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MODELLING OF PERMEABILITY IN CEMENT-BASED MATERIALS: PART 1-UNCRACKED MEDIUM

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ABSTRACT

For a correct prediction of structural durability, it is of first importance to know the transport properties of concrete. In a first section, results of a micromacro model to predict the water permeability of porous materials are presented. This model lays on the concept of a hierarchical lattice. The model is, in a first stage, applied to mortars. Thus it is extended and generalized to cement pastes and concretes. Numerical results are compared with data available in the literature. The model uses two phenomenological parameters: the former is related to the efficient porosity and the latter is related to tortuosity. These two parameters appear to be linked. © 1997 Elsevier Science Ltd

Introduction

Transfer properties of cementitious materials are a key factor for predicting their durability, since it has been shown that corrosion, leaching or carbonation are all related to the way a fluid can pour through the microstructure. Permeation (movement under a gradient of pressure) or diffusion (movement under a gradient of concentration) properties can also be directly related to the limit-state which has been defined for a structural element if limiting the movement of fluids is one of the functions the structure has to fulfill. We will focus on water permeability in this paper. This is the case for instance for dams or for toxic waste containers. In plain concrete, it has been shown that the macroscopic properties have to be, in some way, related to the porosity. It is from that idea that many tests have been developed for evaluating both porosity and permeability (1, 2). A fundamental problem is to relate results obtained on cement pastes (which are usually used for laboratory experiments) and expected properties of mortars and concretes. The solution of this problem requires a careful analysis of pertinent parameters and real mechanisms. Cracking will be treated in a second paper as this parameter can greatly affect the durability of cement-based materials (3, 4, 5).

Uncracked Cementitious Materials

The concept of 'uncracked material' means a cementitious material which has not been subjected, before the measurement of its transfer properties, to any external loading (like me-

chanical load, restrained shrinkage or heating...). At a micro-scale, some microcracks surely exist (due for instance to stress concentrations around agreggates) but they will not be distinguished from the porous structure, and their effect will be studied as that of equivalent pores. Another point is the possible misunderstanding coming with the comparison of different sets of materials-cement pastes, mortars, concretes-which can probably not be directly compared because of the various mechanisms and phenomena they involve (interfaces, pore network, ...) at a microstructural level. Despite this fact, it has been chosen to use the same way to model the microporosity of these different materials. A numerical model fed with experimental data coming from a mercury intrusion test will be built and described. Then it will be used for various cementitious materials and its results will be compared with permeability measurements. This approach will make possible to identify the degree of accuracy/predictibility of the model, the limits of its application field, and to objectively define some subclasses of materials within which submodels will possibly be defined.

Microstructural Information; Porosity; Available Data

The porous microstructure of cementitious materials is very complex, the size of pores varying from 10 angstroms (smaller gel pores) to 10 microns (larger micropores). Larger sizes, one generally considers to be in the domain of microcracking (6).

The measurement of the total porosity raises many questions: the measured value is highly dependent on the technique used (simple drying from saturated samples, mercury intrusion, replacement by a liquid...). The differences can reach 20% to 80% according to the conditions of water extraction (7, 8, 9). Any quantitative assessment of the porous microstructure needs a model, the more common being that of the mercury intrusion porosimetry (m.i.p.) in which the microstructure is considered as being constituted of many cyclindrical pores. Even if both the experimental technique and the model have been widely discussed [9], the data coming from m.i.p. are taken as the input. One problem is that the m.i.p. gives only poor information upon the structure of the porosity itself: how are the pores connected? What is their real geometry? If the transfer properties depend on this structure, useful information will obviously be lacking.

In the following, results given by our model will be compared with previously published results (Table 1). Water permeability and m.i.p. data are given.

In this paper K is the water permeation factor (in m/s, or in 10⁻¹³ m/s) and k is the intrinsic water permeability or the permeation coefficient (in m²)(10). These two parameters are both termed permeability for the sake of simplicity.

TABLE 1
Experimental Data for Comparison

| author | kind of material | method for porosity |
|--------------------|----------------------|---------------------|
| Danyushevsky [11] | cement paste, mortar | drying |
| Mehta [12] | cement paste | m.i.p. |
| Nyame [13] | cement paste | drying |
| Odler [14] | cement paste | drying - m.i.p. |
| Reinhardt [15, 18] | mortar | drying - m.i.p. |
| Jacobs [16] | concrete | m.i.p. |
| Halamickova [17] | cement paste, mortar | m.i <i>.</i> p |

Different Approaches for Linking Porosity and Permeability

The models can be classified following three classes:

- phenomenological models which relate the permeability to other(s) parameter(s), usually built after a statistical analysis of data,
- models lying on physical concepts, like percolation theory and using analytical or semiempirical developments,
- numerical models trying to reproduce the microstructure.

