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* In Kazan State University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Studying the initial stages of gelation process in colloidal silica on basis of synthetic silicates by NMR microimaging and relaxometry

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The acid silicious sols obtained from synthetic silicates were investigated in this work. Using NMR microimaging it was found out the formation of considerable inhomogeneities in optically limpid samples at different stages of gel formation. They were interpreted as silicic acid polycondensation fronts. It was observed the character of spreading and fine structure of the fronts. By means of NMR relaxometry were discovered the some interesting effects at the relaxation dependences in time intervals, corresponding to gel formation transitional stages.

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Keywords: NMR microimaging, relaxometry, colloidal silica, foamed silicate, basalt mineral wool.

1. Introduction

The method of magnetic resonance imaging (MRI) is a novel tool for investigations internal structure of various samples without their destruction. It turns out to be useful when studying the processes of drying and saturation, cementation, transport, adsorption, chemical waves and other [1].

The studying of different colloidal and micro heterogeneous forms of silica with advanced surface (sol, gel and powder) has large significance. Particularly the gel formation initial stages study using indirect methods is complicated [2].

Some preliminary MRI results of gel formation in the systems of colloidal silica received from synthetic wollastonite [3] (foamed silicate) and basalt mineral wool by acid leaching are set out in the present work.

2. Experimental

For MRI investigation two types of samples were used. Namely acid silicious sols obtained from synthetic wollastonite (through the leaching by silica phosphoric acid, H_3PO_4) and basalt mineral wool (basic component is calcium silicate). Experiments were made on the NMR installation based on AVANCE DPX 200 at field 4.7 T with probe PH MICRO 2.5 (coil's diameter 25 mm). An initial solution was filled into glass tube (see the scales in the Fig.1). Samples were placed into foamed plastic for discarding convection and heat exchange with surrounding environment.

The standard spin-echo techniques were used for image acquisitions. For the relaxation times measurements the inversion-recovery (for T_1) and Carr-Pursell-Meiboom-Gill (for T_2) techniques were used, the last being not a volume selective. The concrete parameters are given in the text and captions.

3. Results and discussion

Sols on basis of foamed silicate

Foamed silicate has been powdered, mixed with orthophosphoric acid and filtered after intensive shaking (with large quantity of heat release). The rate of gel formation increases noticeably when the

