Hydrothermal Preparation of a Gehlenite Hydrate

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Hydrothermal treatment of synthetic gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) or of various mixtures of oxides, hydrates, etc., approximating the composition of gehlenite, at 260 to 650° C, produced a hitherto unreported compound having the composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$. Other phases, usually hydrogarnet, were always present in small amounts. A natural gehlenite containing Fe_2O_3 and MgO was partly converted to the same hydrate at 450° C. The compound $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$ was converted to a hydrogarnet at 250 °C, but formed $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$ at 350 °C. The new compound has a body-centered cubic structure, with $a_0 = 8.83$ Å. The index of refraction is 1.628. An x-ray diffraction pattern is given, and some similarities between $CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$ and the ternary compound $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ are pointed out.

1. Introduction

The mineral gehlenite is of relatively uncommon occurrence in nature, but is a common constituent of air-cooled blast-furnace slags and is present in some high-alumina cements [1].[1] The ideal formula is $2CaO \cdot Al_2O_3 \cdot SiO_2$, but other oxides, particularly MgO and Fe_2O_3, may be present in solid solution, forming a group of minerals known as melilites. From a practical standpoint, gehlenite usually has been considered a useless constituent of cements and slags, since it reacts very slowly with water and does not have cementitious properties [1]. There is evidence, however, that glasses having the oxide composition of gehlenite are more reactive with water than is the crystalline mineral. It has been shown by Locher [2] that vitreous slags in the gehlenite area of the system $CaO-Al_2O_3-SiO_2$ develop cementitious properties when activated with lime, cement, or anhydrite.

The cementitious properties of such slags have been attributed, at least in part [2], to the so-called gehlenite hydrate, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$, crystallizing as hexagonal plates. This compound was first prepared by Strätling, whose work was reported by Büssem [3] at the Symposium on the Chemistry of Cements (Stockholm, 1938). It has since been prepared by several investigators, including the author, from various starting materials, at temperatures ranging from 1 to 50 °C. Early attempts to prepare it from gehlenite were unsuccessful. The application of hydrothermal treatment to speed up the hydration resulted in formation of a hydrogarnet [4]. Crystallographic studies [5, 6] indicate that there is no close structural relationship between gehlenite (crystallizing in the tetragonal system [1]) and the so-called gehlenite hydrate.

During the course of some hydrothermal studies in the system $CaO-Al_2O_3-SiO_2-H_2O$, the author observed a series of unidentified x-ray diffraction lines in the powder patterns of several preparations. The present paper gives the results of experimental work leading to the conclusion that the new pattern is produced by a hitherto unreported "gehlenite hydrate," having the composition $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$ and crystallizing in the cubic system.

2. Materials and Procedures

The primary starting materials were reagent grade silicic acid, aluminum hydroxide, and calcium carbonate (low alkali). Glasses of various compositions were prepared by heating the mixed raw materials, in the desired proportions, in an electric furnace. Several preparations were heated below the fusion temperature; these are referred to below as "sinters." Synthetic gehlenite was prepared in this manner by heating the properly proportioned materials at about 1460 °C. The product appeared to be about 95 percent gehlenite by microscopic examination. The compound $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$ was prepared in two ways: (1) by prolonged treatment of a mixture of calcium hydroxide and a lime-alumina-silica glass, in correct proportions, with water at room temperature; (2) by precipitation from a suspension of silicic acid in calcium aluminate solution, also at room temperature.

A sample of natural gehlenite originally from Tyrol was used for a few experiments. The rock was first crushed, treated with hydrochloric acid to remove most of a calcite intergrowth, washed, dried, and pulverized before use. The x-ray diffraction pattern was in close agreement with that obtained from the synthetic gehlenite, except that the natural material showed additional weak lines due to calcite. Chemical analysis, however, revealed 1.8 percent of Fe_2O_3 and 3.7 percent of MgO, indicating that the mineral departed significantly from the ideal gehlenite composition.

