

# Changes of Glass Viscosity in the Course of Phase Separation and Crystallization Observed by a Penetration Viscometer

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## ABSTRACT

Viscosity of glasses is very sensitive to any change of their structure, i.e. phase separation and crystallization. From the point of view of viscosity changes, both the chemical composition of phases, and the arising texture, and the ratio of phases volume, are important, as well. A significant influence on the viscosity change has the phase separation in the form of spinodal decomposition or matrix crystallization.

The above mentioned changes may be well observed on examples of experimentally measured isothermal time dependence on viscosity using a penetration viscometer for various types of glass. In connection with electron microscopy and X-ray diffraction the course of phase separation and/or crystallization of a number of glassy materials, has been studied. The results of a study of time-temperature dependence of viscosity of borosilicate Simax glass, glass in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$ , rock glass based on granite and phonolite nucleated by  $\text{CaF}_2$  and fused basalts from Slapany and Nová Baňa, are briefly given in this paper as typical examples. The combination of the results of above given methods enabled to clarify the principle of proceeding processes in these materials during heat treatment.

## I. INTRODUCTION

Viscosity of glasses varies significantly with temperature and is very sensitive to any change of their structure, i.e. phase separation and crystallization. From the point of view of viscosity changes, both the chemical composition of phases, especially the changes of matrix composition, but also the arising texture and the ratio of phases volume, are important, as well. At a relative concentrating of components decreasing the viscosity in matrix, the viscosity may even decrease, however, in most cases viscosity increases in the course of the process. A significant influence on the viscosity change has the arising texture, as well, especially when a spinodal decomposition or a connection of phase separated particles into a structure of two interconnected phases, appears. In these cases the viscosity may increase even by several orders. The viscosity change appears, as well, in a two-phase system with solid spherical inclusions in glassy matrix but it is much smaller than in the case of two interconnected phases.

The observation of viscosity changes with the time dependence has been used already for a study of a number of phase separating and/or crystallizing glasses, i.e. opal glasses with fluorine and phosphorus content [1], borosilicate glasses [2] or glass ceramic materials [3].

## II. EXPERIMENTAL PART

Time dependence of viscosity of investigated samples at a constant temperature have been measured by the penetration viscometer. This viscometer is based on the principle of recording the time dependence of impression depth of loaded hemispherical penetration indenter to viscous body. The measurement gives absolute viscosity values in the range from  $10^8$  to  $10^{13}$  dPa.s and it is not necessary to introduce either corrections or experimental factors. The principle, description and verification of this instrument function have been published earlier [4].

A sample of glass in the form of polished disk, 30 mm in diameter, was inserted into a preheated furnace of the penetration viscometer and after 20 minutes the

measurement started. This time, according to experimental verification, is necessary for the stabilization of sample and furnace temperature. For the following calculations of activation energies this time of 20 minutes was subtracted. Further measurements have been carried out after turning the sample in the instrument in time intervals adapted to the rate of proceeding processes. The time dependence of viscosity at a constant temperature on the same sample was obtained by this procedure. Maximum temperature variation during measurement (from the 20<sup>th</sup> minute) was  $\pm 1.5$  °C. This procedure was usually repeated at several different temperatures for gaining the time-temperature dependence.

The principle of proceeding processes has been observed on selected heat treated samples by X-ray diffraction and transmission or electron scanning microscopy.

### III. RESULTS AND DISCUSSION

#### Borosilicate SIMAX glass

The time dependence of viscosity at a temperature of 623 °C (see Fig. 1) has been observed on an older industrially melted Simax glass sample from Glassworks Kavalier, Růženín plant. Similar dependence has been found on the older industrially melted Simax glass samples from Glassworks Kavalier, Sázava plant [5]. The curves of time dependence of viscosity in the measured temperature range from 592 to 639 °C have shown a monotonous increase of viscosity with time with typically exponential course. The phase separation has not been observed by electron microscopy, however, it is possible that the phase separated particles were too small with regard to the recognition ability of the instrument used. The crystallization has not been detected by X-ray diffraction.

