Drying of Porous Media: Numerical and Experimental Approach

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ABSTRACT: Drying of porous media, such as cement paste, is observed through different types of experiments at meso- and micro-scales. Important aspect is the transport of water through the porous material. The results from Nuclear Magnetic Resonance (NMR) drying experiments have been numerically modeled by means of Lattice Gas Automaton (LGA) from Statistical Physics. It is shown that numerical modeling with LGA can be an approximate fit to the moisture flow, through the capillaries, in the cement paste samples. For the sake of comparisons, temporal and spatial scales are yet to be found.

1 INTRODUCTION

The behaviour of concrete at early age, and possible micro-crack phenomena, which take place before the application of any mechanical load, influence the durability of concrete structures. The cause of micro-cracks could be the moisture flow in the porous cement structure, which develops due to the differential volume changes and subsequent differential pressures. The physical-chemical processes, in the period of concrete hardening under various environmental conditions, that might cause drying (under high or very low temperatures), freezing and thawing and others, initiate moisture flow. In this research, we focus on drying, as a potential cause of moisture flow and drying shrinkage, which may result in micro-cracking.

Figure 1 and 2 show images of drying shrinkage micro-cracking in Environmental Scanning Electron Microscope (ESEM) experiments, on the top surface of 10 x 10 mm² young cement paste samples. The experiment is performed on very young cement paste sample (4 days of age). In this experiment, a new method of cement paste sample preparation is used, and the preliminary results are described in (Jankovic et al. 2002). After casting 2-mm thick samples in a specially created mould, the samples were polished to the thickness of 1 mm, using a tool, particularly created for this purpose (Jankovic et al. 2002). The sample was wet cured at 20°C and 95% relative humidity (RH). Very thin samples of about 1 mm (1.2 mm in this example) were dried, in order to observe the drying mechanisms that are dependent...
only on the material properties (so-called real mechanisms) and not geometry (Wittmann 1982, Neubauer 1997).

Drying of the sample was performed in ESEM chamber, where the RH was lowered from 100% to 10%, maintaining a constant sample temperature, while slowly reducing the chamber pressure. After the drying period of a few hours, in the artificial ESEM climate, micro-cracks were observed at the end of the experiment at 10% RH (Figs 1, 2). At this point, it is difficult to say more about the period of time when cracking occurred. This is due to the fact that, in ESEM, one small spot of the sample surface is observed, which does not necessarily mean that cracks will occur there. Due to imperfections of the ESEM, such as stage rotation problems, we are still not able to make images at different RH at different spots or to maintain constant observations of the whole sample in order to find a potential crack. Very rapid crack development is observed in drying experiments with acoustic emission (Shiotani et al., in press).

After re-wetting from 10% to 25% and further to 92%RH, the micro-crack started to close. The closure was only partial. Swelling and the microstructure growth, which occurred after re-wetting could not close the crack completely. It is again a question of time if and when the crack could be healed. Regarding previous research experience from the literature, some residual cracks would always be present as an inelastic material deformation. If loaded, these residual cracks might cause later on a catastrophic fracture of the material. It is interesting to mention, that these types of cracks occurred only in the wet cured samples (cured in water at 20°C), while dry cured samples (sealed cured at 20°C and 95%RH), possibly gained sufficient strength, and dried out without cracking.

Due to these potential cement-microstructure deformations at very early age, it is logical to focus concrete research on very small scales (meso-, micro-level), with a potential inclusion of the nanoscale. The application of diverse suitable experimental as well as numerical methods, is a necessity. Usage of electron microscopy is already an advantageous way of microstructure observations. Unfortunately, it is still rather cumbersome to experimentally observe the early age concrete behaviour (deformations) at a very small scale (microscopes like ESEM and similar microscope types are still in the developing phase). To obtain the deformations indirectly, we can use digital image correlation techniques (Jankovic et al. 2002), in order to connect the deformation changes with the decrease of relative humidity.

Other methods, like Nuclear Magnetic Resonance (NMR), can be used as a helpful experimental tool in getting the total moisture content and its distribution, in a specific sample volume, at a certain time (Valckenborg et al. 2001). Additionally, NMR can be used to define the size of the pores with respect to the speed of drying.

