

Hydration of granulated slag-alite in the presence of quartz

M. G. ABD EL-WAHED*, H. EL-DIDAMONY*, A. M. AMIN‡, A. S. TAHA§

*Faculty of Science, ‡Building Research Institute, §National Research Centre, Zagazig University, Zagazig, Egypt

The aim of the present work was to study the effect of quartz on the hydration characteristics of hydrothermally hardened granulated slag-alite pastes. The pastes, of water: solid ratio 0.20, were moulded at a pressure of 50 kg cm^{-2} and autoclaved at 10 atm for 0.5, 2, 6, 12 and 24 h. Compressive strengths of the hardened product were determined, and the kinetics of reaction were studied by the quantitative determination of free lime and combined water contents. The phases formed after autoclaving were determined using XRD techniques. The reaction mechanism of the system under investigation was discussed and correlated to the strength of the hardened product. It can be concluded that the addition of quartz to slag-alite mixture increases the strength of the final product. The strength obtained for samples with high alite content are higher than that of low-alite content. Finally, the addition of quartz assists the formation of tobermorite in the hardened specimens.

1. Introduction

Alite is a rich source of calcium and silica, and thus is an important substance for the manufacture of autoclaved building materials. Generally, the main hydration products of alite are calcium silicate hydrates and calcium hydroxide [1]. The liberated Ca(OH)_2 can be exploited to produce additional amounts of binding materials (calcium silicate hydrates) by its reaction with quartz and/or activation of slag [2-4]. Blast-furnace slag is now widely used in the manufacture of autoclaved products because of the economic validity of this material which lies in the cheapest of raw materials and saving in fuel energy. In studying the hydration of alite in the presence of quartz under different autoclaving temperatures, it was found that the lime produced was reacted with quartz and the main hydration product was tobermorite like hydrated calcium silicate, and the highest strengths were obtained at 160 to 300°C with a CaO/SiO_2 ratio of about one [5]. El-Didamony *et al.* [6] studied the hydration mechanism of hydrothermally hardened slag-alite pastes in relation to mix composition and autoclaving time. The synthesized alite was used as an activator for the granulated slag. It was found that the addition of alite improves the hydration as well as the strength of the granulated slag. In addition, the amount of free lime increases with increasing alite content in the pastes. Other investigators [7] prepared calcium silicate-moulded products with higher strength by mixing granulated blast furnace slag with siliceous materials under hydrothermal treatment.

In this paper, the hydration characteristics of the mixtures of alite-slag-quartz and their relation to compressive strength of the hardened samples were studied under hydrothermal treatment. The compressive strength as well as the hydration kinetics, such as

chemically combined water and free lime contents, were determined. The hydration products were identified using X-ray diffraction.

2. Experimental details

2.1. Materials

The granulated slag used in this work has the following oxide composition: $\text{SiO}_2 = 34.92$; $\text{Al}_2\text{O}_3 = 16.68$; $\text{CaO} = 46.11$; $\text{MgO} = 2.67$ and loss on ignition (LOI) = 1.32% by weight. Its specific surface is $3540 \text{ cm}^2 \text{ g}^{-1}$. The materials used for the preparation of alite were analytical reagent grade (Merk, Darmstadt, West Germany), calcium carbonate, silica gel, aluminium hydroxide and magnesium carbonate. These materials were mechanically mixed according to the alite composition ($\text{C}_{182}\text{S}_{62}\text{A}_2\text{M}_6\text{O}_{315}$) in a porcelain ball mill for 2 h. The preparation of the alite was discussed in an earlier work [6]. The quartz used in this investigation was BDH analytical reagent grade with a specific surface of $3200 \text{ cm}^2 \text{ g}^{-1}$.

2.2. Preparation of the autoclaved samples

Two types of dry mixture were prepared from alite

TABLE I Mix composition of the mixes investigated on a weight basis

Mix no.	Alite	Slag	Quartz (wt %)
MI ₀	1 part	4 parts	00
MI ₂₀	1 part	4 parts	20
MI ₅₀	1 part	4 parts	50
MI ₁₀₀	1 part	4 parts	100
MII ₀	1.86 part	1 part	00
MII ₂₀	1.86 part	1 part	20
MII ₅₀	1.86 part	1 part	50
MII ₁₀₀	1.86 part	1 part	100
MII ₂₀₀	1.86 part	1 part	200