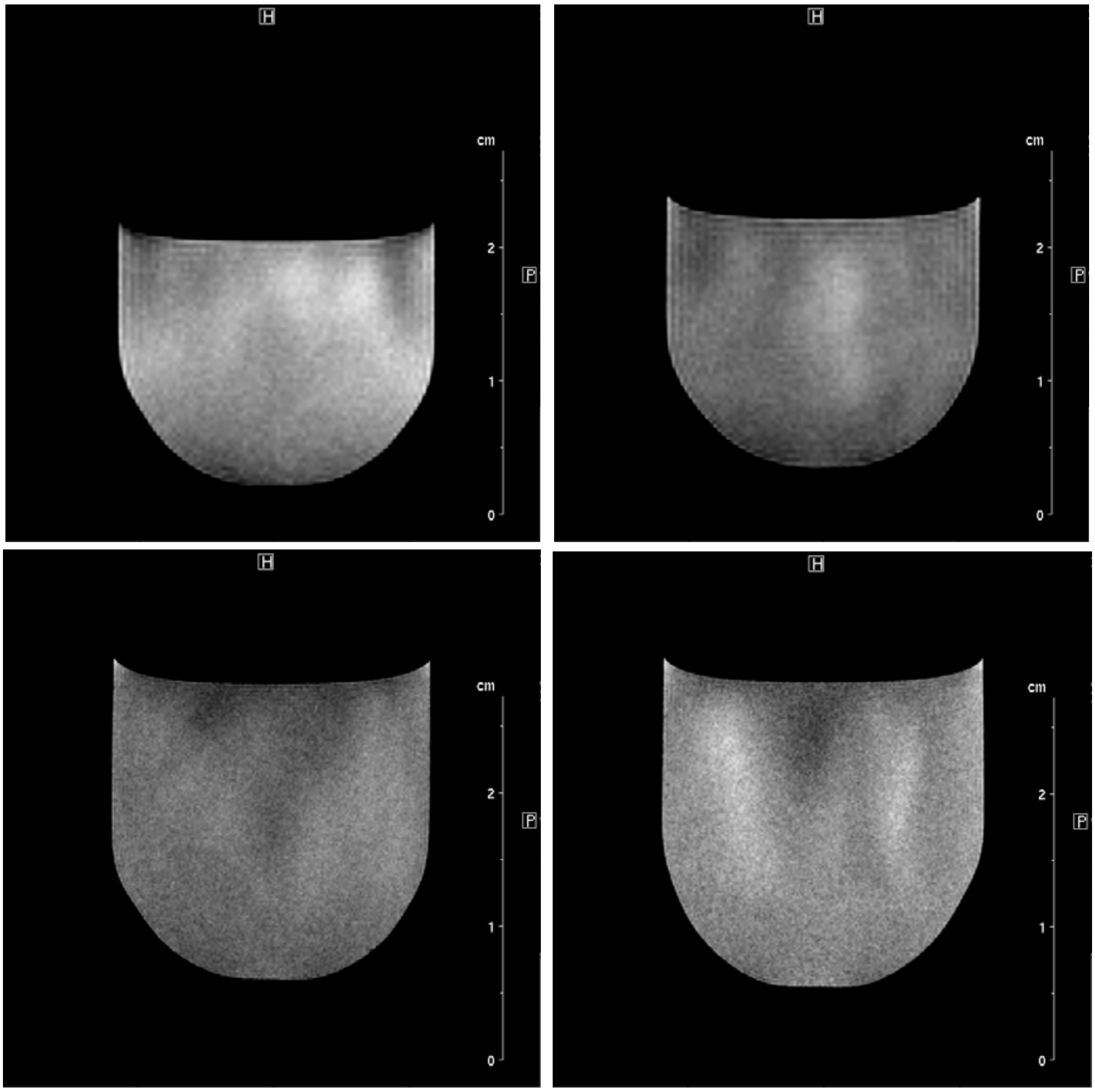


Figure 1. The central longitudinal slices of sample on base of foamed silicate with different initial acid concentrations (from left to right, M: 0.6, 1.2, 1.8, 2.4); FOV 40mm, slice thickness 1mm, 128×128 (two upper) and 256×256 (two lower) matrix

concentration of acid increased. In the Fig. 1 the images of so named T_2-weighted [4] longitudinal slices with different initial acid concentration are presented. The spin-echo technique was used.

One can see a good enough visualization of progressing processes in the system (which is not visible by eyes). They arise as fronts in the near-surface layer which spread vertically into the depth of the tube. It should be noted that the origin, development and disappearance of fronts occurs in the earliest gel formation stages long before the loss of sample fluidity. It's possible to say, that given processes occurs at the stage of transfer from solution to sol, i.e. during the process of silicic acid primary polycondensation.

As it was considered before [2, 5], the mobility loss under the sol-gel transfer occurs not long before the gelling of the system, and the processes of gel formation are insignificant during the whole induction period. In the Fig. 2 the time dependences of spin-lattice relaxation (T_1) for samples with some orthophosphoric acid concentrations are presented. As evident from the date, maximum rate of T_1 decrease has place only during the first four-five hours. Fig.2 shows very slow decreasing of spin-lattice relaxation time after this period. Because the exactness of T_1 measuring is evaluated as ± 2 ms, there are some steps (about 5-9 ms) on T_1 dependences. For convenience we have connected the last

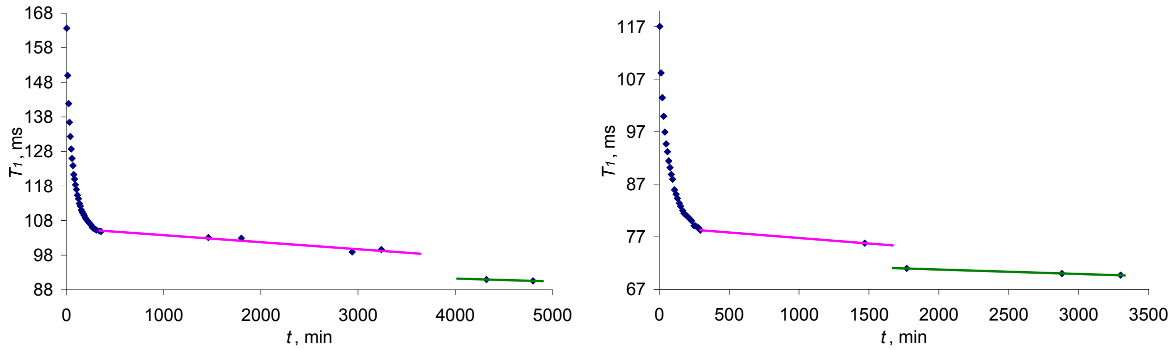


Figure 2. The T_1 dependences on the time for samples with initial acid concentrations 1.6 M (left) and 2.0 M (right)

experimental points with straight lines by different colour: red and green (the samples were not taken from the working installation during whole experiment).

