Investigation of Calcium Aluminate Cement Phases Under High **Gaseous Pressure***

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The chemical degradation of refractory cement castable liners is important in the coal gasification process. The system CaO-Al₂O₃-H₂O has been investigated at high temperature and pressure. A pseudobinary reaction diagram was constructed for the system CaO-Al₂O₃-H₂O in steam at 1000 psig. Several experiments were conducted in the CaO-Al₂O₃-H₂O system in CO₂, CH₄, and CO.

Key words: Alumina cements; CaO · Al₂O₃ · H₂O; coal gasification; refractory cements.

Introduction 1.

The process of coal gasification requires the handling and containment of corrosive gases at high temperature and pressure. Although the chemical composition of the gaseous environment found to occur in coal gasification reactors varies depending on the processes employed, they generally contain CO, CO₂, H₂, H₂O, and CH₄ as major constituents and C₂H₆, H₂S, and N₂ as minor constituents. This investigation was concerned with the chemical degradation produced by the interaction of high pressure H_2O , CO, and CO_2 with some of the phases forming the hot castable high purity calcium aluminate liner material found in many operating coal gasifiers. The principal constituents of this castable liner material are calcium aluminates and alumina.

2. **Specimen Preparation and Test Methods**

For most of the hydration experiments, pure, well-characterized, starting materials were employed. The compositions $3CaO \cdot Al_2O_3$, $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$, and $CaO \cdot 6Al_2O_3$ were prepared from high purity CaCO₃ and Al₂O₃. These admixtures were ground and calcined at 700 °C for 60 hours, 1000 °C for 16 hours, and 1500 °C for 60 hours. The three compositions highest in Al_2O_3 content were reheated for an additional 60 hours at 1550 °C. All of these materials, synthesized in air, were characterized by x-ray powder diffraction techniques and found to be single phase.

These single phase materials were placed in small platinum tubes, with calculated, weighed amounts of H2O and sealed. The tubes were heated by conventional hydrothermal techniques, quenched, opened, and dried. The reaction products were identified by x-ray powder diffraction. Materials reacted in other environments were treated similarly except that they were heated in open platinum tubes in the absence of introduced H_2O .

Results and Discussion 3.

System CaO-Al₂O₃ in Steam 3.1.

Considerable information on the CaO-Al₂O₃-H₂O system has been reported in the literature. The work of Peppler and Wells [1]¹ and Majumdar and Roy [2] summarize most of our present knowledge of this system. Nurse et al. [3] found that 12CaO · 7Al₂O₃ melts congruently at 1392 °C in atmospheric air. In dry air, preformed 12CaO · 7Al₂O₃ melts incongruently to CaO·Al₂O₃ and a liquid at 1374 °C. He further concluded that the $12CaO \cdot 7Al_2O_3$ compound did not have a field of stability in the strictly anhydrous CaO-Al₂O₃ system.

For the purpose of studying the solid state reactions encountered with steam in a coal gasifier the solubility data of Peppler and Wells were reinterpreted with the view of integrating the data with those of Majumdar and Roy. This was accomplished by constructing the diagram, figure 1, from the data given by Peppler and Wells and Majumdar and Roy and from the data in table I. From these low temperature data, it was possible to predict the behavior at 1000 °C. Therefore, it was necessary only to verify that portion of the system which could directly affect the operation of a coal gasifier at 1000 °C and 1000 psig² of steam.

To verify the reactions which occur in the CaO-Al₂O₃-H₂O system at high temperatures and pressures a series of experiments were conducted and the results are given in table II. A pseudobinary reaction diagram, figure 2, was constructed from the data in table II. In constructing figure 2, it was necessary to neglect the starting phases and assume the various starting materials would approach the same equilibrium products in any given temperature, pressure, time sequence.

From figure 2 it can be seen that the first hydrate formed, 3CaO · Al₂O₃ · 6H₂O, is unstable and dissociates, above room temperature, to form $Ca(OH)_2$ and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O_3$.

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 $^{^1}$ Figures in brackets indicate the literature references at the end of this paper. 2 The use of psi, psig, bar, and kbar follows the current common practice of workers in the field. Note that 1 bar = 10^9 N/m² (or pascal) = 0.9869 atm = 14.504 psi. The accepted international standard (SI) unit of pressure is the pascal or newton per square meter.



FIGURE 1. Proposed constitution diagram.

- \otimes Peppler and Wells
- O Majumdar and Roy
- + Waring et al. (this work)

Table I. Experimental Data Used to Construct the Pressure-Temperature Diagram for the System CaO-Al_2O_3-H_2O.

