DEGRADATION OF BRICKS AND TILES

PART 2 - A REVIEW OF MATHEMATICAL MODELS

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INTRODUCTION

Mathematical modelling of degradation processes provides a useful tool for investigating the phenomena. The obtained models enable description of particular system behaviour. They, also, enable a kind of generalization when applying to analogous systems. Once defined mathematical model can be used for numerical simulation of material response to the variable environmental conditions. The results of such a simulation can be used for an optimization as well. The suggestions about quantities of particular raw materials, or about sintering temperature, or about duration of sintering process, etc. (as it is illustrated by few examples in this paper) might be obtained.

Formulation of rigorous mathematical models (such as kinetic models on solid state reactions) requires accurate knowledge on mechanisms of deterioration, which is only sometimes the case. Often, various assumptions, simplifications and idealizations have to be accepted, which leads to approximate models. Typical example is thermodynamic analysis of one-by-one chemical reaction. Finally, there are models (such as D-R functions, frost attack models, etc.) established by pure statistical processing of measured data. Although less rigorous, they can give useful information about system behaviour.

Either the chosen model is rigorous or it is approximate, the valuable source of information is experiment which simulates the degradation. A quantification of the degradation processes is carried out by employing numerous experimental techniques and methods. Differential thermal analysis (DTA) identifies endothermal and exothermal effects typical of phase and/or chemical transformations due to heating. Methods for quantitative and/or qualitative identification of the present phases (such as x-ray diffraction analysis, microscopy, etc.) are useful. Also, the well-known classical methods of chemical analysis are suggested. Data about system porosity are particularly important for better understanding of the degradation. Adequate analytical methods give the information concerning total porosity and porous structure, which includes: shapes of pores, distribution of their volumes, surfaces and diameters, connections among them, etc. Finally, the methods for characterization of final ceramic products, whether required by standard investigation procedures or not, are suitable. For example, methods for measuring compressive- and flexural- strengths and methods for testing water absorption, when comparatively applied to corroded and un-corroded samples, can give essential information. Also, the methods, particularly introduced for degradation examining (as freezing and thawing cycling), are proposed.

Having in mind that this paper considers chemical- and physical degradation of bricks and tiles, following classification of reviewed mathematical models is suggested: 1. chemical degradation models and 2. frost attack models. The chemical models are classified, according to two opposite approaches, into: 1. thermodynamic models and 2. kinetic models. Both groups of chemical models include rigorous as well as approximate models.

THERMODYNAMIC MODELS

Thermodynamic models answer the question which composition of the system can be expected at the end of its deterioration. These models are based on the well-known thermodynamic criterion for equilibrium state which requires minimum of the Gibbs free energy, at given T and P. The criterion can be applied either for determining spontaneity of particular chemical reaction or for defining composition of the entire system. First approach is partial while the second one is general. In both cases, the Gibbs free energies of formation of relevant compounds are required. The reliable sources of thermodynamic data are JANAF tables [1] and similar publications [2, 3].

Thermodynamic analysis of particular chemical reactions

All the degradation processes are spontaneous. This can be proved by calculating the total Gibbs free energy of particular reaction:

$$\Delta G_{\text{reaction}} = \Sigma\Delta G^0_{\text{products}} - \Sigma\Delta G^0_{\text{reactants}} \,, \qquad (1)$$

where $\Delta G^0_{\text{products}}$ and $\Delta G^0_{\text{reactants}}$ are the Gibbs free energies of formation of particular species. In the case when $\Delta G_{\text{reaction}} > 0$ the reaction is not spontaneous and does not occur. But, when $\Delta G_{\text{reaction}} < 0$, reaction takes part spontaneously.

As an example, degradation of feldspar into the micas can be described by the reaction:

$$3KAlSi_3O_8 + 12H_2O + 2H^+ \Rightarrow$$
$$\Rightarrow KAl_3Si_3O_{10}(OH)_2 + 6H_4SiO_4 + 2K^+ \qquad (2)$$

$(\Delta G_{\text{reaction}} = -1.017 \text{ MJ mol}^{-1})$.

Since $\Delta G_{\text{reaction}} = -1.017 \text{ MJ mol}^{-1}$ this reaction is spontaneous. Further degradation processes may convert secondary micas into hydroximuscovite- illite, which K^+ ions can be washed away thus giving kaolinite:

$$\underset{\text{hydroximuscovite}}{4KAl_3Si_3O_{10}(OH)_2} + 6H_2O + 4H^+ \Rightarrow$$
$$\Rightarrow \underset{\text{kaolinite}}{3Al_4Si_4O_{10}(OH)_8} + 4K^+ \qquad (3)$$

$(\Delta G_{\text{reaction}} = -0.017 \text{ MJ mol}^{-1})$.

