ELSEVIER

0958-9465(95)00017-8

Cement & Concrete Composites 17 (1995) 289–300

0958-9465/95/$9.50

Bricks Made of Coal Fly-Ash and Slag, Cured in the Open Air

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(Received 5 September 1994; accepted 11 May 1995)

Abstract

Volume mass, compressive strength, water uptake and water absorption of pressed test samples made of a mixture of coal fly-ash, slag and sodium silicate solution (water–glass) were determined. It was found that such mixtures can solidify in the open air and form water-stable materials. The composition and structure of new formations for the binder and cured material itself were established using X-ray diffraction and a scanning electron microscope. The material has a high water uptake, which may be reduced using a number of different methods, the best of which is short-term impregnation with a hydrophobic material of the siloxane group. The water uptake and water absorption of compressed samples impregnated with such materials are similar to those of comparable building materials, such as lime–sand bricks, clay bricks or concrete blocks.

Keywords: Bricks, fly ash, slag, water–glass, airing, density, compressive strength, water absorption, X-ray diffraction, microstructure, durability, surface impregnation, building materials.

INTRODUCTION

Every year, hundreds of millions of tons of coal are burned in power stations all over the world. Wastes in the form of fly-ash and slag are generated in colossal quantities. These wastes can be used effectively in the building industry and in particular in the manufacture of autoclaved blocks and bricks.[1–3]

Different methods for preparing lime-ash, lime-slag bindings, forming mixtures, and mouldings have been tried, and various temperature conditions for autoclaving such materials have been tested. The technology required is complicated and demands a large capital investment. Thus there is a need for a new, simple but highly effective technology for producing building materials on the basis of fly-ash and slag in which the development of strength should occur in natural conditions at temperatures from 15–30°C, that is in the open air.

Fly-ashes are highly dispersive powders. They consist mainly of round particles of silica–aluminate and ferriferous glass (about 60–80%), and amorphous particles of clay, mullite, β-quartz particles and unburned metamorphic fuel.[4] Their phase and chemical composition makes them active when mixed with materials such as NaOH, Na_2CO_3 and Na_2SiO_3, which contain alkali.[5,6]

Slags consist of particles which are up to 10–15 mm in size. The chemical composition of slags and fly-ashes are similar. Depending on conditions of cooling, the glassy or crystalline phase can predominate in slags. As a rule, slag in its natural state is inert and may act as an aggregate in building mixtures.

Water–glass is a solution of sodium or potassium silicate in water. It may solidify only in contact with air, at temperatures greater than 5–10°C. However, the solids thus formed are not waterproof.

This paper explores the possibility that the combination of water–glass and materials containing silica in the glass phase may under certain conditions form water-stable materials. The process may be described as follows: in the first step of the curing process, silicon–oxygen anions found in fly-ash in the glass phase go into solution and form polymers which begin to coagulate in the liquid. The alkali of the water–glass reacts with silica present in fly-ash in the glass phase, and strengthens this process of polymerization and coagulation, ending with the generation of a water-stable silica binder, mainly in the form of a gel. In the second stage, dehydration of the silica gel takes place, accompanied by consolidation of the structure and an increase in the strength of the bonds. At first, these processes will proceed successively, then simultaneously, resulting in the creation of a hard, solid material.

The objective of the research was the development of a technology for the production of blocks or bricks made of coal fly-ash, slag and water–glass, cured in the open air. This paper presents the results of experiments with pressed laboratory samples. The effect of increasing the compaction pressure and the content of water–glass on the compressive strength and the water uptake were studied. Ways of reducing the water uptake and water absorption were also examined.

EXPERIMENTAL

Samples of fly-ash and slag used in the experiments were obtained from the power station located in Hadera (Israel).

Properties of raw materials

Results of chemical tests on fly-ash and slag as defined in ASTM C311-77 are shown in Table 1. Results of sieve analysis of slag as defined in ASTM C 136 are shown in Table 2.

The water–glass used in these experiments was a solution of sodium silicate, having a density of 1·44 g/cm^3 and silica module of 2·3. Hydrophobic materials used in the experiments were samples of siloxane–polymethylhydrogensiloxane, made by Merck company (Germany) and Siloxane CS (made in Israel).

Experimental procedure

Production of test samples

Several series of test samples were made, differing in their composition, method of moulding, and curing process. Mixing of raw materials (coal ash, slag and water–glass) was done by hand. In order to eliminate the influence of soluble salts usually found in the ashes, the fly-ash was washed five times with distilled water prior to preparation of the samples.

Composition of test samples

Fly-ash (FA) — mixtures consisting of fly-ash and water–glass in varying proportions.

Fly-ash and slag (FAS) — mixtures consisting of equal proportions of fly-ash and slag, with varying amounts of water–glass added. The relative amounts of fly-ash and slag were

Table 1. Chemical composition of fly-ash and slag from the Hadera power station (percentage by weight)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O+K_2O	TiO_2	P_2O_5	MgO	SO_3	*L.O.J*
Fly-ash	45·8	33·5	3·5	5·4	0·8	1·5	1·6	1·6	0·4	5·9
Slag	48·1	34·4	2·8	6·2	0·5	1·2	0·9	1·7	0·2	4·1

The specific surface area (ASTM C204) of fly-ash is 3450 cm^2/g, the bulk specific gravity is 810 kg/m^3 and the specific gravity is 2·3 g/cm^3.

Table 2. Sieve analysis of slag

Sieve size (square opening)	*Percent retained*	*Percent passed*
No. 4 (4·75 mm)	4·90	95·10
No. 10 (2·00 mm)	17·96	77·14
No. 16 (1·18 mm)	18·57	58·57
No. 30 (0·60 mm)	21·10	37·47
No. 100 (0·15 mm)	25·01	12·46
No. 200 (0·075 mm)	8·64	3·82

The bulk specific gravity of slag is 725 kg/m^3 and the specific gravity is 1·95 g/cm^3. Slag was screened on sieve No. 4 before being used in the experiments.

