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Dynamic neutron radiography studies of water migration in beds of natural zeolite

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Abstract. The results of the experiments on water migration in unsaturated beds of natural zeolite (clinoptilolite) performed with a dynamic neutron radiography technique are presented. It was found that the migration of water in zeolites is much slower than in quartz sand composed of the same size grains. The effect is attributed to the enormous grain surface roughness of the zeolite. The influence of gravity was found to be significant only for beds formed by the coarsest grains. It was found that the water imbibition rate increases with time in finest grain zeolite beds. The results show the difficulties of the classical theory of adhesion driven motion of the liquid in the single capillary as a model of water imbibition by zeolite beds.

Key words: natural zeolites • water migration • granular media • neutron radiography

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Introduction

Liquid migration in porous media composed of individual grains is one of the main processes studied in soil science [14, 19, 28] and chemical engineering [4]. The interaction of liquid with the grains' surface is a crucial factor determining the rate of the imbibition of wetting liquid by unsaturated (dry) beds. Zeolites have been used for many years as selective adsorbing materials in catalysis, separation of gases and water recycling [1, 3, 8, 12, 27]. The incorporation of water into zeolitic frameworks is a complex microscopic phenomenon determined by morphology of the zeolite structure [5]. On a macroscopic scale, the enormous microporosity of zeolites yields increased surface roughness of their grains as compared to the smooth grain surfaces of the quartz sand. The large grain roughness should produce slower wetting front motion in the medium [2, 23].

The main aim of the present work was to obtain experimental data on the spontaneous migration of water under gravity in unsaturated beds of natural zeolite of selected grain size. In our studies the dynamic neutron radiography (DNR) was used, which has been proved to be a suitable tool for determination of the wetting front motion and water distribution inside the rigid and granular porous media [6, 7, 10, 11, 15, 21–24, 26]. It is well known that the motion of the wetting front in porous systems complies at least approximately with the square root of time classical law [9, 14, 19, 29]. How-

Table 1. The effective porosity, imbibition rate parameter at 30°C and effective capillary radii of the zeolite and quartz sand beds

Material	Effective porosity	Imbibition rate parameter a (mm·s$^{-1/2}$) at 30°C	Effective capillary radius r_a (μm) determined from a	Effective capillary radius r_H (mm) determined from H
Zeolite 0–0.2 mm	0.55	1.2	0.033	–
Zeolite 0.2–0.5 mm	0.44	3.1	0.22	–
Zeolite 0.5–1.0 mm	0.45	–	–	0.16
Fine quartz 0.06–0.2 mm	0.44	8.0	1.45	–
Coarse quartz 1.0–1.2 mm	0.43	–	–	0.62

ever, the presence of gravity modifies that dependence significantly producing the effect of maximum height of the wet region [9, 14, 19, 23, 28, 29].

Another goal was to study the temperature dependence of the water absorption by zeolite beds. The spontaneous imbibition of liquid by porous media depends substantially on temperature [9, 14, 19, 23, 28] because the interfacial energies as well as other characteristics of the liquid (density and viscosity) depend strongly upon the temperature. The thermal expansion of the grains should also affect the imbibition rate. Since the ratio of the surface tension to the viscosity of water increases with temperature in the region from 5°C to 100°C, according to the capillary motion theory [9, 23, 29], the increase in the water imbibition rate should be observed with increasing temperature. In order to check that effect the water migration in zeolite beds was studied for temperatures within 30–70°C region.

The DNR is a digital, real-time, non-destructive technique with very good temporal (~ 1 s) and spatial (~ 0.1 mm) resolutions suitable for studies of liquid migration in porous media. DNR has now proved to be a valuable research tool in the study of hydrogenous fluid migration [6, 7, 10, 11, 15, 21–24, 26]. It has been applied to the study of water penetration and distribution in natural rocks and building materials [6, 7, 10, 15, 21, 22, 24]. A slightly worse temporal resolution of ~ 10 s, associated with a similar linear resolution of ~ 1 mm, has been provided by X-ray tomography [16]. Much better linear resolution of ~ 50 μm was achieved using X-ray microtomography [20]. A good linear resolution of ~ 1 mm with a temporal resolution of ~ 100 s was obtained by the NMR scanning measurements of water penetration [13, 25]. The usefulness of the DNR in water migration studies is based on the strong scattering of thermal neutrons by hydrogen, which is the main component of water. On the other hand, neutrons are only slightly attenuated by most of the dry materials. These factors determine the neutron transmission through the specimen components producing large optical density differences between regions containing different amounts of water. The available image processing procedures provide many ways in which the digitally recorded images can be quantified and analyzed [18]. A precise linear calibration and determination of distances as well as collection of the distributions of the optical density over the sequences of images is easy and reproducible with contemporary DNR facilities. The main drawback of the DNR technique consists in the application of a strong thermal neutron source such as nuclear reactor or spallation source that at present entails the immobility of the laboratory.