The gel formation time obtained by mechanical methods from the gel fluidity loss, for sols on base of 1.6 M acid solution takes 72-80 h (for 2.0 M – 29-32 h) and "lags" in comparison with step transfer at the relaxation curves. Namely, the first points of the green parts (72 h for 1.6 M and 29 h for 2.0 M) correspond to the viscous but yet mobile sample (not finally consolidated), although the values of T_1 are almost equal for them. For our opinion it is in accord with theoretical conceptions of sol-gel transfer mechanism [5]: the gelation occurs under the ~ 50% gel structure's portion in sol medium.

The time dependences of spin-spin relaxation (T_2) for same samples is almost similar (Fig. 3). From the date it's possible also to conclude that polycondensation of silicic acid with formation of initial particles and their growth practically stops in 3-4 h after sol preparation (the period of maximum rate of T_2 decrease). Particular interest give rise to the transitional period between of maximum rate of T_2 decrease and very slowly decreasing one.

It was carried out the investigation of spin-spin relaxation dependence (T_2) against the time for some samples with different initial acid concentrations. The curves are presented in the Fig. 4. For explain these experimental curves the following model of processes evolution in the system was proposed. After sol initial particles formation the polycondensation and subsequent aggregation took place. In the period between maximum time decrease termination T_1 and T_2 (3-4 h after preparation) and steady state (the period before sol-gel transfer beginning) particles agglomerates aggregation occurs due to formation of weak bonds between separate structures. The aggregation in sols with less acid concentrations and consequently with less concentrations of dissolved silica begins later; the forming structures are unstable and are disintegrated easily; so the system is in balance for 30-40 min. Such effect of T_2 oscillation (greater mobility corresponds to greater T_2) shows that a decomposition of the bigger aggregate into little ones takes place. When increasing the portion of dissolved silica the

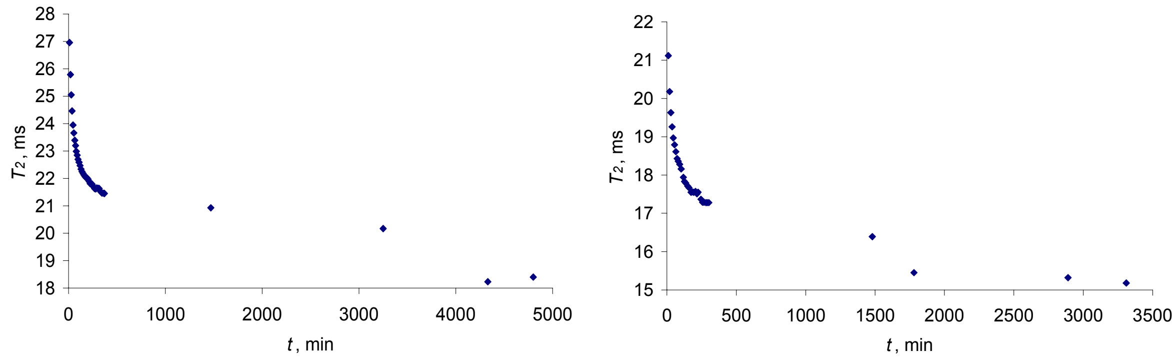


Figure 3. The T_2 dependences on the time for samples with initial acid concentrations 1.6 M (left) and 2.0 M (right)