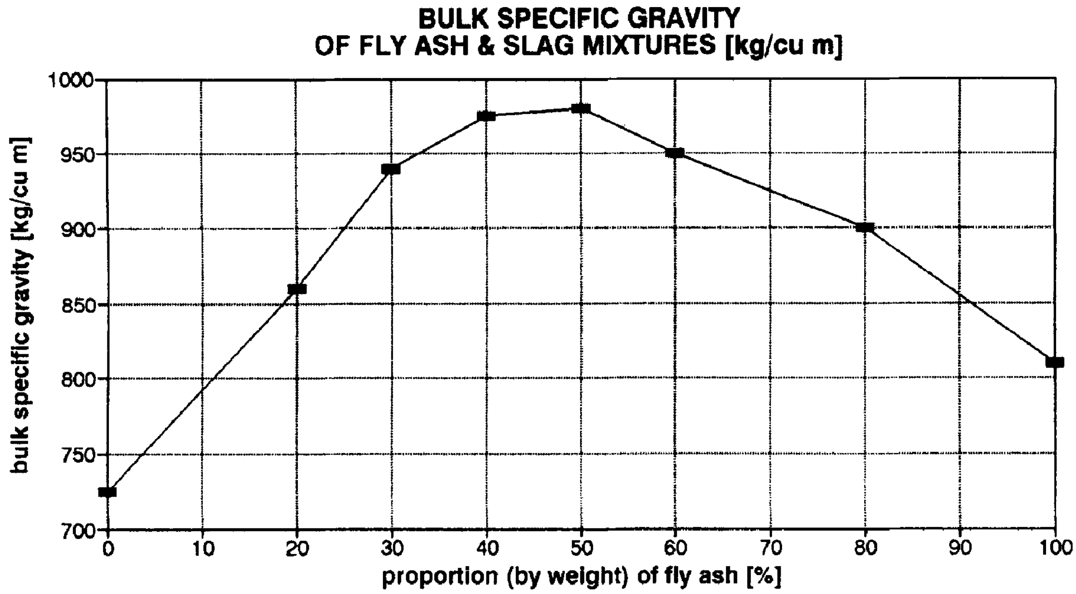


Fig. 1. Bulk specific gravity of fly-ash and slag mixtures.

fixed to achieve the maximum bulk specific gravity which was determined experimentally (Fig. 1).

The amount of water–glass used in the preparation of the test samples mixture was limited by the workability of the mixture. Fly-ash samples contained as much as 50% by weight water–glass, whereas fly-ash and slag samples became too liquid when the proportion of water–glass exceeded 30%. At this point, it became impossible to form test blocks in the hydraulic press since part of the water–glass was lost during compaction. The lower limits of the glass–water content at 10 and 20% for FAS and FA are set by the necessity of obtaining homogeneous mixtures from the constituent materials.

Moulding of test samples

Cast samples — discs 5 mm in height and 30 mm in diameter, from fly-ash and water–glass, in the ratio 2:3 (by weight).

Pressed samples — cylinders 5·71 cm in diameter and about 4 cm in height. These test samples were moulded in a Carver laboratory hand press. The compaction pressure was 40 kg/cm^2, except in experiments designed to test the influence of the compaction pressure on the water uptake and compressive strength of the material.

Curing of test samples. Most of the samples were cured in the open air for 28 days at 20–23°C. A number of cast test discs were cured in a hermetically sealed box, to prevent the absorption of CO_2 found in the open air, and so to isolate its effect on the curing process.

Testing of the samples

Volume mass was determined on freshly moulded samples by measuring their volume and weight. Dry compressive strength was determined for samples cured in the open air for 28 days. Wet compressive strength was tested on the samples cured in the open air for 24 days and then immersed in the water for 4 days.

Water uptake tests were carried out on samples cured in the open air for 28 days, dried to constant weight in an oven at 105°C and then submerged in water. The samples were extracted from the water and weighed every day for the first of five days and every two days for the next 10 days, or until the samples were saturated (weight remained constant). The water uptake was calculated as the ratio of the difference between weights of dried and wet samples to the weight of dried samples.

Capillary water absorption tests were carried out on samples cured in the open air for 28 days, dried to a constant weight in an oven at 105°C and then placed on a constantly water-saturated porous surface enclosed in a moist cabinet. The samples were weighed after one day and then at two-day intervals. The gain in weight due to absorbed water was determined as a percentage of the dry weight.

Analysis of structure and curing process

Analysis of the structure of the test samples was carried out after 180 days, so that the curing process was almost complete and the structure of the material was stable. X-ray diffraction (XRD) analysis was done to determine the presence of crystalline minerals. The analysis was done by a fast scan of $2\theta=2°/\text{min}$, with Cu Kα radiation. Scanning electron microscope (SEM) analysis was carried out to determine the structure of the cured material and the types of chemical bonds formed.