In such a way, diopside, albite, gehlenite and similar high- temperature minerals with alkali- and earth-alkali- metals can alter as well. Ristić and Gržetić [4] applied thermodynamic analysis while investigating the degradation phenomena on bricks and tiles from the Middle Ages Serbian monasteries. From reliable sources it was found that they had been sintered at rather low temperatures (near 900 °C). It is useful to know that Serbia has continental type of climate. It is characterized by very hot and dry summers and very cold and wet winters, with average water precipitates at a level of 500 - 1000 mm per year. Under these conditions, degradation of diopside can be ended by kaolinite (reaction (4)), or by muscovite (reaction (5)). As for gehlenite, it can give muscovite (reaction (6)) or kaolinite (reaction (7)):

$$2CaMgSi_2O_6 + 2Al_2O_3 + 2CO_2 + 4H_2O \Rightarrow$$
$$\Rightarrow Al_4Si_4O_{10}(OH)_8 + 2CaCO_3 + 2\,MgCO_3 \qquad (4)$$

$(\Delta G_{\text{reaction}} = -0.980 \text{ MJ mol}^{-1})$,

$$3CaAl_2Si_2O_8 + 2K^+ + 3CO_3^{2-} + 2H^+ \Rightarrow$$
$$\Rightarrow 2KAl_3Si_3O_{10}(OH)_2 + 3CaCO_3 \qquad (5)$$

$(\Delta G_{\text{reaction}} = -0.384 \text{ MJ mol}^{-1})$,

$$3Ca_2Al_2SiO_7 + 3SiO_2 + 3CO_2 + 2K^+ + 3CO_3^{2-} + 4H^+ \Rightarrow$$
$$\Rightarrow 2KAl_3Si_3O_{10}(OH)_2 + 6CaCO_3 \qquad (6)$$

$(\Delta G_{\text{reaction}} = -0.501 \text{ MJ mol}^{-1})$,

$$2Ca_2Al_2SiO_7 + 2SiO_2 + 4CO_2 + 4H_2O \Rightarrow$$
$$\Rightarrow Al_4Si_4O_{10}(OH)_8 + 4CaCO_3 \qquad (7)$$

$(\Delta G_{\text{reaction}} = -0.160 \text{ MJ mol}^{-1})$.

Degradation of silicate materials is always followed by increase of degree of polymerization of SiO_4^{4-} tetrahedrons. During polymerization, certain quantity of crystal water (as OH^- groups) incorporates into silicate lattice of newly formed compounds. All the reactions (2)-(7) are spontaneous. Taking gehlenite as an example, degradation processes (reactions (6) and (7)) towards mica and kaolinite are possible. Not only that they occur spontaneously but alteration of gehlenite to mica is more probable than its alteration to kaolinite. The reason lies in the fact that: $\Delta G_{\text{reaction 5}} < \Delta G_{\text{reaction 6}}$. However, degradation of mica to kaolinite (reaction (3)) is also a spontaneous process, which very frequently happens in nature.

Degradation of zeolites, in the presence of water, is rather similar. As an example, gismondine degrades to kaolinite in accordance with the reaction:

$$\underset{\text{gismondine}}{2CaAl_2Si_2O_8} + 4H_2O + 2CO_3^{2-} + 12H^+ \Rightarrow$$
$$\Rightarrow \underset{\text{kaolinite}}{Al_4Si_4O_{10}(OH)_8} + 2CaCO_3 + 6H_2O \qquad (8)$$

$(\Delta G_{\text{reaction}} \cong -2.2 \text{ MJ mol}^{-1})$.

Thermodynamic analysis of complete system

Beside the thermodynamic analysis based on the comparison of free energies of particular reactions, there is more general approach. It does not require precisely defined chemical model of degradation processes. Only a list is needed for available reactants as well as potentially obtained products. Values of the Gibbs free energies of all these species are input data. Qualitative and quantitative composition, after the destruction, will be obtained by minimization of the total Gibbs free energy.