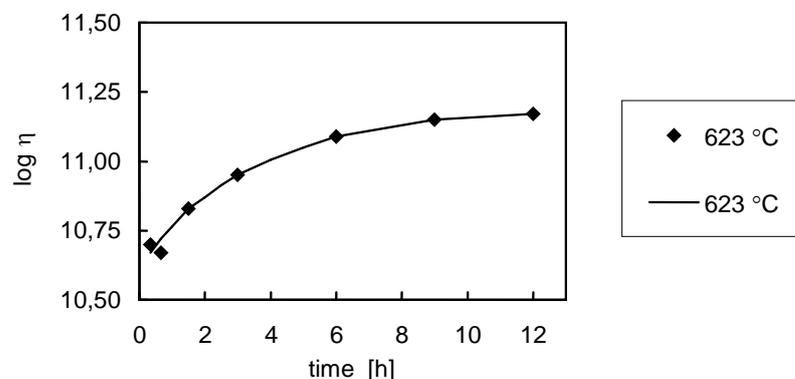


Fig. 1 Isothermal time dependence of viscosity of the Simax glass from Růženín at the temperature 623 °C

Both experimental results obtained and published data for Pyrex glass [2] confirm that the phase separation of this type of glasses is proceeding during the heat treatment in the form of spinodal decomposition and the following growth of isolated particles. The final chemical composition of both phases is given by tie-lines in the phase diagram of immiscibility. Due to the requirement of high chemical durability of this type glass, it is necessary to select their chemical composition so as the matrix was high siliceous and so as the sodium and boron were concentrated in

the phase separated particles and the total volume of phase separated particles was so small that a transition to the region of phase diagram with two interconnected phases could not appear.

From the comparison with published results for Pyrex glass [2] follows that the character and the phase separation rate of Simax glasses, as well, is practically the same. It was also possible to determine the upper critical temperature of phase separation for Simax glass from Sázava plant to  $t = (663 \pm 5) \text{ }^\circ\text{C}$  what is in a good agreement with the published value  $t = 649 \text{ }^\circ\text{C}$  for Pyrex glass [2].

### Glass with fluoride content

The addition of fluorides causes the phase separation and crystallization in a number of glasses. Indications of phase separation in the form of isolated spherical particles have been detected in the glass system  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{CaF}_2$  [6] with 3.60 wt. % of F, marked 1310, by transmission electron microscopy even after preparation. The time dependence of viscosity (Fig. 2) in the measured temperature region have shown a monotonous increase of viscosity with time caused by finishing of the phase separation and crystallization of fluorite  $\text{CaF}_2$  in phase separated particles. After 6 hours at  $812 \text{ }^\circ\text{C}$  the particle size reached a value approx.  $0.5 \text{ }\mu\text{m}$  and the volume of particles from 7 to 8 vol. %. According to the micrographs from the transmission and electron scanning microscope the particles are almost filled with a crystalline material. The crystallization of matrix have not been detected.

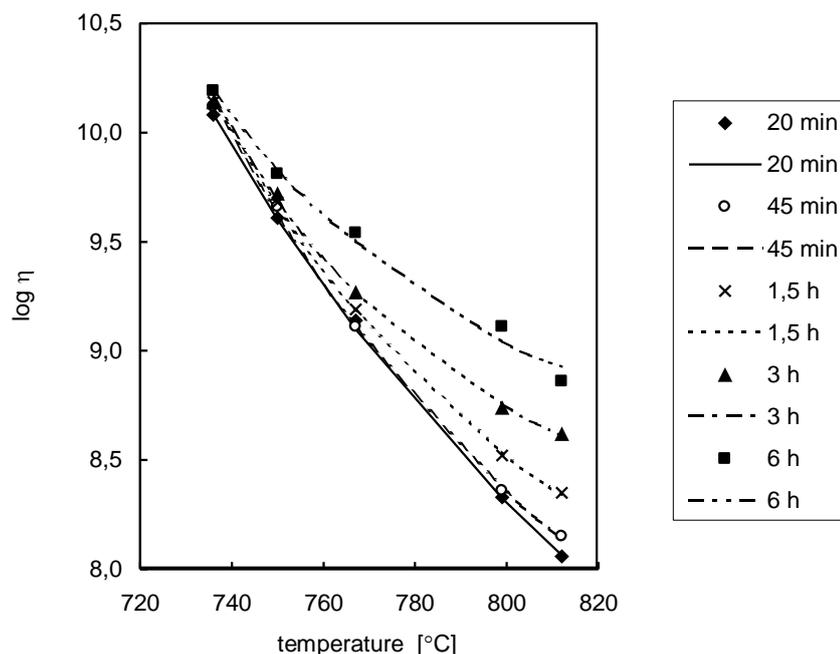


Fig. 2 Temperature dependence of viscosity of the glass, marked 1310 with time isolines

In the case of the given glass the phase separation of isolated particles with an increased calcium and fluorine content and the following crystallization of fluorite in them, has appeared during the heat treatment. The increase of viscosity may be caused both by the change of chemical composition of matrix (increase of its

viscosity by a decrease of fluoride content), and by the physical action of phase separated particles. The influence of the change of chemical composition of matrix is dominant, however.

