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Prefabricated building elements based on FGD gypsum and ashes from coal-fired electric generating plants

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ABSTRACT

Mixtures of fly ash, bottom ash and Flue Gas Desulphurized (FGD) gypsum, all solid wastes from coal-fired electric generating plants, can be combined with lime and 10% of water to produce a damp powder which can be moulded at a pressure of 20-40 MPa and then steam-cured in less than 1 day at 35-80 °C. The resulting building materials – in the form of bricks, blocks or slabs – produced by this Pressure Forming (PF) process, are stronger and sounder than the corresponding materials produced by a slip casting (SC) process.

The physical and mechanical properties of the materials manufactured through the PF process are based on the reaction of amorphous silica and alumina of the ash with lime or lime and gypsum respectively, so that calcium silicate hydrate and ettringite are produced. When the temperature of the steam curing is as low as 35 °C, the hardened material is sound in the air, but it swells and is quickly destroyed by the action of water. This effect can be ascribed to the formation of ill-crystallized ettringite. On the other hand, with thermal treatment at higher temperatures (60-80 °C), the material is stronger and sound even in the presence of water in service. The well-crystallized ettringite fibers, favoured by the higher temperature of the steam curing treatment, are considered to be responsible for the better mechanical performances and the lower change in length.

In general, the physical and mechanical properties of the ash-gypsum-lime cementitious system are better than those of the traditional clay-based ceramic products manufactured at temperatures as high as 1000 °C. Therefore, this process based on steam curing at 60-80 °C appears to be very useful for both the re-utilization of solid wastes and the saving of energy in the production of building materials.

RÉSUMÉ

Un mélange de cendres volantes et de gypse provenant d'installations de désulfuration, déchets solides dérivés de la combustion du charbon dans les centrales thermoélectriques, peut être combiné avec de la chaux et de l'eau (dans un rapport de 10% environ) pour produire une poudre humide qui peut être comprimée à 20-40 MPa et soumise à un étuvage (35-80 °C) pour une durée inférieure à 24 heures.

Le matériau de construction résultant, briques, blocs ou plaques, obtenu par cette mise en œuvre sous pression est plus résistant qu'un matériau analogue produit par coffrage glissant.

Les propriétés physiques et chimiques du matériau produit par mise en œuvre sous pression dépendent de la réaction entre la silice amorphe et l'alumine contenues dans les cendres et, respectivement, la chaux ou la chaux et le gypse, ce qui entraîne une formation de silicate de calcium hydraté et d'ettringite. Quand la température d'étuvage est faible (par exemple 35 °C), le matériau durcit et est stable à l'air mais il se produit un gonflement entraînant la destruction rapide sous l'action de l'eau. Cette dégradation peut être due à la formation d'une ettringite amorphe ou mal cristallisée. Au contraire, quand l'étuvage est conduit à température plus élevée (60-80 °C), le matériau est plus résistant et n'est plus attaqué par l'eau. La formation d'ettringite bien cristallisée, grâce à la température plus élevée de l'étuvage, est responsable des meilleures performances mécaniques et d'une plus grande stabilité dimensionnelle du matériau.

En général, les propriétés physiques et mécaniques du système cendre-gypse-chaux sont meilleures que celles des briques traditionnelles produites à des températures d'environ 1 000 °C. Donc, le procédé proposé, basé sur un traitement thermique à 60-80 °C, semble être valable autant pour la réutilisation des déchets que pour les économies d'énergie dans la production des matériaux de construction.

Editorial note
Prof. Mario Collepardi is teaching at the Dipartimento di Scienza dei Materiali e della Terra, Universita degli Studi di Ancona, which is a RILEM Associate Member. Prof. Collepardi is a member of the Board of Advisors for Materials and Structures.
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1. INTRODUCTION

The amount of fly ash and bottom ash being produced from the burning of powdered coal in electric generating plants is increasing very rapidly. However, less than 25% of the total ash is used, thereby creating a substantial waste-disposal problem. An estimated 80 to 90% of this amount, in the form of fine fly ash, is used by cement and concrete industries, whereas other uses include soil stabilization, road construction and asphalt filling. Table 1 shows the total available ash, the available fine fly ash and the ash used by cement and concrete producers in the USA and in some Western European countries.

Table 1 - Available and utilized fly-ash (million tons/year)

Year	Total available ash		Available fly ash		Fly ash in concrete	
	USA	Europe	USA	Europe	USA	Europe
1970	40	–	30	–	2	–
1980	65	–	50	–	7	–
1985	70	47	55	38	15	7
1990	80	50	65	40	20	10
2000*	85	57	68	46	22	12

— Not available data * Estimated.

