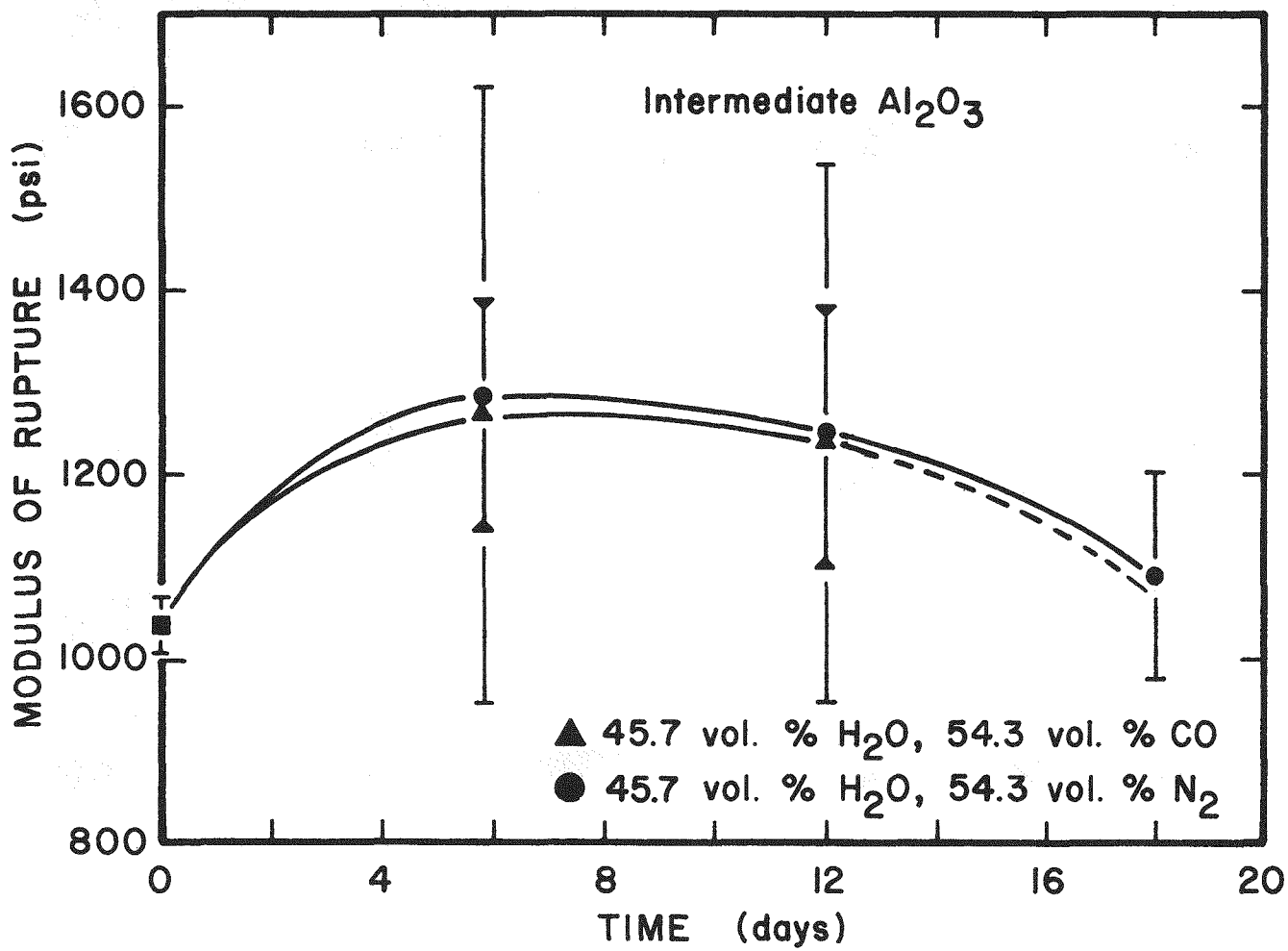


Figure 5. Modulus of Rupture of the Intermediate Al_2O_3 Castable After Exposure to the Atmospheres Shown at 199°C and 450 psi.

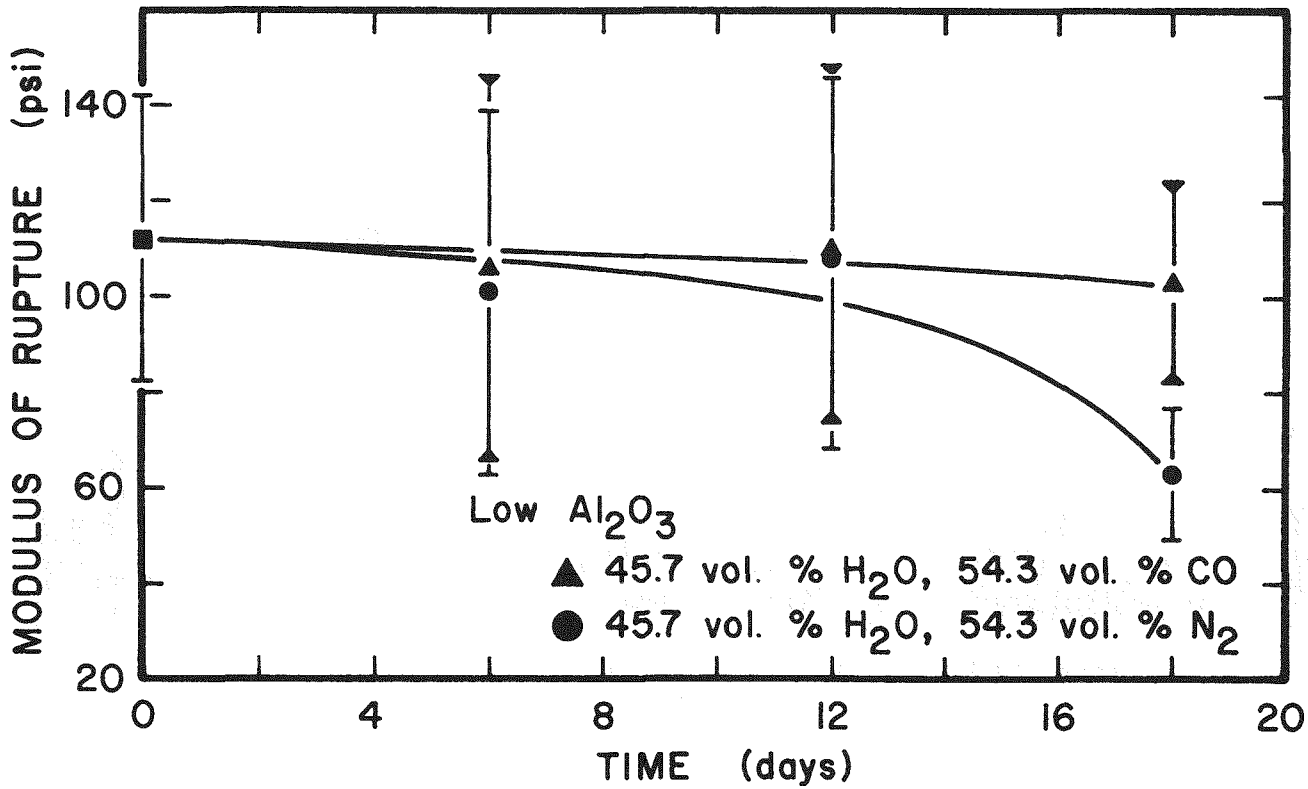
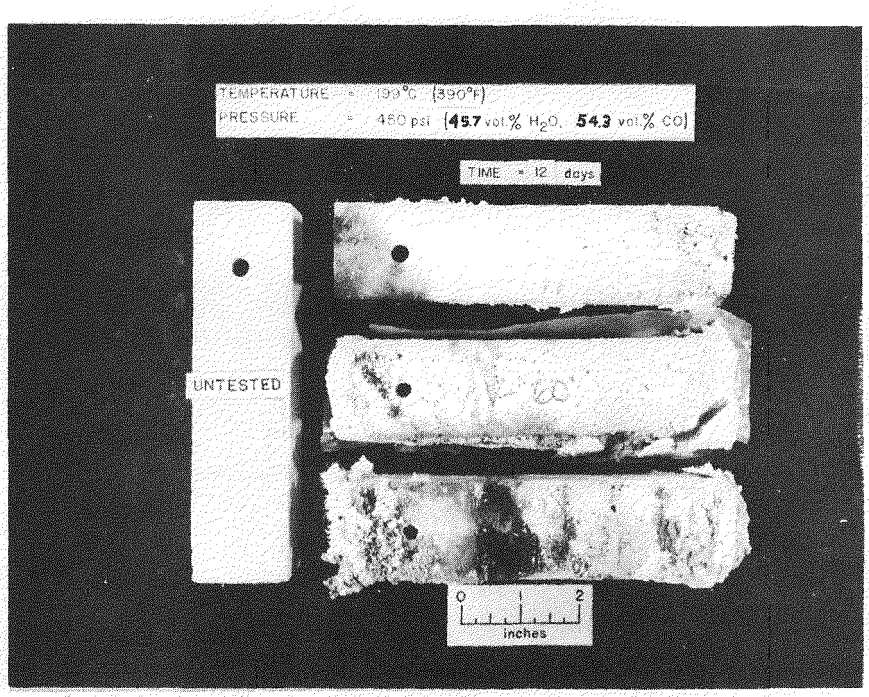
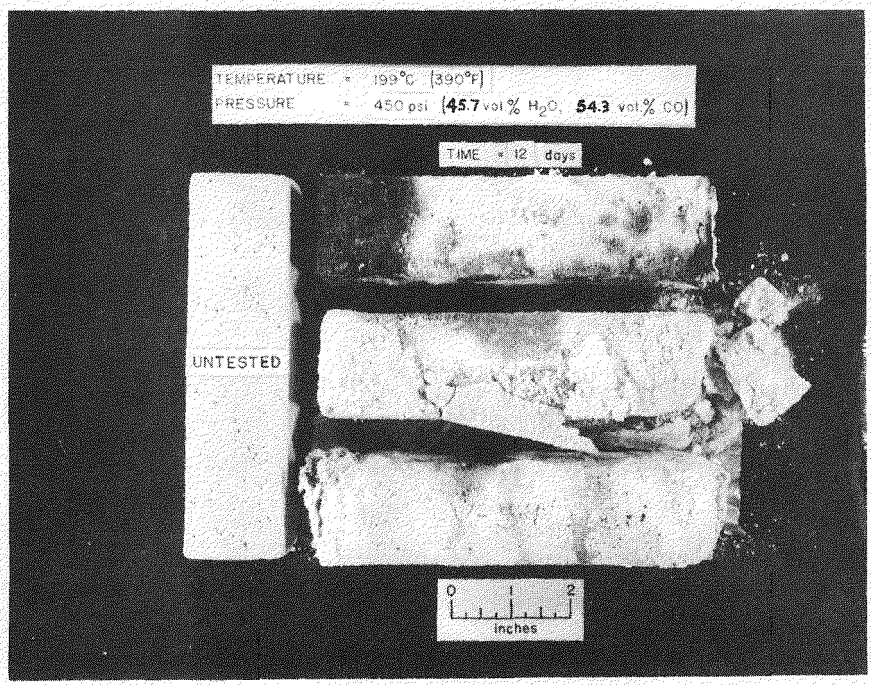