The method can be demonstrated by a simple example [6]. The simple model- system was exposed to the influence of acidic environment and an equilibrium composition was estimated. The results obtained by measurements [5] were taken as data. The raw materials were almost pure kaolinite (92 wt.%) and $CaCO_3$ (p.a.). Their mass ratio was 4 : 1, which corresponded to following molar ratio: 1.55 : 1. The samples were pressed and calcinated at 960 °C for 2 hours. During the calcination kaolinite transformed into metakaolinite while $CaCO_3$ transformed into oxide. So, the reactants (for a degradation process) were: 1.55 mol metakaolinite and 1 mol CaO. The degradation was simulated in a closed cell where the samples were exposed to an influence of mixture of gases (SO_2 and SO_3) in wet atmosphere. Gas concentration was approximately 2 (mg m^{-3}).

On the other hand, composition of the system was determined by XRD- and SEM- methods, after 60 and 100 days. All identified phases are shown in table 1.

Table 1. Experimentally determined composition of the system after 60 and 100 days.

index	name	formula
After 60 days		
1	margarite	$CaAl_4Si_2O_{11}$ H_2O
2	gismondine (zeolite)	$CaAl_2Si_2O_8$ $4H_2O$
3	jugawaralite (zeolite)	$CaAl_2Si_5O_{14}$ $4H_2O$
4	CSH (C_2)	$Ca_3Si_2O_7$ H_2O
5		$CaSO_4$ $2H_2O$
After 100 days		
6	lawbonite (zeolite)	$CaAl_2Si_2O_8$ $2H_2O$
7	CSH (C_1)	Ca_2SiO_4 $0.35H_2O$
	CSH (C_2)	$Ca_3Si_2O_7$ H_2O
8	CSH (C_3)	$Ca_3Si_2O_7$ $2H_2O$
	scawtite	$Ca_6Si_6CO_{20}$ $2H_2O$
		$CaSO_4$
		$CaSO_4$ $2H_2O$

The reactions that take place during the corrosion can be presented by following, general equation:

$$1.55\ \text{metakaol.} + 1\text{CaO} \xrightarrow{\text{(In the presence of } SO_4^{2-} \text{ and } H_2O)} x_1\ \text{marg.} + \\ + x_2\ \text{gismond.} + \ldots + \\ + x_9\ CaSO_4\ 2H_2O + x_{10}\ \text{metakaol.} + x_{11}\ \text{CaO} \quad , \qquad (9)$$

where x_1 - x_9 denote moles of the products (which indexes are given according to the table 1) while x_{10} and x_{11} are moles of the remaining reactants.

Thermodynamic - mathematical model consists of following parts:

Objective function:

$$\Delta G_{TOT} = \sum_{i=1}^{9} x_i \Delta G_i + (1.55 - x_{10}) \Delta G_{KAOL.} + \\ + (1 - x_{11}) \Delta G_{CaO} \Rightarrow \min \quad . \qquad (10)$$

Constraints (balances of all kinds of atoms):

$$\sum_{i=1}^{9} \nu_{i,j} x_i + (1.55 - x_{10}) \nu_{10,j} + (1 - x_{11}) \nu_{11,j} = n_{INIT,j} \\ j = 1, 4 \quad , \qquad (11)$$

where $\nu_{i,j}$ denotes number of atoms of the j-th kind in the i-th compound and ΔG_{TOT} is the Gibbs energy of the whole system. Atoms which balances are taken into account are: Al, O, Ca and Si, whereby quantities of both SO_4^{2-} ions and water are unconstrained.

Additional constraints:

$$x_{10} \leq 1.55 \quad \text{and} \quad x_{11} \leq 1 \quad . \qquad (12)$$

All necessary details can be found in the paper [6]. The solution of the model indicates that the most stable compounds in the system are: *1 $CaSO_4$ $2H_2O$ + + 1.55 kaolinite*. All hightemperature minerals, obtained in the calcination process, decomposed with time in the acidic environment into gypsum and kaolinite. Obviously, states of the system after 60 and 100 days of corrosion are temporary (non equilibrium). Appearance of scawtite in experimental results is probably a consequence of presence of remaining $CaCO_3$ (which is in a collision with thermodynamic expectations). Also, experimentally identified CSH-compounds and zeolites (including thermodynamically most probable gismondine) are present only as intermediate forms (see the reaction (8) and the paper [6]). In this way, a suggestion of the group of authors [5] - that presence of CaO in the system is main cause of its chemical corrosion - is proved.