Phenomenological Models. Several authors have proposed "models" able to predict the permeability. Some of them, following the well known Archie's law used for conductivity have expressed the permeability as a power function of the porosity. For instance Danyushevsky (11) has written that the permeability varies as the porosity to the power 4.75. But the best example of such a model is that suggested by Mehta [12]:

$$K = \exp (3.84 V_1 + 0.20 V_2 + 0.56 10^{-6} TD + 8.09 MTP - 2.53)$$

where V_1 and V_2 refer to the volumes of two classes of pores, TD is the threshold diameter and MTP a modified total porosity. Even if the coefficient of correlation r^2 is equal to 0.95, the predictive power of such a model is low, since five coefficients have been fitted and since the author does not give any information on the way these parameters have to be modified if the context (material, curing, ...) changes.

On the whole set of data referred above (Table 1), the porosity can be correlated to the experimental permeability and assuming a power function under the form $K_{exp} = a p^b$, a linear relation can be established in a log-log diagram. The following results are obtained:

for cement pastes:

$$\ln (K_{exp}) = 9.50 + 5.95 \ln (p)$$
 $r^2 = 0.72$

for concrete and mortars:

$$ln (K_{exp}) = 9.47 + 3.10 ln (p) r^2 = 0.15$$

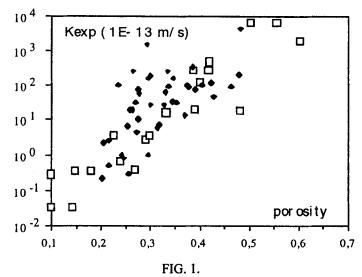
The correlation is poor but it can easily be improved if the porosity p is replaced by the paste porosity p' which is defined by:

$$p' = p / (1 - v_a)$$

where v_a is the volumetric ratio of aggregates (including sand particles). Replacing p by p' is making the assumption that the aggregates are non porous.

Thus, it follows for concrete and mortars:

$$ln (K_{exp}) = 10.80 + 6.41 ln (p') r^2 = 0.41$$



All materials. Correlation between experimental water permeability and porosity. White squares: cement pastes, black spots: mortars and concretes (porosity = effective porosity p').

and for the whole set of data:

$$\ln (K_{exp}) = 10.62 + 6.35 \ln (p') \quad r^2 = 0.64$$

A relatively high scatter remains (see Fig. 1) but this is at least partially due to problems of measurement of the porosity and permeability themselves, as discussed above. It can be noted that the power 4.75 mentioned in (11) is replaced by a power of about 6, which is slightly more. The permeability can also be related to the water cement ratio (w/c). On the same set of data, it has been found:

for cement pastes:

$$\ln (K_{exp}) = -5.39 + 14.73 \text{ w/c} \text{ r}^2 = 0.79$$

for concretes:

$$\ln (K_{exp}) = -1.26 + 8.94 \text{ w/c}$$
 $r^2 = 0.18$

The degree of correlation is quite good for cement pastes but becomes very low for concretes, suggesting that other factors affect the transfer properties. The predictive power of such a model, is a priori limited to materials comparable to those used for identifying the regression law. It is the reason why many works are now devoted to approaches using physical concepts.

Models Based on Physical Concepts. The first help coming from physics was the use of Poiseuille's law for describing the transfer of fluid at the pore scale. Carman and Kozeny have proposed a formula where the permeability is a function of the porosity and of a tor-

tuosity parameter, introducing the effect of the structure of porosity. But their results cannot be applied for cementitious materials (19, 20). The use of percolation theory lead Katz and Thompson to define a threshold pore diameter determined through m.i.p. that they relate to the permeability. Other authors define an equivalent radius from the pore distribution or a "relevant porosity" using arguments related to the flow rules (15, 16, 21) but the fact is that reverse engineering dominates and that the parameters are usually fitted for a good agreement with the experimental data. Recent works (22) show that accounting for the fluid viscosity effects and adsorption will completely modify the behaviour within small pores. In summary, it seems that the complexity of the microstructure is so high that it is not possible to deduce macroscopical properties from a simple flow rule at the micro-scale without trying to model the structure itself. It is the way more commonly followed nowadays.