Sources: American Coal Ash Association for the USA and Enel for Western Europe

Disposal of ash not used in cement and concrete industries or alternative applications can create other kinds of pollution problems, since the drainage of effluents from ash disposal ponds threatens fresh water supplies because trace amounts of toxic products are present in these ashes [1].

More recently, besides ashes, another solid waste material is produced when high sulphur-content coal is burnt in power stations: because of limits on SO_2 emissions, as established by environmental protection agencies and air quality standards, flue gas desulphurization (FGD) plants are required to transform the SO_2 gaseous emissions into scrubber sludge-collected gypsum.

More than 5% of FGD gypsum is produced by using coal with a sulphur content of 1%. Figure 1 shows schematically the approximate amounts of total solid wastes in a coal-fired electric generating plant where a coal is used with total ashes of 10% and sulphur content of about 1%.

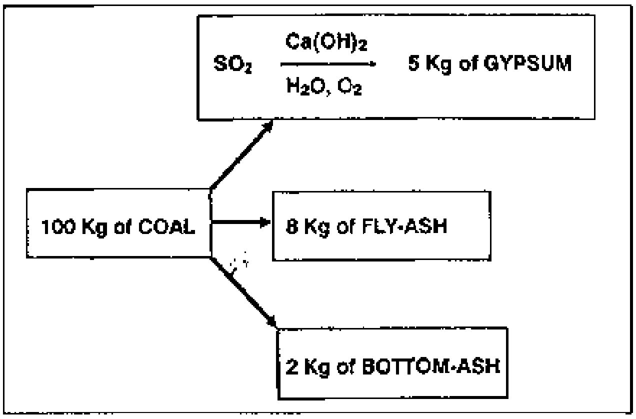

Fig. 1 - Amounts of total solid wastes for 100 kg of coal with 10% of total ashes and about 1% sulphur content.

Theoretically, FGD gypsum could be used in the cement industry as a set regulator of portland cement klinker. However, due to the huge available amounts of alternative calcium sulphate sources from natural mines or other industrial by-products, FGD gypsum should be placed in disposal areas.

Disposal of FGD gypsum is not only expensive but also causes other kinds of pollution problems: since gypsum is relatively water soluble, it should be incorporated into a hydraulic cementitious binder. Yet, even this hardened system in the disposal area can be destroyed by ettringite and/or thaumasite formation [2].

2. NEW STRATEGIES FOR THE UTILIZATION OF FGD GYPSUM AND COAL ASHES

In view of the above mentioned difficulties for the disposal of FGD gypsum, as well as of the ashes not used in industrial applications, new processes have been developed to produce building materials in the form of bricks or prefabricated elements based on the simultaneous utilization of FGD gypsum and fly ash from coal-fired electric generating plants. Ikeda and Tomisaka [3] have studied a slip casting (SC) process where anhydrite ($CaSO_4$) – produced by thermal treatment at 150 °C of FGD gypsum – fly ash, lime and water were combined to produce a flowable mixture which was poured into forms, demoulded after 30 min, and then steam-cured.

By using this technique (Fig. 2), lightweight bricks can be manufactured with a specific gravity of about 1000 kg/m3 and with flexural and compressive strengths of about 1 and 6 MPa, respectively.

An alternative method – pressure forming (PF) process – has been studied by the authors of the present paper in order to minimize the main drawbacks of the slip casting process and to improve the mechanical performances of the materials.

There are several potential advantages to the pressure forming process (Fig. 3) with respect to the slip casting process (Fig. 2).

The most important advantage is based on a productivity aspect: the preliminary thermal treatment at about 150 °C of FGD gypsum in the SC process, which transforms by-hydrate calcium sulphate into anhydrite, is not required in the PF process, and the FGD gypsum can be used as is from the scrubbing equipment.

In the PF process, the "green" precast elements, in the form of bricks for instance, can be immediately demoulded provided that an adequate pressure has been applied in the compaction step of the wet powder into metallic moulds.