Figure 6. Modulus of Rupture of the Low Al_2O_3 Castable After Exposure to the Atmospheres Shown at 199°C and 450 psi.

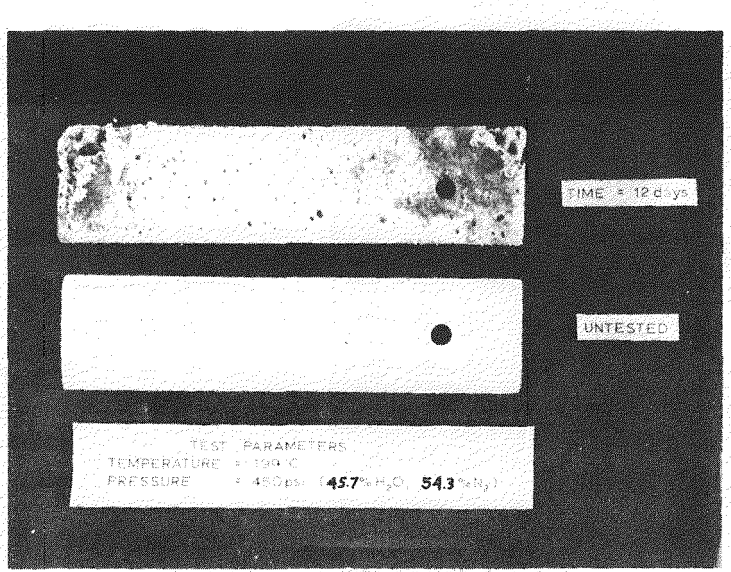


(a). Top

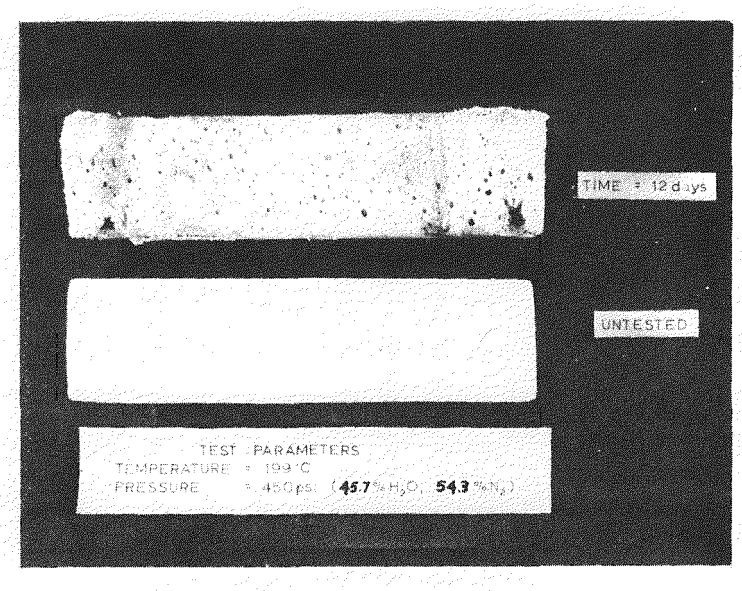


(b). Side

Figure 7. Appearance of a Low Al_2O_3 Castable After Exposure to the Test Conditions Shown.



(a). Top



(b). Side

Figure 8. Appearance of a Low Al_2O_3 Castable After Exposure to the Steam-N_2 Atmosphere at 199° C and 450 psi.

Table I.

Composition (wt.%) and Physical Properties of Refractory Castables*

	High Al_2O_3	Intermediate Al_2O_3	Low Al_2O_3
SiO_2	0.05- 0.15	38.0-41.0	51.0-54.0
Al_2O_3	94.5 -95.0	44.0-47.0	33.0-36.0
Fe_2O_3	0.1 - 0.3	1.0- 3.0	0.6- 0.9
CaO	4.3 - 4.8	8.0- 9.5	8.5-10.0
MgO	Trace- 0.2	0.1- 0.6	0.1- 0.6
TiO_2	------	1.5- 2.5	0.5- 1.5
$Na_2O + K_2O$	0.2 - 0.4	0.5- 1.5	1.0- 2.0
LOI	------	0.5- 1.0	0.5- 1.0
Bulk Density (g/cc)**	2.68-2.76	2.08-2.16	0.82-0.90
M.O.R. (psi)**	1200-1800	700-1000	70-100
Max. Service Temperature (^oC)	1870	1425	1260

* As provided by the A.P. Green Refractories Company.

** Trowelled or poured, cured, and then dried at 104^oC.

Table II.

Test Conditions

Test No.	Atmosphere Composition (vol.%)	Pressure (psi)	Temperature (°C)	Duration (days)	Material Tested
1	45.7 H_2O, 54.3 N_2	450	199	6, 12, 18	* High Al_2O_3
2	"	"	"	"	* Intermediate Al_2O_3
3	"	"	"	"	* Low Al_2O_3
4	45.7 H_2O, 54.3 CO	"	"	"	** High Al_2O_3
5	"	"	"	"	** Intermediate Al_2O_3
6	"	"	"	"	** Low Al_2O_3

* Ten 38.1 x 38.1 x 152.4 mm specimens and one 12.70 x 12.70 x 31.75 mm specimen were used for each time period.

** Ten 38.1 x 38.1 x 152.4 mm specimens, one 12.70 x 12.70 x 31.75 mm specimen, and a sample of each of the raw materials present in the corresponding castables were used for each time period.

Table III.

Compounds Identified in the Untested
High Alumina Refractory Castable

Compounds	Castable	Raw Materials		
		T-61 Tabular Al_2O_3	CA-25*,** Cement (hydrated)	CA-25 Cement (unhydrated)
α-Al_2O_3 (Corundum)	M	M	M	M (2)
CA	m (1)*	-----	m (1)	M (1)
CA_2	-----	-----	tr	m
$C_{12}A_7$	-----	-----	-----	m
AH_3 (Gibbsite)	tr	-----	tr	-----
C_3AH_6	m (2)	-----	m (2)	-----
CAH_{10}	-----	-----	tr	-----
C_3AH_{8-12}	-----	-----	tr	-----

Abbreviation key: M = major, m = minor, tr = trace, A = Al_2O_3, C = CaO, H = H_2O, and S = SiO_2.

* Manufactured by the Aluminum Corporation of America.

** Reacted with 21 wt.% distilled H_2O.

+ The number in parentheses indicates the "comparison" intensity. For example, CA m (1), C_3AH_6 m (2), indicates that CA is the principal minor phase and C_3AH_6 is the secondary minor phase.

Table IV.

Compounds Identified in the Untested Intermediate Alumina Refractory Castable

Compounds	Castable	Raw Materials: Flint Clay	Refcon*,** Cement (hydrated)	Refcon Cement (unhydrated)
α-Al_2O_3 (Corundum)	tr	-----	tr	tr
SiO_2 (α-Quartz)	tr	tr	-----	-----
3 $Al_2O_3 \cdot 2$ SiO_2 (Synthetic Mullite)	M (1)*	M	-----	-----
CA	tr	-----	m (3)	M (1)
CA_2	m (2)	-----	m (2)	M (2)
$C_{12}A_7$	-----	-----	-----	tr
C_2AS (Gehlenite)	M (2)	-----	M	M (1)
CT (Pervoskite)	-----	-----	tr	tr
AH_3 (Gibbsite)	tr	-----	tr	-----
C_3AH_6	m (1)	-----	m (1)	-----
CAH_{10}	tr	-----	tr	-----
C_3AH_{8-12}	tr	-----	tr	-----

Abbreviation key: M = major, m = minor, tr = trace, A = Al_2O_3, C = CaO, H = H_2O, S = SiO_2, and T = TiO_2.

* Manufactured by Universal Atlas Cement.

** Reacted with 23 wt.% distilled H_2O.

+ The number in parentheses indicates the "comparison" intensity. For example, 3 $Al_2O_3 \cdot 2$ SiO_2 M (1), C_2AS M (2), indicates that 3 $Al_2O_3 \cdot 2$ SiO_2 is the principal major phase and C_2AS is the secondary major phase.

Table V.