Experiment and data analysis

The experiments were performed on samples of natural zeolite supplied by Ballagro Sp. z o.o. and containing 84% of clinoptilolite. The beds of three different grain sizes 0–0.2, 0.2–0.5 and 0.5–1 mm were studied. The effective porosity of the beds was determined by the gravimetric method and varied from 0.44 for zeolite of 0.2–0.5 mm grains to 0.55 for zeolite sample composed of the finest (0–0.2 mm) grains (Table 1).

Experiments were performed with the previously described standard DNR station located at the nuclear research reactor MARIA of IAE [6, 10, 11, 22]. The system consists of the neutron beam collimators, fluorescent screen (250 × 250 mm), mirror, optical zoom lenses and high sensitive CCD camera. The commercially available components: AST NDg ^{6}Li:ZnS:Cu,Al,Au screen, Hammamatsu ORCA-ER camera (1280 × 1024 pixels, 12 bit) and LUCIA software were used. The L/D ratio was ~ 165. The exposure time of 1.6 s was applied and the radiograms were acquired periodically during the observed processes. The projection ratio provided by the optical system was 154 μm/pixel. The distance of the sample from the converter screen was about 40 mm.

The material for the samples was initially rinsed with deionized water for 24 h and then dried for 2–5 weeks at 95°C. The experiments were performed in the previously described vertical arrangement [23] with samples placed inside a thermal cell. The samples were cylindrical columns contained in aluminum tubes of 7 mm inner diameter, 135 mm length and 1 mm thick wall. The fresh samples were prepared ~ 1.5 h before start of each experimental run by filling the tubes with a dry granular material. The temperature was chosen from 30°C to 70°C and stabilized within ± 0.1°C. The moment of contact with water (when the water surface touches the appropriate end of the sample) was defined precisely by the inspection of the acquired neutron radiograms. The water migration within samples was registered for the time necessary to saturate the samples, on the average for at least 20 min in the cases of the upward motion. For each of the image sequences, the frames were taken every 2 s with 1.6 s exposition time.

The collected images were analyzed to determine the position of the wetting fronts propagating along the central lines of the samples. The front position defined as the distance d of the edge of the dark region (Fig. 1) from the appropriate end of the sample was determined from the recorded images with an accuracy of 0.2 mm.

The dependence of the wetting front position d on the time t elapsed from the moment of contact with wa-