<u>Numerical Models</u>. The basic idea is to map the material microstructure on a numerical support able to describe the relevant scales for the phenomenon which must be described, to write the good physical rules at the elementary level, and to let the computer make the whole job. Two kind of models can be considered:

Geometrical Representations of the Material. In which the structure is detailed trying to be in agreement with its geometry and topology. The models can be 2D or 3D, the more impressive works having been done in this field on granular media (40), but some results exist on cement paste. Anguy (23) has shown the effect of the structure of porosity, the permeability being highly dependent on the fact that the microstructure is spatially correlated or not, for a given total porosity. Winslow (32), referring to percolation theory has studied the effect of the transition zone on the global permeability. However, for cementitious materials, these approaches remain limited by the fact that it is not possible to describe all scales in the material (a cube of 3*3*3 cm³ of concrete contains about 500 000 tiny sand particles in (23) and it still can not be considered as a representative volume for concrete!).

Models Using a Network of Tubes. In this case, the real geometry is deleted and replaced by a set of (many) elements (tubes, spheres, ...) which assembling rules can vary. Using such models, Quénard (25) and Daian (26) have reproduced the hysteretic sorption in a mortar or the m.i.p. experiment. The limit of such models are fixed by both the validity of the physical description at the elementary level, the representativity of the network and the capacity of the computer.

A more detailed review has recently be published by Marchand and Gérard (10).

The Hierarchical Lattice; Description of the Model

Traditional euclidian lattices (the building rules respecting the euclidian geometry) are confronted with a difficult problem with cementitious materials when the description must include in the same global box elements whose sizes range from fine pore diameters (from 10 angstroems to 0.1 mm) to the specimen size (more than 10⁶ elements leading to very heavy computations with algorithmic problems). An elegant solution is to use a hierarchical lattice, built following a recursive rule, which lowers both requested memory and time computation. The main weakness of this kind of model will be to delete all geometry (in the euclidian meaning). Quantitative results have then to be taken cautiously. However, it will

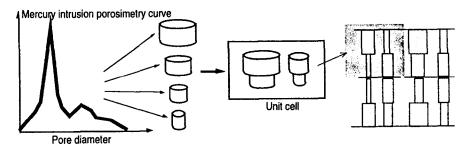


FIG. 2. Principle for building the hierarchical model.

be seen below that if this is true for mechanical problems [27, 28], it is not really a problem when modelling fluid transfer.

The numerical model consists in an ensemble of parallel tubes which are connected into a series and a parallel according veru simple rules:

- at the micro-scale (I = 1) N_1 tubes are considered. They are cylinders of unit length 1 and of random radius r_j (j = 1, N_1). r_j is drawn from the cumulated distribution of pore size (mip data) and its value is in the range 0- r_1 , limiting this distribution to the upper bound $r_{max} = r_1$. r_{max} corresponds to the elementary material scale, let us say l_1 ;
- the building hierarchical rule to get the scale (i + 1) from the scale i consists in to gather in two steps four elements of size l_i to make one of size l_{i+1} . In a first stage two elements i are grouped into a series. This is repeated once for two other elements. The two sets are put in parallel to build the element of size l_{i+1} (Fig. 2). This rule is repeated for all elements of size l_i and iteratively for all scales until all elements of elementary size l_1 are merged into 1 macro-element of total size l_N . It comes that $N_1 = 4^{N-1}$ is the total number of tubes in the model:
- during the building of the model at each scale the process refers to the cumulated distribution of pore size. Each of four elements of size l_i used to build one element of size l_{i+1} can:
 - be a single tube whose radius r is a random value such as $l_i < r < l_{i+1}$ and drawn from mip data;
 - be a 'sum' following an iterative process of elements of size $l_i < r$.

The choice between the two possibilities results from simple statistical rules detailed in (29).

The building process comes to its end when all data contained in the mip curve have been used.

The behaviour at the micro-scale follows a few simple physical laws (25, 26, 29). The Kelvin law (thermodynamical equilibrium between a liquid and its vapor) gives the critical radius under which the fluid is in a liquid form:

$$R_{c} = \frac{-2M\sigma(T)\cos\beta}{RT\Gamma_{1}\ln(HR)}$$

where M is the molar mass, T the absolute temperature, σ the surface tension, R the constant of perfect gases, HR the relative moisture, Γ_1 the volumic mass of the fluid and β the contact angle between solid and fluid.