Modeling of drying and drying shrinkage may be beneficial in defining different parameters, which might influence deformations, due to moisture flow and drying. Needless to say, that these models have to be based on the physics of fluid flow. One of these models, applied in this research is the Lattice Gas Automaton (LGA), a type of Cellular Automata, originating from Statistical Physics. In the existing analyses, LGA models moisture flow and does not include detailed cement microstructure. Different models of the cement microstructure, such as C-S-H models (Wittmann 1973), already exist and will not be discussed here. Goal of the present analysis is to model moisture flow and drying in order to determine similarities with the real moisture flow, as measured in drying experiments, using Nuclear Magnetic Resonance (NMR).

1.1 *NMR: experimental approach to moisture flow*

Gravimetric sampling is the usual (destructive) method for the analysis of moisture content, which is nowadays successfully, replaced by, among others, Nuclear Magnetic Resonance (NMR). NMR is used as a nondestructive method for measuring moisture transport in porous building materials. NMR is applied for first time in the 1960s (Fatt et al. 1967), to determine saturation. It enabled the insight to total moisture content of sample as well as distribution of water in porous materials. The NMR works on the principle of measuring of the absorbed energy, which is proportional to the present distinguishable nuclei of H and hence water. For the moisture transport in time, the size of the pores becomes important. The size classification of pores is into capillaries (size up to 10 µm) and voids (gel pores, size of 10 nm and less), Scheidegger 1960.

The complex network of pores, in different shapes and sizes, has important influence on the speed of drying. It easily influences shrinkage (and creep) due to the status of water presence. This is especially crucial for capillary pores, which present the water-filled space between C-S-H elements (Bažant et al. 1982).

Another important differentiation between the size of pores (capillaries and voids) can be made with respect to the importance of the pore walls. In voids, walls do not play any role, while in capillaries, walls are important for hydrodynamic phenomena in their interior (Scheidegger 1960).

In the tests, the NMR measurement technique was applied to mortars (Valckenborg et al. 2001) pure cement paste, and lately to cement paste combined with additional aggregates (glass pearls, $d = 0.5 \text{ mm}$, in the amount of 35%), see Bisschop et al., in press.
In these NMR experiments (Bisschop et al., in press), drying of the cement paste cylindrical sample (cored from a standard prism), was applied from one side (the top of the sample) while all other sides were sealed (Figs 3, 4).

During drying experiments with mortar (Valckenborg et al. 2001), it was noticed that only capillary pores were emptied in 20 hours time. The duration of the experiment was limited to 3 days. The conclusion from the results was that water could not be taken out from the voids. In the experiments with cement paste (Bisschop et al., in press), drying lasted 12 days. No report was presented on the drying of pores and pore-scales in that experiment.

The NMR results from the experiments in Figures 3 and 4 were chosen for the comparison with the numerical modeling. In order to make comparisons with the NMR results, it would be necessary either to include parameters from the macroscopic flow (velocity, viscosity, Reynolds number and so on), or to observe the trend in moisture flow and drying behaviour. Since extracting of the parameters from the mentioned NMR experiments, which might help in the numerical analysis, is rather complex and doubtful, the trend of the two moisture flows is compared.

2 NUMERICAL APPROACH TO MOISTURE FLOW: LATTICE GAS AUTOMATON

2.1 General notation for steady state

An innovative, numerical way of approaching and describing the problem of fluid flow in complex porous media, dates from 1980s and 90s. The methods are called Lattice Gas Automata (LGA), FHP 2-D models (Frisch 1986, Frisch 1987, d’Humieres 1987). Derived from Statistical Physics, Lattice Gas Automata follow the definitions and basic rules of Cellular Automata. The population of fluid particles in triangular lattice propagates and collides according to certain rules, while conserving mass and linear momentum.