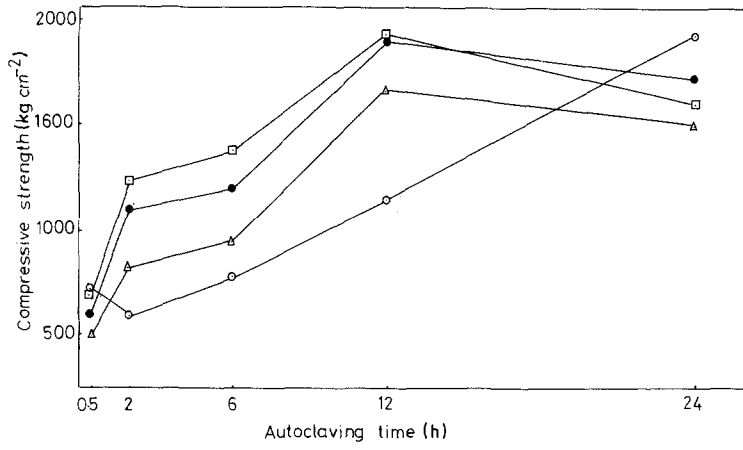


Figure 1 Compressive strength of different mixes made from mix MI and various proportions of quartz as a function of autoclaving time. (○) MI₀, (Δ) MI₂₀, (□) MI₅₀, (●) MI₁₀₀.

Figure 2 Chemically combined water contents of mixes made from mix MI and various proportions of quartz in relation to autoclaving time. (○) MI₀, (Δ) MI₂₀, (□) MI₅₀, (●) MI₁₀₀.

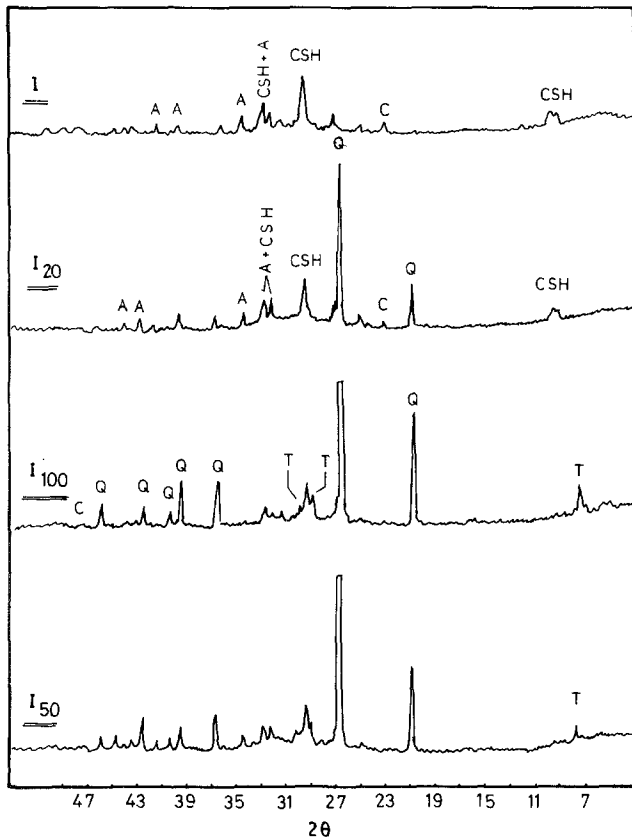
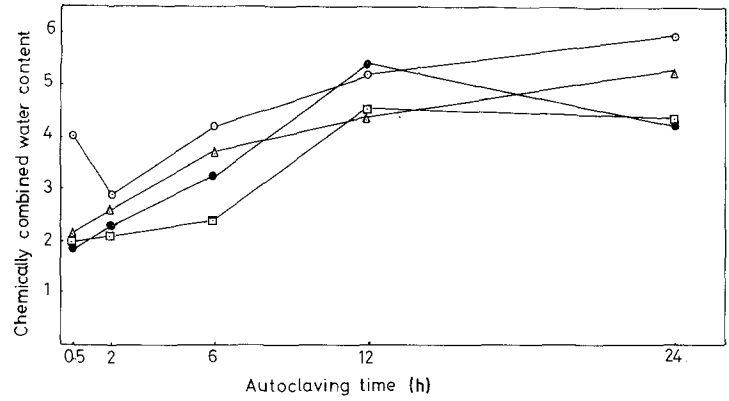


Figure 3 XRD. patterns of hardened specimens made from mix MI and various proportions of quartz autoclaved for 12 h. A, alite; CSH, calcium silicate hydrates; C, calcite; T, tobermorite.