With a few exceptions, the hydrothermal reactions were effected in 18-ml stainless-steel pressure vessels (Morey bombs), the reactants being held in small platinum crucibles. Pressure was estimated from the temperature and the amount of water present.

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[1] Figures in brackets indicate the literature references at the end of this paper.

Expt. No.	Oxide ratio CaO:Al$_2$O$_3$:SiO$_2$	Starting material	Temperature	Pressure [a]	Duration	Relative amount of isometric phase [b] present	Other phases present [b][c]
			°C	atm	Days		
1	2:1:1	Sinter_____	182	10	37	nd_____	hg(s); boh(m)
2	2:1:1	_____do_____	260	45	37	m_____	boh(s); hg(s)
3	2:1:1	Synth. gehlenite___	332	125	20	vs_____	geh(m); hg(w); boh(?)
4	2:1:1	Sinter_____	350	160	16	vs_____	hg(w)
5	2:1:1	Synth. gehlenite___	405	300	16	vs_____	geh(s)
6	2:1:1	Sinter_____	446	400	16	vs_____	hg(vw)
7	2:1:1	Synth. gehlenite___	650	2040	3	vs_____	geh(vw)
8	2:1:1	_____do_____	750	2040	3	nd_____	geh(vs)
9	2:1:1	Natural gehlenite___	348	160	11	nd_____	hg(s)
10	2:1:1	_____do_____	402	290	7	?_____	hg(vs)
11	2:1:1	_____do_____	450	400	11	m_____	hg(w)
12	2:1:1	2CaO·Al$_2$O$_3$·SiO$_2$·8H$_2$O	150	5	34	nd_____	C$_2$ASH$_5$(vs); hg(m)
13	2:1:1	_____do_____	250	40	34	nd_____	hg(s); boh(s)
14	2:1:1	_____do_____	350	160	31	vs_____	hg(vw)
15	2:1:1	Mixed oxides_____	346	150	36	vs_____	hg(w)
16	2:1:1	_____do_____	450	420	35	vs_____	hg(w)
17	1.26:1:1	Glass_____	382	235	21	s_____	hg(vs); boh(s)
18	1.5:1:1	Sinter_____	350	160	135	m_____	hg(s); boh(w)
19	2.5:1:1	_____do_____	406	300	14	vs_____	Ca(OH)$_2$(s)
20	3:1:1	Glass+Ca(OH)$_2$__	355	170	18	vs_____	Ca(OH)$_2$(s)
21	3:1:0.4	Glass_____	365	190	14	vs_____	Ca(OH)$_2$(vs); C$_4$A$_3$H$_3$(s)
22	3:1:2	_____do_____	371	210	18	s_____	hg(m); Ca(OH)$_2$(w)
23	3:1:2	Glass(devitrified)___	350	160	52	m_____	hg(s)
24	3:1:2	_____do_____	448	420	15	m_____	hg(w)
25	3:1:2	_____do_____	570	1020	¼	m_____	hg(s)
26	3:1:2	Dehyd. kaolin+Ca(OH)$_2$	445	400	7	m_____	hg(s); Ca(OH)$_2$(w)
27	2:1:0.5	Sinter+Ca(OH)$_2$__	358	180	28	s_____	C$_4$A$_3$H$_3$(s); Ca(OH)$_2$(w)
28	1.5:1:0.5	Sinter_____	350	160	27	vs_____	C$_4$A$_3$H$_3$(m); boh(w)
29	2.5:1.5:1	_____do_____	400	280	14	vs_____	C$_4$A$_3$H$_3$(m)
30	4:2.5:1	_____do_____	376	220	20	vs_____	C$_4$A$_3$H$_3$(w)

[a] Estimated from temperature and degree of filling, except for Nos. 7, 8, and 25.
[b] Relative amounts of phases estimated from intensities of strongest x-ray lines. The symbols commonly used for relative intensities are here used to indicate estimated amounts of phases present. vs=very strong; s=strong; m=medium; w=weak; vw=very weak; ?=too weak for positive identification; nd=not detected.
[c] boh=boehmite; geh=gehlenite; hg=hydrogarnet; C$_4$A$_3$H$_3$=4CaO·3Al$_2$O$_3$·3H$_2$O; C$_2$ASH$_8$=2CaO·Al$_2$O$_3$·SiO$_2$·8H$_2$O.