On the other hand, the preliminary thermal treatment at about 150 °C of FGD gypsum is absolutely necessary in the SC process since the demoulding of the "green" bricks may occur in about 30 minutes just because of the quick setting caused by the hydration pro-

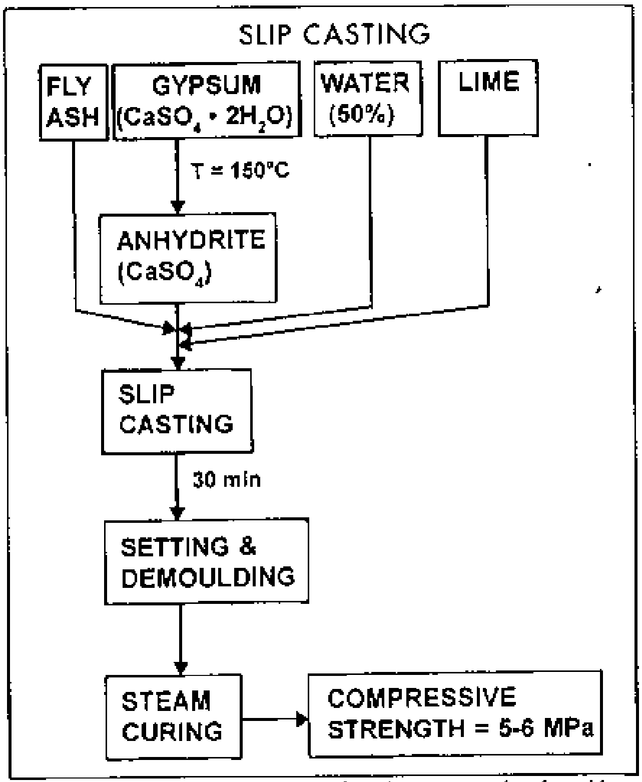

Fig. 2 - Flow chart of the pressure forming process developed by Ikeda and Tomisaka [3].

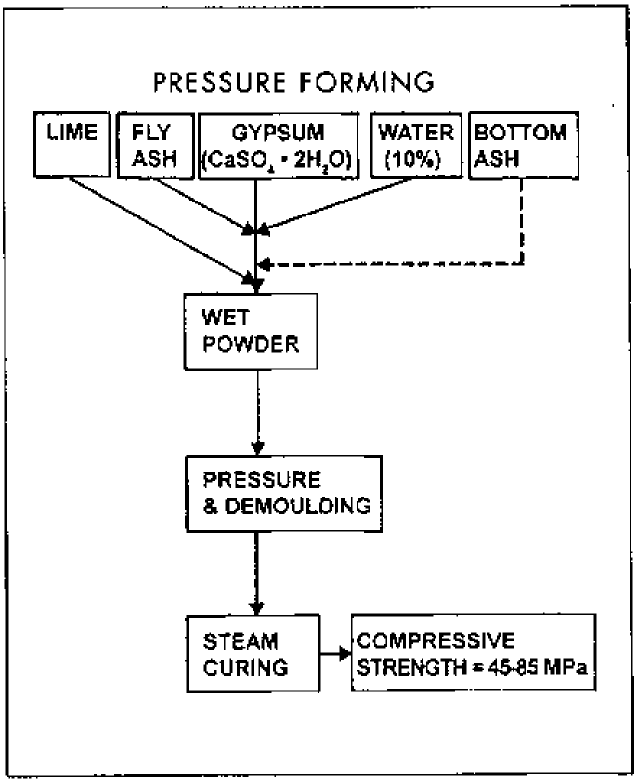

Fig. 3 - Flow chart of the pressure forming process developed by ENCO & ENEL.

cess (1) of anhydrite produced by the preliminary thermal treatment:

$$CaSO_4 + 2H_2O \rightarrow CaSO_2 \cdot 2H_2O \qquad (1)$$

In the absence of the reaction (1), it would take many days to transform the flowable mixture of the SC process into demouldable "green" bricks, since the consolidation process would be substantially based on the formation of calcium silicate hydrate (C-S-H) produced by the relatively slow pozzolanic reaction between lime and the amorphous silica of the fly ash:

$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow C\text{-}S\text{-}H \qquad (2)$$

On the other hand, even the alternative setting process caused by the formation of ettringite produced through the reaction of FGD gypsum with lime and alumina of the fly ash,

$$3CaSO_4 \cdot 2H_2O + 3Ca(OH)_2 + Al_2O_3 + 23H_2O \rightarrow$$
$$\rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \qquad (3)$$

is relatively slow at room temperature, and therefore the demoulding time based on the ettringite formation in the SC process would be very long. Moreover, at room temperature colloidal ettringite is formed instead of crystalline ettringite produced at higher temperature [4], such as that formed in the steam curing process.

Since colloidal ettringite can swell and cause destructive effects in the presence of water [5], the formation of crystalline ettringite through the reaction (3) must occur almost exclusively during the subsequent steam treatment at higher temperatures, in order to produce sound and stable building materials in the presence of water in service.

Another important advantage of the PF process with respect to the SC process is based on the mechanical performances, since strength can be even higher than that of the traditional and more expensive ceramic bricks produced at about 1000 °C.