For any moisture content, an adsorbed layer of liquid water reduces the efficient pore radius. This layer thickness is a function of relative moisture HR:

$$R_{eff} = r - b_{ad}(HR)$$

where r is the pore radius and bad is the layer thickness.

Depending on the value of R_{eff}/R_c ratio, the flow of water respects:

- the Fick's law (diffusion) if R_{eff} / Rc >1: $q_1 = -k_{vap}$ grad P_v , where P_v is the pressure of the vapor and k_{vap} the vapor permeability,
- the Poiseuille's law if R_{eff} / Rc < 1: $q_m = -k$ / μ grad P where P is the pressure and μ the viscosity.

Using the definition of relative humidity (HR = Pv / Pvsat), it is possible to sum both kinds of flow and to deduce an equivalent vapor permeability (29).

$$k_{vap} = \frac{\Gamma_1^2 R_{eff}^2}{8 \, \mu} \frac{RT}{M} \frac{1}{P_v}$$

The hierarchical model computes a global permeability K_0 which refers only to the pore space and does not accounts for the fact that: a) there is matrix around the pores, b) the real geometry/topology is complex and effects of connectivity/tortuosity can not be neglected. Thus some corrections have to be done before deducing the permeability k of the material.

Reinhardt (14) has expressed the permeability under the form:

$$K = a p^n r_e^2 (m/s)$$

where p is the total open porosity, r_e is an equivalent radius of the pore system and where a and n are two scalar coefficients related to the tortuosity and connectivity of the pores. This relation provides a good prediction of the permeability, with the problem that both a and n remain empirical parameters. Using a similar formula, the permeability of the material K is obtained from the computed permeability of the lattice K_o through:

$$K = K_o p'^n$$

where p' is the effective porosity and n is a scalar coefficient under which are summarized all the consequences of the real (not described in the model) structure of the pore system. We will come back later to the meaning of this coefficient and to the concept of efficient porosity.

| TABLE 2 | | | | |
|--------------|--------------|-----|---------|-----|
| Porosity and | Permeability | for | Various | w/c |

| w/c | total porosity | equivalent radius | experimental permeability |
|-------|-----------------|-----------------------|--|
| 1 _ 1 | (average value) | (10 ⁻¹⁰ m) | (average value 10 ⁻¹³ m/s and c.o.v.) |
| 0.4 | 0.175 | 517 | 6 62 % |
| 0.5 | 0.181 | 644 | 59 50 % |
| 0.6 | 0.186 | 885 | 90 12 % |
| 0.75 | 0.213 - | 2553 | 4340 34 % |

Application to Mortars

The first application of the model was to test its predictive abilities on the data that Reinhardt used (15). These data gather twenty mortars of various characteristics (cement content, curing conditions, additives,...). The range of diameters is classically modified towards higher values when w/c increases. The main data and experimental results are summarized in Table 2 (the equivalent radius is a parameter summarizing the whole distribution and defined by Reinhardt). The variability for the measured porosity is small (typical c.o.v. around a few percent) but it is not the case for the permeability measurements (with an averaged c.o.v. from three measurements on twenty different mortars of 37%). The results for K are given in Table 3, with n = 8. In this case, it is assumed that the effective porosity p' is equal to p.

The trends and the values are correct, even if the permeability is underestimated for the last paste. It has also been shown (30, 31) that the model is capable of describing the influence of the relative moisture HR or of varying curing conditions. Fig. 3 summarizes the numerical results (n remaining equal to 8) for twenty pastes which differ by their w/c ratio, their curing conditions, the nature of the binder, the eventual addition of a super-plasticizer... The correlation between experimental and numerical results is satisfying. The parallel lines correspond to an error of +/-20% on the measured value of the open porosity.