Temperature was controlled to about ±2 °C. For hydrothermal treatment at temperatures above 500 °C, a Tuttle cold-seal apparatus was used. X-ray diffraction diagrams of the powdered preparations were obtained on a diffractometer, using CuKα radiation.
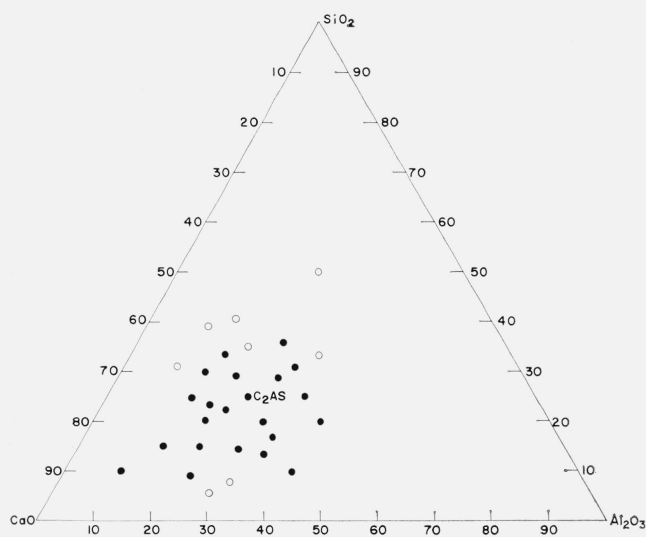

Figure 1. *Compositions of compounds and mixtures given hydrothermal treatment, shown in relation to the anhydrous system* CaO–Al$_2$O$_3$–SiO$_2$. *(Plotted on molar basis)*

Filled circles: new phase (2CaO·Al$_2$O$_3$·SiO$_2$·H$_2$O) observed in product
Open circles: new phase not observed in product.

3. Results

The new isometric phase has been observed in more than 50 preparations obtained by hydrothermal treatment of various materials and mixtures, both hydrous and anhydrous, having compositions near the gehlenite region of the system CaO-Al$_2$O$_3$-SiO$_2$. The location of the various compositions with reference to the ternary diagram is shown in figure 1. Table 1 gives data pertaining to a number of these preparations, selected to show the effects of temperature, composition, and the nature of the starting materials. Experiments 1 to 16 comprise a series in which the molar proportions CaO:Al$_2$O$_3$:SiO$_2$, were held at 2:1:1. Two types of synthetic anhydrous starting materials were used. The one referred to as "sinter" had been heated at about 1040 °C, which is far below the temperature at which complete reaction can be expected. The "synthetic gehlenite," in contrast, had been heated at 1460 °C, and was estimated to be about 95 percent gehlenite. On hydrothermal treatment, both types yielded the same hydration products, but the material which had been heated only to 1040 °C reacted more rapidly with water than did the well-crystallized gehlenite. Formation of the new isometric phase occurred in the temperature range 260 to 650 °C, but in no case was a pure product obtained. Small amounts of hydrogarnet were detected in most of the reaction products. Variation in the x-ray line positions indicated an increase in the silica content of the hydrogarnet phase with increasing temperature, in agreement with results published previously [7].

The synthetic gehlenite was largely converted to the isometric hydrate by hydrothermal treatment at 650 °C, but not at 750 °C. At the latter temperature the irregular gehlenite particles were transformed to well formed crystals, but the x-ray pattern indicated no alteration in structure.

The sample of natural gehlenite was partly converted to the isometric hydrate at 450 °C, but not at 348 °C, only the hydrogarnet phase being formed at the latter temperature. The difference in behavior between the natural and the synthetic materials may reasonably be attributed to the presence of other components in the natural mineral, as disclosed by analysis.

