Evolution of the filling pressure of the porous medium by non-wetting liquid at pulse pressure changes

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Abstract. The paper presents the results of experimental studies of impact filling of nanoporous medium with non-wetting liquid. With increasing the impact energies nontrivial pattern of pressure changes in the system over time is observed. A physical explanation is proposed for the observed phenomena.

1. Introduction
The last few decades systems consisting of nanoporous medium dispersed in a non-wetting liquid cause an increased interest from both the practical and theoretical points of view. Non-wetting liquid can infiltrate into the porous medium only with an excess pressure. Liquid infiltration tends to increase the solid-liquid interfacial energy and thus the absorbed energy can be estimated as $E \sim \Delta \gamma S$, where $\Delta \gamma$ is a solid-liquid interfacial tension, and $S$ is the specific surface area of the medium. Therefore this energy for nanoporous media can reach several orders of magnitude superior to traditional damping materials and shape-memory materials [1, 2]. As a consequence, the prospects of using devices based on systems consisting of a nanoporous medium immersed in a non-wetting liquid associated mainly with the absorption of mechanical energy of impact or explosion. Particularly there are considered the development of automotive dampers [3], the system of protection against strains and by the earthquake [4].

At impact or explosion a rapid growth of pressure is occured in system with rates of $\dot{p} = 10^4 \div 10^5$ atm/s. However, most of modern research is related to the quasi-static regime of infiltration with pressure rate not exceeding $\dot{p} < 10$ atm/s. Not numerous studies [5, 6], that the physics of the infiltration process at high rates of pressure is significantly differ from infiltration at low speeds. Nevertheless, a number of papers [7, 8] studied the dynamic filling by molecular modeling. In [6] shows that the observable system can absorb more energy density in comparison with the case of quasi-static pressure. A lot of papers [3] are devoted to experimentally investigation of the development of car damper. Despite this, a set of experimental data is presented rather poorly and full-fledged studies are missing. The answer is absent to the question of how the system behaves under shock impacts at different energies.
2. Experiment
In the present study we investigated the dynamics of shock filling with water of commercially available silica gels with a random structure of pores obtained in the solgel process Libersorb 23 (L23). L23 was modified in the laboratory headed by Prof. G.V. Lisichkin for obtaining the hydrophobized surface of pores. Using the pycnometry (micro-Ultrapyc 1200e, Quantachrome Instruments) and porometry (Nova 1200e, Quantachrome Instruments) methods, we determined the density ($\rho$), specific surface area ($S_p$), specific volume of pores ($V_p$), and pore size distribution by the classical Barrett-Joyner-Halenda (BJH) method within the cylindrical model of pores and porosity ($\varphi$) of this material. The results are presented in Table 1.

A sample of the porous body weight $2 \div 10$ g was placed in a liquid-permeable container in the pressure chamber with volume of $\sim 60$ cm$^3$. The chamber was filled with distilled water. A falling weight from certain height is designed to impart a load pulse. Impact energy is determined by the variation of height. The direct method of measurement is described in detail at [5].

| Study | $\rho$, g/cm$^3$ | $V_p$, cm$^3$/g | $S_p$, m$^2$/g (BET) | $\varphi = V_p/(V_p + 1/\rho)$ |
|-------|------------------|-----------------|----------------------|---------------------------------|
| L23 (C8) | $1.7798 \pm 0.0016$ | $0.66 \pm 0.02$ | $212 \pm 7$ | $0.66 \pm 0.02$ |

**Table 1.** Characteristics of the studied porous media.

![Figure 1](image-url) **Figure 1.** The dependence of the volume of the trapped liquid on the degree of filling for narrow pore size distribution $f_1(R)$: $\Delta R/R \ll 1$