The 'bad' points on Fig. 3 correspond to very specific pastes: high water cement ratio, severe curing or paste with silica fume. These pastes certainly present a different structure of the porous network and an exact fitting of the experimental data would correspond to a different value of the exponent n. When wanting a predictive model, two possibilities exist:

- the n exponent, being related to the microstructure, can change from one simulation to another,

TABLE 3

K Permeability from the Model for Various w/c

| w/c | permeability K (10-13 m/s) | |
|------|-------------------------------|--|
| 0.4 | 17 | |
| 0.5 | 57 | |
| 0.6 | 131 | |
| 0.75 | 970 | |

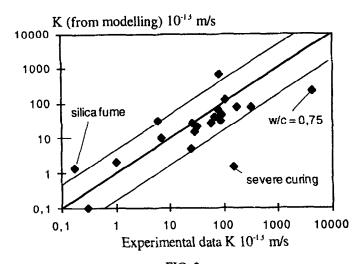


FIG. 3.

Numerical and experimental results for 20 mortars.

- the n exponent has to remain a constant. In a first study (29), Gérard suggested that n is probably higher for a pure cement paste (from 11 to 14) than for a mortar or a concrete (a value of 8 being a good basis in these cases).

Let us now go further in that direction.

Generalizing the Model from Cement Pastes to Concretes

Even if many works theoretically devoted to concrete have just been performed on cement or on mortar, it is a great challenge, when dealing with microstructural related properties (permeability, strength, ...) to deduce the concrete properties from studies on pastes. The presence of aggregates can change the things in average, for instance reducing the amount of porous paste by adding nonporous aggregates, but also in a more subtle manner for transfer problems, by the creation of a the interfacial transition zone of a higher porosity, or for strength problems by the addition of stress concentrators or crack arrestors.

The study on mortars has also shown that all information cannot be summarized in terms of total porosity or by a single scalar value (n = 8), since the microstructure is modified as soon as some additives are used or curing conditions are modified. Since numerical models able to build the resulting microstructure from the only initial conditions (mix) and environment are still in their infancy (32), a semi-empirical way will be followed to improve the results of our model. The challenge is to improve the original formula $[K = K_0 p^n]$ and to see at what point it can be used for permeability prediction in both cement pastes, mortars and concrete.

The reference has to be taken in cement paste, as it is the more homogeneous (and therefore, the less complex) of the three materials but also, even if the parameter n describes some topological paste properties, because the effective porosity is, in this case, the total porosity. Mortars and concrete are deduced from cement paste by adding a volumetric percentage of

aggregates (this word including sand) v_a . Thus, assuming that the aggregates are not porous, the relevant volume is not the total volume V_t , but the volume of the paste:

$$V_p = V_t \times (1 - v_a)$$

If p is the total porosity, the paste porosity is more relevant for transfer. Assuming that the aggregates are not porous or that their porosity is not connected, thus follows:

$$p' = p/(1 - v_a)$$

Another correction can be done considering that the fluid does not go through the whole open porosity but that just a fraction of this porosity is used for transfer (some pores are one-way pores, others are limited by the diameter of their access, others are too small, ...). Let us call α the fraction of efficient porosity. For cement paste, Jambor (33) and Diamond (34) have respectively estimated the value of α to 35 to 65% and 53 to 83%. Brown (35) advances the value of 75% while Meng (21) defines a more complex 'relevant porosity'. Then it is written:

$$p' = \alpha \times p/(1 - v_a)$$
 and $K = K_o p'^n$

Here, the n parameter remains an empirical value, which covers many information: tortuosity, connectivity, existing microcracking, highly porous interfacial zones... (32). A part of this information is also described through α . Thus these two parameters are correlated since it will be verified now. Remaining with a phenomenological point of view, all available data from Table 4 for cement pastes have been treated and the optimal values for α and n have been computed. The results are summarized below.

The values are significatively scattered, and one can remark that the two parameters α and n are not independent. If one eliminates the data from (11)(for which porosity values seem not to be reliable), several sets of parameters (α, n) can then be chosen:

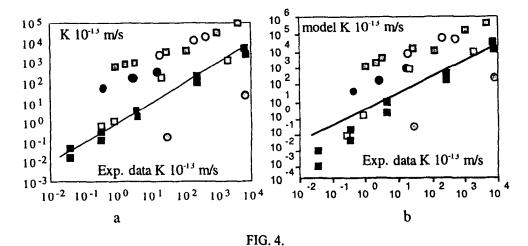
- set A:
$$\alpha = 0.2$$
, $n = 4.9$

- set B:
$$[\alpha = 0.5, n = 7.3]$$

When one considers n (for instance) as the driving parameter and tries to identify the a value which gives the best correlation for all the experimental data, a monotonously in-