Lattice Gas Automaton (FHP model) is often described as a numerical solution of the Navier-Stokes equation. The similarity between LGA and Navier-Stokes equation, for the incompressible fluid flow, is obtained by the introduction of the Chapman-Enskog expansion (Wolfram 1986). This expansion gives the macroscopic behaviour of a fluid by averaging the microscopic (discretized) forms, for mass (density) and momentum (Eqs 1, 2) over the LGA area. The density and linear momentum equation (Eqs 1, 2) are as follows:

\[ \rho(x) = fm \sum_i N_i(x) \]  
\[ \rho u(x) = fm \sum_i N_i(x)c_i \]

where \( \rho(x) \) is a density per node; \( \rho(x) = \rho \) for homogeneous case; \( u \) is mean velocity; \( \rho u \) is momentum; \( f \) is the number of nodes per unit area (\( f = 2 / (\sqrt{3} / l^2) \), \( l = 1 \)); \( m \) is a unit mass; \( c_i \) is the velocity of a single particle in any of 6 directions \( i \) (\( c = l / \tau \)) along the link length \( l \) in time \( \tau \) expressed as \( c_i = (\cos(\pi / 3) i, \sin(\pi / 3) i) \), \( i = 0, ..., 5 \). \( N_i(x) \) is the average particle population of the cell expressed as the Fermi-Dirac distribution in general, as follows:

\[ N_i(x) = \frac{1}{1 + e^{(h+qc_i) / (\beta fm)}} \]

where \( h \) and \( q \) are LaGrange multipliers, nonlinear functions of \( \rho \) and \( u \), \( N_i \) is the probability of particle \( i \) arriving at node \( x \) with velocity \( c_i \). In the case of unit mass \( (m) \) and isotropic velocity distribution, averaging over the lattice area \( (f) \), the probability \( N_i \) will be \( N_i = d \) as in Equation 4

\[ N_i(x) = \frac{\rho}{\gamma fm} = d \]
where $\rho$ is a density (for the homogeneous case, $\rho = nd$; $n$ is a number of particles per node); while $m$ and $f$ are mass and area, as already mentioned in Equations 1 and 2. The probability of a particle leaving the node $x$ will be $N_i'(x)$. Propagation of fluid particles is defined as conservation of the mean population in the equality of probabilities $N_i$ and $N_i'$ as follows:

$$N_i(x + \tau c_i, t = \tau) = N_i'(x, t)$$

where $\tau$ is the time step (usually chosen as 1); in the steady state, the term $t$ vanishes. The macroscopic equations, obtained through the averaging of the mentioned equations, have close similarity to Navier-Stokes equation for incompressible fluid ($\rho = \text{constant}$), in Equation 6 and supplemental continuity equation, Equation 7, as follows:

$$\delta u + (u \nabla)u = -\nabla P + \nu \nabla^2 u$$

$$\nabla u = 0$$

where $u$ is velocity vector; $P$ is pressure; and $\nu$ is kinematic viscosity. More details about Chapman-Enskog expansions, as well as the lack of the Galilean invariance in LGA, in the simulation of Navier-Stokes equations, can be found in other references (Wolfram 1986).

2.2 Lattice gas model (FHP)

The so-called “center hexagonal FHP model”, with 7 particles per cell, is used for our numerical experiment. Maximum one particle is at rest, with zero velocity, while the other six fluid particles can propagate in six directions, displaced by their velocity directions ($c_0 - c_5$). All fluid particles have unit speed, mass and equal initial density ($d_0 = d$), for all particles in each cell, regardless of any of 6 directions.

In order to simulate the porous medium, LGA can be populated, beside fluid particles, also with solid particles in different sizes and percentages. Solid particles are located at fixed positions on the vertices. Applying the conservation law of mass and momentum (Eqs 1, 2), followed by particle propagation and collision, the FHP model produces the result of a macroscopic flow of the real fluid. In the first step, fluid particles propagate, in order to collide. After the collision step, particles continue to propagate further, until the next collision. Collisions are specified as prescribed rules such as: collisions among fluid particles, collisions of fluid with the solid particle, and collisions of fluid particles with the boundaries.

A collision of fluid particles, with any solid is used as either specular- or bounce-back reflection (Jankovic et al. 2001a, Lavallee 1991). The fluid particle collisions are given in the so-called look-up tables, where all possibilities of the particles configuration, at the nodes ($2^2 = 128$), and possible collisions, are presented. Some collision rules in the look-up tables are deterministic, while others have a probability of $p$ ($p = 1/2$), depending on the possible rotations (see for example rule (1) and (5) in Figure 5). In the case of a probabilistic rule, the 8-bit is introduced as a switch, between two probabilities.