Compounds Identified in the Untested
Low Alumina Refractory Castable

Compounds	Castable	Raw Materials: Calcined Al_2O_3	Silica Sand	Perlite	Refcon*,** Cement (hydrated)	Refcon Cement (unhydrated)
α-Al_2O_3 (Corundum)	M(2)*	M	---	---	tr	tr
β-Al_2O_3	---	tr	---	---	---	---
SiO_2 (α-Quartz)	M(1)	---	M	---	---	---
CA	---	---	---	---	m(3)	M(1)
CA_2	---	---	---	---	m(2)	M(2)
$C_{12}A_7$	---	---	---	---	---	tr
C_2AS (Gehlenite)	M(2)	---	---	---	M	M(1)
CT (Pervoskite)	tr	---	---	---	tr	tr
AH_3 (Gibbsite)	tr	---	---	---	tr	---
C_3AH_6	m(1)	---	---	---	m(1)	---
CAH_{10}	tr	---	---	---	tr	---
C_3AH_{8-12}	m(2)	---	---	---	tr	---
$CaCO_3$ (Calcite)	tr	---	---	---	---	---

Abbreviation key: M = major, m = minor, tr = trace, A = Al_2O_3, C = CaO, H = H_2O, S = SiO_2, and T = TiO_2.

* Manufactured by Universal Atlas Cement.

** Reacted with 23 wt.% distilled H_2O.

+ The number in parentheses indicates the "comparison" intensity. For example, SiO_2 M(1), α-Al_2O_3 M(2), indicates that SiO_2 is the principal major phase and α-Al_2O_3 is the secondary major phase.

Table VI.

Summary of Chemical Reactions Observed in the Castables
After Exposure to 45.7 vol. % Steam and 54.3 vol. % N_2 or CO Atmospheres
at 199°C and 450 psi

Castable		Cement Hydration	CaO Dissolution: $CaCO_3$ Formation	CaO Dissolution: $Ca(HCO_2)_2$ Formation	Boehmite Formation	SiO_2 Dissolution	pH	M.O.R.	Wt.	Dimen.
High Al_2O_3	Steam-N_2	M*	m	-----	M	-----	B	I	D → I	-----
	Steam-CO	m	tr	M	M	-----	A	Sl I → D	I	E
Intermediate Al_2O_3	Steam-N_2	M	tr	-----	tr	tr	B	I → D	Sl → D	-----
	Steam-CO	M	tr	M	tr	tr	A	I → D	D	E
Low Al_2O_3	Steam-N_2	m	m	-----	M	m	B	D	D	-----
	Steam-CO	m	tr	M	M	m	A	Sl I	D → I	E

Abbreviation key: M = major, m = minor, tr = trace, A = acidic, B = basic, I = increase, D = decrease, Sl = slight, " → " = followed by, E = expansion.

* The M, m, and tr designations indicate which reactions were most prominent.

Table VII.

pH of Water Recovered After Testing

Test Duration (days)	pH* High Al_2O_3	Intermed. Al_2O_3	Low Al_2O_3
Steam-N_2 Atmosphere at 199°C and 450 psi			
6	6.1/10.4	6.1/10.8	6.5/9.5
12 and 18	6.1/ 9.6	6.1/10.0	6.2/7.4
Steam-CO Atmosphere at 199°C and 450 psi			
6	6.8/ 5.9	5.9/ 6.2	5.8/5.4
12 and 18	6.2/ 5.3	6.3/ 5.7	6.2/4.5

* pH = x/y. x = pH before testing, y = pH after testing.

Table VIII.

Depth at which Boehmite Formed After an 18 Day Exposure to the Atmosphere Shown at 199°C and 450 psi

	Depth (mm)	
Castable	Steam-N_2	Steam-CO
High Al_2O_3	2-4	19*
Intermediate Al_2O_3	2-3	4-5
Low Al_2O_3	19*	19*

* Detected at the center of the specimens.

Table IX.

Average* Expansion After Exposure to Steam-CO Atmosphere at 199°C and 450 psi

Test Duration (days)	Expansion (%) High Al_2O_3	Intermed. Al_2O_3	Low Al_2O_3
6	1.05	0.10	1.57
12	2.50	0.50	1.51**
18	2.81	0.17	1.14

* Average of the length, width, and depth expansion for 10 specimens.

** Average of 7 specimens.

ACKNOWLEDGEMENT

The author gratefully acknowledges: Dr. Delbert E. Day for his guidance, patience, and encouragement throughout the study; the A.P. Green Refractories Company for providing financial support, the refractory materials, and many helpful comments; and Stephen D. Stoddard, of the Los Alamos Scientific Laboratory.

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[9] E.L. Brady, "Chemical Nature of Silica Carried by Steam," J. of Phys. Chem., 57 (7) 706-10 (1953).

[10] T.D. Robson, High Alumina Cements and Concretes, pp. 36, 51, 90-1, John Wiley and Sons, Inc., New York, 1st published in 1962.

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[16] G. Ervin, Jr. and E.F. Osborn, "The System Al_2O_3 - H_2O," J. Geol., 59, 381-94 (1951).

Appendix 1

TEST SYSTEM CONSTRUCTION

The reaction vessel measured 203.2 mm I.D. and 457.2 mm in depth (8 in. I.D. x 18 in. deep), and was capable of 1000 psi at 345°C. A detailed view of the construction of the vessel is shown in Figure A1-1. The water concentration cone shown in Figure A1-1 was made from heavy gage aluminum foil and was used to direct the flow of water, which condensed on the vessel lid, directly onto the center of the test samples. Thermocouples 1 through 5 were used to monitor the temperature gradient throughout the vessel. Thermocouple 1 was also used for temperature control. At 199°C and 450 psi, the temperature within the vessel varied only ±10°C from top to bottom and ±5°C from side to side.

A schematic diagram of the test system is presented in Figure A1-2. Two precautions were taken to insure safe operating conditions. First, the gas system was equipped with an adjustable relief valve, which in case of excessive pressure would open and automatically reduce the pressure to within safe limits. Second, the temperature controller was equipped with thermocouple break protection, so that failure of the temperature controlling thermocouple would cause the controller to reduce the power input.

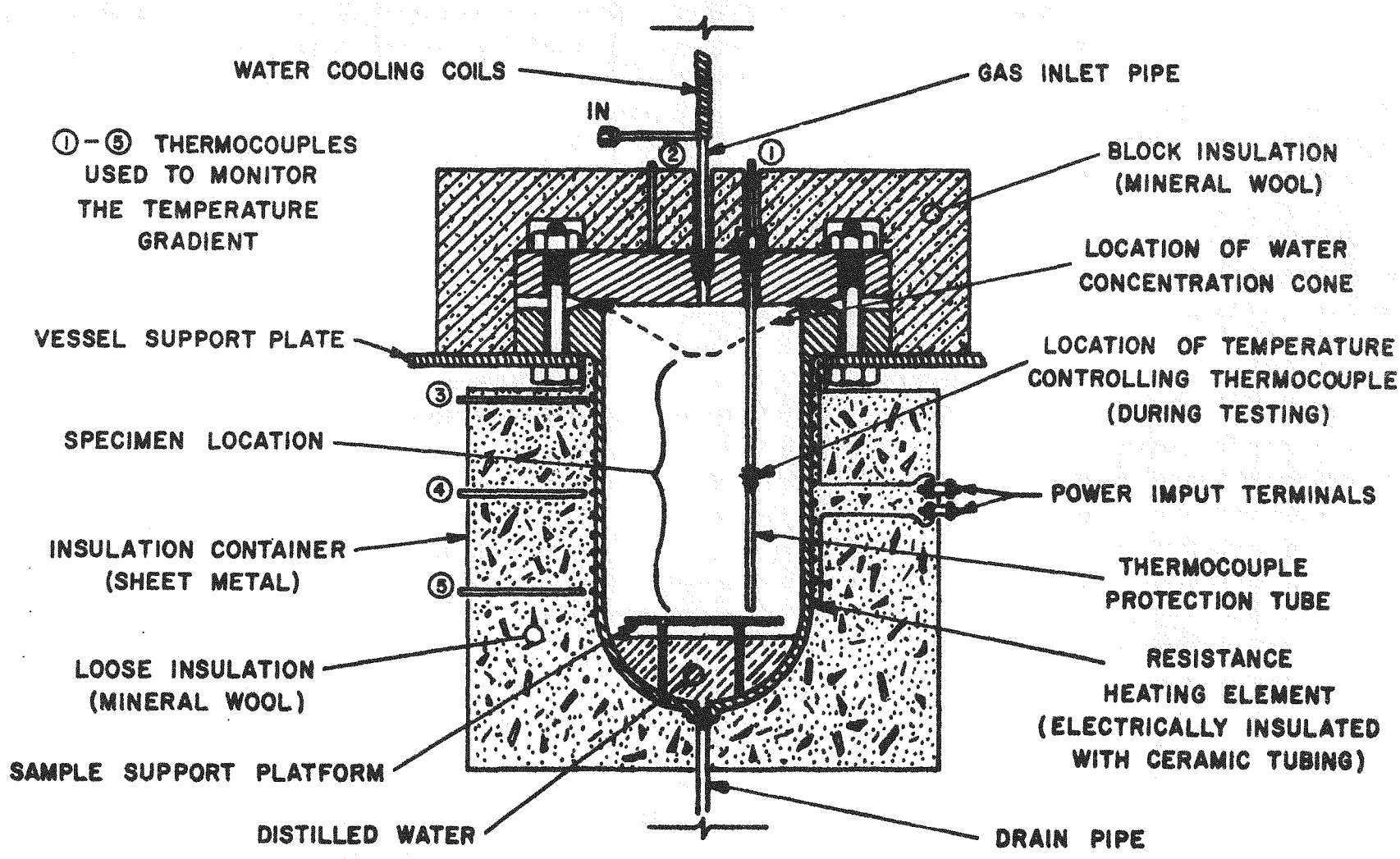


Figure A1-1. Reaction Vessel Construction.