TABLE 4
Best Fitting Values of α for Various Values of Exponent n

| author | n = 1 | n = 3 | n = 5 | n = 8 |
|------------------------|----------------------|-------|-------|--------|
| [10] | 0.02 | 0.30 | 0.65 | > 1.00 |
| [11] | 9.0 10 ⁻⁷ | 0.01 | 0.08 | 0.28 |
| [12] | 2.0 10-5 | 0.03 | 0.19 | 0.58 |
| [13] (m.i.p. porosity) | 2.0 10-5 | 0.04 | 0.26 | 0.78 |
| [13] (drying porosity) | 2.0 10-5 | 0.04 | 0.22 | 0.63 |
| [16] | 2.0 10-7 | 0.01 | 0.10 | 0.35 |



Cement pastes: model predictions. a) a = 0.2, b) a = 0.5. Black squares: data (14), white squares: (13), grey squares: (12), white circles: (17, w/c = 0.5), black circles: (17, w/c = 0.4), grey circles: (11).

creasing 'optimum' curve can be built. Of course, since experimental data are widely scattered, none of these sets will ensure a perfect fitting for all the data, but the aim is here to see what can be done for the larger set of data possible. Fig. 4a and 4b show what are the computed permeabilities for all cement pastes with respectively set A and B. The respective results of statistical regressions are:

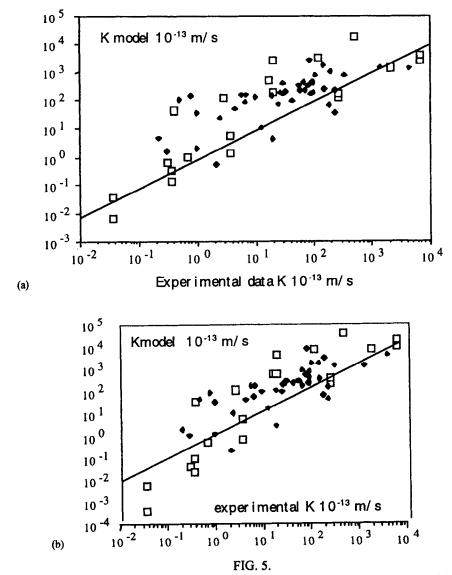
$$\ln (K_{\alpha=0.2}) = 1.89 + 0.857 \ln (K_{\text{exp}}) r^2 = 0.5 \text{ for set A,}$$

 $\ln (K_{\alpha=0.5}) = 1.22 + 1.15 \ln (K_{\text{exp}}) r^2 = 0.6 \text{ for set B}$

When eliminating the "worse data" (those from (11) and (12)), the coefficients of regression jump to 0.75 and 0.79. But a more important remark can come after a closer examination of Fig. 4a (the same would come from Fig. 4b). It can be seen each set of points corresponding to a given author is located along a line quite parallel to the line of slope one, but higher or lower on the diagram. A regression analysis performed separately on each of these groups leads to very high correlation factors (r² around 0.95). This fact proves that the model is indeed very good but that it is still lacking some parameter. This seems to give force to the concept of critical porosity (following the percolation theory framework), which is the value of porosity under which the transfer can not occur since the pore structure is simply not connected. Authors in this field have shown that it is, near the critical porosity pe, possible to write that the permeability is a linear function of (p - p_c)^v where v is a universal exponent. Bentz has shown that this theory can apply to the cement field even if the percolation never strictly holds in cement-based materials since the C-S-H pore space is always open (36). In reality, these range of pores, physical phenomena occurs (surface tension, Van der Waals forces, etc.) which leds to neglect them. A simple look on data indicates that the critical porosity will depend on the structure of the paste, and of course on the experimental way one has measured porosity. For instance, 0.27 would be a good value for the Mehta set (12)

while 0.18 would be good for the Halamickova set (17) and Odler (14) and Nyame (13) sets would need values under 0.10.