Last but not least, in the PF process, all the solid wastes from a coal-fired thermal plant, including bottom ash, may be simultaneously and advantageously used. Bottom ash, in the form of coarse grains and filling material, may be used in the PF process, and the composition of the wet powder mixture needing to be processed (Fig. 3) can be adjusted in order to meet the amounts of solid wastes (Fig. 1) available from the specific thermal plant. The coarse and heavy grains of bottom ash would cause segregation in a flowable mixture, and therefore bottom ash cannot be used in the SC process.

However, the SC process appears to be more advantageous than the PF process when high strength is not required and building materials are needed with better thermoinsulating properties related to a more porous and lighter weight. Another advantage of the SC process pertains to the shape of the precast elements which can be very complicated, whereas in the PF process, only building materials with relatively simple geometry can be moulded and manufactured.

3. EXPERIMENTAL

Although in the present paper only few specific results can be shown for the sake of brevity, a synthetic picture of the general program will be given in the following sections.

3.1 Materials and Mixture Proportions

Fly ash, bottom ash and FGD gypsum (Table 2) from coal-fired electric generating plants of ENEL in Italy have been used. These solid wastes have been combined with an adequate amount of lime, $Ca(OH)_2$, so that different mixtures, whose composition corresponds to the shaded area of the ternary diagram of Fig. 4, have been produced.

The SO_3/CaO molar ratio of the investigated ternary system has been changed from 0.05 (point C of Fig. 4) to 1.29 (point A of Fig. 4). The percentage of total ash indicated in Fig. 4 can be derived from three different situations:

i) only fly ash;
ii) 85% of fly ash and 15% of bottom ash;
iii) 70% of fly ash and 30% of bottom ash.

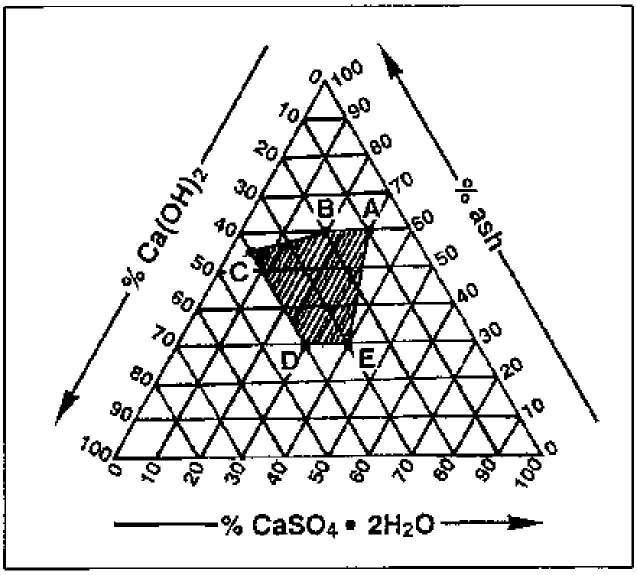

Fig. 4 - The shaded area ABCDE in the ternary diagram indicates the investigated mixture composition. Point A, for instance, corresponds to 60% of ash, 30% of gypsum and 10% of lime.

3.2 Manufacturing and test procedures

From each mixture a wet powder has been produced by using 10% of water, including the moisture contents of the individual components (Table 2).

Specimens in the form of prisms (40 x 150 x 300 mm) or cylinders (diameter 80 mm, height 40 mm) have been moulded by pressing for 5-10 seconds the wet powder into metallic moulds at a pressure in the range of 0.5-40 MPa.

The demoulded specimens have been steam cured at 35, 60 or 80 °C according to the thermal treatment illustrated in Fig. 5. Then, the specimens have been cured at 5 or 20 °C and characterized at 1 day up to 2 years by carrying out tests of compressive and tensile strength, elastic modulus, specific weight, water absorption, shrinkage and swelling, X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).

Table 2 - Chemical composition of solid wastes from coal thermal plant

Component (%)	Fly ash	Bottom ash	FGD gypsum
SiO_2	46	43	–
Al_2O_3	29	30	–
Fe_2O_3	5	7	–
CaO	4	5	31
MgO	1	1	–
Na_2O	0.3	0.2	–
K_2O	0.5	0.4	–
SO_3	0.5	0.4	40
Moisture	1	2	8
LOI	8	9	20
Retained on 45 μm sieve (%)	5	99	4

