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Chemical Corrosion Phenomena of Roofing Tiles

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Abstract: The deterioration phenomena of roof tiles in model systems, formed from clay minerals and Ca-carbonate component, have been investigated. The systems after a specific thermal treatment were exposed to real atmospheric conditions, i.e. to attack of sulphurous acidic rains.

The dual action, of SO_2 and atmospheric humidity, on roofing tiles, supporting the destruction phenomena of samples, elucidated the formation of specific phases: gel of calcium silicate hydrates and crystals of aluminate hydrates, cancrinite, scawtite and zeolites. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

The ability of roof tiles to resist the attacks of a wet and freezing environment is of primary importance. Their other main qualities, i.e. strength, became secondery in a case where the roof tiles fail in such an environment.

For several years the appropriate connection among mechanical properties, resistance of roof tiles to physical corrosion and their pore size distributions have been developed,[1,2] specifying particular methods of investigations. The phenomena of chemical deterioration of ceramic systems were not included in those considerations.

The attack of water as well as of the acid gases on the ceramic systems has, however, a remarkable influence on their resistance. The present article analyses these phenomena, which are very specific for systems with remarkable pozzolanic character[4–6] and fired clay materials, elucidating a wide range of new crystalline forms.

The presence of CaO in ceramic systems (obtained after thermal decomposition of $CaCO_3$) as well as its contact with water, in a specific environment, and the polluted atmosphere, are the main factors controlling the deterioration step of these systems. Some of these phenomena are known in the field of cement chemistry. Using this knowledge, particularly as for the formation of calcium silicate hydrate and ettringite phases,[3,7,8] the factors controlling chemical corrosion and deterioration of roof tiles have been determined.

2 EXPERIMENTAL

Two different industrial raw materials (Table 1 and Fig. 1), one based on quartz, mica, feldspars, calcite, dolomite and hydromica clay material (*H* raw material) and the other based on montmorillonite clay material, feldspars, mica, quartz and peat component (*M* raw material) were applied in the designing procedure of three different model-systems: A, B and C.

Previous investigations[9] confirmed that the mixture of raw materials *H* and *M* in the specific mass ratio ($H/M = 1/3$) gave the industrial product, roof tile, which failed in wet and freezing environments. The chemical compositions of fresh and used roofing tiles from this bacth (Table 2) show the difference in the content of SO_3, which might be considered as an important factor in the deterioration phenomena in the system.

Model systems A, in the form of polyhedra ($10 \times 10 \times 60$ mm), were prepared using calcined *H* and *M* raw material, calcium hydroxide and water

Table 1. Chemical composition of raw materials *H* and *M*

Component	*H* raw material	*M* raw material
L.O.I.	17.70	10.57
SiO_2	46.29	54.36
Al_2O_3	11.74	21.13
Fe_2O_3	2.64	3.91
CaO	13.54	0.56
MgO	4.63	3.55
K_2O	2.35	4.08
Na_2O	0.89	1.56
Sum.	99.75	99.72

(standard procedure for pozzolanic activity determination, ASTM C311/77). The calcination of raw materials has been done in a laboratory kiln ($T = 960°C$, firing time 2 h) and the obtained samples were ground to obtain the desired particle size (< 63 μm). The ratio of calcined raw material (CRM) to calcium hydroxide was 2.33, and the ratio of water to solid components was 0.65. These mixtures were cast into Plexiglas moulds and cured in water for 2, 7 and 28 days at 24°C. After defined time of curing, mechanical testing of obtained polyedra was done (Fig. 2).

Model systems B, homogeneous samples, were formed from the mixtures of calcium carbonate, peat component and purified *H* and *M* clay raw material in different ratios (Table 3). Purification was performed by wash sieving procedure ($d = 63$ μm), aimed to enrich the raw material with clay minerals (Table 4). The obtained samples, pressed under 10.5 MPa (diameter of die, $d = 25$ mm, mass of sample 1 g) and calcined at 960 °C for 2 h, were exposed to real atmospheric conditions. The contents of acidic oxide, SO_2 (0.0006 up to 0.345 mg/m^3) and the variation of temperature of the environment (−13°C up to +8.4°C) have been followed for a period of 45 days (January–March).