Lacking information for introducing the critical porosity values, the model will not be modified and, keeping the values of its coefficients unchanged, it can now be seen up to what point the modified formula can predict the response of mortar and concrete (the aggregates play a role directly through the value of v_a , which is a data of the problem and no degree of freedom is added in the model at that stage). For only mortars and concrete, it is found:



(a) All materials: model predictions with a = 0.2, white squares: cement-pastes, black spots: mortars and concretes; (b) All materials: model predictions with a = 0.5, white squares: cement-pastes, black spots: mortars and concretes.

$$\ln (K_{\alpha=0.2}) = 2.74 + 0.61 \ln (K_{exp}) r^2 = 0.50 \text{ for set A,}$$

 $\ln (K_{\alpha=0.5}) = 2.22 + 0.77 \ln (K_{exp}) r^2 = 0.55 \text{ for set B}$

The same parameters applied for the whole set of data (Table 1) gives:

$$\ln (K_{\alpha=0.2}) = 1.77 + 0.85 \ln (K_{exp}) r^2 = 0.65 \text{ for set A},$$

 $\ln (K_{\alpha=0.5}) = 0.989 + 1.09 \ln (K_{exp}) r^2 = 0.70 \text{ for set B}$

Fig. 5a and 5b illustrate these results. The values of r^2 can be compared to those given by phenomenological porosity/permeability models. For concrete as well as for the whole set of data, it is the model developed which offers the best prediction of the experimental permeability. However, it remains partly empirical, since the value n (taken at n=7.3 for $\alpha=0.5$) remains fitted. This parameter recovers the mixed influence of connectivity, tortuosity and of the local geometry (the shape of microcracks widely differs from that of cylindrical pores). Work has to be done such as to provide a wider physical basis for this parameter and to compare it to 'tortuosity parameters', defined in the literature (37-39) and whose values range from 2 to 9 according to the material.

The more important fact is that a predictive model has been developed. It has a physical basis and it uses measurements of the microstructure, which can be applied, without any change, to cement pastes, mortars and concretes. It would be possible to improve the fitting with experimental data, identifying different sets (n, α) for different classes of materials (concretes, mortars, cements, and in the future clays, rocks, ...), since these materials have different microstructure and, therefore, react differently to the transfer. However, it was not the aim followed here, and it has been preferred to show that, conceptually, this kind of approach can cover a wide range of materials. To identify the relevant subclasses and the correct values of parameters only needs further experimental work (mainly permeability measurements), which will be usefully helped by microstructural analysis. The advantage of such an approach is that it opens doors for predicting the evolution of material properties, once a first measurement has been performed. Applications in the field of modelling hydration, leaching or healing processes can be considered.

Conclusions

The most important problems for describing and predicting the transfer properties on cementitious materials have been introduced. The discussion was not limited to cement paste and mortar but also applied to concrete. It has been shown that, even if it is possible to write phenomenological models relating the permeability to the water/cement ratio, these models give no explanation about the physics of the phenomena and they have only a small predictive power. A micro-macro hierarchical model capable of predicting the response of all cementitious composites (including concrete), with an identical (or better) degree of correlation, and with underlying physical explanations for the parameters used in the model, has been developed. The development of such an approach will open avenues in the field of predicting the evolution of material properties in given contexts: hydration, leaching, healing, and effect of thermal stresses. It has been pointed out that the introduction of a percolation threshold value would probably improve the model. However experimental information

for varying mixes and curing conditions is still lacking on this point and will have to be drawn from specific experiments. It has also been shown that different scales can be used for modelling, according to the scale at which it is chosen to introduce the experimental data (total porosity, mip curve) and to describe the observed and measured phenomena. The predictive power of these various models will depend on the ability for getting the required data. Micro-macro models, based on a description of the microstructure in its initial stage, could lead to the prediction of the evolution of the transfer properties, from their initial value to their ultimate one.