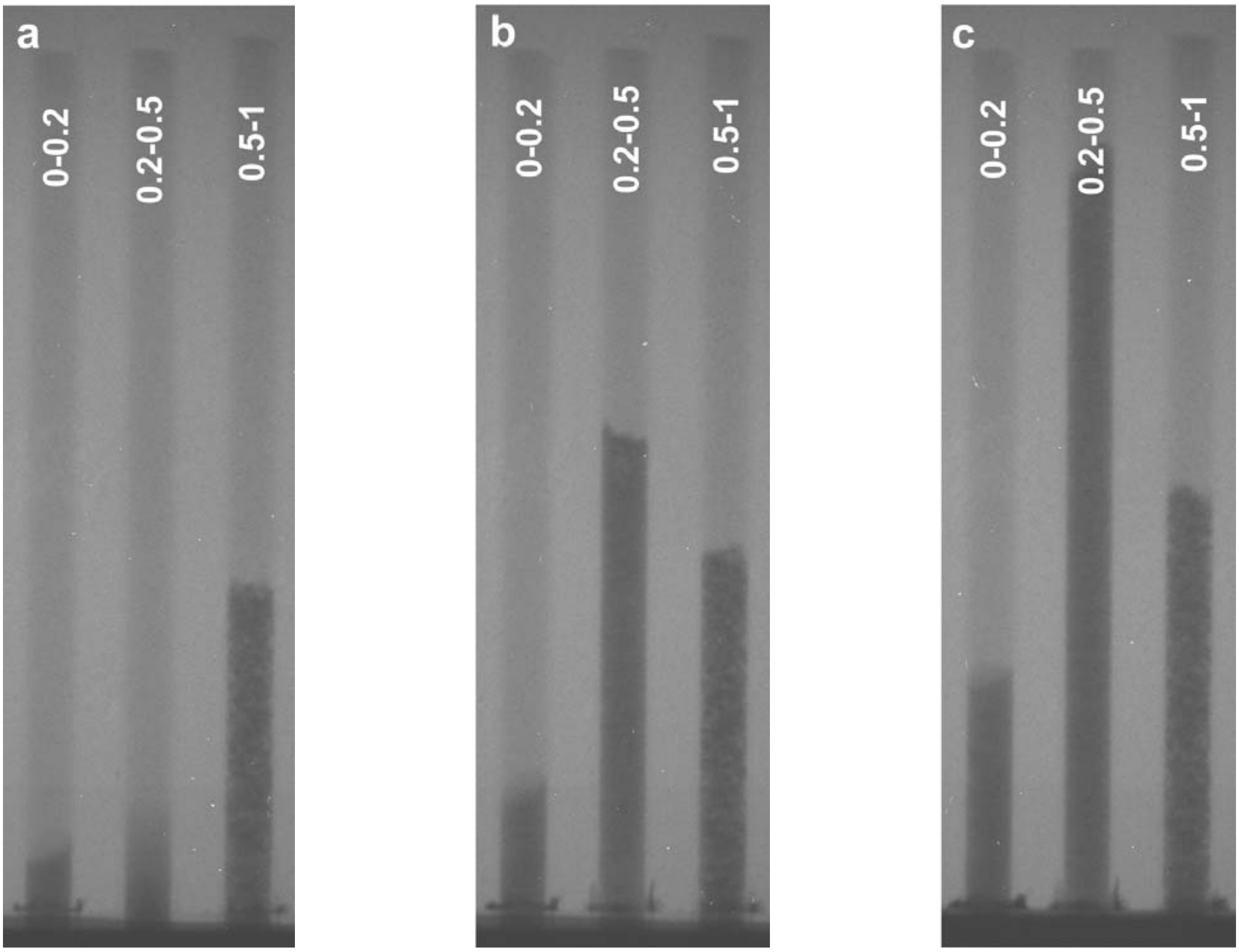

Fig. 1. Neutron images of water migration in three vertical samples of zeolite beds formed by grains of different sizes, from the left: 0–0.2, 0.2–0.5 and 0.5–1 mm. The radiograms represent the system at different times of the process: a – 70 s after moment of contact with water of the finest grain sample; b – 270 s; c – 870 s after that moment. Dark regions are imbibed with water.

ter is highly non-linear (Fig. 2). For the upward motion of the wetting front in beds composed of grains larger than 0.5 mm the saturation of the imbibed region height was observed (Fig. 2).

Bearing in mind the well known prediction of the classical theory [29] that $d \propto \sqrt{t}$, the detailed analysis of the front position motion was performed to check whether the simple power law

$$d(t) \propto t^{\alpha} \tag{1}$$

is applicable. It was revealed that only in the case of the zeolite bed composed of finest grains (0–0.2 mm) the simple power law exponent $\alpha \approx 0.5$ can describe that time dependence for the observation period (Figs. 3a and 4a). For medium grain (0.2–0.5 mm) samples, the classical exponent is applicable in limited time intervals (Figs. 3b and 4b). For samples composed of the coarsest grains (0.5–1 mm), no single power law exponent can describe the experimental results (Fig. 3c).