KINETIC MODELS

Investigations on kinetics of chemical degradation of building materials are almost at the beginning. However, degradation of selected minerals with alkali- and earth-alkali- metals was thoroughly investigated in early eighties. The minerals were considered as acceptors of rejected radioactive elements - waste materials from nuclear power plants. Thanks to the mentioned investigations, very precious kinetic data were acquired. They can be used for solving some kinetic problems of degradation of bricks and tiles [7,8]. As it will be shown, kinetic models can be rigorous, based on description of reaction mechanisms. However, due to the lack of information related to mechanisms, kinetic models which apply a degree of deterioration are introduced.

Rigorous kinetic models

Kinetics of dissolving of solid particle

One of the simplest rigorous kinetic models was suggested by Lasaga [7]. He proposed a model which considers dissolving of small particle of mineral in water. It is based on the assumptions that the degradation rate depends on following factors: *pH* value, temperature and dissolution constant- k for particle in contact with water. The constants are given in table 2.

So, if k_i (mol m^{-2} s^{-1}) represents rate constant of dissolution of i- th mineral than decrease of number of its moles (n_i) will be proportional to the surface of spherical particle ($4\ \pi r_i^2$):

$$-dn_i / d\tau = 4\ \pi r_i^2\ k_i\ . \qquad (13)$$

Multiplied by the molar volume V_i^0 , equation (13) gives change of particle real volume ($V_i = n_i\ V_i^0$):

$$-dV_i / d\tau = 4\ \pi r_i^2\ k_i\, V_i^0\ . \qquad (14)$$

On the other hand, volume of spherical particle is as follows: $V_i = 4/3\ \pi r_i^3$. Time derivative of this quantity will be obtained by differentiation:

$$dV_i / d\tau = 4/3\ \pi 3 r_i^2\ dr_i / d\tau. \qquad (15)$$

Since: $4\ \pi r_i^2\ k_i\ V_i^0 = -\ 4\ \pi r_i^2\ dr_i / d\tau$, equation which defines reduction of particle radius due to dissolution is obtained:

$$-dr_i / d\tau\ = k_i\ V_i^0\ ,$$

$$-\int_{r_i^0}^{r_i} dr_i = k_i\ V_i^0 \int_0^{\tau} d\tau \Rightarrow r_i^0 - r_i = k_i\ V_i^0\ \tau\ . \qquad (16)$$

So, if radius of one particle at the beginning of dissolution process (τ = 0) has r_i^0 value and at the end of the same process ($\tau = \tau$) has r_i value than period of time (τ), necessary for reducing size of each particle from r_i^0 to r_i , can be easily estimated from equation (16). By applying described model "life time" of all the minerals listed in table 2 was predicted.

"Life time" data give real picture about the rate of degradation processes - they are slow but take place. Presented data are very important with respect to kinetics of degradation processes of compounds obtained by sintering, since certain minerals from table 2 exist in bricks and tiles. For example, anortite, which "life time" is very short, appears during sintering (together with diopside) in small quantities. But even these small quantities might initialize degradation.

Kinetics of solid state reactions in the presence of liquid and/or gas phase

Deterioration of building materials might be regarded as the solid state reactions that occur at the surface of solid particle in the presence of gas and/or liquid phase. This allows following assumptions. Reaction starts by nucleation when molecules from gas and/or liquid phase meet solid particle. The nucleation was considered by Avrami [16] and Erofe'ev [17] who suggested the theoretical equations:

Table 2. Average rate of release of SiO_2 from chosen minerals during degradation processes and their average "Life time". (size of particle: 1 mm^3, *pH* = 5, t = 25 °C)

mineral	formula	average rate (mol m^{-2} s^{-1})	average "Life time" (years)	ref.
quartz	SiO_2	4.10×10^{-14}	34.000.000	[9]
muscovite	$KAlAl_2Si_3O_{10}(OH)_2$	2.56×10^{-13}	2.700.000	[10]
forsterite	Mg_2SiO_4	1.20×10^{-12}	600 000	[11]
K-feldspar	$KAlSi_3O_8$	1.67×10^{-12}	520 000	[12]
albite	$NaAlSi_3O_8$	1.19×10^{-11}	80 000	[13]
enstatite	$Mg_2Si_2O_6$	1.00×10^{-10}	8 800	[14]
diopside	$CaMgSi_2O_6$	1.40×10^{-10}	6 800	[14]
nepheline	$(Na,K)AlSiO_4$	2.80×10^{-9}	211	[7]
anortite	$CaAl_2Si_2O_8$	5.60×10^{-9}	112	[15]