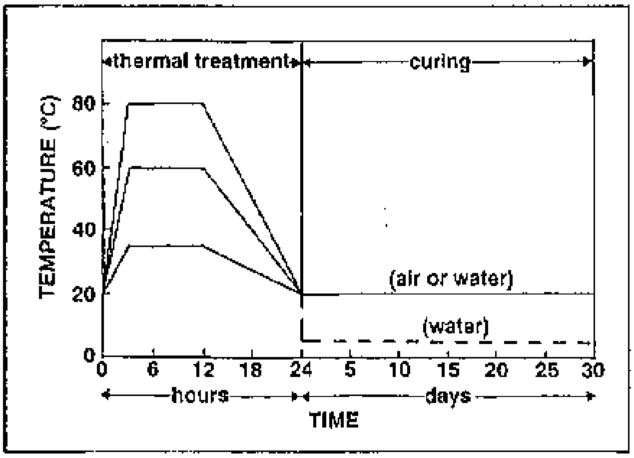

Fig. 5 - Steam curing at 35, 60 or 80 °C and then curing at 5 or 20 °C.

4. RESULTS

In the present paper, only the results of one specific mixture, among the more than 300 available mixtures, will be examined in some detail, whereas the general performances of the ternary system (ash-gypsum-lime) investigated in the research program will be briefly discussed in the concluding section.

The specific mixture examined in the present report contains: 55.7% of fly ash, 30% of FGD gypsum and 14.3% of lime, with an SO_3-CaO molar ratio of 0.9. The performances of this mixture, whose composition is very close to that at point A in Fig. 4, are not the best and are representative of the average behaviour of the total investigated system when the powder has been moulded at a pressure of 20-40 MPa. The partial replacement of fly ash by 15 or 30% of bottom ash does not significantly change the performance.

Only compressive strength, shrinkage and swelling tests will be examined in the present report. Prism specimens

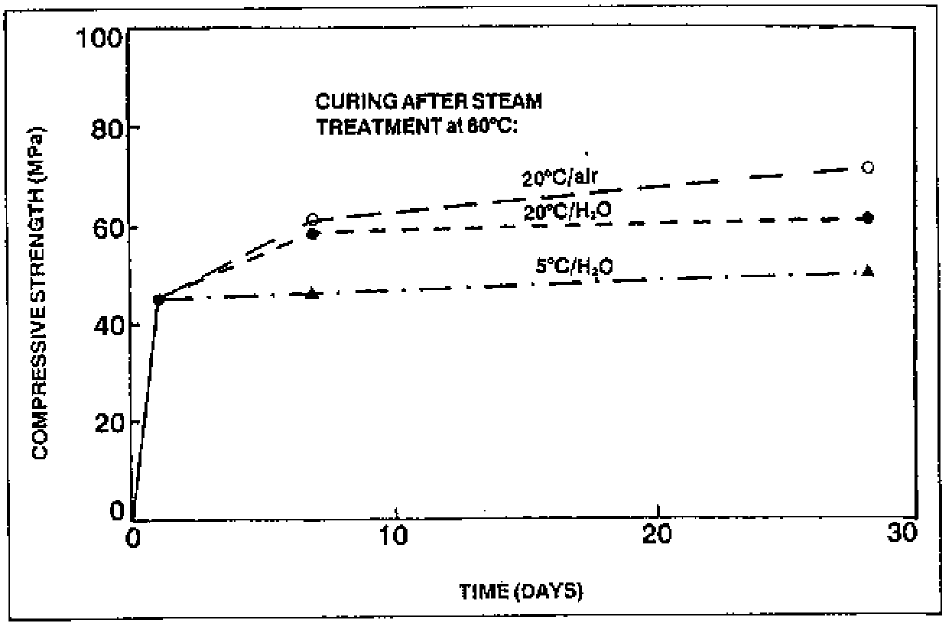

Fig. 6 - Compressive strength of the fly ash-gypsum-lime system after a steam curing at 80 °C.