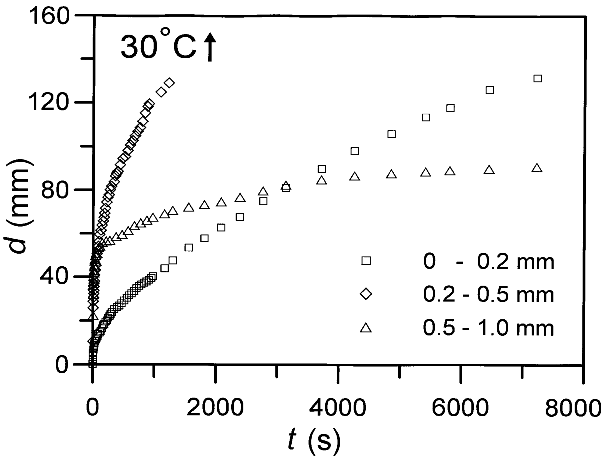

Fig. 2. An example of the time dependence of the wetting front position in three zeolite beds of different grain size. The experiment was performed at 30°C with water migrating upwards.

In order to discuss the temperature dependence of the imbibition rate in terms of the classical theory [29], we analyzed the wetting front motion in finest grain beds in terms of the generalized square root law

$$d = a\sqrt{t} + b \tag{2}$$

where a is the imbibition rate parameter.

The results of our analysis (Fig. 4) revealed that the imbibition rate parameter a for the finest grain zeolite bed increases with temperature (Fig. 5).

Discussion

The simplest theoretical description of the wetting front motion in dry porous medium under capillary force is that of Washburn based on the Poiseuille-Hagen description of the viscous flow in a straight capillary tube of radius r [29]. According to the classical theory [9, 14, 19, 23, 28], the imbibition rate parameter a is determined by the effective capillary radius r_a, the ratio of the surface tension σ to the viscosity η and the wetting angle ϑ.

$$a = \sqrt{\frac{\sigma r_a \cos\vartheta}{2\eta}} \tag{3}$$

In an attempt to model the imbibition process of the granular medium by the effective single straight capillary, the radius r_a of such model tube was calculated from the rate parameter a given by Eq. (3). The effective radius was obtained with zero wetting angle ϑ assumption and the NIST data on the surface tension and viscosity of water [17]. The determined values of r_a are within 0.03–0.25 μm range (Table 1).