### Glass ceramic material

During the previous study of the properties of rock glasses based on granite and phonolite nucleated by  $\text{CaF}_2$  [6], an intensive phase separation and a following crystallization has been observed. A selected rock glass in the system  $\text{Na}_2\text{O-K}_2\text{O-MgO-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-CaF}_2$ , marked 1383, has been studied earlier by electron microscopy and the X-ray diffraction. The penetration viscometer has been used for further study of proceeding processes.

Examples of obtained time dependence of viscosity of rock glass at selected temperatures are given in Fig. 3. The curves of temperature dependence of viscosity for selected measurements are documented in Fig. 4. A three-dimensional diagram completely depicting the time-temperature dependence of viscosity is given in Fig. 5.

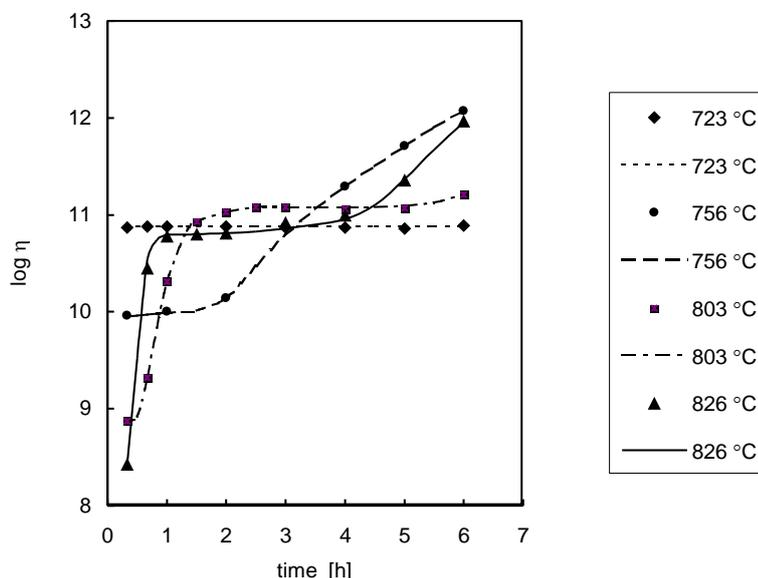


Fig. 3 Examples of isothermal time dependence of viscosity of the rock glass, marked 1383

On the detected time-temperature dependence of rock glass viscosity, four consequential characteristic regions were recognisable. These processes were preceded by a phase separation which proceeded very quickly already during annealing of melted glass and the following stabilization of temperature in the penetration viscometer. According to the results of X-ray diffraction and micrographs from the transmission electron microscope, the glass in the first region was phase separated and X-ray amorphous. Both the initial reannealed sample, and the sample in the 20<sup>th</sup> minute tightly before the beginning of measurement at the lowest temperature, were in an advanced stage of the phase separation in the form of small particles, size about 0.5  $\mu\text{m}$ . During the heat treatment at 723 °C, the average size of phase separated particles was growing, and after 6 hours it reached the size of about 20  $\mu\text{m}$ .