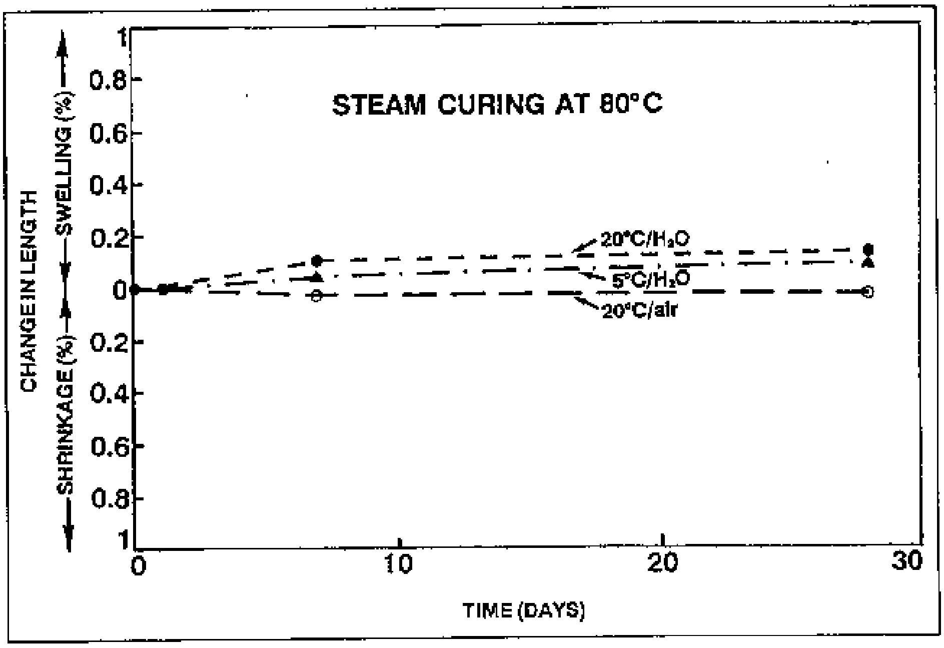

Fig. 7 - Shrinkage and swelling properties of the fly ash-gypsum-lime system after the curing at 80 °C.

have been used to measure shrinkage in air (at 20 °C with R.H. of 65%) and swelling under water at 5 or 20 °C. Cylindrical specimens have been used to determine the compressive strength. Since the height-diameter ratio is 0.5, the compressive strength values are about twice as much as those of the corresponding standard cylindrical specimens with a height-diameter ratio of 2, which cannot be easily produced by the PF process. However, the compressive strength values of cylindrical specimens with a height-diameter ratio of 0.5 can be used for comparative purposes to study the influence of the different parameters (composition, forming pressure, steam curing, etc.) on the performances of the material.

Compressive strength and change in length measurements are shown in Figs. 6-9 for the mixture moulded at a pressure of 40 MPa, steam-cured at 80 °C (Figs 6, 7) or 35 °C (Figs 8, 9) and then cured at 5 °C or 20 °C under water or in air with a R.H. of 65% at 20 °C.

Figure 6 shows that the compressive strength at the end (1 day) of the thermal treatment at 80 °C is about 45 MPa and then it increases up to 70 MPa at 28 days when the specimen is cured at 20 °C in air. With respect to the air curing, the strength increase of water-cured specimens is a little lower at 20 °C (60 MPa at 28 days) and much lower at 5 °C (49 MPa at 28 days).

The change in length measurements indicate that with a steam curing at 80 °C, the drying shrinkage in air of the hardened material is negligible, whereas the swelling under water is less than 0.1% at 20 °C and even lower at 5 °C (Fig. 7).

The steam curing at a lower temperature (35 °C instead of 80 °C) changes the behaviour of the material in a dramatic way. In particular, the compressive strength, which is about 18 MPa at the end of the thermal treatment, is reduced to zero in less than 1 week of water curing at 5 °C (Fig. 8). Moreover, the specimens signifi-

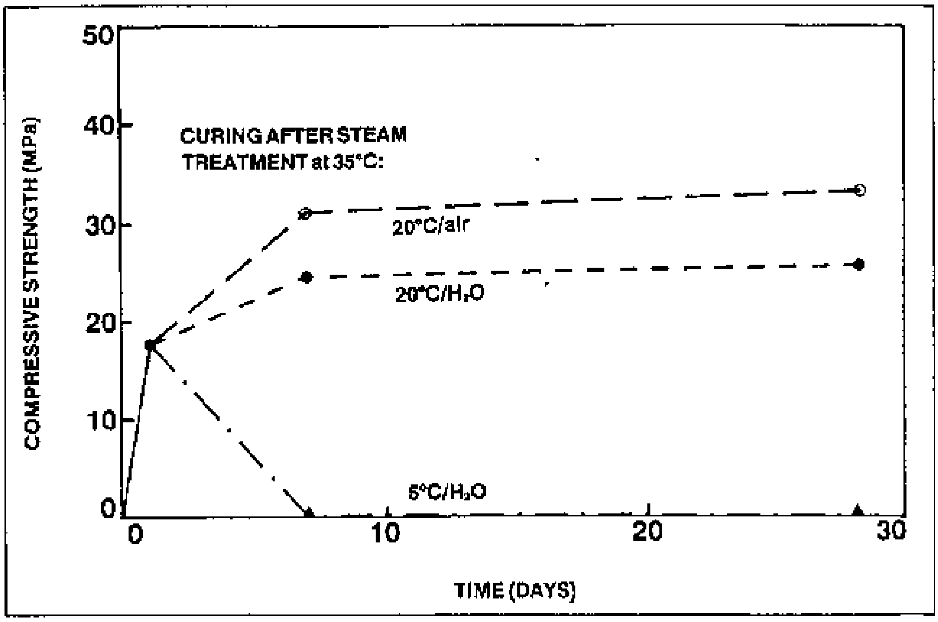

Fig. 8 - Compressive strength of the fly ash-gypsum-lime system after a steam curing at 35°C.