$$\alpha = 1 - \exp\left[-(k_1\,\tau)^n\right] \qquad \begin{cases} n=2 \text{ Avrami} \\ n=3 \text{ Erofe'ev}\ , \end{cases} \qquad (17)$$

where α denotes the fraction of total products, formed to the time τ, while k_1 is the rate constant of nucleation. During time, available space at the reacting surface of particle decreases so that the reaction becomes phase- boundary controlled. The proposed model, for polysize system, is [18]:

$$\alpha_i = 1 - \left[1 - \frac{k_2\,\tau}{r_i}\right]^3,\ i = 1, n \Rightarrow \alpha = \sum_{i=1}^{n} g_i\,\alpha_i\ , \qquad (18)$$

where r_i corresponds to the radius of i-th particle, while g_i is its mass fraction. Finally, products of degradation cover each particle thus forming a protective layer. So, diffusion through this barrier starts and lasts till the end of deterioration. It seems that this diffusion- controlled reaction is correctly described by Ginstling and Brounshtein [19]:

$$\alpha_i = 1 - \left[1 - \left(\frac{k_3\,\tau}{r_i^2}\right)^{1/2}\right]^3,\ i = 1, n \Rightarrow \alpha = \sum_{i=1}^{n} g_i\,\alpha_i\ . \qquad (19)$$

Deterioration is always governed by the slowest mechanism. Transition from one mechanism to another occurs when rate of one reaction becomes equal to the rate of the other. Data that are very difficult to acquire are kinetic constants. Attempts are made towards their calculation from the measured data [20].

Kinetic models with degree of deterioration

Fundamental concept of such models is a kind of quantification of the deterioration by introducing a degree of deterioration. Its cumulative increase with time gives information about system behaviour. As degree of deterioration, mass loss can be taken, as well as loss of mechanical characteristics, increase of quantity of some undesired compound (e.g., $CaCO_3$ in the case of carbonation), etc.

Model of Matsufuji, Koyama and Harada

The most general model was proposed by Matsufuji et al. [21]. The model intends to predict the degradation progress for various building materials. The degradation usually starts at the surfaces in contact with the environment. Therefore, the exposed parts are covered with the products of degradation (see figure 1). The surface between deteriorated and defect- free, internal parts is exposed to the influence of both the environmental factors at the outer surface and the characteristics of deteriorated parts:

$$pf = p0 + f(D, A)\ , \qquad (20)$$

where $f(D, A)$ is a function of two variables; D is degree of degradation and A is property of deteriorated part.

It can be assumed that the rate of degradation ($dD/d\tau$) is proportional to pf:

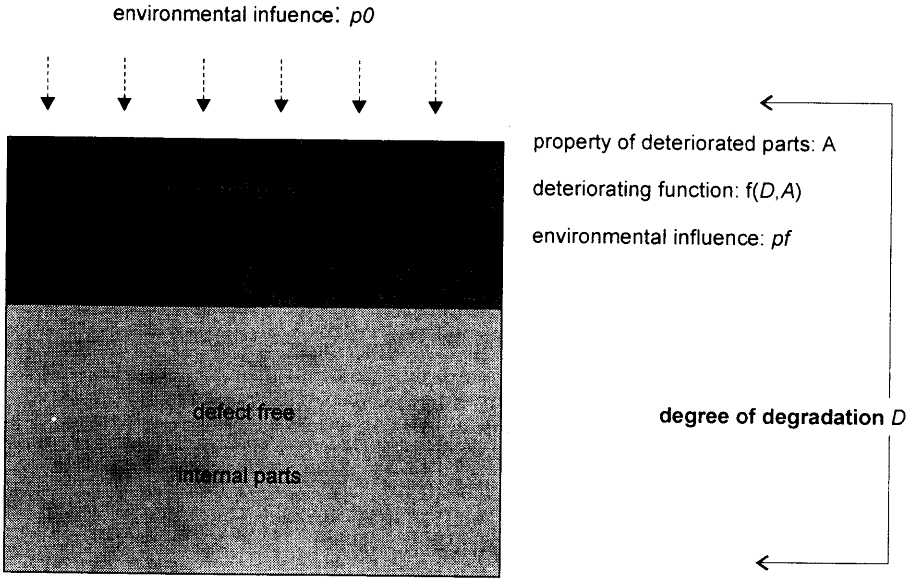

Figure 1. Progress of degradation and relevant factors.

$$\frac{dD}{d\tau} = kpf = k[p0 + f(D, A)] = b + aD \ . \qquad (21)$$

This is a general kinetic model with constants: a and b. They represent influence of deteriorated parts and influence of environment itself. The model has following solutions:

$$\frac{dD}{d\tau} = b + aD \Rightarrow \begin{cases} a=0 & D=b\tau \\ a\neq 0 & D=(b/a)[\exp(at)-1] \end{cases} . \qquad (22)$$

In accordance with the solutions (22), deterioration of all building materials can be classified into three patterns (as presented in figure 2):

Alignment type (a=0) has deterioration rate that does not depend of the current status of degradation. As an example, deterioration of floor concrete can be taken.