References

- 1. R. Berissi, G. Bonnet, G. Grimaldi, Bull. Liaison LPC, 142, 59-67, 3/4 (1986).
- 2. D. Ludirdja, R.L. Berger, J.F. Young, ACI Mat. J., 433-439, 9/10 (1989).
- 3. Y. Malier, M. Moranville-Regourd, Ann. ITBTP, 502, 137-168, 3/4 (1992).
- 4. G. Ithuralde, Material to Structure, ed. Y. Malier, E. & F.N. Spon, pp. 276-293, 1992.
- 5. P. Locoge, M. Massat, J.P. Ollivier, C. Richet, Cem. Concr. Res., 22, 431-438, (1992).
- 6. E.K. Attiogbe, D. Darwin, ACI Mat. J., 491-500, 11/12 (1987).
- 7. R.F. Feldman, Huang Cheng-Yi, Cem. Concr. Res., 15, 765-774, (1985).
- C.D. Lawrence, Int. RILEM Symp. on Pore Structure and Properties of Materials, Prague, D167-D176, 1973.
- 9. D. Breysse, Rapp. Int. 113, 46, LMT Cachan-France, 3/1991.
- 10. J. Marchand, B. Gérard, Second CANMET/ACI International Symp. on Advances in Concrete Technology, Las Vegas, USA, 1995, 46 pages.
- V.S. Danyushevsky, K.A. Djabarov, RILEM Int. Symp. on Pore Structure and Properties of Materials, Prague, D97-D114, 18-21/9/1973.
- 12. P.K. Mehta, D. Manmohan, 7th Int. Cong. Chemistry of Cement, Paris, III, 1-5, (1980).
- 13. B.K. Nyame, J.M. Illston, 7th Int. Cong. Chemistry of Cement, Paris, VI, 181-185, (1980).
- 14. I. Odler, H. Köster, Cem. Concr. Res., 16, 893-901, (1986).
- 15. H.W. Reinhardt, K. Gaber, Mat. Str., 23, 3-15, (1990).
- 16. F. Jacobs, F.H. Wittmann, Nucl. Eng. and Design, 138, 157-164, (1992).
- 17. P. Halamickova, Th. Master Appl. Sc., Univ. Toronto, Canada, 1993.
- K. Gaber, 1989, Einfluβ der Porengrößenverteilung in der Mörtelmatrix auf den Transport von Wasser, Chlorid und Sauerstoff im Beton, Ph. D., Univ. Darmstad.
- 19. E.J. Garboczi, Cem. Concr. Res., 20, 591-601, (1990).
- 20. J.P. Ollivier, M. Massat, Cem. Concr. Res., 22, 503-514, (1992).
- 21. B. Meng, Mat. Str., 27, 125-134, (1994).
- 22. L. Tang, L.O. Nilsson, Cem. Concr. Res., 22, 541-550, (1992).
- 23. Y. Anguy, Thesis Univ. Bordeaux I, 1993.
- 24. J. Holly, D. Hampton, M.D.A. Thomas, Cem. Concr. Res., 23, 1317-1330, (1993).
- 25. D. Quénard, H. Sallée, Cahiers du CSTB, 323, 10-1991.
- J.F. Daïan, X. Ke, Quénard D., COPS III, IUPAC Symp. on the Characterization of porous solids, Marseille, 9-12/05/1993.
- 27. D. Fokwa, Matériaux hétérogènes: analyse expérimentale et modélisation numérique par une approche hiérarchique, Thèse Université de Paris 6, LMT Cachan, 1992.
- 28. D. Breysse, B. Gérard, RILEM-UNESCO Int. Congress on the Conservation of Stone and Other Materials, Paris, 29/6-1/7.1993.
- G. Schlatter, Durabilité des bétons: analyse de la perméabilité à la vapeur d'un modèle de milieu poreux, DEA Mécanique et Matériaux, LMT Cachan, 1991.
- 30. B. Gérard, Influence de la microstructure sur les propriétés de transfert des matériaux poreux: le cas des matériaux à matrice cimentaire, DEA MAIS, LMT Cachan, 7.1992.

- 31. D. Breysse, Coll. René Houpert, Nancy, France, 10-11/09/1992.
- D.N. Winslow, M.D. Cohen, D.P. Bentz, K.A. Snyder, E.J. Garboczi, Percolation and pore structure in mortars and concrete, 24, 25-37, (1993).
- J. Jambor, Int. RILEM Symp. on Pore Structure and Properties of Materials, Prague, D75-D96, 1973.
- S. Diamond, Int. RILEM Symp. on Pore Structure and Properties of Materials, Prague, pp. B73-B88, 1973.
- P.W. Brown, D. Shi, J. Skalny, Materials Science of Concrete II, 83-109, Amer. Sc. Soc., ed. Skalny & Mindess.
- 36. D.P. Bentz, E.J. Garboczi, Mat. Str., 25, 523-533, (1992).
- 37. M.R. Wyllie, M.B. Spangler, Bull. Amer. Ass. of Petr. Geol., 36, 2, 359-403, (1952).
- 38. S.C. Carniglia, Journ. of Catalysis, 102, 401-418, 1986.
- 39. N. Epstein, Chem. Eng. Sci., 44, 3, 777-779, 1989.
- 40. L.M. Schwartz, S. Kimminau, Geophysics, 52, 1402, 1987.