Experiments 12 to 14, in which the hexagonal gehlenite hydrate was treated hydrothermally for about a month, are of interest for two reasons. First, the low temperature hydrate underwent little or no alteration at 150 °C. A moderate amount of hydrogarnet was observed in the product, but the same phase was present in the starting material. Second, the low temperature hydrate was decomposed to hydrogarnet and boehmite at 250 °C, indicating that it is not converted to the high temperature hydrate directly by loss of water. The new isometric phase was formed at 350 °C.

Mixtures of the hydrated oxides (experiments 15 and 16) also produced the new phase along with small amounts of hydrogarnet.

The rest of the experiments listed in table 1 cover a range of oxide proportions other than 2:1:1. In Nos. 17 and 18, with the proportion of CaO reduced, the new phase was accompanied by larger amounts of hydrogarnet and a considerable quantity of boehmite. In Nos. 19 and 20 the excess lime appeared as $Ca(OH)_2$. In the remainder of the experiments listed, the proportions of all three solid components were varied. Here the phase relationships naturally became rather complex. No attempt was made to define phase boundries, as the primary purpose here was to ascertain what proportions of oxides gave the best yield of the new phase. It is evident that the 2:1:1 composition satisfied this condition better than any other investigated.

The last three experiments listed were designed to explore the area between the compositions represented by the oxide proportions $2CaO:Al_2O_3:SiO_2$ and $4CaO:3Al_2O_3$, which is of interest because of certain similarities between the new phase and the ternary compound $4CaO·3Al_2O_3·3H_2O$. The X-ray patterns indicated that both phases were present in the products, with no detectable shift in position of the lines, and hence no evidence of solid solution.

The new isometric phase occurred typically as octahedral crystals, usually with rounded edges. Cubo-octahedra were also observed, and in some preparations some of the crystals were elongated into prisms. The index of refraction was found to be 1.628 ±0.003.

The water content of five of the more nearly homogeneous preparations was determined from the loss on ignition. The results, in terms of moles of H_2O per mole of $2CaO·Al_2O_3·SiO_2$, ranged from 1.00 to 1.19, averaging 1.08. Preparations judged to be the most nearly homogeneous had the lowest water contents. Most of the water was driven off between 550 and 750 °C.

The X-ray diffraction pattern of one of the powdered preparations is given in table 2. The pattern indicated a body-centered cubic structure, with $a_0=8.83$Å. A pattern of a new preparation of $4CaO·3Al_2O_3·3H_2O$ is also given in the table to show the similarities between the strongest lines of the two. Tungsten was used as internal standard in both cases. The pattern of $4CaO·3Al_2O_3·3H_2O$ is

TABLE 2. *Interplanar spacings of* $2CaO·Al_2O_3·SiO_2·H_2O$ *and* $4CaO·3Al_2O_3·3H_2O$

	$2CaO·Al_2O_3·SiO_2·H_2O$		$4CaO·3Al_2O_3·3H_2O$	
hkl	d	I	d	I
	$\AA$		$\AA$	
200	4.42	7		
211	3.607	93	3.61	100
			3.50	9
			3.274	81
			3.207	3
220	3.122	9	3.109	5
			3.029	28
			2.849	51
310	2.793	100	2.797	66
			2.741	4
			2.614	11
222	2.549	32	2.545	22
			2.419	21
			2.386	5
			2.354	8
321	2.360	29	2.290	26
400	2.208	15	2.225	35
			2.182	4
			2.169	17
			2.137	10
411	2.081	42	2.088	37
			2.071	17
			2.066	5
			2.053	5
			2.019	2
			1.986	3
420	1.974	8	1.970	8
			1.931	4
			1.914	8
332	1.882	4	1.838	5
			1.823	4
422	1.801	12	1.801	6
			1.776	4
510	1.730	13	1.738	6
			1.726	3
			1.681	5
			1.668	3
			1.643	4
			1.619	5
521	1.611	10	1.601	20
			1.597	9
			1.572	44
440	1.559	38	1.552	30
			1.540	7
530	1.513	21	1.511	11
			1.486	5
600	1.470	7	1.470	5
			1.466	6
611	1.431	13	1.429	3
			1.416	3
			1.396	2
			1.375	2
541	1.362	4	1.367	5
622	1.330	7	1.331	3
			1.308	2
			1.289	14
710	1.248	4	1.224	3
			1.219	3
721	1.201	3	1.185	5
642	1.179	3	1.170	6
			1.167	4
730	1.158	11	1.158	3
			1.116	8
800	1.103	3	1.113	3
			1.085	2
			1.083	2
			1.081	2