The results of experimental measurements of pressure versus time with a porous medium L23 are shown in Fig. 1, the range of variation of energy ranged from 5 to 80 J. The analysis of
the experimental data shows that the pressure does not behave in a trivial way with increasing impact energy. Under quasi-static compression system nanoporous medium – non-wetting liquid there is a threshold pressure $p_{0}$ at which the liquid infiltrate to the pores of the porous medium [9]. This forms an inhomogeneous front of porous media filling. This process is typical at filling macroscopic porous medium by non-wetting liquid. The threshold infiltration character was set for non-wetting liquids by [10], as well as for granular porous bodies - zeolites having a pore size ($R = 0.3 \div 1.4$ nm) and silochrome ($R = 4 \div 120$ nm) when filled with liquid (molten) metals, hydrophobized porous media with a framework of a silicon oxide ($R = 3 \div 50$ nm) when filled with water, a solution of ethylene glycol and salt solutions [4,9,11,12]. At the same time, at the rapid compression $p = 10^4 \div 10^5$ atm/s, as shown in the work [5,6] for the systems ”granular porous body Silohrom CX 1.5 - Wood’s alloy” and ”Fluka 100 - water”, it was found that infiltration occurs at the percolation threshold at a pressure far above the threshold pressure at quasi-static mode $p_{0}$. So far the first system pressure threshold value of $p_0 = 1.6p_0$ [5], and for the second — $p_0 = 2p_0$ [6].

3. Discussion
These experiments (Fig. 1) shows that at the energy of 5 J pressure is not reached value $p_{0}$, corresponding to the beginning of the infiltration pressure at quasi-static mode [13], and at an energy of 10 J maximum pressure is in the interval $p_{0} < p < p_c$, where the value $p_c$ corresponds to the pressure of the beginning of infiltration at impact infiltration. The magnitude of the change in volume of the system within the measurement error coincides with a change in volume due to deformation, and this means that there is no filling of the porous body. With increasing impact energy is observed infiltration to the porous medium with a pronounced plateau in the pressure versus time. At higher energies, where the energy of compression exceeds the maximum value determined by the energy density of the porous body filling, fill mode at constant pressure is not realized. In these circumstances, as the filling of the porous body is not provided the necessary speed energy absorption characteristic growth time pressure and response system wetting liquids - nanoporous medium is elastic deformation, which is accompanied by the end of the filling pressure increases to a maximum and then only outflow.

Let us consider the characteristic times of the system: $\tau_p$ is the time of pressure changes; $\tau_z$ is the hydrodynamic time of clusters available barrier-free filling of pores; $\tau_v$ is the the time of change of volume; $\tau_d$ makes sense to the characteristic time of formation of the available pore changes over time. The relations between these times in case of impact of filling should be arranged as follows: $\tau_z > \tau_p \gg \tau_d$.

In times $t$, which satisfy the inequality $\tau_v > \tau_z > t \geq \tau_p > \tau_d$, arising accessible pores do not have time to fill with liquid, causing the porous body is in a state above the percolation threshold at affordable pores. In times $\tau_v > t \geq \tau_z > \tau_p > \tau_d$ begin the process of filling the infinite cluster available now through clusters filled pores of finite size.

Conclusion
Thus, with the rapid change in pressure ($\tau_z > \tau_p \gg \tau_d$) filling the porous body occurs by rapid (taking place simultaneously throughout the volume of pellets filled clusters of finite size at times $t \sim \tau_z$) and slow (taking place at times $t \sim \tau_v \gg \tau_z$) the process of filling the infinite cluster of available pore fluid flowing through the pores filled with clusters of finite size. Consequently the dynamics of filling granules of a porous body can be represented as formation of the environment for filling, i.e. as the formation of clusters available since then filling some of these clusters. As in the experiments recorded by filling granules of porous medium occurs when the correlation length $\xi = R/|\theta - \theta_{cl}|^v$, $v = 0.8$ [14] becomes comparable to the size of the granules $L$ or higher than the ($\xi \geq L$), the process of filling the granules can be considered as a homogeneous and
at the same time flowing throughout the space since the formation of clusters of granules filled pores.

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