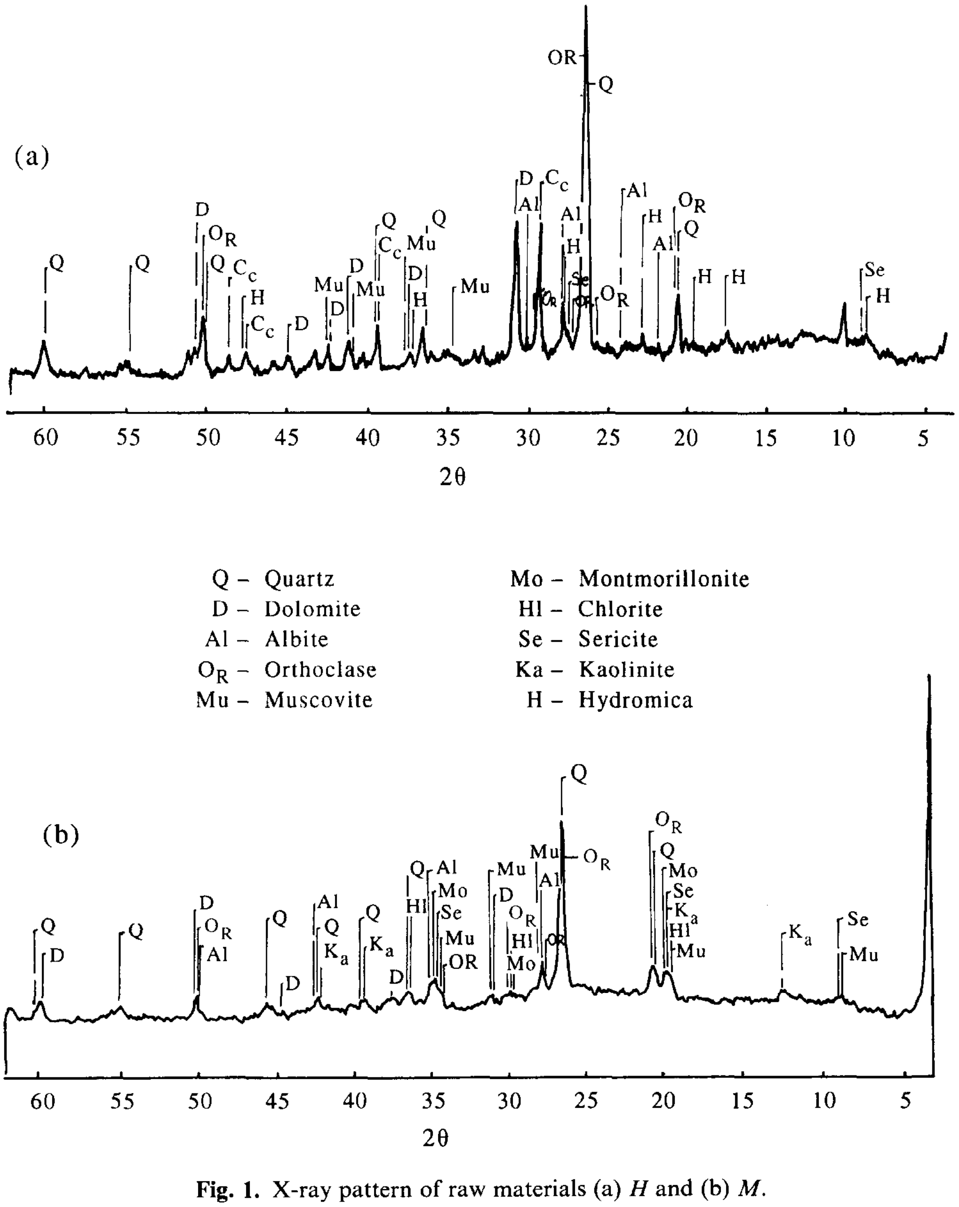

Fig. 1. X-ray pattern of raw materials (a) *H* and (b) *M*.