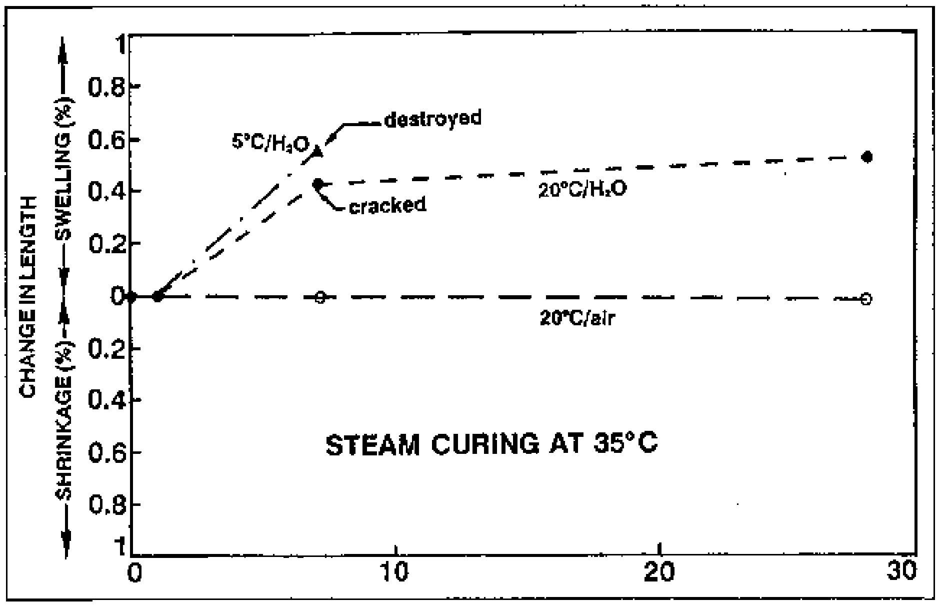

Fig. 9 - Shrinkage and swelling properties of the fly ash-gypsum-lime system after the steam curing at 35 °C.

cantly swell when being exposed to water before being cracked at 20 °C or destroyed at 5 °C (Fig. 9). Only air-cured specimens are sound (about 33 MPa at 28 days) and do not show significant changes in length.

The significant reduction in the performances caused by the decrease in the temperature of the steam treatment to 35 °C (at 60 °C, the material performs as well as at 80 °C) can be ascribed more to the morphology change rather than to the composition of the hydrated phases formed after the steam curing. The XRD pattern of the steam-cured specimens does not seem to be substantially affected by the temperature of the thermal treatment. In particular, the XRD peaks of ettringite at the lower temperature (35 °C) are essentially the same as those at higher temperatures (60-80 °C). However, the SEM observations show that the ettringite fibers produced at higher temperatures (Fig. 10) are much more crystallized and show less specific surface area than those formed at 35 °C (Fig. 11). Therefore, it seems that the subsequent exposure to water caused more swelling (Fig. 9) and is more destructive (Fig. 8) when ettringite with a higher specific area is produced by steam curing at a temperature as low as 35 °C.

This explanation, for the effect of the steam curing temperature upon the behaviour of the ash-gypsum-lime mixture (Figs 6-9), is in agreement with the Mehta theory for the ettringite expansion mechanism in the portland cement mixture (5).

However, this mechanism cannot explain, for a given temperature of the steam treatment (35 °C) and therefore for a given ettringite morphology, the drop in compressive strength (Fig. 8) as well as the increase in swelling (Fig. 9) by reducing the temperature from 20 °C to 5 °C in the water curing after the thermal treatment.

Although a clear explanation is not yet available, the data from the present work confirm the behaviour of the portland cement concrete which appears to be much more deteriorated by the chemical attack of sulphate [4] as well as of calcium chloride [6] at lower temperatures.