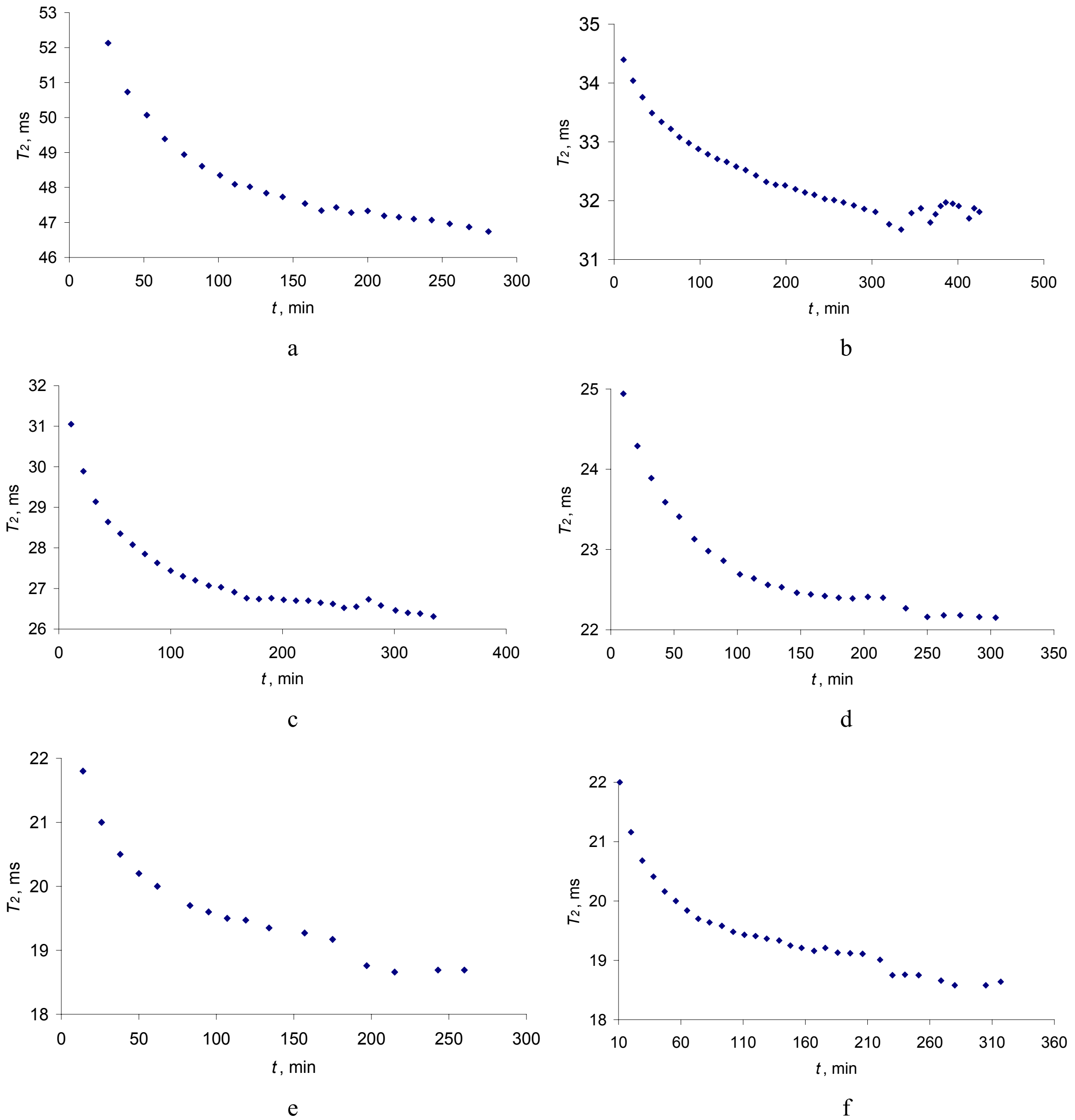


Figure 4. The T_2 dependences on the time for samples with different initial acid concentrations (a – 0.6 M, b – 1.2 M, c – 1.4 M, d – 1.65 M, e – 1.7 M, f – 1.8 M)

aggregation begins earlier, and under such conditions the forming structures are more stable; so oscillation T_2 is insignificant and transfer is stronger.

If the concentration of dissolved silica is more than defined value, the aggregation occurs avalanche-like, the formed agglomerates are stable – there is a “step” on the relaxation dependence.

Sols on basis of basalt mineral wool

In sols of second type the fronts also arise in the near-surface layer, but they have more clear expressed “finger-like” thin structure (Fig. 5, T_2-weighted images, spin-echo). One sample is in a narrow tube with flat bottom (right). Irrespective of the tube’s diameter the front propagation character remains, at the same time the first front reaches the bottom already in 2 hours after preparation.

The appearance of the second front can be observed after the first front sufficient evolution (Fig. 6). The structure of the second front differs by central intensive thick finger which has sometimes some less side branches.