In our model, the LGA is used to simulate moisture flow during drying of a 2-D homogenous and heterogeneous sample. Drying can be treated simply as mass transfer. The flow occurs due to the difference in the density concentrations, which leads to a paradox called “uphill diffusion” (Pihlajavaara 1965), from lower to higher concentration. In the model, the difference, in the density concentration, is created by “inputting” lower density particles in the higher density environment (Jankovic et al. 2001a).

2.3 Collision rules (look-up table)

Standard collision rules include collisions in the 6-particle model, such as FHP1 rule (collision of 2 and 3 particles) and 7-particle model (all possible 76 collisions from 2 to 5 fluid particles, including collisions with a particle at rest), d’Humieres, 1987.

In this research, the so-called FHP2 collision rule, with higher viscosity, is applied in order to keep a low Reynolds number to model porous media. Su-
perposition of the rules in Figures (5a) and (5b) results in the rule FHP2. Usually, all FHP collision rules are defined in the “look-up” tables, listed as the input and output set of \( n = 6 \) velocities (expressed in Boolean notation as either 0 or 1), per each of 128 lines. The FHP2 rule includes 22 collisions: double, triple and collisions with the particle at rest, which amounts to 17.2% collisions (out of 128 velocity configurations).

2.4 Boundary conditions

Boundary conditions (BC) are essential for the LGA, but also significant for the modeling of drying. The boundary is defined in the vertical and horizontal direction, as periodic or as a wall (barrier) condition. In the presented examples, the wall is always located on the left-hand side. In the vertical direction, both periodic and top/bottom wall conditions were applied and compared.

Collision of fluid particles with solid particles is also treated as a boundary problem, where fluid particles, after being bounced from solid, reflect either as bounce-back \((r = 0)\) or they have specular-response \((r = 1)\). Both cases have been studied.

3 LGA ILLUSTRATIONS

The size of the LGA mesh is 1024 x 1024 nodes in X and Y direction. In the triangular mesh, a non-orthonormal way of coordinate labeling is used, such that the \( x \) coordinates, in the odd rows, are shifted for \( l/2 \), in order to form a mesh under angle of 60°. Although the size of the NMR sample was 40 x 20 \( \text{mm}^2 \) (ratio = 2: 1), the LGA mesh is chosen to have equal number of nodes in horizontal and vertical direction. This provides an easier running of the averaging analysis, in the presence of the higher percentage of solid particles.

Two simulations of drying will be presented: drying of homogenous (Figs 6) and heterogeneous sample (Figs 8). The percentage of solid particles for the homogenous sample is 3%, occupying the size of only one LGA node. For the heterogeneous sample, the size of the solid particles is increased to 20 x 20 LGA nodes. The total percentage of solid population is 0.01%. In both cases, the solid particles are placed at random.

Different analyses have been performed, in order to find the best fit for the boundary conditions, that would give the closest numerical approximation to the experiment. In all presented cases in (Figs 6-10), boundary conditions were as mentioned in 2.4. Regarding the collision with the solid wall, the bounce-back boundary rule is applied in all cases. Two possibilities of fluid-solid collision (bounce-back or specular-reflection) were applied and compared. The LGA works on the principle of averaging over area and time in steps. In that sense, this is a truly statistical approach. The time averaging is made at every 500 steps (Figs 6-9) and 250 steps (Fig. 10). Regarding the averaging over the LGA area, we make an average in the vertical direction. By increasing the size of the sample, the noise in the results reduces (see Jankovic et al. 2001a).

3.1 Drying of homogeneous LGA sample

In Figure 6, the homogenous sample with 3% of small, solid particles, illustrates drying from the left-hand side. The initial density of particles is \( d = 0.9 \). Drying curves (Fig. 7) indicate regular smooth drying. The smoothness of the curves is due to using a larger LGA size. Due to the application of the FHP2 collision rule, drying goes very slowly. The analysis ran only for 5000 steps, since the tendency was to examine the shape of the drying curves. We want to compare the shape and trend in this “drying” analysis (Fig. 7) to the NMR drying experiment (Fig. 3).