Convergence type (a<0) has gradually falling rate, due to preserving influence of layers of deteriorated material. This type is typical of carbonation progress in building materials.

Multiplication type (a>0) is an accelerated type of deterioration. Actually, deteriorated parts accelerate further degradation. As an example, periodical freezing and thawing can be taken.

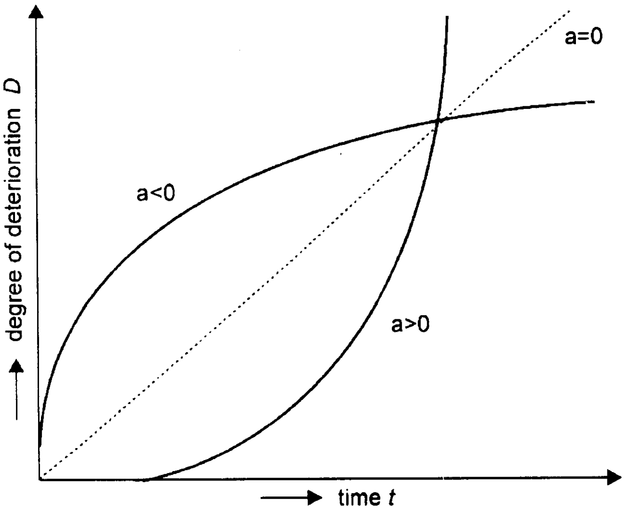

Figure 2. Three types of deterioration, according to Matsufuji et al. [21].

Dose - response (D-R) models

Response of material to the influence of any factor from the environment can be mathematically described by introducing so called "dose - response" functions. Such *D-R* functions has following form:

$$M = a\tau^{b} \ , \qquad (23)$$

where M is corrosion at time τ, while a and b are constants, calculated from measured data. Many studies have been performed both on national and international level to establish such functions [22-24]. A review of *D-R* functions can be found in Haagenrund's paper [22]. Here, 4-year dose - response function for unsheltered limestone is presented:

$$^{4}\mathrm{ML} = 34.4 + 5.96\mathrm{TOW}[\mathrm{SO_2}] + 338\mathrm{Rain}[\mathrm{H^+}] \ , \qquad (24)$$

where ML (g m^{-2}) denotes mass loss, TOW (hours $year^{-1}$) is time of wetness, $[SO_2]$ ($\mu m\ m^{-3}$) and $[H^+]$ (g l^{-1}) are concentrations while $Rain$ (m $year^{-1}$) is amount of atmospheric precipitation.

While investigating sulphate corrosion of Portland cement, Djuric et al. [25] applied *D-R* concept to describe concrete response to the influence of aggressive SO_4^{2-} ions. Data basis was acquired by measurements on three types of Portland cement with defined content of C_3A. The cements were examined pure and blended with 30 wt.% of fly ash. In this way, six systems were obtained. They were used for preparing test samples (10 × 10 × 30 mm prisms with cement/sand ratio 1/3.5 and water/cement ratio 0.4). The samples were moist cured *14* days and tested for flexural strength. Afterwards, according to the plan of experiments, the samples were immersed into two solutions with 1000 mg l^{-1} and 2000 mg l^{-1} of sulphate ions. Also, a referential group of samples was examined. These were immersed into water.

Corrosion process lasted 1, 2, 4 and 6 months. Afterwards, flexural strengths were measured and following corrosion resistance factors (*CRF*) were calculated:

$$CFR = \frac{\text{flexural strength of corroded sample}}{\text{flexural strength of the sample immersed into water}} \qquad (25)$$

Adequate *D-R* function have following form:

$$D = 1 - CRF \ , \qquad (26)$$

where D denotes dimensionless degree of deterioration. The *CRF* correlation was defined as a function of three independent variables:

x_1 (wt.%) content of C_3A compound in a mixture,

x_2 (month) time period of exposure,

x_3 (g l^{-1}) concentration of SO_4^{2-} ions.