Table 2. Chemical composition of fresh and used roofing tile

Component	Fresh tile	Used tile
L.O.I.	0.74	0.68
SiO_2	60.89	61.10
Al_2O_3	15.41	15.61
Fe_2O_3	6.26	6.61
CaO	8.83	8.31
MgO	3.44	3.44
SO_3	0.24	0.34
K_2O	1.38	1.40
Na_2O	2.35	2.37
Sum.	99.54	99.86

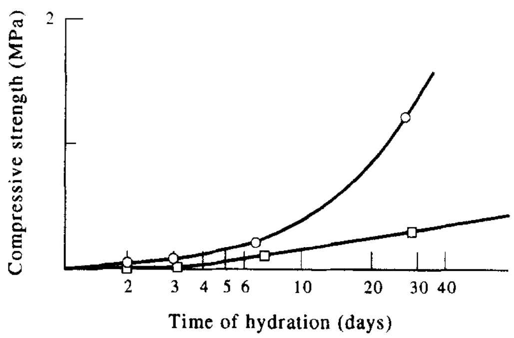

Fig. 2. Compressive strength of systems A prepared using calcined *H* and *M* raw materials. (□) *H* calcined raw material + portlandite; (○) *M* calcined raw material + portlandite.

Table 3. The results of XRD and SEM investigations of model systems B and C after exposure to atmospheric conditions

Type of model	Mass ratio Clay/Peat/$CaCO_3$	Cryst./Amorph. ratio in initial sample	Type of crystalline phase in the model system
Hydromica model system (*H*)	1/0/1	70/30	Calcium silicate hydrate(C_1); Hydrogarnet*; Scawtite*; $Ca(OH)_2$; $CaCO_3$
	2/2/1	64/36	Calcium silicate hydrates(C_1, C_2, C_3); Cancrnite*; $CaSO_4$; $CaSO_4x1.5H_2O$;$CaSO_4x2H_2O$;$Ca(OH)_2$; $CaCO_3$
Montmorillonite model system (*M*)	1/0/1	67/33	Calcium silicate hydrates(C_1, C_2); Hydrogarnet; Margarite*; Zeolite* (Lawbonite)
	1/2/2	57/43	Hydrogarnet; Margarite; Zeolites (Gismondine, Epistilbite, Jugawaralite, Scolezite, Analcite);$CaSO_4$
	2/1/2	63/37	Calcium silicate hydrates(C_1, C_2); Cancrinite; Margarite; Zeolites (Lawbonite, Laumontite, Epistilbite, Jugawaralite); $CaSO_4$; $CaCO_3$
	2/2/1	58/42	Zeolites (Laumontite, Gismondine, Heulandite, Epistilbite); Cancrinite; $CaSO_4$; $CaSO_4x2H_2O$

* Hydrogarnet, $3CaO\ Al_2O_3x6H_2O$; Skawtite, $5CaO\ 6SiO_2\ CaCO_3x2H_2O$; Vishnevite, $Na_8Al_{12}Si_{12}O_{24}SO_4x3H_2O$; Margarite, $CaO\ 2Al_2O_3\ 2SiO_2xH_2O$; Lawbonite, $CaO\ Al_2O_32SiO_2x2H_2O$; Laumontite, $CaO\ Al_2O_3\ 4SiO_2x4H_2O$; Gismondine, $CaO\ Al_2O_3\ 2SiO_2x4H_2O$; Heulandite, $CaO\ Al_2O_3\ 7SiO_2x6H_2O$; Epistilbite, $CaO\ Al_2O_3\ 6SiO_2x5H_2O$; JugawaraliteCaO $Al_2O_3\ 5SiO_2x4H_2O$; Scolozite, $CaO\ Al_2O_3\ 3SiO_2x3H_2O$; Analcite, $CaO\ Al_2O_3\ 4SiO_2x2H_2O$; Cancrinite(Na, Ca, K)$_8$ (Al, Si)$_{12}O_{24}(SO_3,CO_3)x3H_2O$. Calcium silicate hydrates: C_1 $2CaO\ SiO_2x0.35H_2O$; C_2 $2CaO\ SiO_2xH_2O$; C_3 $2CaO\ SiO_2x0.5H_2O$

