

Effects of Carbonation and Hydrothermal Treatments on some Properties of Calcium Monoaluminate Mortars

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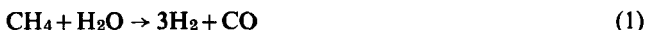
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To produce suitable catalyst supports for the steam reforming of hydrocarbons, the effect of curing calcium monoaluminate in both steam and carbon dioxide has been investigated. The green strengths of steam cured samples were no higher than those of air-cured samples, but the strengths under steam reforming conditions (850°C in steam) were very much higher. The green strengths of carbon dioxide cured samples were higher than those of air cured samples and under steam reforming conditions the strengths were similar to those of the steam cured samples. An explanation of the behaviour is proposed in terms of the hydration mechanisms and the reactivities of the decomposition products.

1. Introduction

The reaction of hydrocarbons with steam in the presence of catalysts at high temperatures has been recognised as a possible source of hydrogen since the early years of the 20th century. The steam reforming of hydrocarbons is now an important and well-established process and can be typified by the methane-steam reaction¹



followed by



Glaud *et al.*² have calculated that for reaction (1) to go virtually to completion the operating temperature should exceed 900°C.

The catalyst most commonly used is nickel mounted on a refractory support. The most satisfactory supports have been found to be α - and/or γ -alumina, with a refractory aluminous cement as binder. The catalyst support is usually shaped by pelleting or extrusion.

A major difficulty that occurs with catalyst supports or refractory castables, in which a refractory cement based on calcium aluminates has been used as a binder, is the low strength at temperatures between that at which the hydraulic bond is destroyed and that at which the cement begins to form a ceramic bond. This loss in strength is most marked between 600 and 1000°C.³

To produce a gas with a low concentration of methane by the catalytic steam reforming process requires temperatures in the reformer to be in the region of 900°C and this temperature is unfavourable for the strength of an aluminous cement bonded support. It would seem to be of primary importance for the development of strength at high temperatures that dehydration or decomposition products be formed in quantity and of high reactivity.⁴

Work by Tseung and Carruthers⁵ has indicated that high temperature strength is very dependent on the curing conditions. They attributed this to the differing hydration mechanisms and reactivities of the dehydration products. Some work involving curing in carbon dioxide⁶ also indicated that improved strength could be obtained at intermediate temperatures. Again this improvement could be attributed to the formation of reactive decomposition products.

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Since it would be economically desirable to be able to produce a catalyst support which did not lose strength, it was thought useful to investigate the effect of varying the curing conditions of pure calcium aluminate compounds with a view to obtaining a material having a high strength at intermediate temperatures. In particular the effect of carbonation was to be examined as a means of producing active products and thus, perhaps, of lowering the temperature at which the ceramic bond begins to occur.

To avoid complicating the results, this work was confined to pure synthetic calcium monoaluminate. To simplify the discussion the commonly used shorthand notation for the phases encountered is used: $\text{CaO} = \text{C}$; $\text{Al}_2\text{O}_3 = \text{A}$; $\text{H}_2\text{O} = \text{H}$.

2. Experimental

2.1. Materials used

2.1.1. Synthesis of calcium monoaluminate

Pure calcium monoaluminate was synthesised from Analar grade calcium carbonate and Analar grade aluminium oxide using the method of Tseung and Carruthers. The materials were first dried by heating to 150°C for 6 h and then a mixture having a 1:1 molar ratio of calcium carbonate and aluminium oxide was fired at 1500°C for 7 h in an electric furnace. The resulting material, which passed a 300 mesh BS sieve, was checked for identity and mineralogical purity by optical examination, X-ray analysis, and chemical means. The X-ray diffraction data showed that the only detectable impurity was C_{12}A_7 , and that this was present only as a very minor phase. Unstable orthorhombic C_5A_3 was not detected.

To minimise possible contact with atmospheric carbon dioxide and water vapour the ground aluminate was stored under vacuum in a vacuum desiccator. No obvious deterioration in the properties of the aluminate was observed over the period of this investigation.

2.1.2. Fused Alumina Aggregate

Fused alumina was chosen as the aggregate for the concrete mixes because of its relatively high purity and its refractoriness. The alumina was crushed to less than 22 mesh BS sieve. The X-ray diffraction data showed that the major impurity was $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$.

2.2. Preparation of the mortar specimens

Calcium monoaluminate and the alumina aggregate were mixed in a weight ratio of 1:3. Water was added in a ratio of water to cement of 0.50 (w/w) and 12 identical rectangular prisms cast. The size of each prism was $15.5 \times 15.5 \times 25.4$ mm. To minimise the possibility of contamination, deionised water was used which had been previously boiled to expel dissolved carbon dioxide.