Chosen *CRF* function has polynomial form:

$$CRF = \sum_{i=1}^{3} b_i x_i + \sum_{1 \le i < j \le 3}^{3} b_{ij} x_i x_j + \sum_{i=1}^{3} b_{ii} x_{ii}^2 \ , \qquad (27)$$

where *b* coefficients were obtained by the regression analysis as shown in table 3.

Ranking of the significances of particular coefficients (last column in table 3), shows that the third and the last coefficients have dominant influence to corrosion resistance. It means that the concentration of SO_4^{2-} ions is the most influential independent variable. Adequacy of the correlation (27) was tested by statistical methods (by ANOVA test and by time independent test) and satisfactory result was obtained.

Table 3. Coefficients of the *CRF* function (27).

coefficients		
symbol	value	significance
b_1	0.04525	0.0406
b_2	-0.05612	0.05211
b_3	1.64554	0.27127
b_{12}	-0.00404	0.00291
b_{13}	-0.00176	0.01116
b_{23}	0.01008	0.01548
b_{11}	-0.0036	0.00226
b_{22}	0.00458	0.00572
b_{33}	-0.57452	0.11112

PHYSICAL DEGRADATION

Frost attack

A relationship between frost resistance of brick and its total porosity as well as pore structure had been investigated by number of authors, but Maage [26] was first who made an attempt to express it in a mathematical form. He introduced the frost resistance factor *F*:

$$F = \frac{3.2}{VP} + 2.4\ VP3 \ , \qquad (28)$$

where *VP* ($cm^3\ g^{-1}$) denotes total volume of pores while *VP*3 (% of the total *VP*) represents volume of pores greater than 3 μm. The equation was derived by processing experimentally acquired data basis, on samples which specific surface values and porosity data were as follows:

$$0.65 \le S\ (m^2\ g^{-1}) \le 2.11 \ , \qquad (29)$$

$$0.045 \le VP\,(cm^3\ g^{-1}) \le 0.1505 \ ,$$
$$1.2 \le VP3\,(\%) \le 32.4 \ . \qquad (30)$$

When suggesting the correlation, Maage combined theoretical knowledge with pure statistical approach. Namely, his expression takes obviously into account a fact noticed by many investigators that total porosity as well as number of pores less than 3 μm has dominant influence on resistance of brick. So, both theoretical knowledge and empirical experience enable a selection of adequate type of the correlation, which coefficients (3.2 and 2.4) were obtained by the regression analysis.

According to Maage, resistant bricks have $F > 70$; those which are not resistant have $F < 55$, while bricks with questionable resistance have *F* factors between two boundary values. Application of expression (28) to some Yugoslav bricks, based on illitemontmorilonite clays and sandy- carbonate clays, gives rather low results indicating relatively low resistance to frost action. It was proved that CaO from carbonates significantly contributes to chemical corrosion. This brings us to a conclusion: low values for Maage's factors (in table 4) result from a combined effect of physical and chemical corrosion.

Table 4. Porosity data and calculated Maage's factors for some of Yugoslav bricks.

comp. mass fraction		sintering temperature	test*	*S*	*VP*	*VP*3	*F*
$x_{\text{illite-mont.}}$	$x_{\text{carbonat.}}$	(°C)		($cm\ g^{-1}$)	($cm^3\ g^{-1}$)	(%)	
0.573	0.427	960	before	1.49	0.140	7.65	41.2
			after	4.74	0.124	14.40	60.4
0.5	0.5	960	before	0.96	0.116	13.10	59
			after	1.34	0.120	7.44	44.5
		1000	before	2.12	0.124	12.24	55.2
			after	2.10	0.100	4.46	42.7
0.378	0.622	1000	before	1.48	0.145	8.42	42.3
			after	3.57	0.144	15.06	58.4

* Frost resistance of samples was tested by 30 cycles of freezing and thawing, in accordance with JUS B.D1.010 (1979).

Those who have criticized Maage's equation have mostly proposed lowering of critical diameter from 3 μm to 1.4 μm and lower [26].

Djuric et al. [28] demonstrated an application of Maage's equation as a part of a complex optimization model. Solution of the model suggests minimal energy consumption in producing bricks which are resistant to frost attack and posses acceptable other characteristics. The model was applied to: 1. two sets of Yugoslav bricks (which mechanical characteristics were controlled), 2. two sets of Canadian bricks (which water absorption was controlled) and 3. one set of Ohio- bricks (without any control with respect to other characteristics). The only independent variable was sintering temperature. Mathematical model was defined by processing of experimentally obtained data. The functions- parts of the mathematical model were defined:

$Q(t)$, energy consumption as a function of working temperature,

$VP(t)$ and $VP3(t)$, total and partial porosity as functions of temperature,

$F(t)$ in terms of: $VP(t)$ and $VP3(t)$, that is, from Maage's equation,

y_{COMP}, y_{FLEX}, y_{ABS} product characteristics as functions of sintering temperature.