![Figure 6. Moisture distribution in the homogeneous sample, (a) after 1000, and (b) after 4500 LGA steps.](image)

![Figure 7. LGA simulation of drying of the homogeneous 1024 x 1024 sample, with FHP2 collision rule. Periodic boundary conditions, with wall on the left-hand side. Drying in maximum of 5000 steps.](image)
3.2 Drying of heterogeneous LGA sample

In Figure 4, the NMR result of drying of a heterogeneous sample is given. Due to the presence of solid particles (35%), the content of cement paste was reduced to 65%. This means that, there will be less cement paste to dry, which will result in quicker drying. This logic was followed in the numerical analysis.

Drying in the Lattice Gas Automaton, with 0.01% of solid particles, is given in Figures 8. In order to simulate quicker drying and less percentage of present moisture in the sample, the initial density was reduced from 0.9 to 0.5.

The difference in the results can be observed in the diagrams (Figs 9), where the LGA results are averaged every 500 steps. The sample with $d = 0.9$ was dried to 5000 steps (Fig. 9a) and to 3000 steps with the density from $d = 0.8$ to 0.5, (Figs 9b, d).

![Figure 8](image-url)  
(a) $d = 0.9$  
(b) $d = 0.8$  
(c) $d = 0.7$  
(d) $d = 0.5$

Figure 8. Moisture distribution in the heterogeneous sample, with different initial density $d$, after 1000 LGA steps.

![Figure 9](image-url)  
(a) Initial density, $d = 0.9$. Drying to 5000 steps.  
(b) Initial density, $d = 0.8$. Drying to 3000 steps.  
(c) Initial density, $d = 0.7$. Drying to 3000 steps.  
(d) Initial density, $d = 0.5$. Drying to 3000 steps.

Figure 9. Moisture LGA profiles for different initial densities. Applied FHP2 collision rule. Periodic BC in vertical direction. Solid wall on the left-hand side. $r = 0$ (on the wall) and $r = 1$ (collision with solid particles).
The following can be observed: if the difference between the initial density (0.9, 0.8, 0.7 and 0.5) and the ultimate density (0.2) was smaller, the drying was quicker, and smaller number of steps is necessary to dry the sample. In the case of \( d = 0.9 \) (Fig. 9a), 5000 steps are necessary to get to \( d = 0.3 \), while in the Figure 9d, only 3000 steps will give approximately the same drying condition. Some spurious behavior, in the drying curves, can be observed in the case of smaller initial densities (Figs 9c, d). The reason might be the lowering of the initial density, compared to the ultimate density, which was fixed to 0.2. On the other hand, drying to the lower fixed values \( (d = 0.05 \text{ instead of } d = 0.2) \) in the smaller steps, would cause quicker drying (Fig. 10).

4 MOISTURE LOSS

Moisture content (loss) and moisture distribution, as presented in the drying curves in the LGA sample, depend on:

- different boundary conditions (collisions) of fluid particles with the solid wall: specular- or bounce-back reflection, or periodic boundary conditions
- boundary conditions with the solid obstacles
- initially prescribed density of the fluid particles
- content and size of solid particles (a simple representation of the cement/concrete microstructure)
- prescribed collision rules

Some of the mentioned parameters have been compared in Figure 11. The same boundary condition (bounce-back, \( r = 0 \)) is kept on the solid wall, while the conditions with the solid obstacles run with either \( r = 0 \) or \( r = 1 \), specular-reflection.

The drying analysis shows that the number of lost particles decreases, as the speed of drying decreases. In the case of “pure cement paste” (CP), for the initial density \( (d = 0.9) \), drying goes rather slowly and the moisture loss is also slow. Wall barrier on the top and bottom slowed the process of drying but not significantly (Fig. 11b).

In the experiments, the speed of drying would depend, among other parameters, on the w/c-ratio. In the LGA analysis, the w/c-ratio can be taken into account by applying different collision rules, and subsequently different number of collisions. Lower w/c-ratio means slower drying (see for example FHP2 rule, in Fig. 7), while higher w/c means quicker drying (application of FHP5 rule, in Jankovic et al. 2001a).