The specimens were stored at 20°C and a relative humidity of 93% for 5 h after which period they were randomly allocated to the different forms of treatment (Figure 1). By retaining four of the 12 specimens for air curing it was ensured that a continual check could be made on the strengths of the air cured samples and thus the constancy of the experimental procedure.

In the work all the specimens were cured for the same length of time and there was no attempt to determine the optimum water to cement ratio. The value of 0.50 was chosen on the basis of the work of Tseung and Carruthers.

The procedures used were standardised to ensure that the results would be comparable and could possibly be altered by choosing a different set of standard conditions.

2.3. Hydrothermal treatment

Since the carbonation treatment was to be carried out in the presence of saturated steam it was first necessary to try to determine the physical and chemical effects due to the hydrothermal treatment alone.

A Baskerville high pressure hydrogenation autoclave was used which was modified slightly by removal of the stirrer to allow sufficient space for the specimens. The capacity of the pressure vessel was 1 litre. Distilled water (50 ml) was put into the vessel to ensure that the steam was saturated. The specimens for treatment were placed in a stainless steel wire basket of a size sufficient to hold

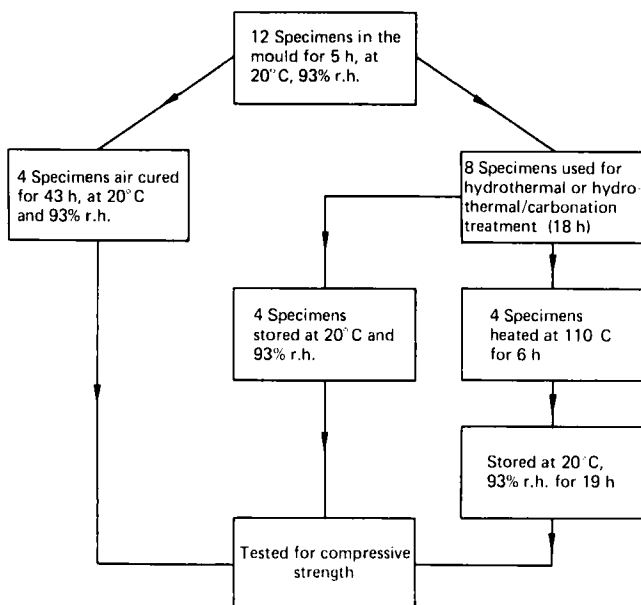


Figure 1. Allocation of specimens for treatment.

eight of the rectangular prism specimens. The basket and its contents were protected by a nickel cover to prevent condensation from falling on to the specimens. The rate of heating was such that the desired temperature was attained in 3 h and then maintained constant for 15 h. The heaters were then switched off and the vessel and its contents left to cool to 60°C before opening. Cooling was not accelerated by any method in order that the samples would not be weakened by too drastic a change in temperature.

The temperatures of the treatment range from 107 to 170°C. In all the experiments saturated steam was used; on no occasion was superheated steam used.

2.4. Hydrothermal-Carbonation treatment

For the steam/carbonation treatment of the samples the same apparatus as described for the hydrothermal treatment was used, the only difference being that 20 g of solid carbon dioxide in a small beaker was placed in the vessel as well as 50 ml of distilled water. The autoclave was assembled and the relief valve controlled so that the pressure within the vessel was 300 kPa. When conditions were steady at 300 kPa the valve was closed and the vessel then left for a further 30 min to ensure that all solid carbon dioxide had sublimed. The vessel was then brought up to the required temperature using the same heating programme as for the hydrothermal treatment. The pressure of carbon dioxide within the vessel at a particular temperature was assumed to be the gauge pressure less the steam pressure given by steam tables. Specimens were again allocated as indicated in Figure 1. The temperature of the treatment ranged from 77 to 167°C. No specimen was removed from the autoclave until the temperature had dropped to 50°C. The pressure on the gauge was noted immediately before opening, and this pressure was considered to be the pressure of the residual carbon dioxide. This residual carbon dioxide pressure was relatively high for two of the experiments, those done at 77 and 97°C, but the residual pressures for higher treatment temperatures were either zero or quite small.

2.5. Heat treatment of samples

Since the object of the work was to try to improve steam-reforming catalyst supports it was thought desirable to subject the specimens to elevated temperatures in an atmosphere of steam. Work carried

out by Imperial Chemical Industries Ltd⁷ indicates that this is a much more stringent test than simply firing in air.