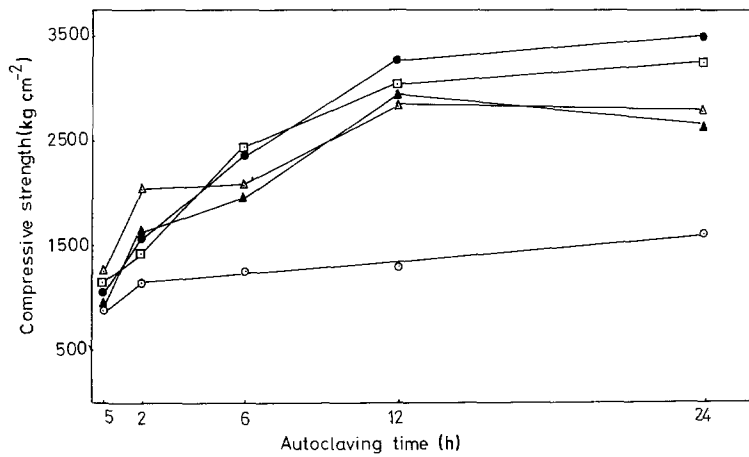


Figure 4 Compressive strength of mixes MII and various proportions of quartz as a function of autoclaving time. (○) MI₀, (△) MI₂₀, (□) MI₅₀, (●) MI₁₀₀, (▲) MI₂₀₀.

and slag with various proportions of quartz, as shown in Table I.

Each dry mixture was mixed with water for 3 mins at a water/solid ratio of 0.20 by weight. Cylindrical specimens of 3.14 cm² cross-section and 1 cm height were moulded at a pressure of 50 kg cm⁻². After moulding, the specimens were cured in a humidity cabinet (100% relative humidity) at room temperature. The specimens were autoclaved at 10 atm for 0.5, 2, 6, 12 and 24 h. At the end of each autoclaving period, the specimens were dried in a CO₂-free atmosphere at 105°C for 24 h.

Compressive strength tests were carried out on the dried samples, then free CaO and chemically combined water contents were determined using the ground dried samples [6].

3. Results and discussion

3.1. Mix MI₀: slag–low alite–quartz–water system

The values of compressive strength of the different hardened mixtures are graphically represented against autoclaving time in Fig. 1. The results show that the strength increases as autoclaving time increases. After 0.5 to 2 h autoclaving, the strength gained is mainly attributed to the hydration of alite. Although the alite content decreases from mix MI₂₀ to MI₁₀₀, the strength of the hardened product does not decrease. This is due to the acceleration of hydration of alite as a result of the presence of quartz [8]. After 2 h autoclaving, the slag is activated with the hydration product of alite whereas some of the liberated Ca(OH)₂ reacted with quartz. As a result, a new amount of CSH will be produced which is responsible for the increase in the strength of the hardened product over 2 to 6 h. The development of strength after 6 h autoclaving is mainly associated with the formation and later stabilization of CSH. The decrease in strength between 12 and 24 h autoclaving may be due to the transformation of part of CSH into tobermorite, hence the ratio between the semicrystalline phases (CSH) and crystalline phase (tobermorite) at which maximum strength can occur will be changed, and the strength decreases [9].

The kinetics of reaction of the system under investigation was studied by determining the free lime and chemically combined water contents. The results of free lime of the hydrated samples are given in Table II. It shows that the liberated lime is present as traces in the samples up to 2 h autoclaving. Then it disappears completely with increasing autoclaving time, which indicates its reaction with quartz and/or slag. Fig. 2 shows the variation of the content of chemically

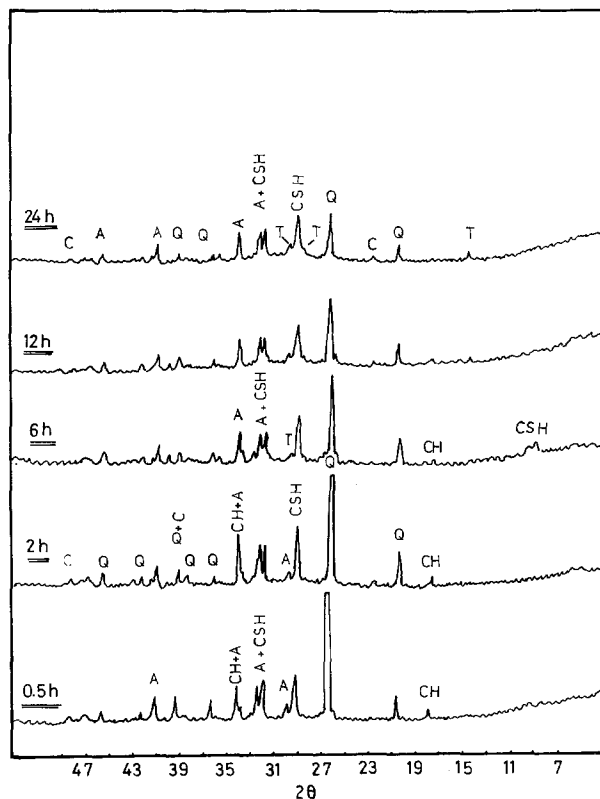


Figure 5 XRD patterns of autoclaved mix MI₂₀ in relation to autoclaving time. For notation, see Fig. 3.