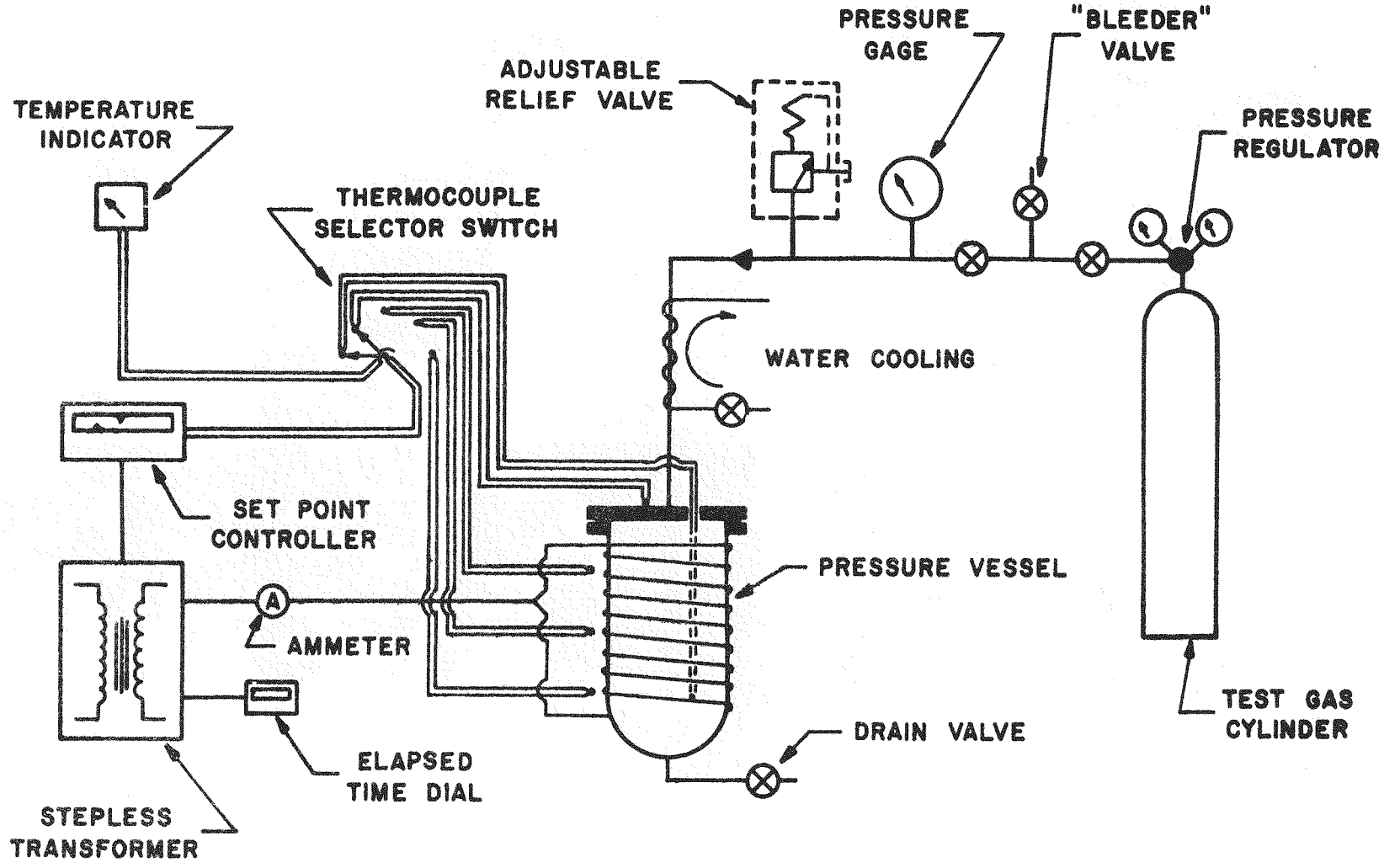


Figure A1-2. Schematic Diagram of the Test System.

Appendix 2

SEM ANALYSIS

Solid samples were carefully removed from the test specimens and cemented to a mounting fixture using silver paste. The mounted samples were then examined using a JEOLCO JSM-2 scanning electron microscope. While still mounted in the vacuum chamber, the elemental constituents of the samples were determined using an Ortec Si (Li) elemental analyzer.

Appendix 3

X-RAY DIFFRACTION ANALYSIS

a. EXPERIMENTAL PROCEDURE

X-ray diffraction analyses were performed with a General Electric x-ray diffractometer, model XRD-700, using Cu and Co K_{α} radiation. Three sample preparation methods were utilized: bulk, powder, and vaseline-powder.

The 12.70 x 12.70 x 31.75 mm specimens and sections of approximately the same dimensions, removed at different depths from the 38.1 x 38.1 x 152.4 mm specimens, were prepared by the bulk method. This method consisted of mounting the specimens in an opening in a glass slide with modeling clay, as shown in Figure A3-1(a). The exposed surface of the sample was then analyzed. Progressive-depth analyses were made by successively grinding and analyzing the sample surface. Two problems were encountered with this method. Since the sample was a polycrystalline aggregate, there was no control over the distribution and/or orientation of particles in the surface being x-rayed. Therefore, the observed intensities were subject to an uncontrollable variation.[A3-1] Second, only a small portion of the sample surface, approximately 2 x 8 mm (0.1 x 0.3 in.) was analyzed, and it could only be assumed that this area was representative of the entire sample. Both of these problems could have been minimized by rotating the

sample. This would have randomized the orientations within the sample plane and increased the area being analyzed, but such a device was not available. Consequently, large variations in peak intensities were observed, resulting in much difficulty in compound identification and peak ratio comparisons.

The powder method was used when a substantial amount of sample was available. The material was ground to -100 mesh in a mortar and pestle and placed in an opening in a glass slide. The material was pressed into position from the back side, the excess material removed, and then covered with a piece of transparent tape (refer to Figure A3-1(b)). The exposed surface of the sample was then x-rayed. The advantage of this method was that preferred orientation at the exposed surface was prevented.

The vaseline-powder method was used only when a small amount of sample was available. The material was ground to -100 mesh in a mortar and pestle and mixed with a very small amount of vaseline. The vaseline-powder mixture was then removed from the mortar and uniformly spread as a thin film on a glass slide (refer to Figure A3-1(c)).

The Hanawalt method was used for compound identification.[A3-2] Comparisons between diffraction patterns were made using peak ratios. Due to the large number of components present in each castable and the resulting complex absorption and scattering effects, quantitative analysis and comparisons based upon integrated intensity data was virtually impossible.

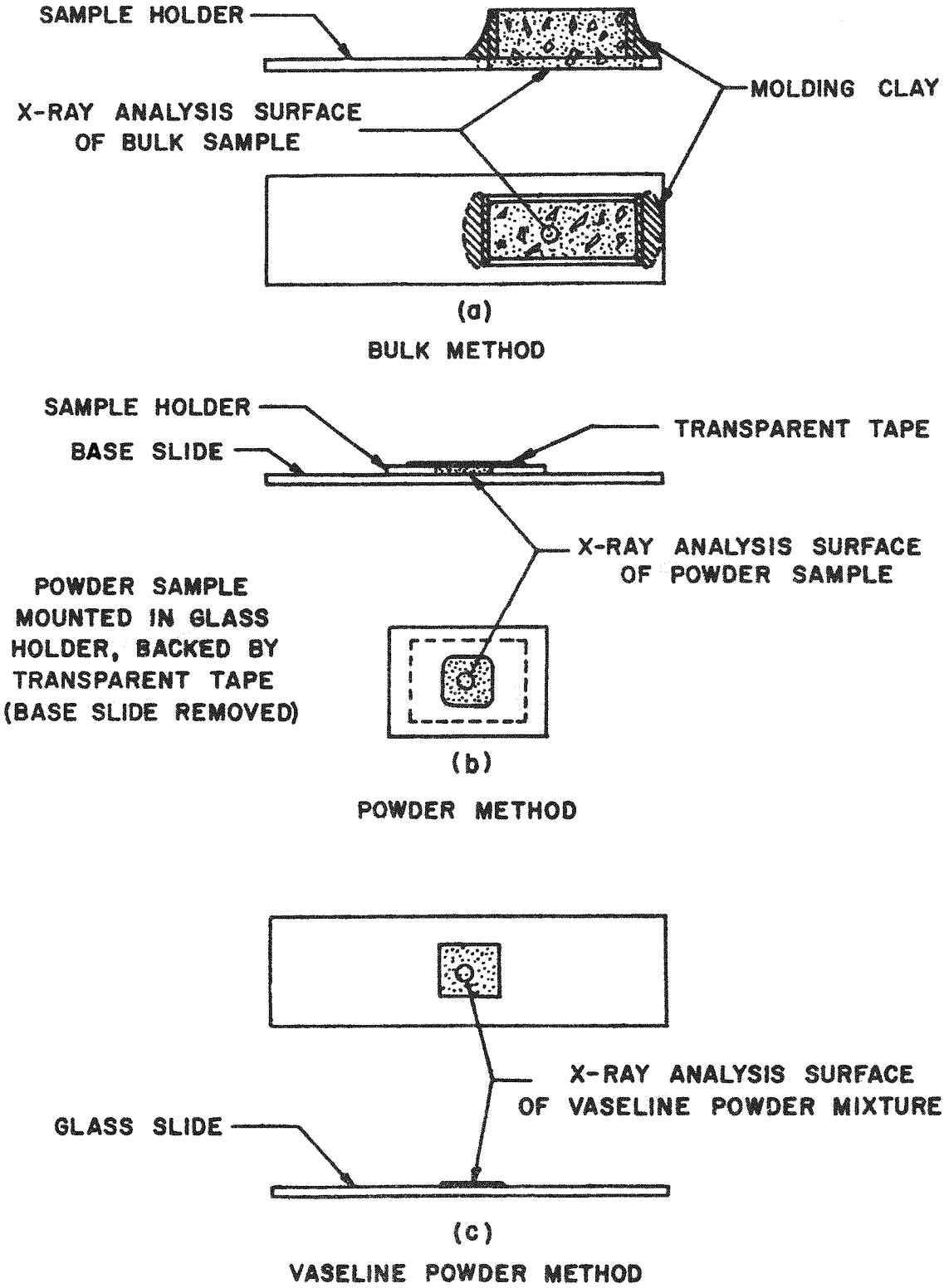


Figure A3-1. Sample Preparation Methods for X-ray Diffraction Analysis.

b. REFERENCES

A3-1 B.D. Cullity, Elements of X-ray Diffraction, pp.379-86, 398-9, Addison-Wesley, Reading, Massachusetts, 1956.