Model systems C, sandwich model systems, prepared from components as in the case of homogeneous B model samples, with particle sizes below 63 μm, but composed of layers of clay/Ca-carbonate/peat (total mass of sample 1 g, $p = 10.5$ MPa). These models simulated the inhomogeneous parts in the industrial products. Parameters of calcination and acidic treatment were the same as in the case of the B models.

Table 4. Chemical composition of purified raw materials *H* and *M*

Component	*H* raw material	*M* raw material
L.O.I.	17.98	9.90
SiO_2	47.47	56.56
Al_2O_3	5.74	19.65
Fe_2O_3	6.39	7.75
CaO	13.65	0.56
MgO	7.05	2.86
K_2O	1.66	2.87
Na_2O	0.17	0.14
Sum.	100.11	100.29

After the specified period of exposure to atmospheric conditions, the model systems B and C were analysed by X-ray diffraction (Table 3) and SEM (Figs 3 and 4). The latter method, in the case of C model systems, was used for certain samples only. The choice of the samples has been made on the basis of X-ray diffraction and SEM investigations of the homogeneous model systems B. The presence of specified crystalline forms within the structure of the model systems with specific ratios of components has been confirmed (Table 3).

3 RESULTS AND DISCUSSION

The chemical composition of raw materials *H* and *M* (Table 1), was the basic parameter for the designing procedure of model systems A. Average values of compressive strength of model systems A (Fig. 2) as controlling parameter, confirmed their pozzolanic activity. In the next step of investigation, this property together with chemical compositions