TABLE II Free lime content of the different hardened mixtures in relation to autoclaving time

Mix	Autoclaving time (h)				
	0.5	2	6	2	24
MI ₀	0.33	0.38	0.09	0.05	0.03
MI ₂₀	0.12	–	–	–	–
MI ₅₀	0.06	0.06	–	–	–
MI ₁₀₀	–	–	–	–	–

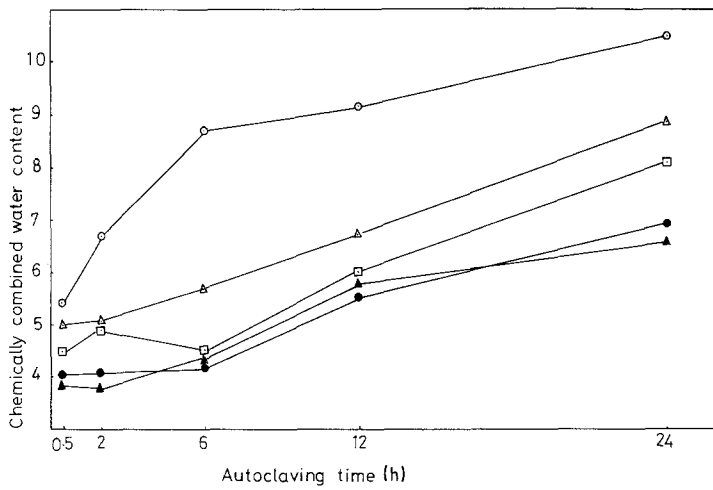


Figure 6 Chemically combined water contents of mixes made from mix MII and various contents of quartz as a function of autoclaving time. (○) MII₀, (△) MII₂₀, (□) MII₅₀, (●) MII₁₀₀, (▲) MII₂₀₀.

combined water of the different samples as a function of autoclaving periods. Generally, it increases for increasing autoclaving time. This is associated with hydration of alite, slag and sand–lime reaction as the autoclaving time proceeded. The decrease occurring for the samples autoclaved at 24 h (Fig. 2) may be attributed to the adsorption of part of the water on the surface of CSH as a result of its high surface area in the later stage of hydration. This adsorption makes determination of water inadequate [10]. Thus it can be concluded that for a certain mixture, the strength of the hardened product is related linearly to the chemically combined water content.

The diffractograms of the different mixtures autoclaved for 12 h are given in Fig. 3. They indicate the presence of quartz, alite, CSH, tobermorite and calcite. Tobermorite can hardly be detected for mix MI₂₀,

increases for mix MI₅₀ and can be detected easily for mix MI₁₀₀. The amount of calcite detected may be due to partial carbonation of Ca(OH)₂ during autoclaving. The variation in the intensity of the peaks of tobermorite can be correlated with the strength of the different hardened mixtures. Maximum strength cannot occur at maximum content of CSH (mix MI₂₀, Fig. 2) or at maximum content of tobermorite (mix MI₁₀₀), but can occur in the presence of both phases (mix MI₅₀).

Alite can be detected throughout all the samples and at a relatively high autoclaving period. This may be associated with the formation of calcium silicate hydrates at the beginning of hydration of alite. It tends to form an almost impermeable thin layer which coats the alite grains. This hinders the diffusion of water through the coat into the unhydrated part [11, 12]. Again the hardened product autoclaved at 12 h shows unattacked cores of alite surrounded by a layer of hydrated calcium silicate hydrates.