A3-2 L.V. Azároff, Elements of X-ray Crystallography, pp. 531-2, McGraw-Hill, St. Louis, 1968.

Appendix 4

ATOMIC ABSORPTION SPECTROSCOPY

a. EXPERIMENTAL PROCEDURE

A Varian-Techtron AA-5 atomic absorption spectrometer,[A4-1] using a Ca light source and an acetylene-air flame, was utilized to determine the Ca content of the residual water in the reaction vessel (test 6). The water samples were prepared by filtering through No. 40 filter paper to remove the particulate material. Both a sample of the distilled water added before testing and a sample of the water recovered after testing were checked for the presence of Ca.

b. REFERENCES

A4-1 Varian - Techtron AA-5--Instruction Manual, sections 1, 3, 6, Varian Techtron, Park Ridge, Illinois.

Appendix 5

GAS CHROMATOGRAPHY

a. EXPERIMENTAL PROCEDURE

The test atmospheres were analyzed with a Victoreen 4000 Series gas chromatograph[A5-1] at the conditions shown in Table A5-I. Prior to each analysis, standards, composed of the gases in the test atmosphere, were analyzed to calibrate the retention times for the various gases (air, CO, CO_2, H_2, H_2O, and N_2).

The liquid displacement method, shown in Figure A5-1, was used to obtain a sample of the test atmosphere. The reaction vessel "bleeder" gas line was purged for 30-40 seconds to allow gas from within the vessel to flow through the outlet valve. A gas sampling bottle, filled with distilled water, was then connected to the outlet valve and the test atmosphere allowed to displace the water. Upon complete displacement of the water, the outlet stopcock was closed and the pressure in the bottle allowed to increase slightly. The inlet stopcock was then closed and the sampling bottle disconnected. A gas-tight syringe was used to remove the test atmosphere from the sampling bottle for injection into the gas chromatograph.

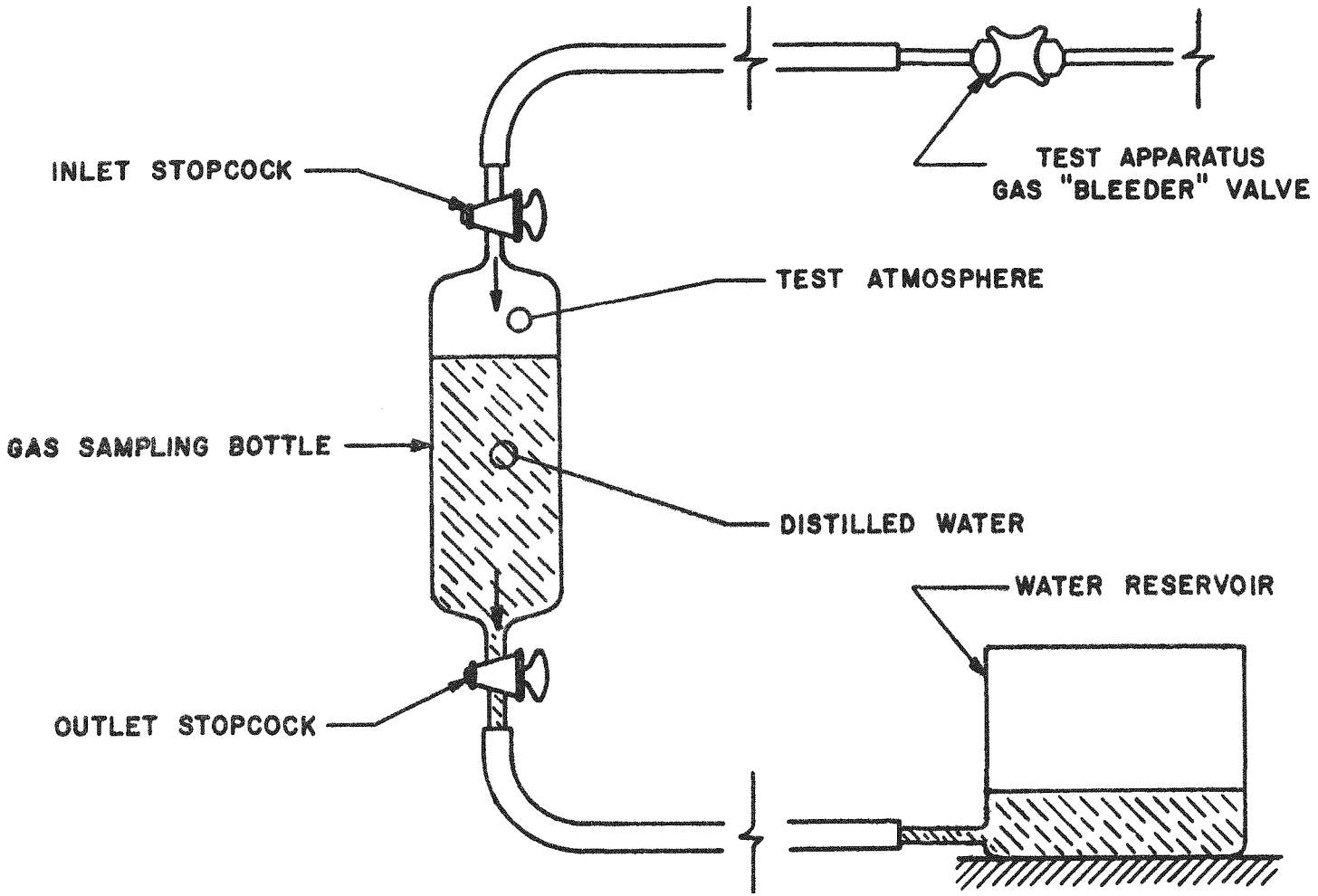


Figure A5-1. Liquid Displacement Method of Gas Sampling.

b. REFERENCES

A5-1 Victoreen 4000 Series Gas Chromatographs--Instruction and Maintenance Manual, The Victoreen Instrument Co., Cleveland, Ohio.

A5-2 Porapak, Gas Chromatography Column Packing Materials, Bulletin PB-71-205, Waters Associates Inc., Framingham, Massachusetts.

Table A5-I.

Gas Chromatography Analysis Conditions

COLUMN	:	1524 mm long x 3.175 mm O.D. (60 in. long x 0.125 in. O.D.), stainless steel
SUPPORT	:	Ethylvinylbenzene polymer beads (Porapak Q),[A5-2] 100/120 mesh (Packed column conditioned at 230°C for 1 hour)
CARRIER	:	Helium Inlet pressure = 28 psi Flow rate = 15 ml/min.
DETECTOR	:	Thermal conductivity cell
TEMPERATURES:		Injection port = 190°C Column = 30°C Detector = 230°C

Appendix 6

CEMENT HYDRATION

a. RESULTS and DISCUSSION

Robson[A6-1] reported that during cement hydration, metastable calcium aluminate hydrates appear readily, and once formed are extremely persistent, except at higher temperatures. Therefore, the metastable CAH_{10}, which resulted from the reaction of the CA and CA_2 in the cements and the steam in the test atmospheres, should have transformed to the stable C_3AH_6. However, it did not, and it is believed that the elevated pressure conditions in this study may have helped suppress this metastable - stable transformation.

$C_{12}A_7$ was detected only in the unhydrated castables, which indicates it hydrates rapidly and completely.

The C_2AS, which is present in only the Intermediate and Low Al_2O_3 castables (Refcon cement), proved to be unreactive. This was expected, since it has been reported that crystalline C_2AS reacts extremely slowly, if at all, with water.[A6-1]

The CT, pervoskite, present in only the Refcon cement, was also unreactive. The occurrence of this compound in the Refcon cement is due to the reaction of lime with small amounts of TiO_2, present in the bauxites used for the manufacture of high Al_2O_3 cements.

b. REFERENCES

A6-1 T.D. Robson, High Alumina Cements and Concretes, pp. 36, 51, John Wiley and Sons, Inc., New York, 1st published in 1962.