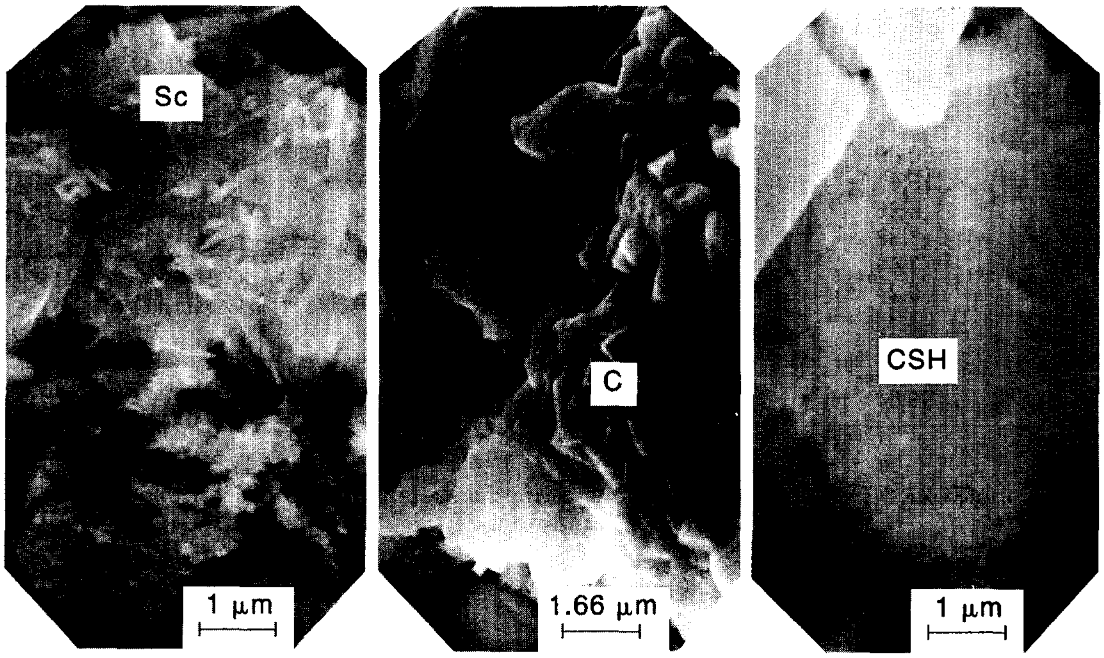

Fig. 3. SEM images of the model systems containing *H* clay component: (a) 1/0/1 model system; (b) 2/2/1 model system. (Sc) scawtite; (C) cancrinite; (CSH) calcium silicate hydrate.

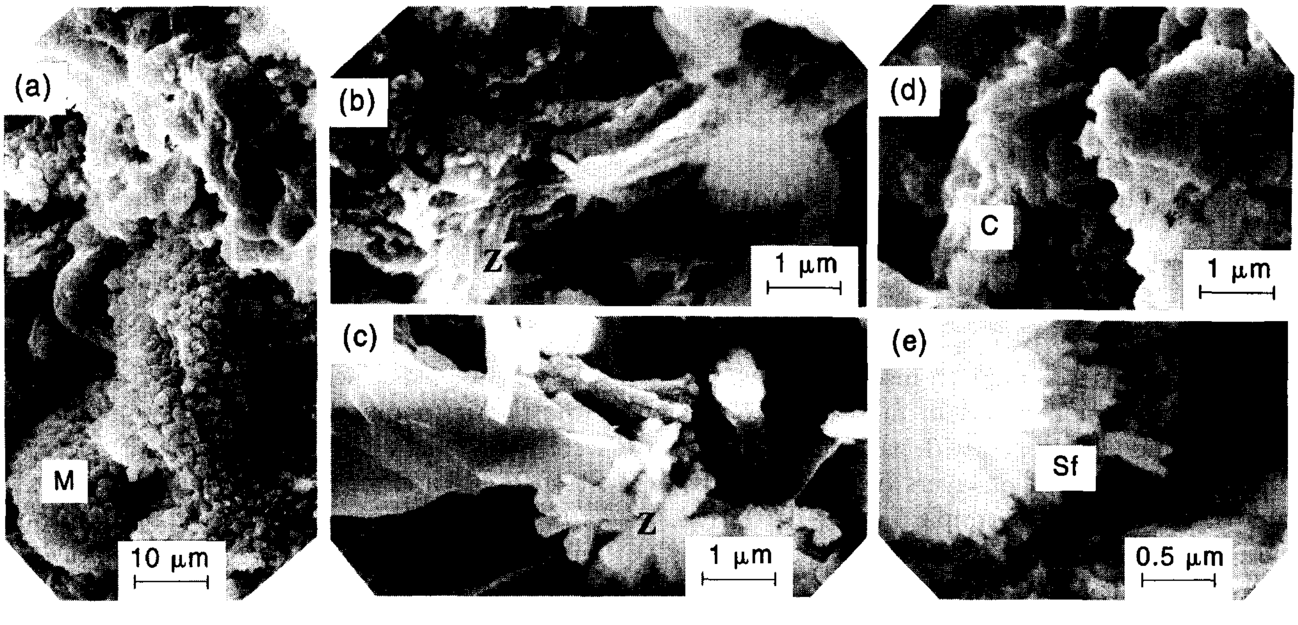

Fig. 4. SEM images of the model systems containing *M* clay component: (a) 1/0/1 homogeneous model; (b) 2/1/2 homogeneous model; (c) 2/1/2 sandwich model; (d) 2/2/1 homogeneous model; (e) 2/2/1 sandwich model. (M) Aggregates of margarite crystals; (Z) zeolite crystalline phases; (C) cancrinite crystal form; (Sf) crystals of Ca-sulphate in the model.