The model, introduced for Yugoslav bricks, contained following parts:

Two objectives

$Q(t) \Rightarrow$ minimum

$F(t) \Rightarrow$ maximum

Constraints upon quality of product

$y_{\mathrm{COMP.\ STRENGTH}}(t) \geq y_{\mathrm{STANDARD\ COMP.\ STRENGTH}}$

$y_{\mathrm{FLEX.\ STRENGTH}}(t) \geq y_{\mathrm{STANDARD\ FLEX.\ STRENGTH}}$

Constraints upon temperatures

$t \geq t_{MIN}$

$t \leq t_{MAX}$

For one set of Yugoslav bricks [28], the optimization model has following form:

Two objectives

$-0.6543\ t + 1.9716 \times 10^{-3}\ t^2 \Rightarrow$ minimum

$68.7 + 1.8 \times 10^{-2}\ t \Rightarrow$ maximum

Constraints upon product quality

$12.278 + 2.896 \times 10^{-2} t \geq 25$

$23.220 - 4.9 \times 10^{-3} t \geq 2.5$

Constraints upon temperatures

$t \geq 900$ °C

$t \leq 1050$ °C

By solving the model, it was proved that even the lowest sintering temperature (and consequently the lowest energy consumption) guarantees obtaining a frost resistant product ($F = 85 > 70$).

By applying an analogy between phenomena that cause degradation of bricks and concrete, an attempt has been made towards defining a correlation that can be used for estimation of frost resistance of cements and concrete. So, a correlation, for frost resistance factor of cement (FC), was suggested:

$$FC = 11.2 \;/\; VP + 7.7VP3 \qquad (31)$$

after processing the data obtained by measurements conducted on samples made of Portland cement (pure and blended with 30 wt.% of fly ash), as presented in paper [29]. The samples have porosity data:

$$0.183 \leq VP\ (\mathrm{cm^3\ g^{-1}}) \leq 0.325\ ,$$
$$3.175 \leq VP3\ (\%) \leq 6.618\ . \qquad (32)$$

CONCLUSION

The models which simulate chemical degradation are based on thermodynamic and kinetic principles. They are complementary, i.e. both applied to the same system give complete picture about its behaviour related to degradation. Thermodynamic analysis of particular chemical reactions (one by one) is less accurate than complete analysis. Not only that complete thermodynamics gives more precise results but it does not require complete chemical model which is tremendous advantage. In both cases, providing of exact values of the Gibbs free energy of formation for all relevant compounds is serious problem.

Kinetic models of chemical reactions among solid material and gas and/or liquid surroundings have a correct theoretical background. They simulate three mechanisms (nucleation, phase boundary controlled reaction and diffusion controlled reaction) which correspond to three steps of any degradation process. However, there is a serious problem. All the models assume spherical shape of solid particles. However, building materials (as bricks and tiles) are porous systems which contain great number of pores, micro capillaries, tunnels, etc. In this case, the reacting surface has form of cylinders (of pores) instead of spheres (of particles). So, it would be useful to modify leading equations having this fact in mind.

There is a class of kinetic models which introduce a degree of deterioration. They simulate dynamics of deterioration by calculating this degree as a function of time and other relevant variables. Since the function (mathematical model) is obtained by using data acquired by measurements on particular system, it can be very precise. The problem is that the applicability of such models is limited to the particular system.

The equation which estimates resistance of bricks to frost attack is, also, derived by processing of measured data but number of experiments was rather great. Therefore, it can be applied to all bricks and tiles but the results are often questionable. Similar conclusion concernes the equation for estimation of concrete resistance to frost attack.

Degradation of bricks and tiles is very complex problem, not yet satisfactory explained. In spite of this fact, there is impressive number of mathematical models used to simulate the phenomenon. Great number of models do not have theoretical base. They were obtained by processing of measured data. Very small number of models are based on rigorous description of degradation, mostly because of lack of necessary knowledge about degradation mechanisms. It can be expected that further investigations on deterioration mechanisms will provide development of new, much more rigorous mathematical models.

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