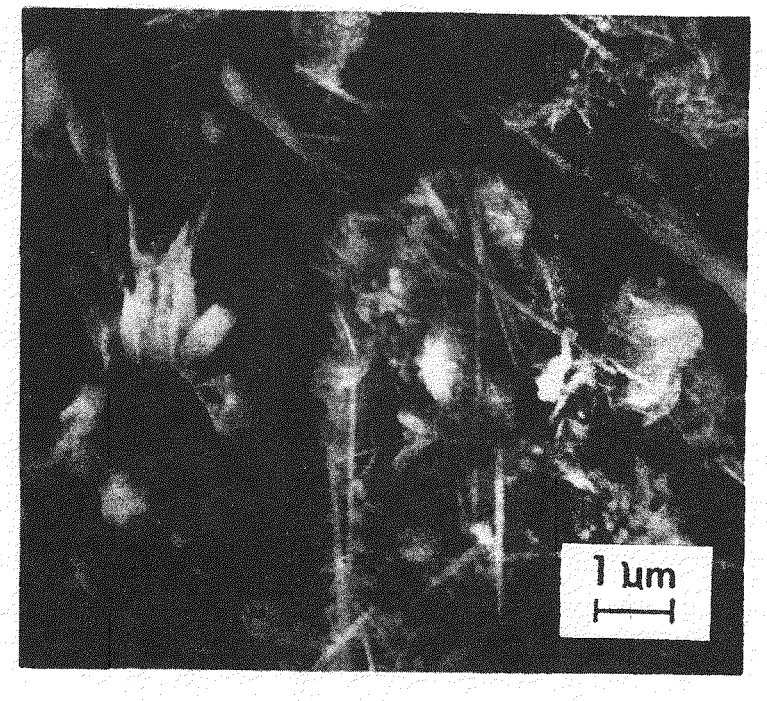
Appendix 7

REACTION OF THE CEMENT BOND PHASES

In the steam-N_2 atmosphere, the $CaCO_3$ was observed both as well delineated crystals and globules. An example of both forms, present on the surface of a Low Al_2O_3 sample after a 12 day exposure to the test conditions (test 3), is shown in Figure A7-1(a).

An additional example of $Ca(HCO_2)_2$ fibers observed in the steam-CO atmosphere is given in Figure A7-1(b).

(a).



(b).

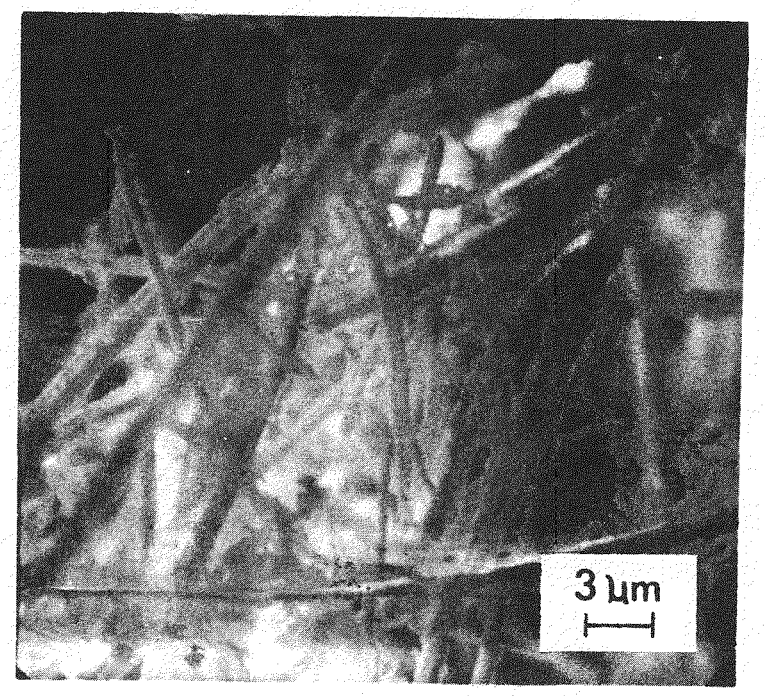


Figure A7-1. (a). $CaCO_3$ Crystals and Globules (1000x) on the Surface of a Low Al_2O_3 Castable After a 12 Day Exposure to the Steam-N_2 Atmosphere at 199°C and 450 psi.

(b). $Ca(HCO_2)_2$ Fibers (300x) on the Surface of a Low Al_2O_3 Castable After a 6 Day Exposure to the Steam-CO Atmosphere at 199°C and 450 psi.

Appendix 8

BOEHMITE FORMATION

a. RESULTS and DISCUSSION

In addition to the boehmite observed in the interior of the castables, as explained in the text, boehmite also occasionally formed on the exterior of the castables. In these instances, it appeared as a deposit-like formation, as shown in Figure A8-1. The area between the brackets was identified as pure boehmite.

Although data in the literature indicate that boehmite is a stable phase at the test conditions used in this study, the kinetics of formation at such a low temperature and pressure are very slow.[A8-1] Yanagida and Yamaguchi[A8-2] stated that spontaneous nucleation of boehmite cannot occur below 300-400°C or 590-5990 psi. However, they also reported that transformations in the system Al_2O_3 - H_2O can be accelerated considerably by seed crystals of the product phase. Therefore, two mechanisms are proposed for the formation of boehmite in this study.

One mechanism is believed to be a two step process, involving first the dehydration of gibbsite to form boehmite, which serves as seed crystals for the subsequent hydration of the free α-Al_2O_3 to form additional boehmite. This mechanism is plausible for two reasons. First, gibbsite, present in trace amounts in the hydrated cements in

each castable, spontaneously transforms to boehmite at temperatures and pressures as low as 150°C and 90 psi.[A8-2] Second, α-Al_2O_3 has been reported to transform into boehmite at temperatures below 300°C and pressures below 1100 psi, with the coexistence of boehmite grains.[A8-2] This boehmite formation mechanism is also supported by the fact that, in general, the amount of the gibbsite detected in the castables decreased with increasing testing time, which suggests that the gibbsite was transforming to boehmite.

The second mechanism is also believed to be a two step process. It involves, first, the hydration of β-Al_2O_3 to form gibbsite and/or boehmite, and then proceeds in the same manner as the first mechanism. The key to this second mechanism is the transformation of the β-Al_2O_3 which is known to be very reactive,[A8-1] and which is present in trace amounts in the calcined Al_2O_3 aggregate in the Low Al_2O_3 castable. This mechanism accounts for the formation of boehmite in the calcined Al_2O_3, even though no gibbsite of boehmite were detected in the unexposed samples.

b. REFERENCES

A8-1 W.H. Gitzen, Alumina as a Ceramic Material, pp.7-28, American Ceramic Society, Columbus, Ohio, 1970.

A8-2 H. Yanagida and G. Yamaguchi, "A Discussion on the Phase Diagram of the System Al_2O_3 - H_2O, Considering the Transformation Mechanisms of the Polymorphs Appearing in It," J. Ceram. Assoc. Japan, 74 (3) 94-9 (1966).

Figure A8-1. Appearance of a High Al_2O_3 Castable After Exposure to the Test Conditions Shown.

Appendix 9

SiO_2 DISSOLUTION

a. RESULTS and DISCUSSION

The mechanism considered responsible for the removal of SiO_2 from the Intermediate and Low Al_2O_3 castables is a SiO_2 dissolution process, involving the reaction of the free SiO_2 (α-quartz) with the steam in the test atmospheres to form a silica hydrate. A general form of this reaction is:

$$n\ SiO_2(s) + m\ H_2O(g) \rightleftharpoons n\ SiO_2 \cdot m\ H_2O(g) \qquad (A9\text{-}1)$$

The type of silica hydrate is unknown. However, Brady[A9-1] suggested that equation (A9-2) is favored below 4410 psi.

$$2\ SiO_2(s) + 3\ H_2O(g) \rightleftharpoons Si_2O(OH)_6(g) \qquad (A9\text{-}2)$$

Since the pressure in all the tests conducted in this study was $<<$ 4410 psi, $Si_2O(OH)_6$ is a reasonable choice.

b. REFERENCES

A9-1 E.L. Brady, "Chemical Nature of Silica Carried by Steam," J. of Phys. Chem., 57 (7) 706-10 (1953).

Appendix 10

CASTABLE WEIGHT CHANGE DATA

The weight change data for each castable is presented in Figures A10-1 through 3 and Table A10-1.

Figure A10-1 shows that the High Al_2O_3 samples exposed to the steam-N_2 atmosphere initially exhibited a 3.85% weight loss, followed by an approximately linear weight gain. The initial loss is attributed to the removal of both "dust" (i.e., the loose castable material on the exterior of the sample) and some CaO by the steam. The subsequent weight gain is attributed to the hydration of the free Al_2O_3 and cement compounds, and the formation of some $CaCO_3$. The magnitude of the $Ca(HCO_2)_2$ reaction is verified by the weight increase exhibited by the High Al_2O_3 samples exposed to the steam-CO atmosphere (shown in Figure A10-1), since the magnitude of the reactions observed in the steam-N_2 atmosphere were approximately the same in the steam-CO atmosphere.

The Intermediate Al_2O_3 samples exposed to the steam-N_2 atmosphere continually lost weight, as shown in Figure A10-2. This weight loss is attributed to dissolution of the SiO_2 and CaO, and removal of some castable "dust" by the steam. In the steam-CO atmosphere, $Ca(HCO_2)_2$ formation also occurred, resulting in a reduction in the weight loss.

It should be recalled that cement hydration was considered a major reaction in this castable. However, Figure A10-2 suggests that cement hydration had little effect on the weight change of the Intermediate Al_2O_3 castable.

Reference to Figure A10-3 shows that the Low Al_2O_3 samples exposed to the steam-N_2 atmospheres exhibited a weight decrease, which became relatively stable after 6 days. Apparently, the loss of SiO_2 and CaO was compensated by a weight gain associated with alumina hydration, i.e, boehmite formation. In the steam-CO atmosphere, the initial weight increase in Figure A10-3 is attributed to formation of $Ca(HCO_2)_2$. As time increases, more CaO is removed from the castable, resulting in some additional $Ca(HCO_2)_2$ and also easier SiO_2 removal. Therefore, the weight change data shows a decrease with increasing time.