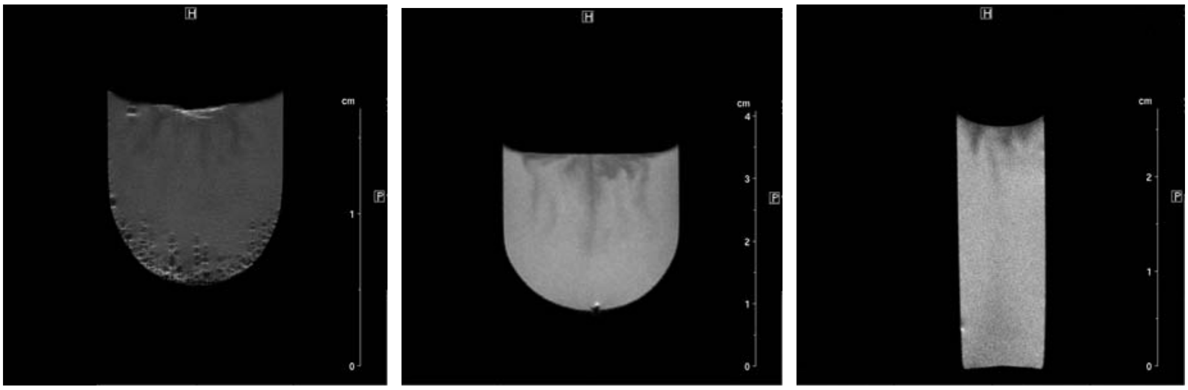


Figure 5. The central slices of three different samples during the first hour after preparation; FOV 40 mm, slice thickness 1 mm, 256×256 matrix

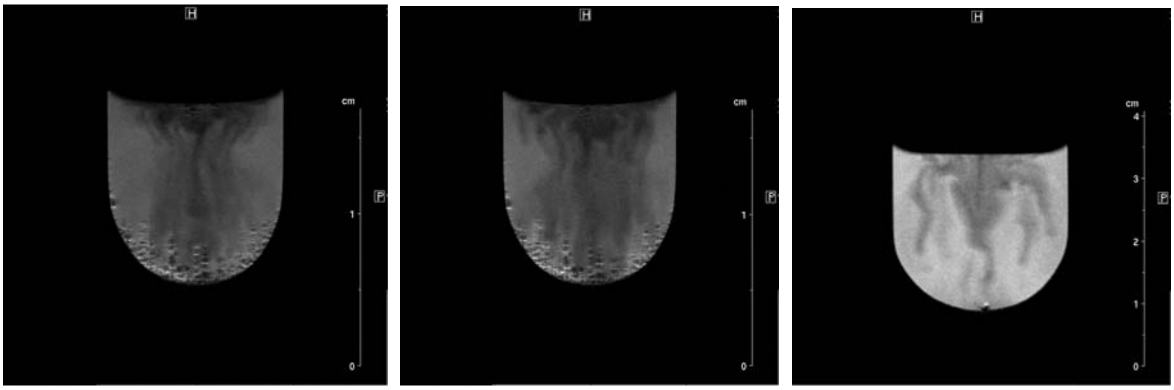
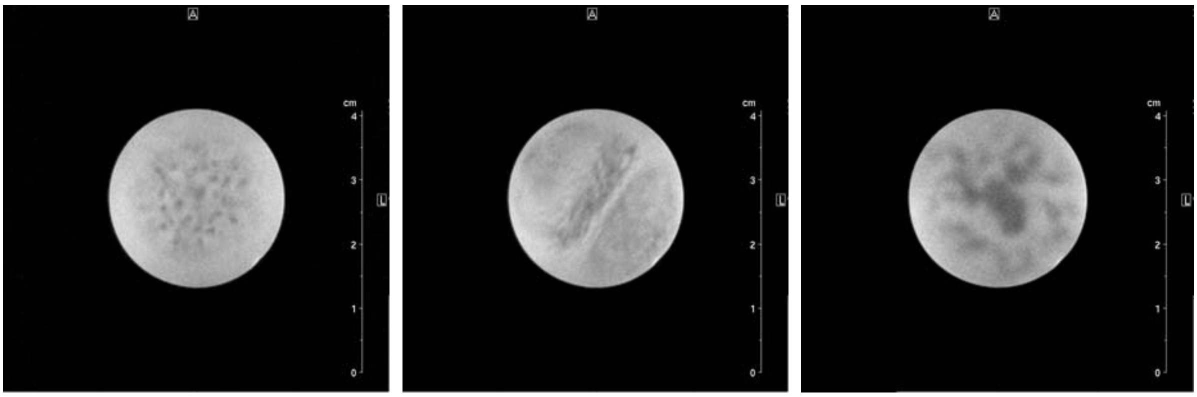