Consequently the samples were heated in a tube furnace through which steam was passed. The outlet temperature of the furnace was controlled at 850°C and the rate of temperature rise to this maximum was 350°C h⁻¹. The inlet temperature tended to be about 30 to 50°C below the outlet temperature.

The specimens were kept at 850°C for 4 h; the furnace was then switched off and allowed to cool to 130°C with steam passing, and finally cooled to room temperature with no passage of steam.

2.6. Measurement of compressive strength

It was considered that crushing strength would be the simplest property of the set cements that could be used to give a measure of their relative strengths. The samples were crushed using a Hounsfield Tensometer, the spring beam used being capable of taking a maximum load to 2 t. The samples were crushed by manual operation of the machine. The load was applied, so far as was practicable, at a rate of 2000 kPamin⁻¹. Care was taken to ensure that the rate of loading was the same for all samples. Four prisms were tested from each batch and the mean of the four determinations was taken to be the compressive strength.

2.7. Analysis of samples

X-Ray diffraction was the principal technique used for the identification and relative quantitative estimation of the phases present. The powder diffraction patterns of the various specimens were investigated using a counter diffractometer and supplemented on occasions by the use of a Debye-Scherrer powder camera.

Differential thermal analysis and thermogravimetric investigations were also carried out to check and extend the X-ray results.

To measure the amount of carbon dioxide present in some of the samples, the carbonate phase was decomposed by acid treatment and carbon dioxide determined by quantitative absorption in a mixture of benzylamine, ethanol and dioxan (Patchornik and Shalitin).⁸

3. Results

3.1. Phase analysis

From the X-ray, DTA and TGA results it was possible to make the following deductions about the phases present in the various samples.

The major phase present in the air-cured samples was CAH₁₀ although much remained unhydrated. After drying the samples at 110°C for 6 h the CAH₁₀ was fully converted into C₃AH₆ and gibbsite. Heating at 850°C in steam gave C₁₂A₇ and some CA₂. The latter was presumably formed by combination of CA and alumina resulting from the dehydration of gibbsite.

C₃AH₆ was the major phase in the steam cured samples. Those samples cured above 132°C also contained boehmite whereas those cured at lower temperatures contained gibbsite. No unhydrated CA was detected in any of the steam cured samples. Heating at 110°C for 6 h produced no detectable changes. After heating at 850°C in steam, C₁₂A₇ was formed together with minor amounts of CA. Since all the original CA had been hydrated, some CA must have been regenerated during the 850°C treatment.

All the carbon dioxide cured samples showed CaCO₃ as the major phase (in the form either of calcite or aragonite). Gibbsite or boehmite was also present depending on the curing temperature. No gibbsite was observed in samples cured above 160°C. Some unhydrated CA was also present but the amount varied from sample to sample and did not appear to depend on the temperature of treatment. Small amounts of C₃AH₆ were also present. Heating at 110°C for 6 h produced no detectable changes. After heating to 850°C in steam, C₁₂A₇ and CA were formed together with minor amounts of CA₂. The formation of CA₂ suggests that the gibbsite and boehmite formed on

Table 1. Compressive strengths of air-cured samples ($\text{kPa} \times 10^3$)

Green strength		Heated to 850°C in steam after curing	
	32.3		10.0
	33.8		10.4
	31.0		11.0
	29.1		11.7
	31.1		11.0
	32.4		11.1
Average	31.6 ± 1.5		10.9 ± 0.5

Table 2. Compressive strengths of steam-cured samples ($\text{kPa} \times 10^3$)

Temp. of curing (°C)	Green strength		Strength after heating to 110°C		Strength after heating to 850°C in steam	
	Mean	σ	Mean	σ	Mean	σ
111	19.1	0.7	35.0	1.80	34.6	3.2
127	29.3	1.0	44.5	1.41	32.9	1.1
132	27.9	0.8	42.9	2.10	27.6	0.9
135	23.9	0.7	40.8	1.10	29.7	1.6
144	26.9	0.6	42.0	0.60	28.0	1.0
152	23.9	0.8	40.7	0.60	30.3	1.2
158	21.3	3.2	39.2	0.63	28.2	0.8
167	25.6	0.8	41.0	0.8	29.6	0.6
170	30.6	0.5	41.0	0.8	37.3	1.3
Average over all temperatures	25.4	3.7	40.8	2.6	30.9	3.3

Table 3. Compressive strengths of carbon dioxide-cured samples ($\text{kPa} \times 10^3$)