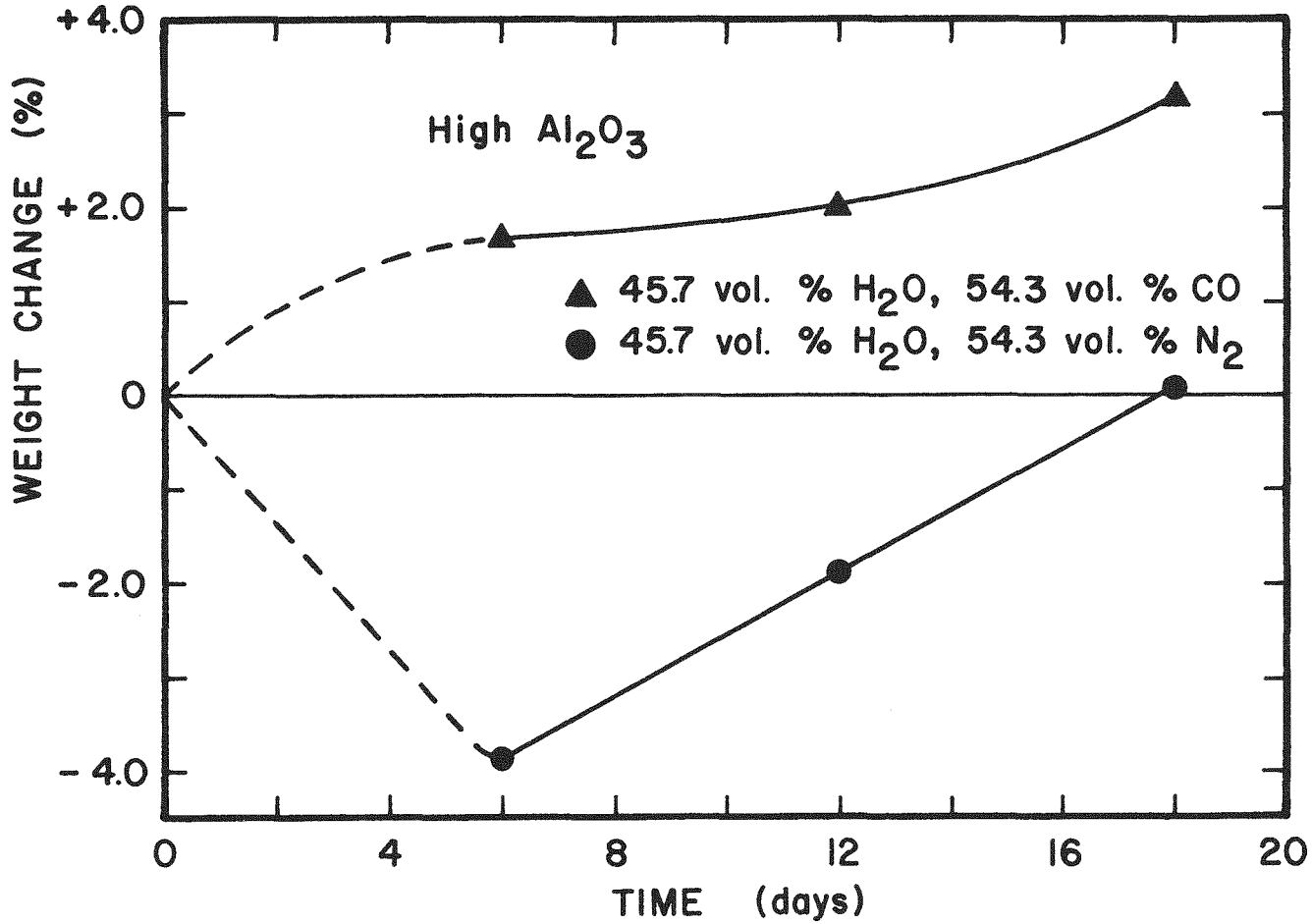


Figure A10-1. Weight Change for the High Al_2O_3 Castable When Exposed to Atmospheres Shown at 199°C and 450 psi.

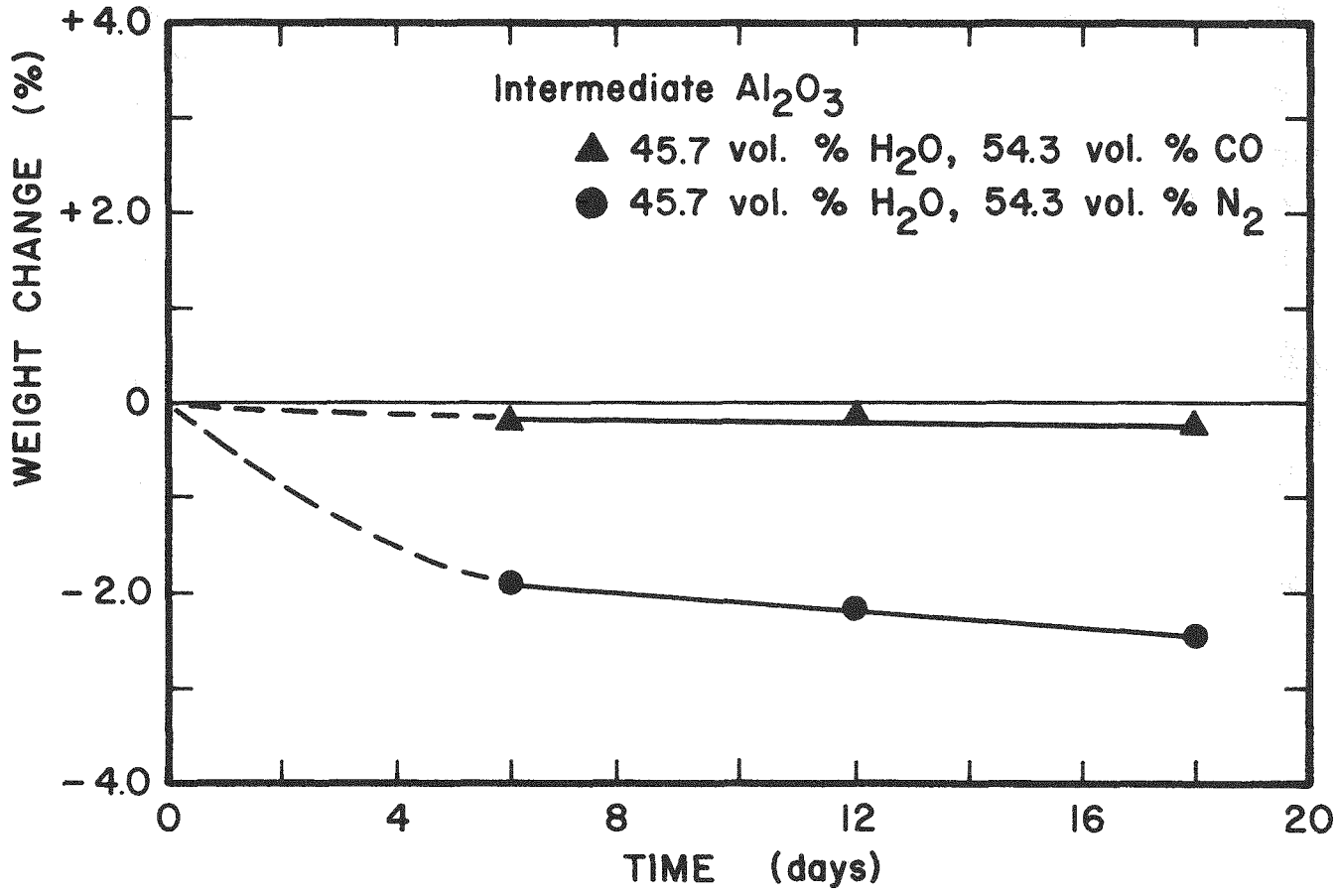


Figure A10-2. Weight Change for the Intermediate Al_2O_3 Castable When Exposed to Atmospheres Shown at 199°C and 450 psi.