Figure 6. The central slices of some different samples with the forming second aggregation front; FOV 40 mm, slice thickness 1 mm, 256×256 matrix



a b c

Figure 7. The central transverse slices of one sample after about 1 (a), 4 (b), and 6 (c) hours; FOV 40 mm, slice thickness 1 mm, 256×256 matrix

In the Fig.7 the noted above peculiarities of the finger-like fronts are illustrated by the transverse slices.

Some unexpected interesting picture (Fig. 7b) is visible in transitional period when the first front (Fig. 7a) is changed by the second front (Fig. 7c). The mean diameter of the most thin "fingers" estimated from the Fig. 7a is about 1.0 – 1.5 mm.

More clear «fingers» at this type of samples allowed the rate of their spreading to evaluate quantitatively. The dynamics of first and second fronts propagation is presented in the Fig. 8 (l is length of finger). As seen from presented data, the first front propagation rate does not depend on specific position. As for the second front (it is not divided into clear fingers), its rate has two periods; there is a transitional part after which the rate become to be equal to the rate for the first front. By comparing this period with Fig. 7b it is possible to conclude that the transitional processes result in second front intensive propagation into the depth of tube. It is necessary to note that the model described above for the first type of samples might be extended to the given system.

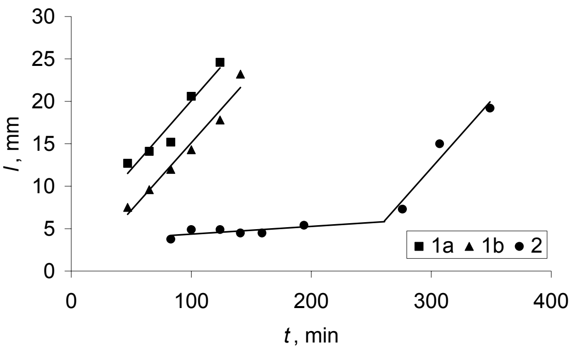


Figure 8. The front dynamics in sols on basis of basalt mineral wool; 1a – central finger of the first front, 1b – fingers of the outlying districts, 2 – the second front

Mechanical fluidity loss of formed gel is accompanied by uniform horizontal fogging front in images (not shown). This front extends from the surface to the bottom. The time dependence of the given front depth propagation is presented in the Fig. 9, where *l* is the depth of propagation. The shrinkage of gel is not significant during the period of time dependences in Fig. 9. As evident from presented dependence, when losing water the front penetration rate decreases. It is connected with the activity of capillary forces holding the remains of liquid water in the interstices within the solid gel mass. Even after long period (about a month) of time the front amount to only 15 mm.

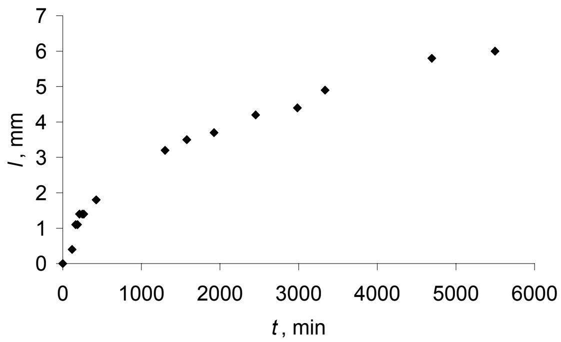


Figure 9. The horizontal front propagation, conditioned by water loss near the surface

Note in conclusion that, as is well known, gradients switching during image acquisition cause significant mechanical vibrations. The contribution of fluid vibration in a sample can not be excluded completely, but it can be modified. So the foamed plastic vessel partially reduce them. Besides, using the set of tubes with different diameters as well as samples with different concentration of acid (consequently with different T_1, T_2 and TR, TE), we have the same effect. As a whole it helped us to be sure, that the effect of mechanical vibrations, conditioned by gradient coils, on a character of studying heterogeneities is not too significant.

The described results show that the MRI opens some unusual heterogeneities in absolutely limpid systems, which reflect complicated dynamic of processes in the initial stages of gel formation.

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