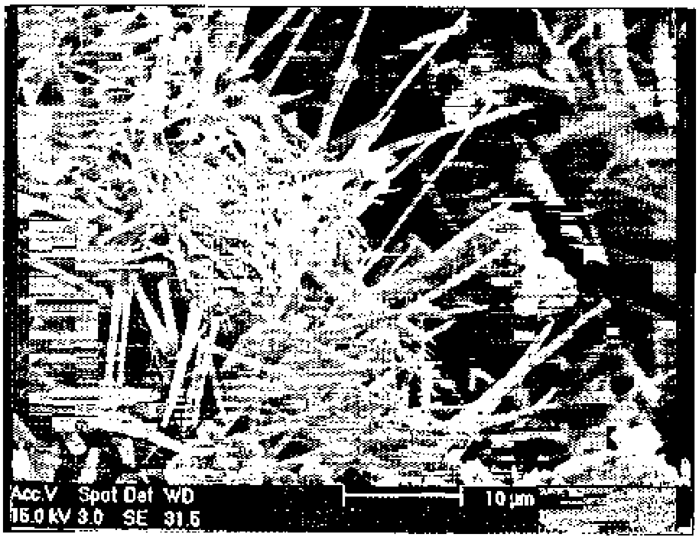

Fig. 10 - SEM observation of the ettringite phase in a specimen steam-cured at 80 °C.

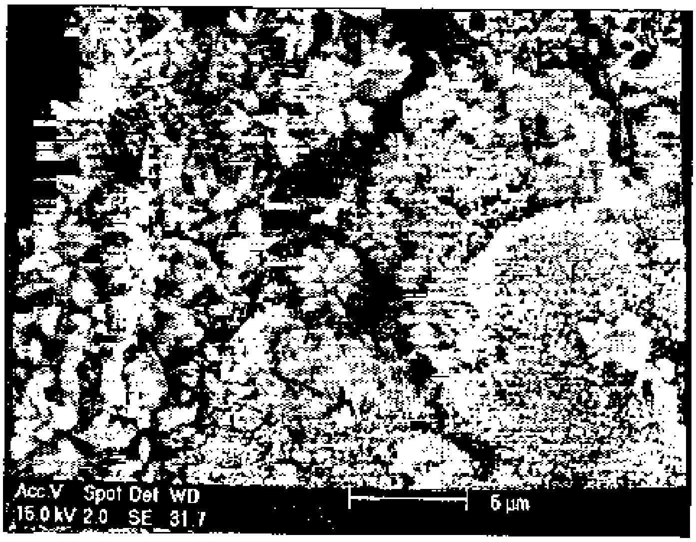

Fig. 11 - SEM observation of the ettringite phase (on the right hand side) in a specimen steam-cured at 35 °C.

5. CONCLUSIONS

The solid wastes from coal-fired electric generating plants (including fly ash, bottom ash and FGD gypsum) can be simultaneously and advantageously used in combination with lime to produce prefabricated building materials, such as bricks, slabs or blocks through a moulding forming process (at 20-40 MPa) followed by thermal treatment at 35-80 °C.

The hydration products which are formed through the pozzolanic reaction of amorphous silica of the ash with lime (C-S-H), as well as the reaction of alumina of the ash with lime and gypsum (ettringite), are responsible for the soundness of the hardened material. However, if the temperature of the steam-curing treatment were as low as 35°C, the ettringite would be produced in the form of ill-crystallized fibers able to swell in the presence of water and then to cause very severe deterioration, particularly at temperatures as low as 5 °C.

The building materials manufactured through this pressure forming process are sounder and stronger than those produced by a slip casting process based on a similar thermal treatment [3] and can be compared with traditional ceramic products generally produced at temperatures in service as high as 1000 °C (Table 3).

Therefore, this process based on steam curing at temperatures lower than 100 °C appears to be very useful for the re-utilization of solid wastes as well as for the saving of energy in the production of building materials.

A compressive strength of 45-85 MPa, a tensile strength of 6-8 MPa, an elastic modulus of 10-12 GPa, a specific gravity of 1600-1800 kg/m^3, water absorption of 8-9%, negligible drying shrinkage and water swelling of about 0.1% can all be attained provided that: a) the composition of the mixture is that corresponding to the ABCDE area of the ternary system ash-gypsum-lime as shown in Fig. 4; b) the amount of the bottom ash is not higher than 30% of the total ash; c) the moulding pressure of the wet powder mixture is at least 20 MPa and d) the temperature of the thermal treatment is not lower than 60 °C.

Table 3 - Properties of ash-gypsum-lime based mixtures and traditional ceramic materials

Property	Ash-gypsum-lime material	Ceramic material
Compressive strength (MPa)	45-85	10-45
Tensile strength (MPa)	6-8	1-4
Elastic modulus (GPa)	10-12	8-15
Specific weight (kg/m^3)	1600-1800	1700-1800
Water absorption (%)	8-9	8-28
Drying shrinkage (%)	0.01	negligible
Water swelling (%)	0.1	negligible

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