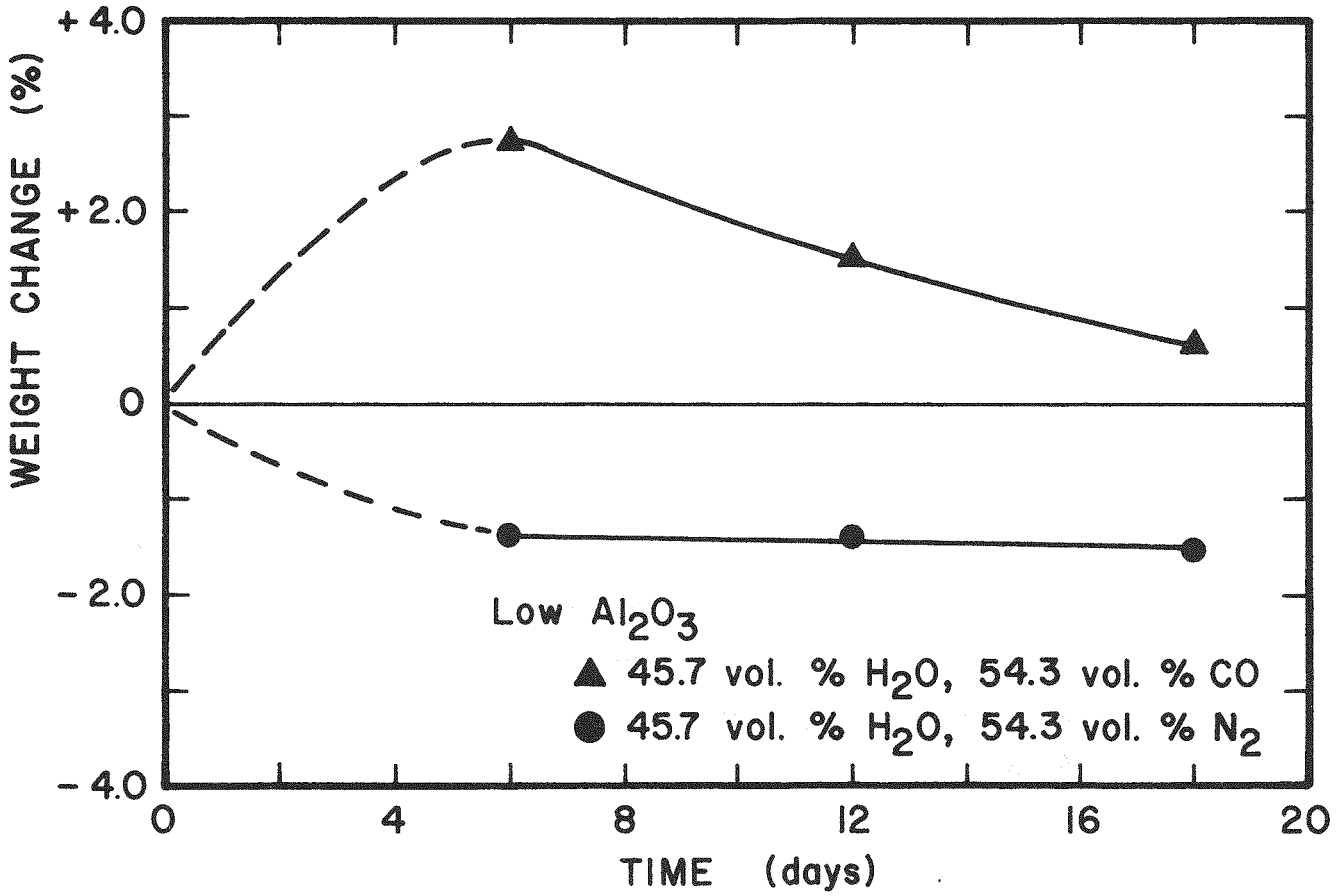


Figure A10-3. Weight Change for the Low Al_2O_3 Castable When Exposed to Atmospheres Shown at 199°C and 450 psi.

Table A10-I.

Average* Weight Change After Exposure
to the Atmosphere Shown at 199°C and 450 psi

Test Duration (days)	Weight Change (%) High Al_2O_3	Intermed. Al_2O_3	Low Al_2O_3
Steam-N_2 Atmosphere at 199°C and 450 psi			
6	-3.85	-1.90	-1.38
12	-1.78	-2.14	-1.38
18	+0.11	-2.44	-1.52
Steam-CO Atmosphere at 199°C and 450 psi			
6	+1.70	-0.17	+2.76
12	+2.03	-0.13	+1.55**
18	+3.18	-0.20	-0.64

\+ = Weight gain

\- = Weight loss

* Average of 10 specimens.

** Average of 7 specimens.

Appendix 11

M.O.R. DATA

The mechanical strength data used in Figures 1,5, and 6 in the text, is given in Table A11-I.

Table A11-I.

Mechanical Strength Data

Test Duration (days)	M.O.R.* (psi) and Standard Deviation (σ) High Al_2O_3 M.O.R.	σ	Intermed. Al_2O_3 M.O.R.	σ	Low Al_2O_3 M.O.R.	σ
0**	1748	109	1034	33	112	30
Steam-N_2 Atmosphere at 199°C and 450 psi						
6	3312	310	1286	336	101	38
12	3212	357	1245	292	108	40
18	3640	268	1090	113	63	14
Steam-CO Atmosphere at 199°C and 450 psi						
6	2065	1123	1266	124	106	40
12	1362	484	1241	142	110+	36
18	1007	383	----	---	103	21

* Average of 10 specimens.

** Trowelled or poured, cured and then dried at 104°C.

+ Average of 7 specimens.

Appendix 12

ADDITIONAL INVESTIGATIONS

a. EXPERIMENTAL PROCEDURES

Additional investigations were conducted at higher temperatures and pressures, and with different atmospheres, to determine what effect atmosphere composition, temperature, and pressure had on the various reactions. A summary of these test conditions is presented in Table A12-I.

All of the tests listed in Table A12-I, except test 9, were performed using a second reaction vessel, constructed from AISI 316 stainless steel. This vessel measured 44.5 mm I.D. and 184.14 mm in depth (1.75 in. I.D. x 7.25 in. deep) and was capable of 5400 psi at 345°C. The second vessel was operated in the same manner as the first vessel. However, the overall system differed in that the gas line was equipped with a rupture disc instead of an adjustable relief valve, and the temperature control system was not equipped with thermocouple break protection or additional thermocouples to monitor the temperature gradient.

The "stained" samples, referred to in test 7 (Table A12-I), were iron stained by boiling the samples in saturated ferrous sulfate ($FeSO_4 \cdot 7\ H_2O$) and ferric sulfate ($Fe_2(SO_4)_3 \cdot n\ H_2O$) solutions for 16-24 hours. This method produced a stain which penetrated 1-2 mm into the samples. After staining, the samples were dried at 104°C for 24

hours.

The analysis procedures were the same as those used in tests 1-6 (as described in the text).

b. RESULTS and DISCUSSION

(1). Refractory - Vessel - Atmosphere Interactions

The interior of both the carbon steel vessel and the stainless steel vessel (the "second" vessel) reacted with the test atmospheres to form Fe_3O_4 and Fe_2O_3, but the greatest amount of oxidation occurred in the carbon steel vessel.

In addition to metal oxidation differences, the $Ca(HCO_2)_2$, detected in the steam-CO atmosphere, was observed only in the carbon steel vessel. There are two possible explanations for this difference. First, perhaps substantial amounts of Fe_3O_4 or Fe_2O_3 were necessary to catalyze $Ca(HCO_2)_2$ formation. However, this does not seem likely, because the largest amounts of $Ca(HCO_2)_2$ formed on "clean" or unstained areas on the castable surfaces, as shown in Figures 3(a) and (b), the top samples (in the text). The other explanation is that perhaps excess CO was necessary for $Ca(HCO_2)_2$ formation (equation (3) in the text) to occur. This could very well be the case, since the ratio of test gas volume to sample volume was approximately 3 times greater in the carbon steel vessel.

Therefore, it is believed that the reactions observed

in the castables were not dependent upon the metal used in reaction vessel construction, but rather were influenced by the test gas volume available for reaction.

(2). Catalyzed Boehmite Formation

Deteriorated samples of castables removed from the cold face of NH_3 plant transfer lines were usually iron stained and often contained substantial amounts of boehmite.[A12-1] Test 7 was conducted to determine if iron catalyzed boehmite formation. The test results showed that iron had no effect. Similar amounts of boehmite were detected in the iron stained and unstained samples.

(3). Effects of Atmosphere Composition, Temperature, and Pressure

The test atmosphere used in test 12 closely approximates that found in the secondary transfer line of an NH_3 production plant. It was anticipated that the results obtained in this study would more closely simulate those which occur in an NH_3 plant. From the chemical reaction standpoint, the results proved to be the same as those observed in the steam-CO atmosphere at 199°C and 450 psi.

Increasing the pressure affected only $CaCO_3$ formation in the steam-CO atmosphere (tests 9 and 10), which increased in magnitude. This result was expected, since increasing the pressure in the steam-CO atmosphere results in an increase in the amount of CO available to form CO_2. The physical properties of the castables remained much the same,

as can be seen by comparing the data in Tables A12-II, III, and IV to that in Tables IX (text), A10-I (Appendix 10), and A11-I (Appendix 11), respectively.

Increasing the temperature, with or without increasing the pressure, appeared to have little effect on the reactions.

Table A12-I.

Additional Investigations - Test Conditions

Test No.	Atmosphere Composition (vol.%)	Pressure (psi)	Temperature (°C)	Duration (days)	Materials Tested
7	66.6 H_2O, 33.4 N_2	1000	260	1, 8, 16	* High Al_2O_3
8	66.6 H_2O, 33.4 N_2	1000	260	6,12, 18	** High, Intermediate, and Low Al_2O_3
9	29.4 H_2O, 70.6 CO	700	199	6	+ High, Intermediate, and Low Al_2O_3
10	20.6 H_2O, 79.4 CO	1000	199	6,12, 18	** High, Intermediate, and Low Al_2O_3
11	66.6 H_2O, 33.4 CO	1000	260	6,12, 18	"
12	45.7 H_2O, 37.1 H_2, 4.7 CO, 5.9 CO_2, 6.6 CH_4	450	199	6,12, 18, 24, 30, 40	"

* Three 12.70 x 12.70 x 31.75 mm specimens were used for each time trial. One bar was unstained, the second bar was stained with ferrous sulfate, and the remaining bar was stained with ferric sulfate.

** One 12.70 x 12.70 x 31.75 mm specimen was used for each time period.

\+ Five 38.1 x 38.1 x 152.4 mm specimens and two 12.70 x 12.70 x 31.75 specimens were used for each time period.

Table A12-II.

Average* Expansion After Exposure
to Steam-CO Atmosphere at 199°C and 700 psi (test 9)

	Expansion (%)		
Test Duration (days)	High Al_2O_3	Intermed. Al_2O_3	Low Al_2O_3
6	3.15	1.74	1.49

* Average of the length, width, and depth expansion for 5 specimens.

Table A12-III.

Average* Weight Change After Exposure
to Steam-CO Atmosphere at 199°C and 700 psi (test 9)

	Weight Change (%)		
Test Duration (days)	High Al_2O_3	Intermed. Al_2O_3	Low Al_2O_3
6	+2.76	+1.17	-0.61

\+ = Weight gain

\- = Weight loss

* Average of 5 specimens.

Table A12-IV.

Mechanical Strength Data After Exposure to Steam-CO Atmosphere at 199°C and 700 psi (test 9)

Test Duration (days)	M.O.R.* (psi) and Standard Deviation (σ)					
	High Al_2O_3 M.O.R.	σ	Intermed. Al_2O_3 M.O.R.	σ	Low Al_2O_3 M.O.R.	σ
6	2197	480	1822	660	99	28

* Average of 5 specimens.

c. REFERENCES

A12-1 D.E. Day, personal communication from the Bechtel Corporation and the A.P. Green Refractories Company.

☆ U.S. GOVERNMENT PRINTING OFFICE: 1976—677-343/216