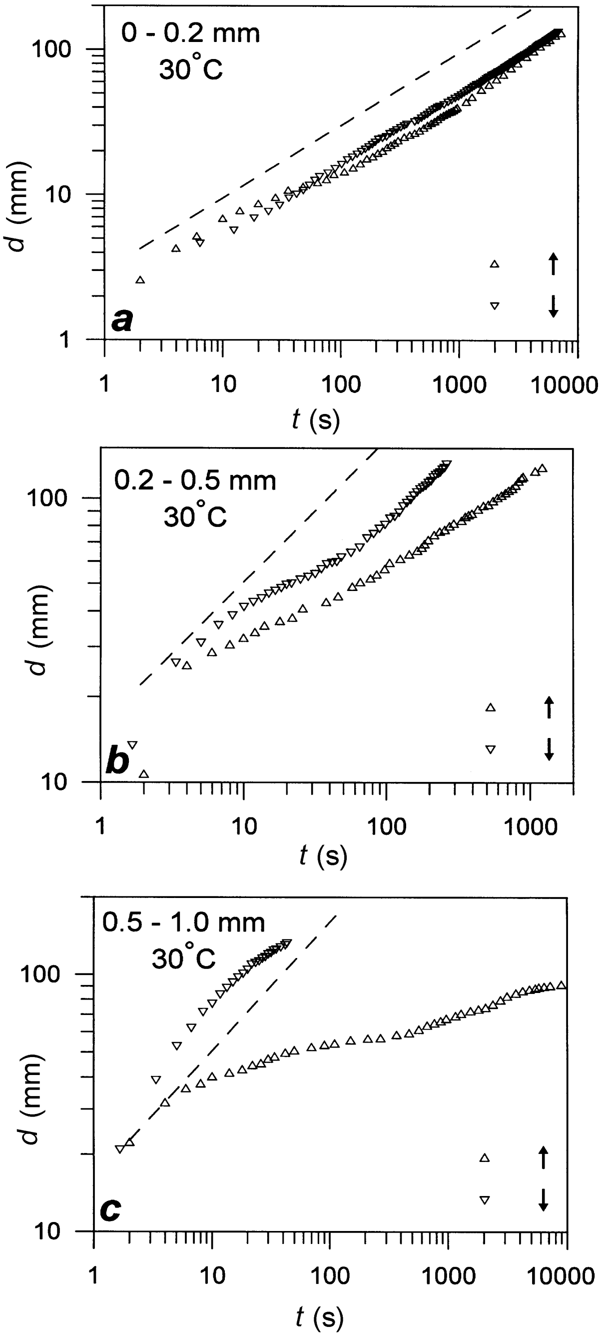

Fig. 3. Logarithmic plots of the wetting front position vs. the time for three different grain size zeolite beds at 30°C. The vertical arrows ↓ and ↑ indicate the direction of the wetting front motion according (downwards) and opposite (upwards) to the gravity, respectively. The dashed lines indicate the classical $d \propto \sqrt{t}$ dependence.

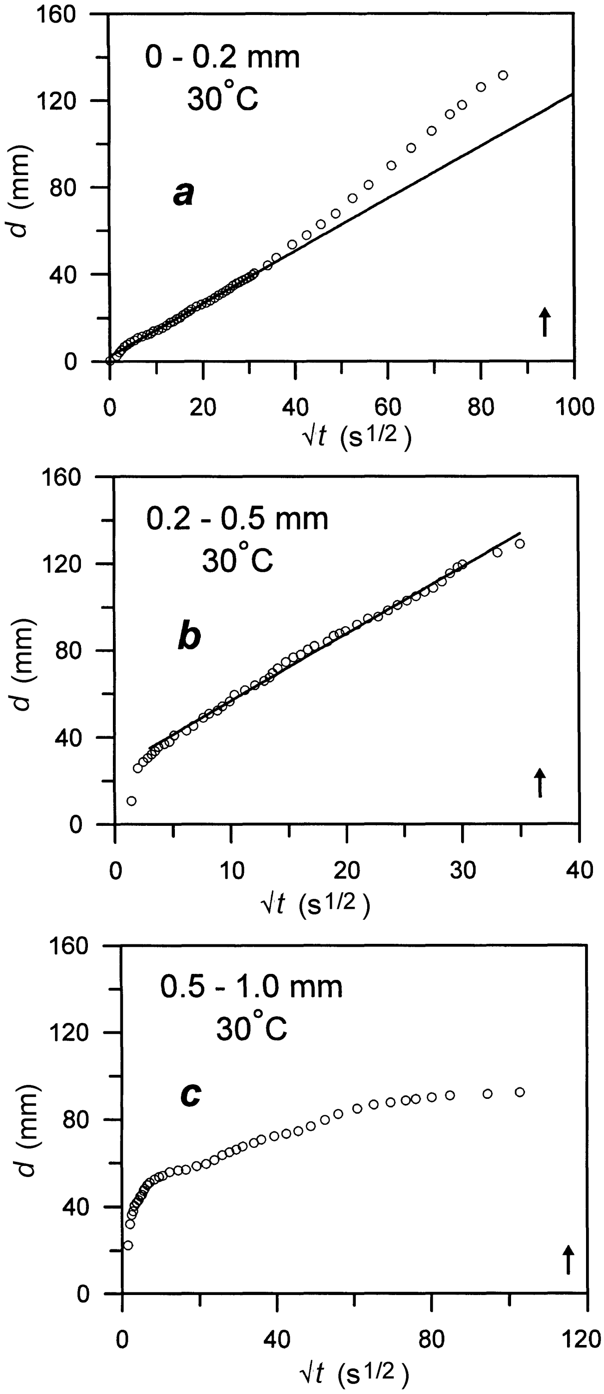

Fig. 4. Examples of the wetting front position during upward motion plotted vs. square root of time. The lines are best fits of $d = a\sqrt{t} + b$ to experimental data for a time interval of 10–1000 s.