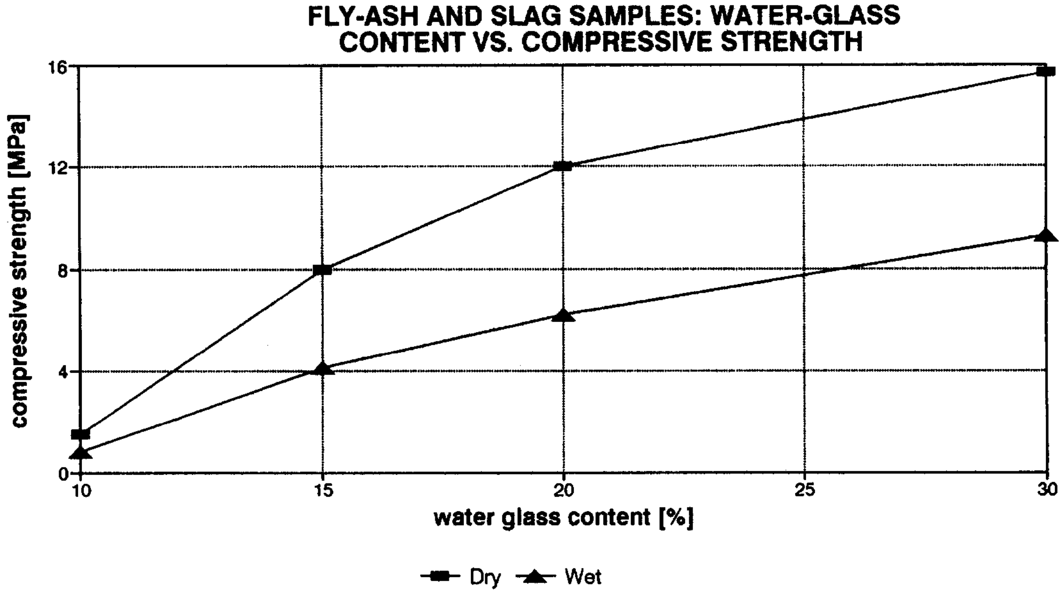
RESULTS

Compressive strength

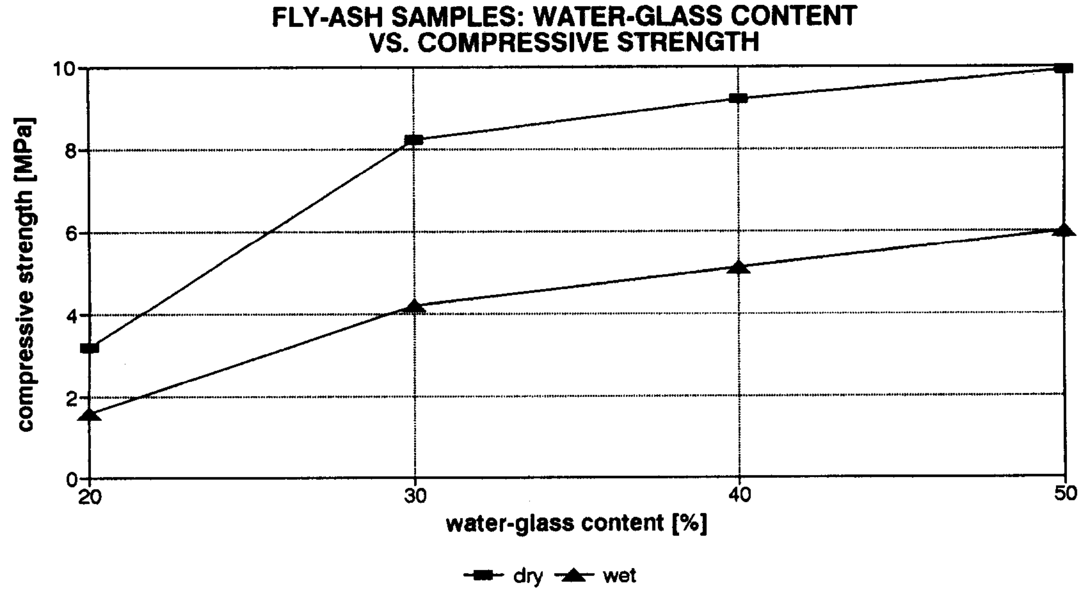
The effect of varying the water–glass content

The effect of the water–glass content on the compressive strength of fly-ash samples (FA) and fly-ash and slag samples (FAS) is shown in Figs 2(a) and 2(b).

It may be clearly seen that both materials harden in the open air and are stable in water to a certain extent. The fly-ash and slag samples



(a)



(b)

Fig. 2. (a) The effect of water–glass content on compressive strength of test blocks made of fly-ash. (b) The effect of water–glass content on compressive strength of test blocks made of fly-ash and slag.

(FAS) had a higher compressive strength than those made of fly-ash alone (FA): the dry compressive strength of FA rose from approximately 3·5 to 9·8 MPa when the water-glass content was increased from 20 to 50%, while that of FAS rose from 1·5 to 15·6 MPa as the water-glass content was increased from 10 to 30%. The wet compressive strength of the samples was approximately 52–60% of dry compressive strength. The lower limits of the water-glass content at 10 and 20% for FAS and FA are set by the necessity of obtaining homogeneous mixtures from the component materials.

The effect of increasing compaction pressure

Experiments were carried out with mixtures of fly-ash (FA) and fly-ash and slag (FAS) containing 30% and 15% water-glass, respectively. Samples containing these amounts of water-glass were found to have similar compressive strengths at low compaction pressures, and could therefore be used as a basis for comparison.

As compaction pressure was increased from 20 to 200 kg/cm^2 the compressive strength of fly-ash (FA) samples increased from 5·3 to 20·0 MPa, and that of fly-ash and slag (FAS) from 6·0 to 12·8 MPa (Fig. 3).

Water uptake

Figures 4(a) and 4(b) show the relationship between the content of water-glass in the mixture and the water uptake in the cured FA and FAS test samples. In the fly-ash (FA) samples, increasing the water-glass content from 20 to 50% reduces the water uptake from 36·6 to 16·8%. For the fly-ash and slag samples, increasing the water-glass content from 10 to 30% diminished the water uptake from 24 to 17%. The reduction in water uptake may be explained by the increase in the volume mass of the test cylinders, which was calculated for freshly moulded samples.

A comparison of the two types of test cylinders shows that the water uptake of FAS is much smaller than the water uptake of FA having the same water-glass content. For example, when the water-glass content of both types of cylinders was 20%, the water uptake of the fly-ash samples was about 37%, while that of the fly-ash and slag samples was less than 20%. The corresponding figures for a water-glass content of 30% were 30% for FA samples and 17% for FAS samples. The lower water uptake of FAS samples should be attributed to their higher density: the volume mass of freshly moulded FAS is greater by approximately 16%.

Several steps were taken in an attempt to reduce the water uptake of both types of mixtures, in view of its high absolute value:

1. Increasing the compaction pressure used in moulding the samples.
2. Adding hydrophobic materials to the initial mixtures.

