Investigation of Calcium Aluminate Cement Phases Under High Gaseous Pressure*

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(August 2, 1977)

The chemical degradation of refractory cement castable liners is important in the coal gasification process. The system $CaO-AI_2O_3-H_2O$ has been investigated at high temperature and pressure. A pseudobinary reaction diagram was constructed for the system $Ca\bar{O}-A_1_2O_3+H_2O$ in steam at 1000 psig. Several experiments were conducted in the CaO-Al₂O₃-H₂O system in CO₂, CH₄, and CO.

Key words: Alumina cements; $CaO \cdot Al_2O_3 \cdot H_2O$; coal gasification; refractory cements.

1. Introduction

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 C_2H_6 , H_2S , and N_2 as minor constituents. This investigation was concerned with the chemical degradation produced by the interaction of high pressure H_2O , CO, and $CO₂$ 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 $\mathrm{Al}_2\mathrm{O}_3$ 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 H_2O 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 .

3. Results and Discussion

3.1. System CaO-A I_2O_3 in Steam

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 $12CaO \cdot 7Al_2O_3$ melts congruently at 1392 °C in atmospheric air. In dry air, preformed $12CaO \cdot 7Al_2O_3$ melts incongruently to $CaO \cdot Al_2O_3$ 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 $CaO-Al_2O_3$ - $H₂O$ 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, $3CaO \cdot Al_2O_3 \cdot 6H_2O$, is unstable and dissociates, above room temperature, to form $Ca(OH)_2$ and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$.

^{*} This work was supported in part by ERDA:FE Contract No. 14-32-0001-1749 and shorter versions of this paper have been included as parts of ERDA Quarterly Reports.

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 = 10⁵ N/m² (or

FIGURE 1. Proposed constitution diagram.

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

Table I. Experimental Data Used to Construct the Pressure-Temperature Diagram for the System CaO-Al₂O₃-H₂O.

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

 $\frac{1}{2}$ 1:2 = Ca0.2A1₂0₃

1:1 = $CaO - A1_2O_3$

 $4:3:3 = 4CaO \cdot 3Al_2O_3 \cdot 3H_2O$

 $Al_2O_3·H_2O =$ 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 compl

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

 $4:3:3 = 4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ $3:1 = 3CaO \cdot Al_2O_3$ $12:7 = 12CaO \cdot 7Al_2O_3$ $1:1 = \text{CaO} \cdot \text{Al}_2\text{O}_3$ $1:2 = \angle A_2O_3$ $1:6 = \text{CaO} \cdot 6 \text{Al}_2\text{O}_3$ $\mathrm{Al}_2\mathrm{O}_3 \cdot \mathrm{H}_2\mathrm{O} = \mathrm{boehmite}$ $\overline{\mathbf{m}}$ = region of undetermined equilibria \bullet = experimental points

of 1000 $^{\circ}$ C and to hydrate below 400 $^{\circ}$ 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 $(\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O})$ and $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. 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 $CO₂$ (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 $4CaO \cdot 3\text{A}l_2O_3 \cdot 3\text{H}_2O$ phase at 500 °C is stable in steam but in CO_2 partially decomposes to $CaCO_3 + Al_2O_3$. At 600 °C/ 860 psig CO_2 , that portion of the $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$, which has not reacted with the $CO₂$, dehydrates to form a cubic phase with $a \approx 8.9$ A, which is apparently the aluminate analog of sodalite $(Ca_4A1_6O_{13}$, analogous to $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}$ Cl). 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.

1:6 = CaO \cdot 6A 1_2 O₃ hydrate = hydrated calcium aluminate of unknown composition

3.3. System CaO-Al₂O₃-H₂O in CH₄

1:1 = $CaO-A1_{2}O_{3}$

Two specimens consisting of CA-25, a commercially available calcium aluminate cement, and $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ 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 Al₂O₃, CaO \cdot 2Al₂O₃ and Al₂O₃ 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 llO hours. The x-ray pattern of the

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

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 a conventional hydro-
thermal bomb in open Pt tube and were quenched by water immersion from the temperatures indicated.

 $\frac{b}{c}$ 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.

 \mathcal{L} The following short notations were used for clarity:

 $3:1 = 3Ca0 - A1_20_3$ 3:1:6 = $3CaO - A1_2O_3 - 6H_2O$ 12:7 = 12Ca0 \cdot 7A1₂O₃ $4:3:3 = 4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ 1:1 = $CaO-A1_{2}O_{3}$ 1:2 = $CaO.2AI₂O₃$ 1:6 = $Ca0.6Al_2O_3$

 $\frac{df}{dx}$ The "sodalite" dehydration product (major peak, d = 3.642)

 $\frac{e}{c}$ Unknown dehydration product (major peak, d = 3.697)

 f Unknown dehydration product (major peak, d = 3.620)

sample which was initially $CaO \cdot Al_2O_3$ showed a mixture of $CaO \cdot Al_2O_3$ and $CaO \cdot 2Al_2O_3$. The $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ showed the same decomposition products as those heated in $CO₂$. The CA-25 x-ray pattern showed mixtures of CaCO₃, Al_2O_3 , CaO·2Al₂O₃ and CaO·Al₂O₃. The CaO·2Al₂O₃ showed no reaction.

Summary 4.

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 CO2 or CO and directly to the stable phases in steam.

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

 $\frac{d}{dt}$ 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

 $\frac{b}{c}$ 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.

 $C/$ 4:3:3 = 4CaO·3A1₂O₃·3H₂O

1:2 = CaO - 2A1₂O₃

1:1 = CaO - A1₂₀₃

12:7 = 12CaO·7A1₂O₃

 $CA-25$ = A commercial cement containing 1:1, 1:2 and α -Al₂O₃

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

Table V. Experimental Data for Compositions in the System CaO-Al₂O₃-H₂O in CO.

 $\frac{\partial f}{\partial t}$ 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 plati

 $\frac{b'}{c}$ 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.

 $\frac{C}{c}$ This material is a dehydration product which appears to be the calcium aluminate analog of sodalite.

 $4:3:3 = 4CaO \cdot 3Al_2O_3 \cdot 3H_2O$

1:2 = $CaO - 2Al_2O_3$

1:1 = $CaO-A1_2O_2$

 $CA-25 = A$ commercial cement containing 1:1, 1:2 and α -Al₂O₃

4. Most of the phases in the $CaO-Al_2O_3-H_2O$ system are not stable in $CO₂$ (860 psig) with respect to the system $CaCO₃-Al₂O₃$.

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

 $CaO-Al_2O_3-H_2O$ system, especially in CH_4 and in various

gaseous combinations.

5. **References**

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