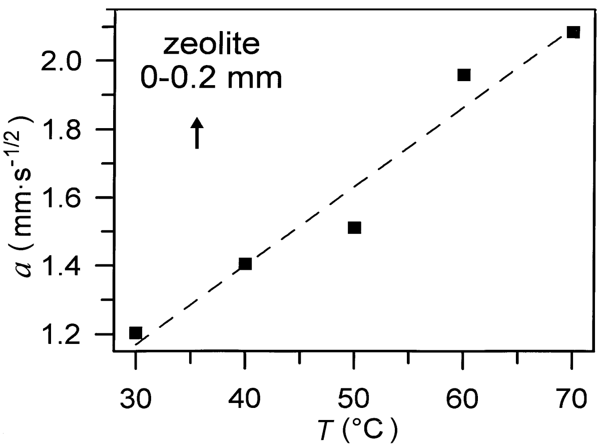

Fig. 5. Temperature dependence of the imbibition rate parameter a for the finest grain (0–0.2 mm) zeolite. The line is a linear fit to the data.

The detailed examination of the $d \propto \sqrt{t}$ dependence reveals that for the finest grain beds two stages of the process occur and the process rate increases in the advanced migration period (Fig. 4a). This rate enhancement is probably due to the water film developing on the grain surfaces in effect of condensation of water vapor migrating much faster than the liquid through the medium. The water film enhances the flow velocity of liquid water. It was found that the classical law can be applied to the medium size grain zeolite except the initial period of migration (Fig. 4b). Nevertheless, the square root of time dependence is inapplicable to the water migration in beds composed of largest grains (Fig. 4c).

The beds formed by the coarsest grains (0.5–1 mm) exhibit much more complicated behavior characterized by the maximum height H of wetted region at later stages of the process. Since the height saturation effect is due to the balance between capillary suction and gravity, the effective radii of the straight capillary tubes