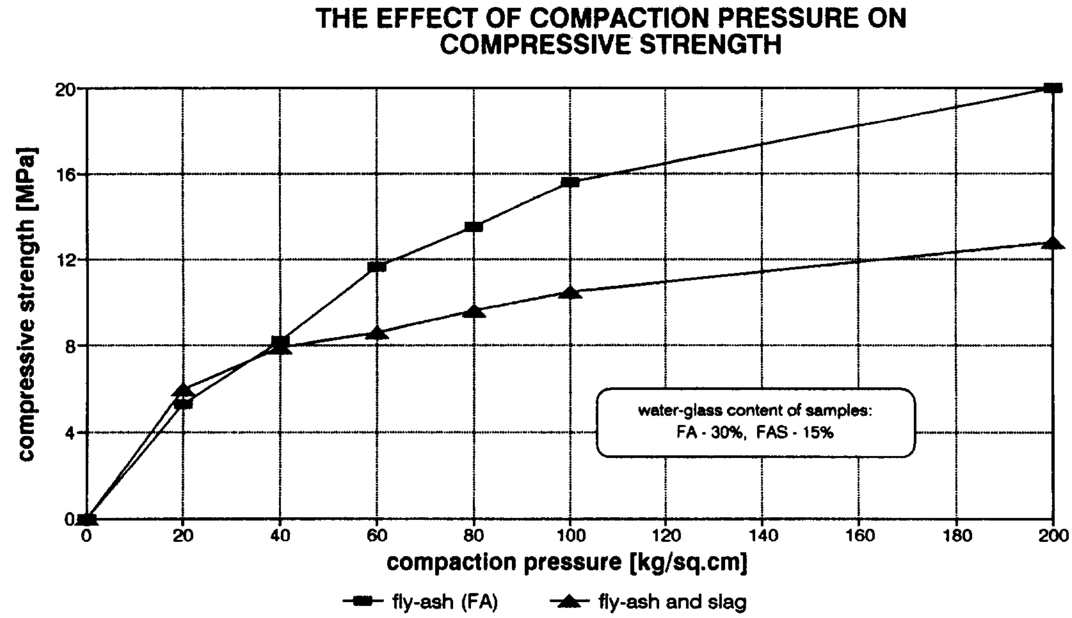
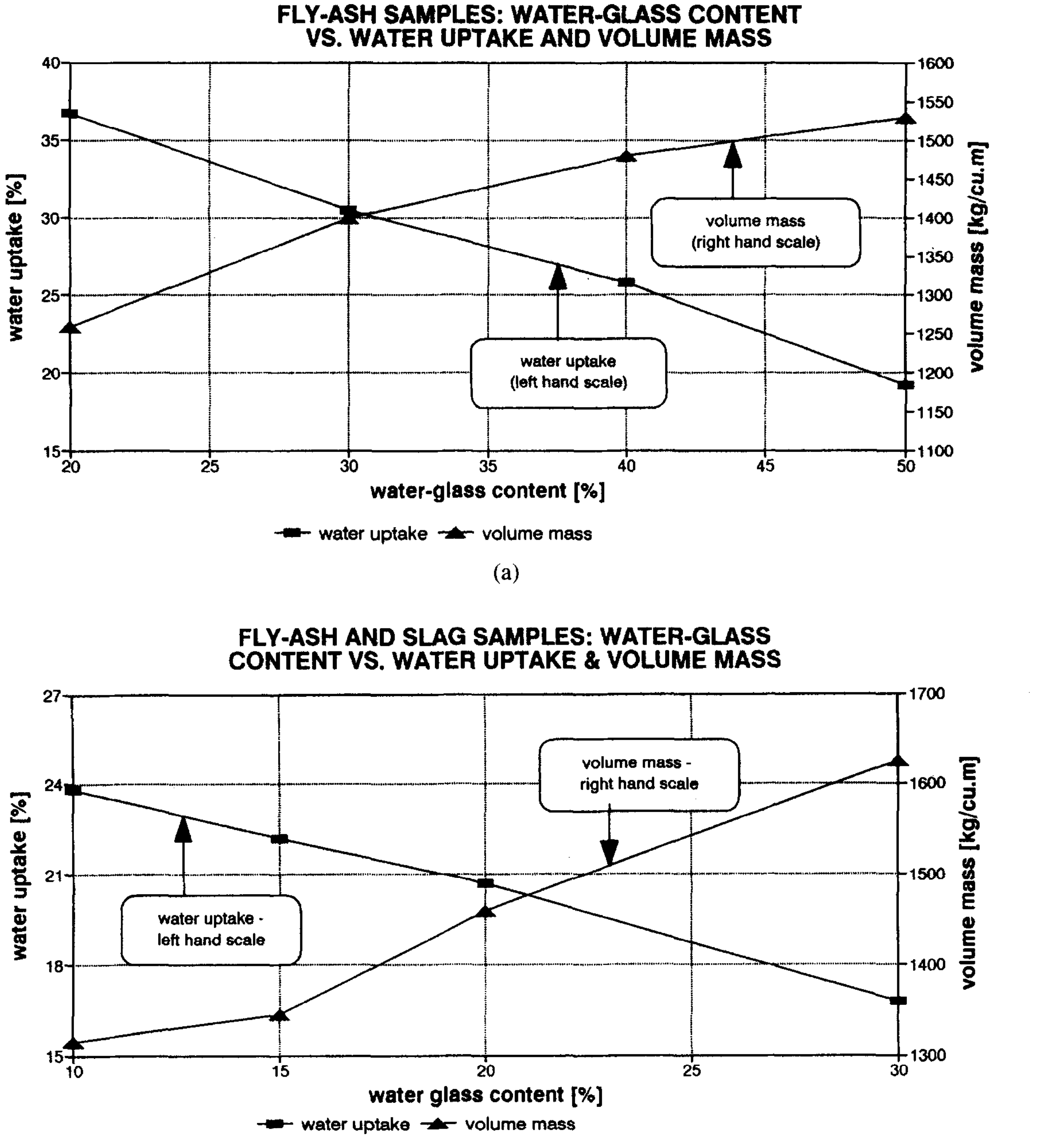


Fig. 3. The effect of compaction pressure on compressive strength of test blocks.



(a)

(b)

Fig. 4. (a) The effect of water–glass content on water uptake and volume mass of test blocks made of fly-ash. (b) The effect of water–glass content on water uptake and volume mass of test blocks made of fly-ash and slag.

3. Short-term impregnation of moulded samples with a hydrophobic material, which would repel the water but would allow the surface to breathe.

The effect on water uptake of increasing the compaction pressure

Figure 5 shows the relationship between the compaction pressure and the water uptake of FA samples. When compaction pressure was increased from 20 to 200 kg/cm^2, the water uptake was reduced from 32·2 to 22·6%. This behaviour may be explained by the increase in density of the material formed.

Reducing the water uptake by using a hydrophobic additive

Figure 6 shows the effect on the resulting water uptake of adding a hydrophobic material to the mixture.