Starting Material $\frac{1}{}$	Temperature °C	Pressure psig	Time days	X-ray Diffraction Analysis	Conclusion
1:2	300	1000	7	1:2 + 4:3:3 + boehmite	1:2 → boehmite + 4:3:3
1:2	700	1000	7	1:2	1:2 → 1:2
1:1	700	1000	7	1:1 + trace 1:2	1:1 → 1:1
1:2	400	1000	11	1:2 + boehmite + 4:3:3	$1:2 \rightarrow \text{boehmite} + 4:3:3$
1:2	500	1000	11	1:2	1:2 → 1:2
1:1	400	1000	11	1:1	1:1 (?)
1:1	500	1000	11	1:1 may have faint trace of 1:2	1:1 + 1:1

 $\frac{1}{1:2} = Ca0.2A1_{2}0_{3}$

 $1:1 = Ca0 \cdot A1_20_3$

 $4:3:3 = 4Ca0 \cdot 3A1_20_3 \cdot 3H_20$

 $A1_20_3 \cdot H_20 = boehmite$

Preformed $3CaO \cdot Al_2O_3$ was found to have a minimum dissociation temperature in excess of 1000 °C and 1000 psig steam. The 1000 °C and 1000 psig data were obtained using a TZM (titanium-zirconium-molybdenum alloy)³ apparatus.

The maximum and minimum dissociation temperatures for the $12CaO \cdot 7Al_2O_3$ have not been established. However, the minimum dissociation temperature is probably in excess of 400 °C and the compound should be stable up to the melting point of 1392 °C. The hydrate $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ forms in a wet atmosphere at about 20 °C and is stable up to about 600 °C in 1000 psig steam. The compounds $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$ were found to exist at temperatures in excess

³ Certain commercially available materials or instruments are identified in this publication for the purpose of providing a complete description of the work performed. The experiments reported do not constitute a complete evaluation of the performance characteristics of the products so identified. In on case does such identified in mply recommendation or endorsement by the National Bureau of Standards nor does it imply that the items identified are necessarily the best available for the purpose.



FIGURE 2. Tentative pseudobinary reaction diagram of the system CaO-Al₂O₃-H₂O at 1000 psig. $3:1:6 = 3CaO \cdot Al_2O_3 \cdot 6H_2O$

of 1000 °C and to hydrate below 400 °C. The compounds $CaO \cdot Al_2O_3$, $CaO \cdot 2Al_2O_3$ and $CaO \cdot 6Al_2O_3$, experimentally, appear to have the same minimum temperature of stability since at these relatively low temperatures the reactions occur very slowly. It has not been possible to delineate these boundaries; therefore, the region of uncertainty is shaded in the diagram, figure 2. At a temperature below approximately 400-450 °C, these phases dissociate into boehmite ($Al_2O_3 \cdot H_2O$) and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$. The phase transition between boehmite and Al_2O_3 in the pressure range of 1000 psig was not determined.

In a cement which initially consists of $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$ with Al_2O_3 grog, the $3CaO \cdot Al_2O_3 \cdot 6H_2O$ originally formed after the addition of H_2O will transform rapidly upon the increase of pressure and temperature to form $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$. This phase will then react at slowly increasing temperatures to form, first, $12CaO \cdot 7Al_2O_3$ plus $CaO \cdot Al_2O_3$ and then, eventually, $CaO \cdot 6Al_2O_3$ plus Al_2O_3 , if the whole product attains equilibrium.

3.2. System CaO-Al₂O₃-H₂O in CO₂

Several experiments were conducted at high temperature in CO_2 (860 psig) and the results are given in table III.

The data given in table III indicate that the reactions which occur in a CO₂ environment are similar to those occurring in steam. There are several exceptions. The 4CaO·3Al₂O₃·3H₂O phase at 500 °C is stable in steam but in CO₂ partially decomposes to CaCO₃ + Al₂O₃. At 600 °C/ 860 psig CO₂, that portion of the 4CaO·3Al₂O₃·3H₂O, which has not reacted with the CO₂, dehydrates to form a cubic phase with $a \cong 8.9$ A, which is apparently the aluminate analog of sodalite (Ca₄Al₆O₁₃, analogous to Na₄Al₃Si₃O₁₂Cl). The occurrence of the calcium aluminate analog of sodalite was reported by Ponomarev, Kheiber, and Belov [4] to form by dehydration in air from hydrothermally grown single crystals. Several experiments indicate that other CaO-Al₂O₃ phases may also be stable with respect to the CaCO₃-Al₂O₃ system under these conditions.