$a_0=8.83$ Å.

in fair agreement with the one published by Majumdar and Roy [8], the chief difference being that the spacings given in table 2 are consistently slightly greater.

4. Discussion

Even the most nearly homogeneous preparations of the new compound contained significant amounts of at least one other phase, most frequently hydrogarnet. This fact makes it impossible to state with certainty that the proposed formula, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$ actually is correct. The amount of hydrogarnet present was estimated to be 10 percent or less in a few cases. Because of the nearness of the oxide ratios in the two phases, the error introduced in the calculated composition resulting from the presence of 10 percent of hydrogarnet is relatively slight. In consideration of this fact, the ignition loss values lead to the conclusion that the new phase has the formula $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$. Thus it may be considered a hydrate of gehlenite.

The relative ease of preparation of this gehlenite hydrate raises the question as to why it was not discovered earlier. A reexamination of the x-ray patterns obtained in a previous investigation [7] showed that the isometric phase was unquestionably present in many of the preparations. Unfortunately, it had been mistaken for the ternary compound, $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$, with which it usually was associated. The x-ray patterns (see table 2) are somewhat similar. Many of the strongest lines are practically coincident, while others are shifted only slightly. It should be noted, also, that diffraction diagrams of different preparations of $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ may vary widely unless great care is taken to avoid orientation effects when mounts are prepared. This fact tended to obscure the significance of the differences that should have been recognized as arising from the presence of another compound. The patterns given in table 2 were obtained on mounts of powders prepared in such a way as to minimize orientation effects; hence the differences between the two patterns are more obvious. Optically, the two phases are also similar, the isometric phase having $n = 1.628$, while the 4:3:3 compound is very slightly birefringent, with n (average) = 1.627. Even in crystal habit there is some similarity, in that the cubic phase was observed in some cases to form prisms like those typical of the aluminate.

Owing to these similarities, it was thought that there might be a structural relationship between the two phases. Experiments 27 to 30 (table 1) were intended to permit formation of an intermediate solid solution, but no evidence of such formation was observed.

To the extent that the isometric phase was mistakenly identified as $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$, the data given and the conclusions drawn in the earlier work cited above [7] need to be modified. [2]

The hydrothermal synthesis of gehlenite at temperatures as low as 450 °C has been reported recently [9], but no mention was made of a hydrate. The experimental conditions were somewhat different from those of the present work, in that calcium carbonate was used as one of the starting materials, with lime present as a receptor for the carbon dioxide evolved. Nevertheless, from the data given above, it would be expected that the isometric gehlenite hydrate, rather than gehlenite itself, would be formed at 450 °C. The reasons for the apparent conflict in results probably cannot be clarified without additional information regarding experimental details in the work cited.

The existence of the high temperature gehlenite hydrate needs to be taken into account in any future study of phase relations in the system $CaO \text{-} Al_2O_3 \text{-} SiO_2 \text{-} H_2O$ at elevated temperatures.

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[2] The correction applies to the following experiments reported in the paper cited [7]: in table 4, Nos. 6 and 7; in table 6, Nos. 16, 24, and 26; in figure 2, the point at the right end of the curve. In each case the phase reported as $4CaO \cdot 3Al_2O_3 \cdot 3H_2O$ ($C_4A_3H_3$) actually was the isometric phase, $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot H_2O$.

5. References

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