Temp. of curing (°C)	Green strength		Strength after heating to 110°C		Strength after heating to 850°C in steam	
	Mean	σ	Mean	σ	Mean	σ
77	34.4	0.8	42.8	2.0	19.6	0.8
97	33.4	1.9	58.7	1.9	34.8	1.7
112	27.6	0.8	51.7	2.6	28.6	1.8
120	27.4	0.8	42.9	1.5	30.6	1.6
130	27.9	0.5	45.2	2.4	30.4	1.9
137	28.4	0.9	43.5	1.1	28.6	1.1
144	28.7	0.9	41.8	0.5	27.9	0.9
156	36.6	0.6	53.5	1.0	35.8	1.4
160	34.2	0.8	47.4	0.9	34.3	1.3
167	34.6	0.4	49.7	0.6	34.5	1.9
Average over all temperatures	31.1	3.6	47.7	5.6	30.5	4.8

curing are highly reactive and react very readily with the decomposition products of calcium carbonate.

The results of carbon dioxide determinations on the carbon dioxide-cured samples indicated that at curing temperatures above 110°C over 60% of the CA had been converted into CaCO_3 . At lower temperatures the conversion was only of the order of 38%.

3.2. Compressive strength

The average compressive strengths of the various groups of specimens are given in Tables 1, 2 and 3.

By neglecting the effects of variations due to different curing temperatures, the results can be grouped together to obtain average compressive strengths for each form of treatment.

4. Discussion

The results confirm that air cured samples suffer a dramatic loss in strength on heating in steam at 850°C. Serious consequences of this loss in strength can be avoided by curing either with steam or with carbon dioxide which gave samples having compressive strengths after the 850°C treatment as good as air cured samples not subjected to any heat treatment.

The observed increase in strength of both the steam and carbon dioxide cured samples after heating to 110°C was not unexpected. This is attributed by Schneider⁹ to an increase in crystallinity of the hydrates.

The carbon dioxide cured samples, with or without the drying treatment at 110°C, had greater green strengths than the corresponding samples which had been steam cured. The calcium carbonate present in the sample had thus conferred increased strength even though practically all of the carbonated samples contained unhydrated CA. Some carbon dioxide initiated retardation process may have gone on, but there was no direct evidence of this.

Tseung and Carruthers⁵ have attributed the high fired strengths of the steam cured samples to the fact that steam curing results in a high degree of hydration, and the great quantity of dehydration products produced on firing assists in the formation of a ceramic bond. This is confirmed in the present work. The air cured samples contained significant quantities of unhydrated CA, whereas the steam cured samples contained none. After the 850°C treatment the steam cured samples contained significant amounts of CA obviously formed by the interreaction of the dehydration product.

Although all the original CA was not hydrated in the carbon dioxide cured samples the fired strength was still as good as for the steam cured samples. This is presumably due to the great reactivity of any CaO formed on decomposition of CaCO_3 . This rapidly reacted with any alumina to give a ceramic bond. In view of this it would be interesting to see the strength of samples cured in carbon dioxide if full utilisation of the CA were attained.

For optimum fired strength it would appear best to steam cure either at 110–120°C or alternatively above 170°C.

For carbon dioxide curing these ranges are displaced to slightly lower temperatures, namely 90–100°C or above 150°C.

The superior strength of the carbon dioxide-cured samples after heating at 110°C suggests that such treatments could be applied to advantage where high alumina cements are used as binders in steam reforming catalyst supports. The resultant stronger catalyst supports could be handled and stored with a reduced risk of breakage. The results for the compressive strengths after the 850°C treatment do not indicate any great difference between the steam curing and carbon dioxide curing but the strengths are very much higher than those of air cured specimens subjected to the 850°C treatment. This relatively high strength at high temperature implies obvious advantages in the steam reforming process or in most applications where alumina is used at temperatures in the region 800–900°C.

5. Conclusions

For an alumina support to be suitable for a steam reforming catalyst it must have reasonable strength at 850°C in steam.

It has been shown that CA cured at room temperature at a water:cement ratio of 0.5 is only partially hydrated in 48 h to CAH_{10} . Whilst possessing adequate green strength the material has low strength after 850°C treatment.

Curing in steam produces complete hydration to C_3AH_6 but the green strength is not improved by the greater utilisation of CA, unless the sample is heated to 110°C to increase the crystallinity of the hydrates. However the greater quantity of dehydration products, consequent on the complete hydration, assists in the formation of a ceramic bond and the fired strength is high.

Curing in carbon dioxide uses part of the CA, giving largely CaCO_3 and some C_3AH_6 . The cementitious properties are favourable and the green strength is good and can be still further improved by heating to 110°C . In spite of the incomplete utilisation of the CA, the decomposition products are extremely reactive. This favours the formation of a ceramic bond and the fired strength is high.

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