Table II.	Experimental	Data	for	Compositions	in	the System	Ca0-A120	3-H20	at	1000 psig Steam Pressure.	
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Starting <u>1</u> / Material	Temp. °C	Pressure psig	Time hrs	X-ray Diffraction Analysis	Conclusions
3:1:6	350	1000	720	$4:3:3 + Ca(OH)_{2} + hydrate$	3:1:6 → 4:3:3 + hydrate
3:1:6	450	1000	720	4:3:3 + Ca(OH) ₂ + 3:1:6 + hydrate	3:1:6 → 4:3:3 + hydrate
3:1	350	1000	720	3:1 + Ca(OH) ₂ + 12:7	$3:1 \rightarrow 12:7 + Ca(OH)_2$
3:1	450	1000	720	3:1 + Ca(OH) + 12:7	$3:1 \rightarrow 12:7 + Ca(OH)_2^{-1}$
3:1	500	1000	168	3:1 + 12:7 + Ca(OH) ₂	$3:1 \rightarrow 12:7 + Ca(OH)_2^{-1}$
3:1	600	1000	168	12:7 + 3:1 + Ca0	3:1 → 12:7 + CaO
3:1	700	1000	168	3:1 + 12:7 + CaO	3:1 → 12:7 + CaO
3:1	1000	945	120	12:7 + CaO	3:1 → 12:7 + CaO
4:3:3	350	1000	720	4:3:3 + boehmite	Ca(OH)_ + amorphous Al₂O3 + 4:3:3 → 4:3:3 + boehmite
4:3:3	400	1000	86	4:3:3 + Ca(OH) ₂	4:3:3 + amorphous Ca(OH) ₂ + amorphous A1 ₂ O ₃ → 4:3:3 ¥ Ca(OH) ₂
4:3:3	450	1000	720	4:3:3	4:3:3 + amorphous Ca(OH) ₂ + amorphous Al ₂ O ₃ \rightarrow 4:3:3
4:3:3	500	1000	86	4:3:3 + Ca(OH) ₂	4:3:3 + amorphous Ca(OH) ₂ + amorphous Al ₂ O ₃ + 4:3:3 + cryst Ca(OH) ₂
4:3:3	500	1000	168	4:3:3	4:3:3 + amorphous A1 ₂ 03 + amorphous Ca(OH) ₂ \rightarrow 4:3:3
4:3:3	600	1000	168	4:3:3 + 12:7 + CaO	4:3:3 + 12:7 + CaO
4:3:3	700	1000	168	(leaked) 12:7 + 1:1	
1:1	300	1000	168	4:3:3 + 1:1 + boehmite	1:1 → boehmite + 4:3:3
1:1	400	1000	240	1:1	1:1(?)
1:1	450	1000	240	1:1 + 4:3:3	1:1 + 4:3:3
1:1	500	1000	264	1:1	1:1 + 1:1
1:1	700	1000	168	1:1 + 1:2	1:1 + 1:1
1:1	1000	945	120	1:1	1:1 + 1:1
1:2	300	1000	168	1:2 + 4:3:3 + boehmite	1:2 → boehmite + 4:3:3
1:2	400	1000	264	1:2 + boehmite + 4:3:3	1:2 → boehmite + 4:3:3
1:2	450	1000	240	1:2	1:2 -> 1:2
1:2	500	1000	264	1:2	1:2 → 1:2
1:2	700	1000	168	1:2	1:2 → 1:2
1:2	1000	945	120	1:2	1:2 -> 1:2
1:6	350	1000	945	1:6 + 4:3:3 + A1 ₂ 0 ₃	$1:6 \rightarrow 4:3:3 + A1_20_3$ (+ boehmite-?)
1:6	450	1000	945	$1:6 + A1_20_3$	$1:6 + 1:6 + A1_20_3$
<u>1</u> / 3:1:6 =	3Ca0.A1_0			$A1_2O_3 \cdot H_2O = boehmite$	
1:2 =	Ca0.2A1_0	3			
3:1 =	3Ca0.A1_0	2			
4:3:3 =	4Ca0.3A1	03.03H20			
12:7 =	12Ca0•7A1	203			