(Table 3) was used in developing the systems B and C. These samples (B and C) were exposed to atmospheric conditions. The XRD and SEM analyses of the samples, after a defined time of exposure, identified a number of new crystalline forms (Table 3, Figs 3 and 4).

The destruction of initial hydromica clay mineral lattice during calcination was the basic parameter for obtaining calcium silicate and aluminate hydrates, as well as scawtite crystal form, obtained in the model system 1/0/1 (Fig. 3(a)). The next model system, 2/2/1, of the same group is characterized by the absence of crystals of hydrogarnet (calcium aluminate hydrate) and the presence of new crystalline forms as $CaSO_4$, $CaSO_4{\times}1.5H_2O$, $CaSO_4{\times}2H_2O$ and crystals of cancrinite (Fig. 3(b)). The presence of $Ca(OH)_2$ and $CaCO_3$ phases, in both model systems, is the result of the unfinished process of hydration. The absence of hydrogarnet form, in the case of 2/2/1 model system, and the formation of crystalline phases containing SO_4 ions (cancrinite, $CaSO_4$, $CaSO_4 \times 1.5H_2O$ and $CaSO_4 \times 2H_2O$ forms) are the consequence of the presence of peat component in the initial system. This component, during the period of burning process, is the real source of SO_2 and SO_3 phases in the analysed model systems. These gases entering the structure of calcium silicate hydrates ($2CaO\ SiO_2\ 0.35 \times H_2O$; $2CaO\ SiO_2 \times H_2O$ and $2CaO\ SiO_2 \times 0.5H_2O$) (Fig. 3(c)) supported the elucidation of crystalline phases as cancrinite and vishnevite.

Deterioration of model samples containing montmorillonite (*M* type) clay mineral, thermally treated at 960°C, was different from the phenomena in the case of the previous group of models. This fact is in connection with the particular chemical composition of the *M* type clay, which causes the appearance of new crystalline like forms: margarite and zeolite crystalline phases (Fig. 4 (a)–(e)). The group of zeolite crystals (lawbonite, laumonite, gismondine, heulandite, epistilbite, stilbite, jugowaralite, scolozite, analcite and analcime) were identified by X-ray analysis (Table 3). The formation of zeolite forms containing CaO is the consequence of the destruction phenomenon of calcium silicate hydrates, formed in the early period of hydration in these ceramic systems. The ratio of components in model samples has the greatest influence on the type of zeolite form, which emerges from the ceramic system after its contact with water (Table 3, Fig. 4(b) and (c)).

The parameter that complicates the whole situation is the level of acidity of the environment. The presence of SO_2, SO_3 and CO_2 plays the main role in the appearance of $CaSO_4$, $CaSO_4 \times 2H_2O$, cancrinite, vishnevite and scawtite crystalline forms. Sulphuric acid, formed after the reactions of SO_2 and SO_3 with the defined quantity of moisture present in the systems, transforms the crystals of calcium silicate hydrate into an assemblage of amorphous silica, gibbsite and gypsum. In this way, the reactions progressively change the starting microstructure of the systems, giving $CaCO_3$ and gypsum form as a result, supporting the deterioration process of the heavy clay materials by the pressure of crystallization.

4 CONCLUSIONS

The pressure created during the formation of calcium silicate hydrates, cancrinite, hydrogarnet, scawtite and zeolite crystals, as well as transformation of the latter phase into $CaCO_3$, $CaSO_4 \times 2H_2O$ and $CaSO_4$, are the main causes of the deterioration phenomena.

Hydromica type clay mineral has been the basis for the formation of calcium silicate hydrates, montmorillonite type for zeolite crystalline phases.

The ratio, of the raw components in the investigated models, simulating the specific crystalline structure of roof tiles, are identified as the initial cause and the main factor of the wide range of crystalline phases formed during particular processes of hydration and zeolitation.

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