After the first day the water uptake of FAS containing 0·5% Siloxane CS was equal to 4·7%, less than a quarter of the water uptake of FAS without the additive. After 8 days the water

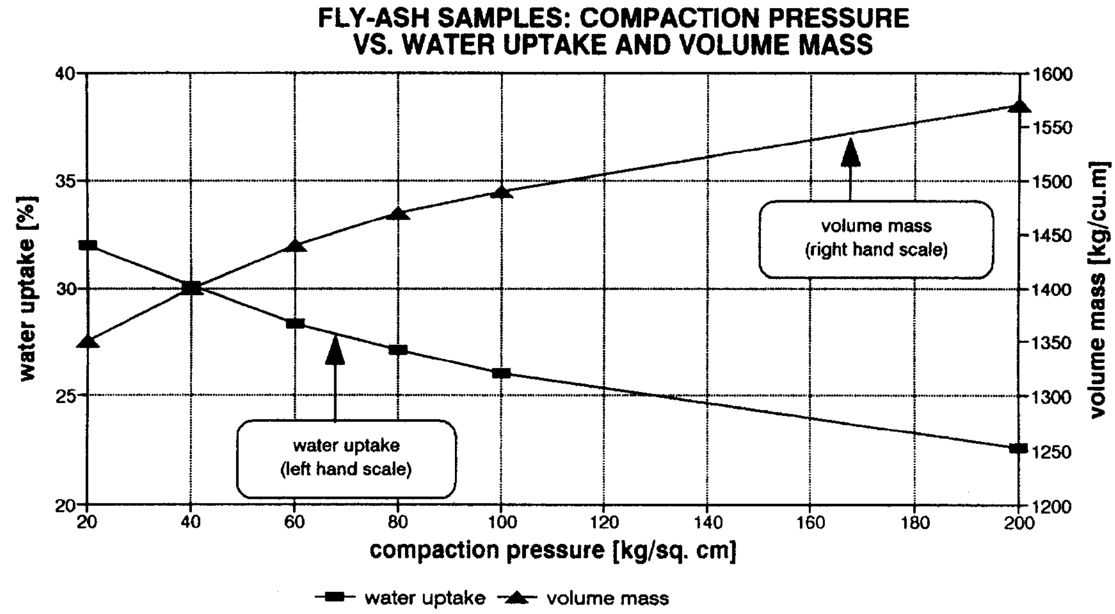


Fig. 5. The effect of compaction pressure on water uptake and volume mass of test blocks made of fly-ash.

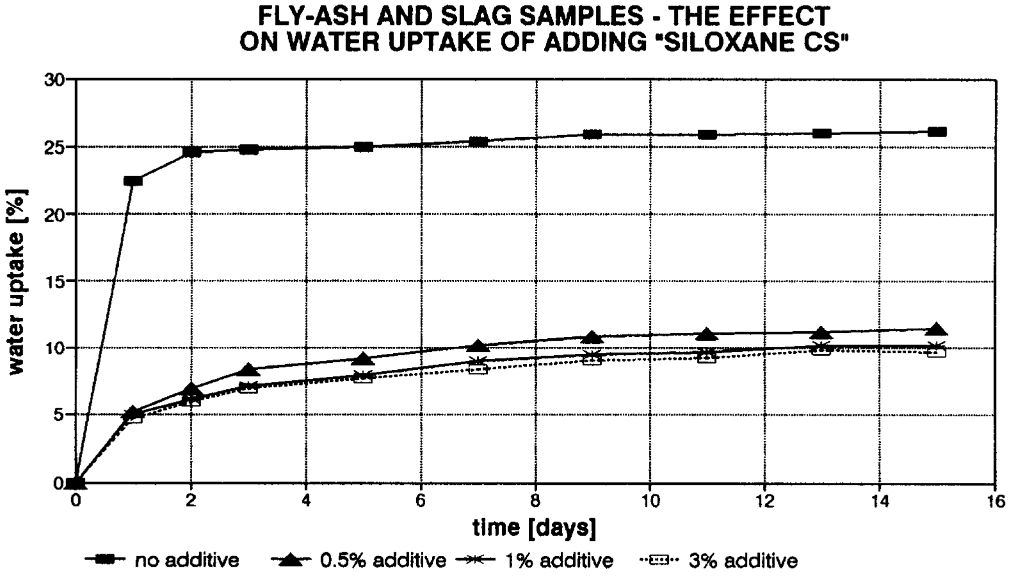


Fig. 6. The effect of using a hydrophobic additive on the water uptake of test blocks made of fly-ash and slag.

uptake stabilized at about 10·7% of the dry weight of the samples, and showed little further increase over time. Increasing the amount of the hydrophobic additive to 3% of the mixture produced only a very small reduction in the water uptake of the FAS samples, which was 4·7% after the first day, and 8·6% in the stable state.

While the use of Siloxane CS reduced the water uptake of the samples made from coal fly-ash and slag, it also caused a significant decrease in their compressive strength. When the amount of additive used was 3% of the mixture, the dry compressive strength of FAS was reduced to only 2·2 MPa (Fig. 7). However, when a smaller amount of the hydrophobic additive was used — 0·5% by weight — the reduction in dry compressive strength was much smaller, and the test samples could withstand a pressure of nearly 5 MPa. However, the wet compressive strength of these samples, tested after submersion in water for 4 days, was only 3 MPa, or 60% of their dry strength.

The combined effects of the hydrophobic additive and increased compaction pressure

For a given proportion of the hydrophobic additive, an increase in the compaction pressure

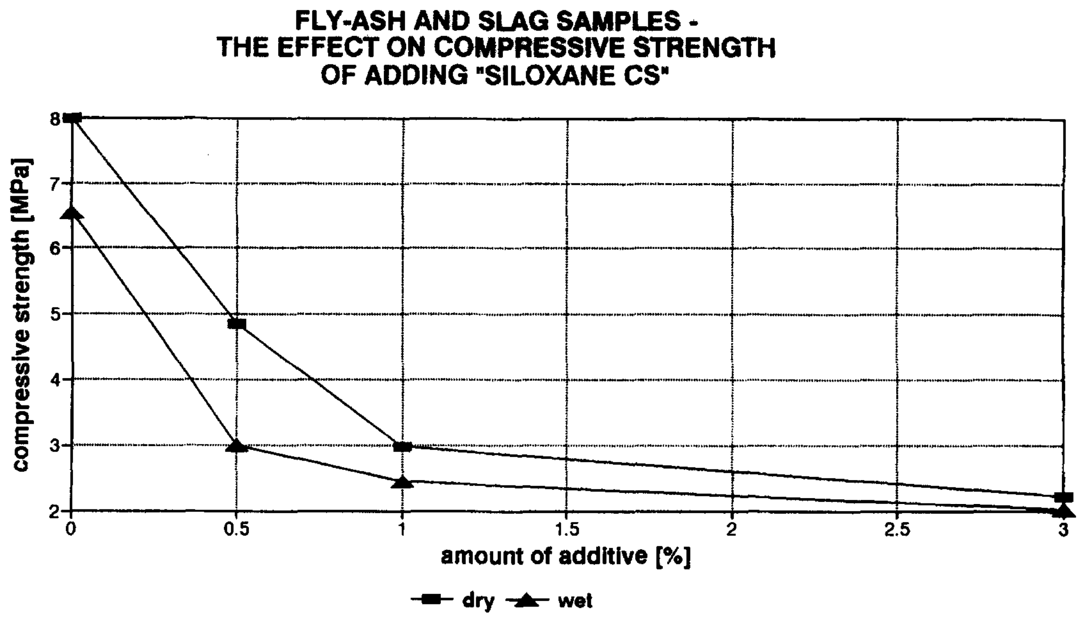


Fig. 7. The effect of using a hydrophobic additive on the compressive strength of test blocks made of fly-ash and slag.