hydrate = hydrated calcium aluminate of unknown composition

3.3. System CaO-Al₂O₃-H₂O in CH₄

 $1:1 = Ca0 \cdot A1_20_3$ $1:6 = Ca0 \cdot 6A1_20_3$

Two specimens consisting of CA-25, a commercially available calcium aluminate cement, and $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ were heated in a methane environment at 800 °C for two weeks at 1000 psig. The x-ray powder pattern of the CA-25 specimen showed the CaO $\cdot \text{Al}_2\text{O}_3$, CaO $\cdot 2\text{Al}_2\text{O}_3$ and Al $_2\text{O}_3$ which were present in the original CA-25 plus an unknown phase with a line at about 24° 2θ (CuK α radiation). This unknown phase did not appear to be calcium formate. The $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ contains $12CaO \cdot 7Al_2O_3$ and $CaO \cdot Al_2O_3$. These are the same reaction products as those occurring under 1000 psig steam at the same composition and temperature. Table IV summarizes the results.

3.4. System CaO-Al₂O₃-H₂O in CO

Four compositions were heated in CO (Table V) at 1000 psig and 700 °C for 110 hours. The x-ray pattern of the

Table III. Experimental Data for Compositions in the System CaO-Al₂O₃-H₂O in 860 psig of CO₂.

Starting Material <u>a</u> /	Temp. °C	Pressure psig	Time hrs	Results <mark>b,c/</mark> X-ray Diffraction Analysis	Conclusions
3:1	600	860	72	3:1	3:1 → 3:1
3:1	700	860	72	3:1 + 12:7 + CaCO ₃	$3:1 \rightarrow 12:7 + CaCO_3$
3:1	700	860	144	3:1 + 12:7 + CaCO ₃	$3:1 \rightarrow 12:7 + CaCO_3$
3:1:6	500	860	336	CaCO ₃ + 4:3:3	$3:1:6 \rightarrow CaCO_3 + 4:3:3$
3:1:6	600	860	384	$CaCO_3 + 12:7 + 1:2$	$3:1:6 \rightarrow CaCO_3 + 12:7 + 1:2$
3:1:6	800	860	144	CaCO ₃ + unknown <mark>e</mark> / + 1:2	$3:1:6 \rightarrow CaCO_3^3 + unknown^{\underline{e}/} + 1:2$
4:3:3	500	860	288	4:3:3 + A1 ₂ 0 ₃ + CaC0 ₃	$4:3:3 \rightarrow CaCO_3 + Al_2O_3$
4:3:3	600	860	384	"sodalite" $\frac{d}{d}$ + CaCO ₃	4:3:3 → "sodalite" $\frac{d}{}$ + CaCO ₃
4:3:3	700	860	1 4 4	1:1 + CaCO ₃ + unknown(s) e,f /	$4:3:3 \rightarrow 1:1 + CaCO_3 + unknown(s) e,f$
4:3:3	800	860	144	1:1 + 1:2 + CaCO ₃ + unknown ^{e/}	4:3:3 → 1:1 + 1:2 + CaCO ₃ + unknown <u>e</u> /
1:1	500	860	288	$1:1 + A1_{2}0_{2} + CaC0_{2}$	$1:1 \rightarrow A1_20_2 + CaC0_2$
1:1	600	860	72	1:1	1:1 → 1:1
1:1	700	860	72	1:2 + CaCO ₂	$1:1 \rightarrow 1:2 + CaCO_3$
1:1	800	860	144	1:1	1:1 → 1:1
1:2	500	860	720	1:2	1:2 → 1:2
1:2	700	860	192	1:2	1:2 → 1:2
1:6	500	860	720	1:6 + tr α -A1 ₂ 0 ₃	1:6 → 1:6

<u>a</u>/ All bulk starting materials, which were spectrographically pure, were mixed and calcined for sufficient time and at a temperature to obtain single phase materials. These specimens were heated in a conventional hydrothermal bomb in open Pt tube and were quenched by water immersion from the temperatures indicated.

 $\frac{b}{}$ The phases identified are given in order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to which the specimen was heated.