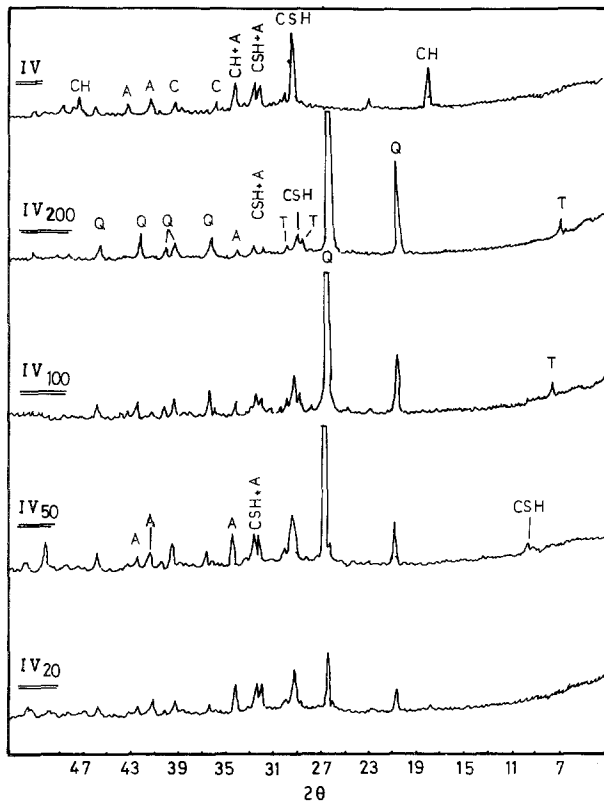


Figure 7 XRD patterns of hardened samples made from mix MII and various proportions of quartz autoclaved for 12 h. For notation, see Fig. 3.

3.2. Mix MII₀: slag-rich alite–quartz–water system

The compressive strengths of the different autoclaved mixtures are drawn as a function of autoclaving period in Fig. 4. The results obtained are very similar to those in Section 3.1. Consequently, the proposed mechanism and its relation to strength can be treated by the same way. The reduction in the strength for sample MII₂₀₀ autoclaved for 24 h may be associated with the formation of larger amounts of tobermorite at the expense of CSH (semi-crystalline phases). This transformation depends upon the CaO/SiO₂ ratio of the mixture [13]. The result obtained indicates that the alite–quartz ratio for mix MII₂₀₀ may be suitable for forming a relatively higher content of tobermorite.

TABLE III Free lime content of the different hardened samples as a function of the autoclaving period

Mix	Autoclaving time (h)				
	0.5	2	6	24	24
MII ₀	1.29	1.59	1.31	1.54	1.49
MII ₂₀	2.21	2.50	2.33	1.22	–
MII ₅₀	2.21	2.33	0.87	–	–
MII ₁₀₀	1.16	0.87	–	–	–
MII ₂₀₀	0.87	–	–	–	–

The proposed mechanism, with respect to hydration of alite, releasing Ca(OH)_2 , its activation to slag and its reaction with quartz, can be clarified by examining the X-ray diffractograms for sample MII₂₀, as an example, autoclaved at various autoclaving periods, Fig. 5. Alite, Ca(OH)_2 , quartz, CSH, tobermorite and calcite can be detected from Fig. 5. Alite appears clearly in the early stages of reaction, i.e. 0.5 h, and its intensity decreases with autoclaving time. The peak area of Ca(OH)_2 increases from 0.5 to 2 h and can hardly be detected from 6 to 12 h whereas it disappeared completely after 24 h. The peak area of quartz may not be changed up to 2 h and decreases gradually up to 24 h autoclaving. This indicates that the strength obtained in the early stages of reaction (0.5 to 2 h) is mainly attributed to the hydration of alite. After that (2 to 6 h) Ca(OH)_2 will react with quartz to produce an additional amount of CSH, at the same time some of the quartz reacts with CSH to complete the hydration reaction of the alite product to form tobermorite. This indicates that CSH and tobermorite increase with autoclaving period.

The free lime content of the different hardened samples autoclaved for different periods are listed in Table III. The free lime contents decrease as the autoclaving time increases and are consumed completely after 24, 12, 6 and 2 h for mixes MII₂₀, MII₅₀, MII₁₀₀ and MII₂₀₀, respectively. This may be attributed to the decrease of the alite content in the mixture and/or the increase in the content of available silica which reacts with Ca(OH)_2 . The results obtained are being monitored with the above-mentioned mechanism.

Chemically combined water contents of the different autoclaved samples are graphically plotted as a function of autoclaving time in Fig. 6. The results are similar to those obtained in Section 3.1.

To illustrate the variation in the hydration product due to the presence of quartz in the mixture of alite

and slag, XRD analysis was carried out on the samples of Mix MII autoclaved at 12 h, Fig. 7. It indicates that no free lime can be detected and part of it may be carbonated to form calcite. Alite can be detected for all the samples and its peak area decreases from mix MII₂₀ to MII₂₀₀. CSH behaves in a similar manner to alite, whereas tobermorite can hardly be detected for mix MII₂₀ and increases gradually up to MII₂₀₀.

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Received 27 November 1987

and accepted 29 April 1988