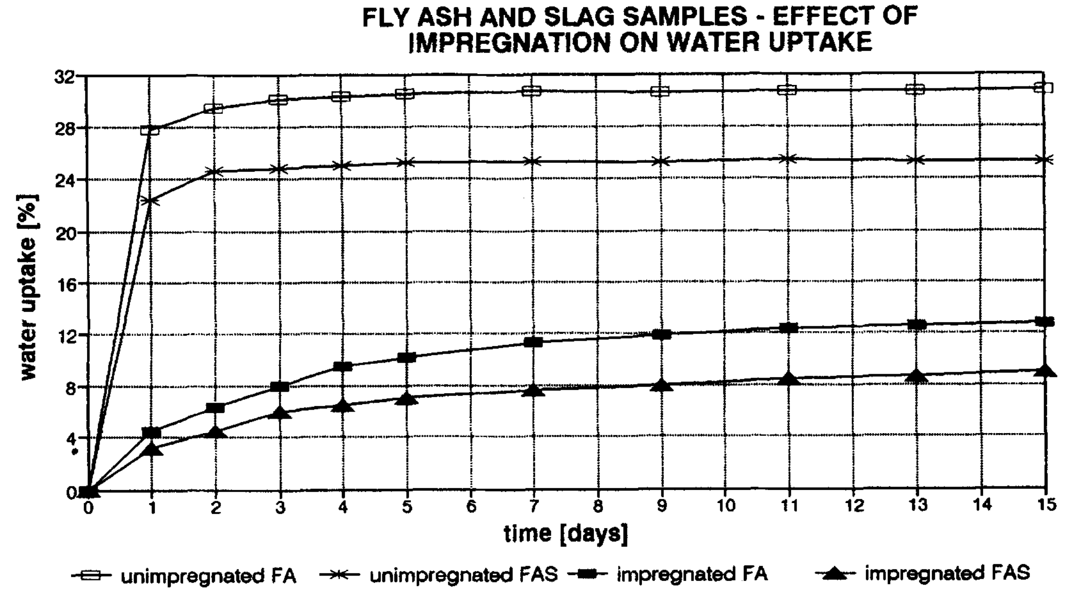


Fig. 8. The effect of impregnation with a hydrophobic material on the water uptake of test blocks.

resulted in a reduction of the water uptake and an increase in the compressive strength. Thus, for example, FAS test samples which contained 0·5% Siloxane CS and which were formed with a compaction pressure of 200 kg/cm^2 had dry and wet compressive strengths of 9·4 and 5·6 MPa, respectively. These values are nearly twice as high as the corresponding values for samples with the same amount of additive formed at a pressure of 40 kg/cm^2. The ratio between the wet and dry compressive strengths remained at 60%, even though the maximum water uptake was reduced to 7·5% of their dry weight. The water uptake for the corresponding samples formed at a pressure of 40 kg/cm^2 was 10·7%.

Partial impregnation with a hydrophobic material
Immediately after moulding, the fresh test cylinders were immersed for 2 s in polymethylhydrogensiloxane — a hydrophobic substance. It was found that the liquid had penetrated to a depth of 2–3 mm. In this layer, the pores and capillaries were partly clogged with the hydrophobic additive, so that their cross-secton was narrowed. As a result, the rate and extent at which test samples took up water

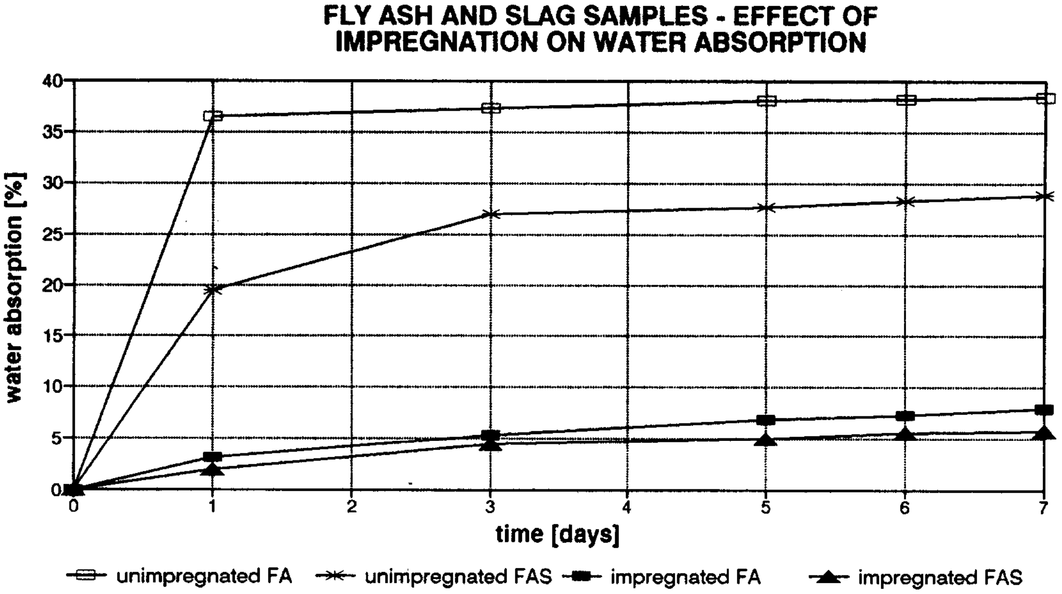


Fig. 9. The effect of impregnation with a hydrophobic material on the water absorption of test blocks.