 \underline{c} The following short notations were used for clarity:

 $3:1 = 3Ca0 \cdot A1_{2}O_{3}$ $3:1:6 = 3Ca0 \cdot A1_{2}O_{3} \cdot 6H_{2}O_{3}$ $1:7 = 12Ca0 \cdot 7A1_{2}O_{3}$ $4:3:3 = 4Ca0 \cdot 3A1_{2}O_{3} \cdot 3H_{2}O_{3}$ $1:1 = Ca0 \cdot A1_{2}O_{3}$ $1:2 = Ca0 \cdot 2A1_{2}O_{3}$ $1:6 = Ca0 \cdot 6A1_{2}O_{3}$

 \underline{d} The "sodalite" dehydration product (major peak, d = 3.642)

- \underline{e} / Unknown dehydration product (major peak, d = 3.697)
- $\frac{f}{d}$ Unknown dehydration product (major peak, d = 3.620)

sample which was initially CaO·Al₂O₃ showed a mixture of CaO·Al₂O₃ and CaO·2Al₂O₃. The 4CaO·3Al₂O₃·3H₂O showed the same decomposition products as those heated in CO₂. The CA-25 x-ray pattern showed mixtures of CaCO₃, Al₂O₃, CaO·2Al₂O₃ and CaO·Al₂O₃. The CaO·2Al₂O₃ showed no reaction.

4. Summary

Many questions remain unanswered which could not be investigated in this study. However, the following observations should be noted:

- 1. At 1000 psig steam pressure, the phase boundaries are essentially those which can be predicted from a combination of the published data of Peppler and Wells [1] and Majumdar and Roy [2].
- 2. The cementitious phases $3CaO \cdot Al_2O_3 \cdot 6H_2O$ and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ are not stable at any higher temperature in 1000 psig steam than they are at atmospheric pressure.
- 3. The compound $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ decomposes to metastable phases in dry atmospheres such as CO_2 or CO and directly to the stable phases in steam.

Table IV. Experimental Data for Compositions in the System CaO-Al₂O₂-H₂O in CH₄.

Starting Materials <u>a</u> /	Temp. °C	Pressure psig	Time hrs	Results <mark>b,c/</mark> X-ray Diffraction Analysis	Conclusions
CA-25	800	1000	316	$1:2 + 1:1 + \alpha - A1_20_3 + unknown \frac{d}{d}$	
4:3:3	800	1000	316	12:7 + 1:1	4:3:3 → 12:7 + 1:1

 $\underline{a}/$ All bulk starting materials, which were spectrographically pure, were mixed and calcined for sufficient time and at a temperature to obtain single phase materials. These specimens were heated in an open platinum tube in a conventional hydrothermal bomb.

 \underline{b}' The phases identified are given in order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to which the specimen was heated.

 $\underline{c}/4:3:3 = 4Ca0.3A1_20_3.3H_20$

 $1:2 = Ca0 \cdot 2A1_20_3$

1:1 = Ca0.A1203

 $12:7 = 12Ca0.7A1_{2}O_{3}$

CA-25 = A commercial cement containing 1:1, 1:2 and α -A1₂0₃

 $\frac{d}{2}$ Specimem contains an unknown phase with the major x-ray diffraction powder line occurring at about 3.70Å.

Table V. Experimental Data for Compositions in the System $CaO-Al_2O_3-H_2O$ in CO_2

Starting "ateria!s <u>a</u> /	Temp. °C	Pressure psig	Time hrs	Results <u>b</u> / X-ray Diffraction Analysis	Conclusions
1:1	700	1000	110	1:1 + 1:2	
4:3:3	700	1000	110	1:1 + "sodalite" ^{C/} + CaCO ₃	4:3:3 → 1:1 + CaCO ₃
1:2	700	1000	110	1:2	1:2 → 1:2
CA-25	700	1000	110	CaCO ₃ + α-A1 ₂ O ₃ + 1:2 + 1:1	

 \underline{a}^{\prime} All bulk starting materials, which were spectrographically pure, were mixed and calcined for sufficient time and at a temperature to obtain single phase materials. These specimens were heated in an open platinum tube in a conventional hydrothermal bomb.

 \underline{b}' The phases identified are given in order of the amount present (greatest amount first) at room temperature. These phases are not necessarily those present at the temperature to what the specimen was heated.

 $\underline{C}/$ This naterial is a dehydration product which appears to be the calcium aluminate analog of sodalite.

 $4:3:3 = 4Ca0 \cdot 3A1_20_3 \cdot 3H_20$ $1:2 = Ca0 \cdot 2A1_20_3$

1:1 = CaO.A1203

CA-25 = A commercial comment containing 1:1, 1:2 and α -A1₂0₃

4. Most of the phases in the CaO-Al₂O₃-H₂O system are not stable in CO₂ (860 psig) with respect to the system CaCO₃-Al₂O₃.

5. References

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In order to determine the possible deleterious effects of the combined gaseous atmospheres present in a coal gasifier, a considerably more detailed study must be made of the CaO-Al₂O₃-H₂O system, especially in CH₄ and in various gaseous combinations.