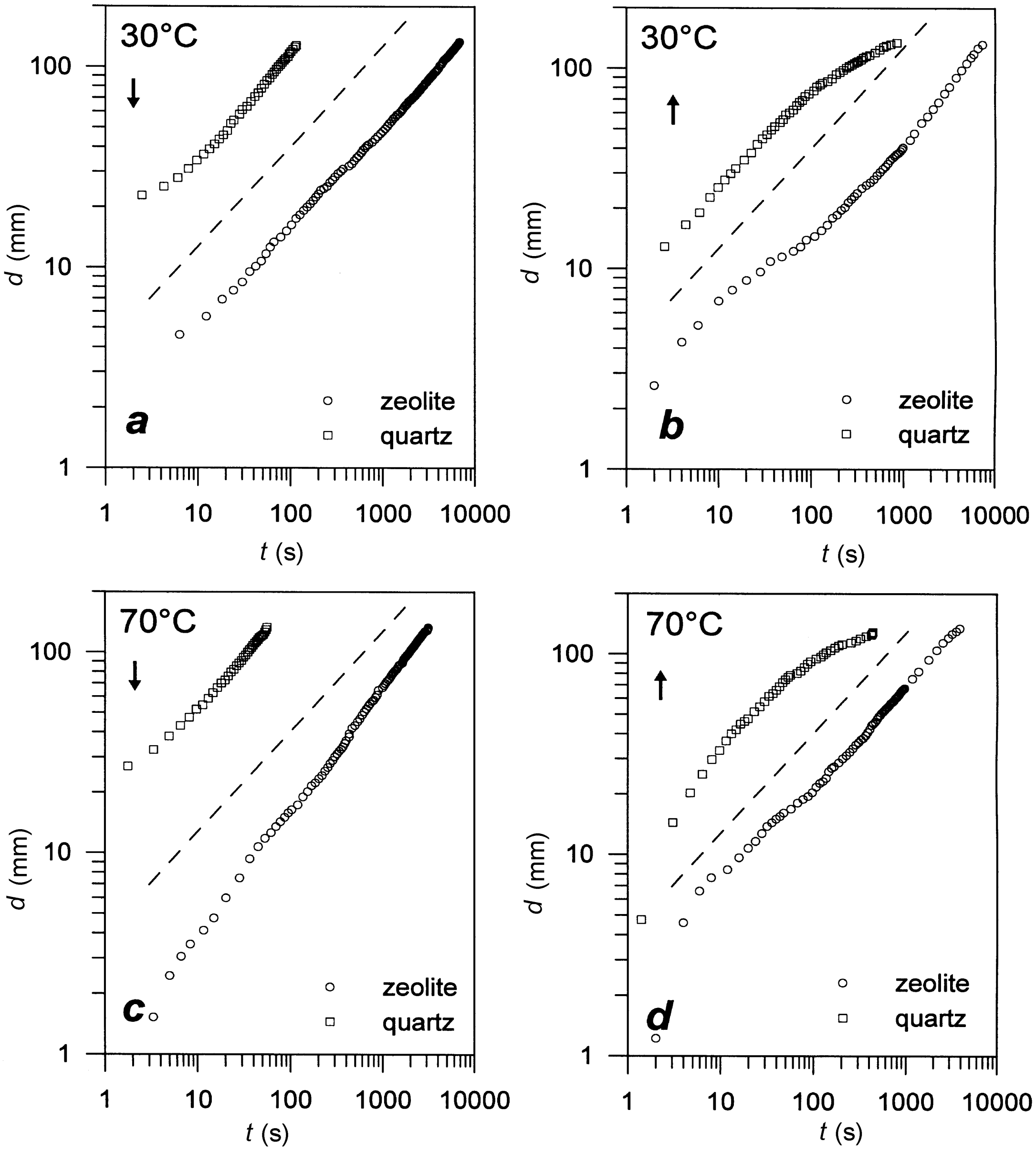

Fig. 6. Comparison of the wetting front motion at 30°C (a, b) and 70°C (c, d) for the zeolite bed composed of 0–0.2 mm grains and quartz sand of 0.06–0.2 mm grain size. The vertical arrows, ↓ and ↑, indicate the direction of the wetting front motion, according (a, c) and opposite (b, d) to the gravity, respectively. The dashed lines indicate the classical $d \propto \sqrt{t}$ dependence.

representing the sample were calculated according to the formula [14, 19, 23, 29]

$$r_H = \frac{2\sigma \cos \vartheta}{H \rho g} \tag{4}$$

with the same zero wetting angle assumption as before. The effective radius r_H determined from the maximum height H amounts to 0.16 mm, and is approximately a thousand times larger than the radius r_a determined from the initial imbibition rate in finer grain samples. This difference should be considered as the main drawback of the classical theoretical description of imbibition by porous media under the influence of gravity and can be attributed to improper account for the pore surface roughness by simple capillary theory [2, 23]. This r_H value is four times less than the determined for the coarse quartz beds [23].

The rate of water migration in the finest grain zeolite beds is almost ten times slower than the one observed in quartz sand of similar grain size [23] (Fig. 6 and Table 1). This effect should be attributed to the different roughness of the pore boundary surfaces in zeolite and quartz sand as well as the surface adsorption that also impedes the migration process.

The fastest water migration observed (Fig. 2) for beds of medium grain sizes (0.2–0.5 mm) can be explained as the result of trade off between the capillary and viscous forces. The capillary theory predicts the fastest flow rate for capillaries of largest radius unless the gravity gets into play. The viscous force impedes the capillary flow for small size pores. The gravity is of no importance during most of the time for finest pores and becomes the important factor at advanced stages of the migration for beds composed of largest grains. For medium size grains, the gravity plays still a minor role as compared to the capillary forces.

We should mention that the observed increase of the imbibition rate with increasing temperature (Fig. 5) does not match the expected dependence on temperature described by the square root of the surface tension to viscosity ratio and is approximately twice the increase predicted by Eq. (3).

Summary

The dynamic neutron radiography is a non-destructive testing technique which provides ideal tool for real time studies of kinetics of hydrogenous liquids migration inside macroscopic systems. In this work we have demonstrated the applicability of neutron radiography for studies of the water imbibition in zeolite beds. The main aim of obtaining data on the kinetics of the process and its dependence upon temperature for granular zeolite beds was achieved.

Presented results indicate that the capillarity is the main driving force of the imbibition in granular zeolite with fine grains and that the gravity has a strong effect on the imbibition only in the beds composed of large grains (Table 1). The maximum imbibition region height yields estimation of the effective pore size that is at variance with the estimates based on the imbibition rate which are reasonable for fine grain granular beds and rigid porous materials. The difference should be attributed not only to the differences in the media structure, but mainly to the simplistic reasoning underlying the effective capillary tube picture.

For the first time, the increase in water migration rate at advanced stages for fine grain beds was observed and interpreted as the effect of water condensation on the grain surfaces.

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