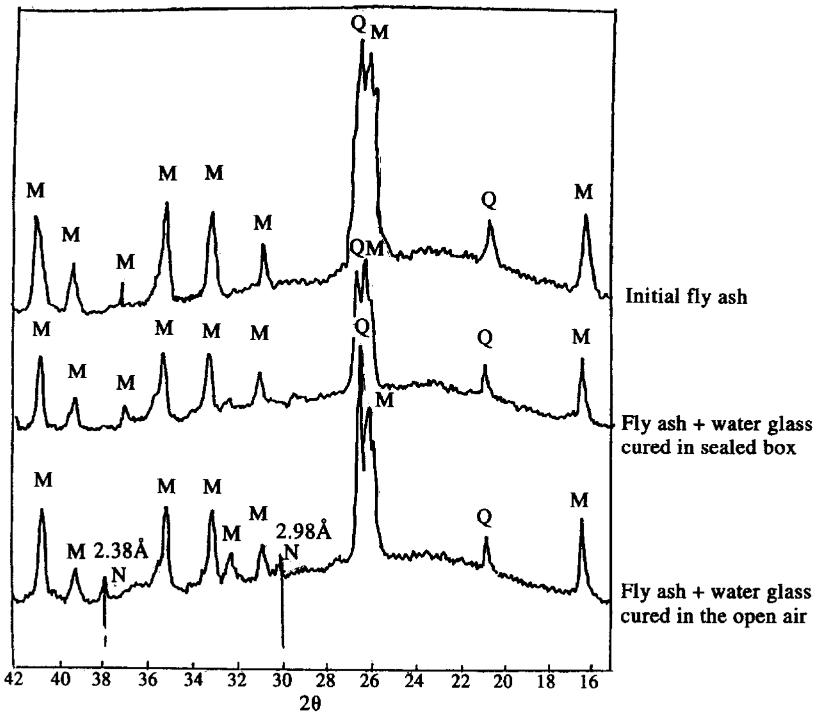


Fig. 10. Typical XRD patterns of fly-ash and water–glass test blocks cured for 180 days.

was reduced, both for samples immersed in water or by capillary absorption.

Figure 8 shows the rate of water uptake for FA and FAS impregnated with a hydrophobic material. While the water uptake of the untreated cylinders was both rapid and extensive — they absorbed water corresponding to over 20% of their dry weight within the first day — the rate at which the impregnated samples absorbed water was much lower. Only after 8 days did they reach equilibrium conditions, the FA cylinders taking up 11·3% water, and the FAS cylinders only 7·6%. The total water uptake of untreated FA and FAS cylinders was 31 and 25%, respectively. Since the depth of impregnation was very shallow, no negative effect was observed on the compressive strength.

Water absorption

Impregnated FA and FAS samples absorbed less water by capillary action than samples which had not been impregnated, and at a

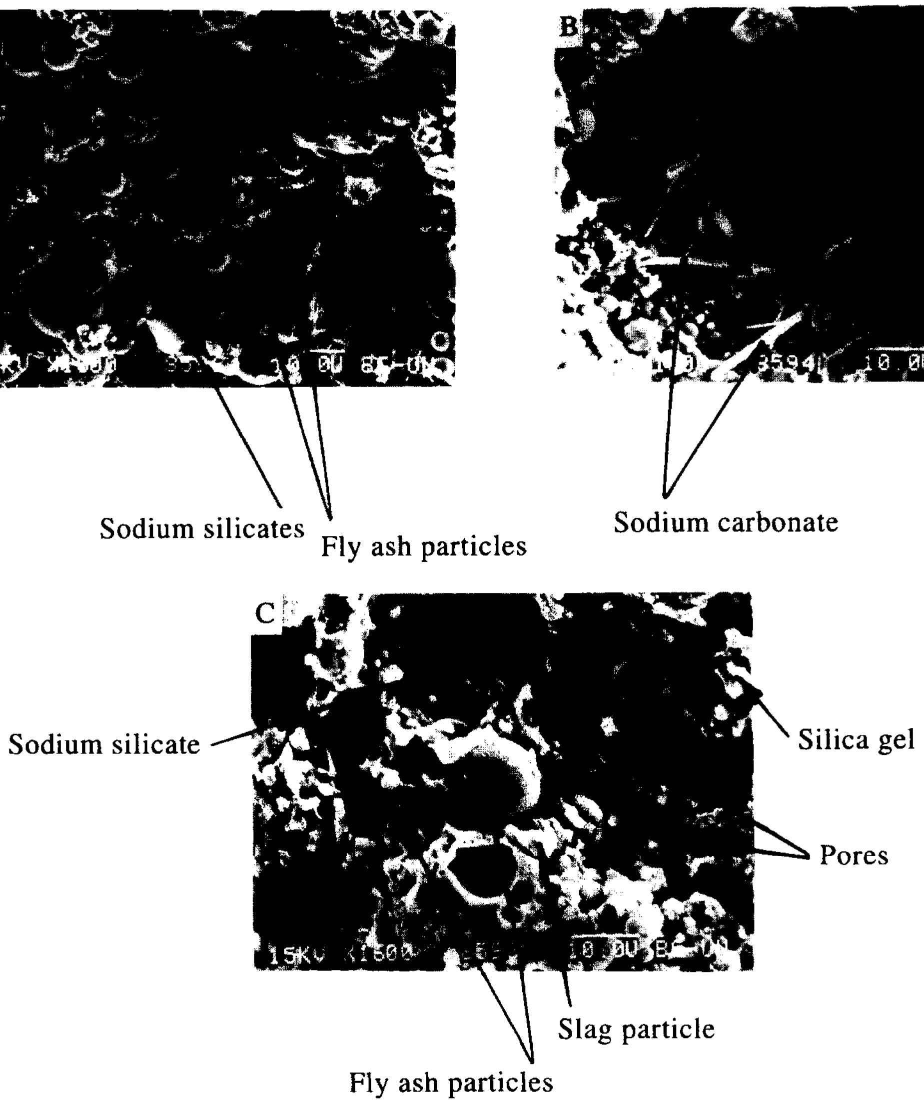


Fig. 11. SEM photographs of the micro-structure of test blocks.

slower rate (Fig. 9). Water absorption in the untreated samples stabilized after 1–3 days, whereas water absorption in the impregnated FA and FAS samples stabilized only after 5–6 days. At the end of the experiments, the water absorption was 7·9 and 5·8%, respectively for impregnated FA and FAS samples, and 38·4 and 28·9%, respectively, for unprotected FA and FAS samples.