On the other hand, the moisture loss increases, when more solid particles are added (cases of different density \( d \)). This implies that as more/bigger ob-
staces are added, larger porous interface zones are created around the obstacles, which speeds up the moisture flow and drying, when and if the interfaces are connected. Cement paste is not as compact as in the case when no or very small solid particles are added. The use of solid particles, which are smaller in size, would create slower drying and lower percentage of cracking.

Implementing the collision rule of specular-reflection ($r = 1$), among fluid and solid particles, moisture loss slightly increases, compared to the case of $r = 0$ (bounce-back reflection), see Figure 11. The difference in moisture loss is due to the different surfaces of the obstacles. If obstacles are rough, than a bounce-back rule ($r = 0$) can be applied. If they are perfectly smooth, the specular-reflection rule ($r = 1$) is more applicable, implying that smooth surfaces do have much lower resistance than rough surfaces.

5 DISCUSSION AND CONCLUSIONS

In this research, we have showed that the use of a 2-D, isotropic FHP hexagonal Lattice Gas Automaton, with maximum of 6+1 fluid particle at rest (per node), can produce good comparisons with NMR experiments on drying of the cement paste samples. There are still many open questions to which we have to address.

Some remarks should be made regarding the type of LGA (6 and 7-particle LGA model). The maximum number of particles per node (6 or 7) influences the Reynolds number $R_e$ (Rivet et al. 1986) which is significant in modeling of porous media. In order to model porous media correctly, $R_e$ needs to be very low. In that case, the viscosity term should be higher, by introducing a lower number of collisions. As a result of this discussion, FHP2 rule, with a low number of collisions is applied.

In general, collision rules influence drying behaviour in the model. New collision rules may improve the moisture gradient, during the modeling of drying.

At this moment, no temporal or spatial scale is derived from the analyses. Regarding the temporal and spatial scale, it is important to say that the LGA model has no intrinsic temporal or spatial scale. By implying the law of similarity between the real and fluid in the model, where $R_e$ number must be the same, it would be possible to find out about the temporal and spatial scale. It is important to keep in mind that, due to the lack of Galilean invariance in the microscopic derivations of Navier-Stokes equation, re-scaling had been applied (Frisch et al. 1987) such that new re-scaled $R_e$ number is as follows:

$$R_e = \frac{\mu \rho_0}{\rho_0 \nu} \frac{L_0^2}{v(\rho_0)} \quad (8)$$

The Reynolds number, re-scaled in this way, plays the same role as $R_e$ number in real fluids. Re-scaling of the $R_e$ number and subsequently of the space, time, velocity and pressure, makes smooth transformation of incompressible macrodynamical equation for Lattice Gas, into classical Navier-Stokes, for the real fluid.

Due to the existence of different sizes of solid particles (in different percentages), moisture gradients as well as drying mechanisms (compare Figs 7 and 9a) will be influenced. The size of the solid particles also plays an important role. The bigger the size of solid particles the quicker the drying, and the lower the moisture gradient. Due to the smaller size of particles and smaller circumferential, interfacial transition zone (compared to bigger size of particles in Jankovic et al. 2001b), the moisture gradient around the particles is much less steep.

The number of averaged LGA steps has an effect on moisture gradient. If the number of averaged steps is 250 (Fig. 10), instead of 500 (Fig. 9c), increase in moisture gradient in the early phase is noticed. Taking into account the experiments on drying shrinkage cracking (Bisschop et al. 2001), this can be explained by the fact that drying in the early phase (surface drying) is more critical for the possible crack occurrence, than later stages of drying.

Use of periodic or wall boundary conditions, has an effect on the drying simulation, while the use of bounce-back or specular-reflection, has an effect on the speed of drying as well as on the moisture gradient (Fig. 11).

The distinction between capillaries and voids may be important in the numerical simulations, regarding the boundary conditions. Maybe the combination of both bounce-back and specular-reflection can be the right solution for this type of analysis, although it is still not clear how these matters are related.

Time seems to be the key factor in the experiments as well as in modeling. Some progress should be expected from the experiments in the ESEM. Deformations, due to drying at the small scale, can properly model standard drying experiments at the larger scale. Our experiments on drying are always limited in time. Basically, drying in cementitious materials is a never finished process, but the initial phase, where rapid crack propagation may occur (within hours) is considered very important.

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