These results indicate that a water repellent such as polymethylhydrogensiloxane can lower the water absorption rates of materials made from fly-ash and slag to values found in conventional building materials made of clay, silicate or concrete — 4–20% by weight[7] — provided the exterior surface of the bricks is undamaged.

Structure and chemical composition

XRD analysis shows only minor differences between the raw fly-ash and the cured product. Typical XRD diagrams of the initial fly-ash and of samples cured in a hermetically sealed box and in the open air show identical peaks of quartz and mullite of practically the same intensity (Fig. 10). The diagram representing the mineral composition of the material cured in the open air shows clear lines at 2·38 and 2·98 Å, which may be attributed to sodium carbonate formed during the carbonation process in the open air.

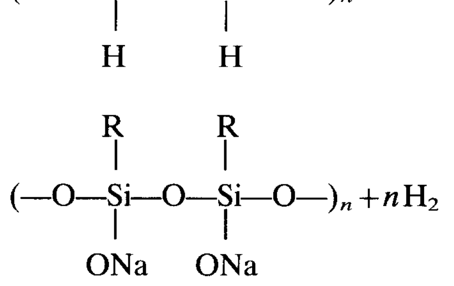
SEM observations have shed further light on the structure and composition of new binding substances formed during the curing process and of the building material obtained as a whole. From scanning electron micrographs it may be concluded that the solidified material is an artificial conglomerate containing a matrix and pores of different configurations and length. The matrix consists of particles of fly-ash and slag which had not participated in the reaction, surrounded by the inorganic polymer binder formed on the basis of silica present in the water–glass and fly-ash (Fig. 11).

The main mass of the binder is a water-stable silica gel. Also found are water-stable, high-module sodium silicates in the form of colourless scales, thin plates, lamellar crystals and a negligible quantity of needle-shaped sodium carbonates.

DISCUSSION

Results indicate that, as expected, use of a hydrophobic material as an additive to the raw mixture reduces the water uptake of the hardened inorganic building materials. The mechanism by which these materials produce the hydrophobic effect may be described as follows: when the additive Siloxane CS is added to a mixture of fly-ash, slag and water–glass, molecules of the hydrophobic material (siloxane) are absorbed by the ash and slag particles. Chemisorption may then occur throughout the mixture. Finally the carbon–hydrogen, non-polar, hydrophobic part of the siloxane molecules fixes on the surface of the hard phase strongly, completing the hydrophobic action throughout the material. The interior surface of air pores and capillary walls of such a material becomes hydrophobic and its water uptake will be greatly reduced.

The reduction of the water uptake described above has an undesirable side effect, namely a decrease in the compressive strength of the resulting solid material. Evidently, it is connected with the blockading effect of the hydrophobic films on the space of fly-ash particles, which interferes with curing processes. In addition, bubbles of hydrogen gas may also have a negative effect. These bubbles are formed in the mixture due to the reaction between the alkali of water–glass and Siloxane CS, as follows:



$$(\text{—O—}\underset{\text{H}}{\overset{\text{R}}{\text{Si}}}\text{—O—}\underset{\text{H}}{\overset{\text{R}}{\text{Si}}}\text{—O—})_n + n\text{NaOH} \rightarrow$$

$$(\text{—O—}\underset{\text{ONa}}{\overset{\text{R}}{\text{Si}}}\text{—O—}\underset{\text{ONa}}{\overset{\text{R}}{\text{Si}}}\text{—O—})_n + n\text{H}_2$$

The reduction in compressive strength caused by the addition of Siloxane CS to the mixture limits its value as a hydrophobic additive. While the dry compressive strength of the FAS test samples with only a small amount (0·5%) of this material was sufficiently high, the further reduction in strength caused by exposure to water would suggest that the use of such bricks is limited to dry conditions, or to structures where they can be protected against water by an external waterproofing barrier. The combined effects of high compaction pressure (200 kg/cm^2) and the hydrophobic additive were promising — the wet compressive strength of test cylinders formed in this manner was 5·6 MPa — but it remains to be seen whether these results can be duplicated under normal production line conditions.

The negative effect of the hydrophobic substances on the compressive strength of the building material may be avoided by using it only for impregnating the surface of the blocks after they are moulded. Test samples treated in this way showed no decrease in compressive strength, but the rate and extent of their water uptake was reduced significantly, relative to the untreated samples. This effect was observed both for samples immersed in water and for those exposed to capillary absorption.

The application of an external hydrophobic coating may be an effective means of improving the water resistance of the coal fly-ash based building blocks. However, it also has some serious drawbacks:

- — The finished blocks may be chipped or broken while they are transported from the production plant to the building site, and even more so during the construction process. As a result, their water resistance may be significantly reduced, unless great care is taken to preserve their surface intact.
- — The hydrophobic effect of the coating applied to the blocks may cause problems in the adherence of mortar to the blocks, reducing the strength and stability of a wall built with them. Likewise, commonly used plaster or other rendering materials may not adhere to these blocks. Both aspects of this problem may be treated by developing compounds or additives which form stable bonds with blocks in spite of the surface coating. The lack of such materials, should they be required, is an

obvious drawback to the proposed technology and could hinder the successful introduction of building blocks based on coal fly-ash and slag to the market.

CONCLUSIONS

Water resistant building materials may be made out of mixtures of coal fly-ash and slag, to which water–glass has been added, and which are cured in the open air. Their strength (2·0–20·0 MPa) and water resistance are attributable mainly to the formation of a water stable binder consisting of silica gel and high-module potassium silicate. However, such materials characteristically have a large water uptake — up to 40% — which is due to the high absorbing capacity of fly-ash. The reduction of water uptake to within acceptable limits for comparable wall materials, such as clay bricks, silicate bricks and concrete blocks, can be achieved by adding a hydrophobic material such as Siloxane CS to the mixture in very small quantities. However, this reduces the compressive strength of the blocks considerably. The reduction of the water uptake to acceptable levels without causing a great reduction in the wet compressive strength may also be achieved by a combination of higher compaction pressure and the use of hydrophobic additives. Partial impregnation with a hydrophobic material such as polymethylhydrogensiloxane also reduces the water uptake to about 6–10%, and since it is applied only to the surface of the finished blocks, it causes no reduction in their strength.

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