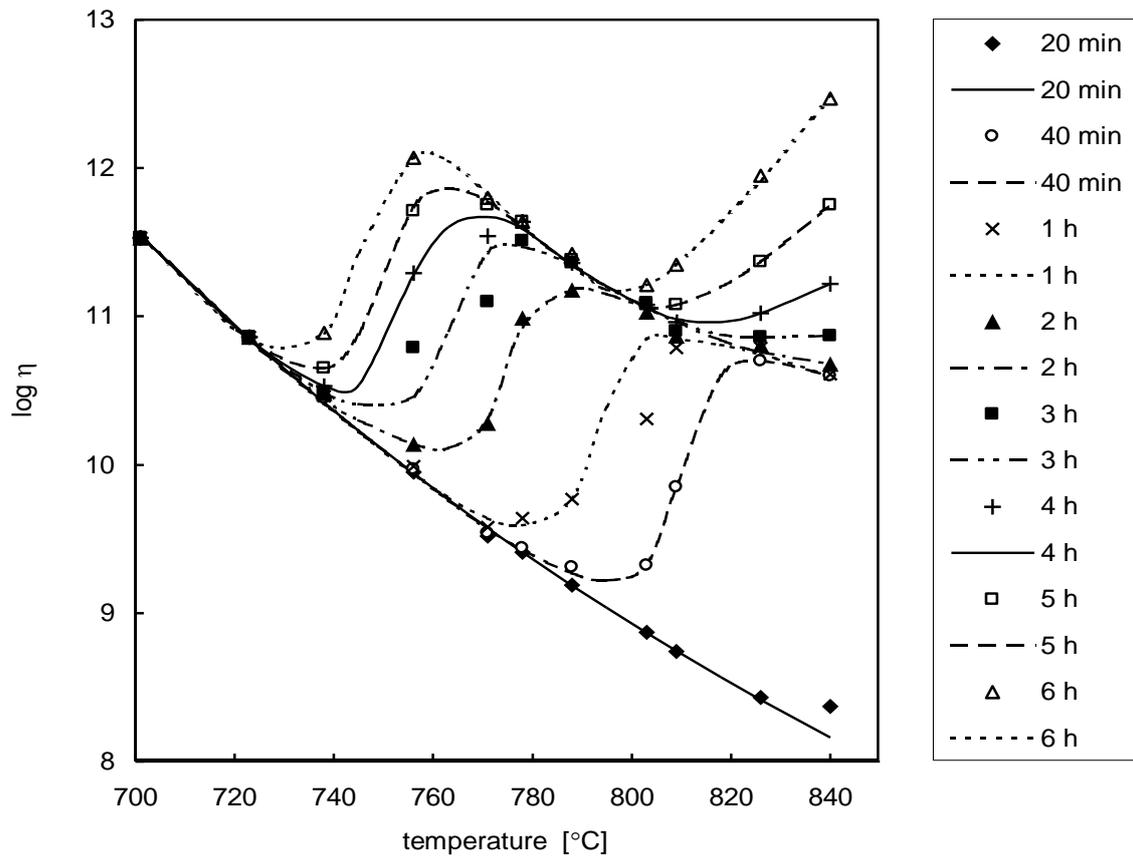


Fig. 4 Temperature dependence of viscosity of the rock glass, marked 1383 with time isolines

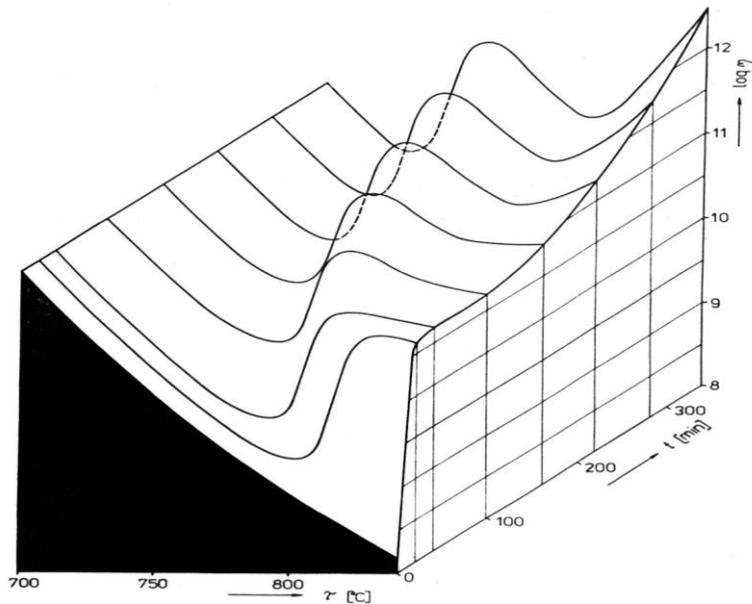


Fig. 5 Time-temperature dependence of viscosity of the rock glass, marked 1383 (without the initial 20 minutes)

In the first region the viscosity did not change noticeably and contemporary with the growth of the average size of phase separated particles by the Ostwald process of growth, the nucleation of the following crystallization proceeded. The second region was connected with a fast viscosity increase by two orders and with the crystallization of fluorite  $\text{CaF}_2$  and fluorphlogopite  $\text{KMg}_3(\text{Si}_3\text{AlO}_{10})\text{F}_2$  in phase separated particles. The first and second region represented the 1<sup>st</sup> crystallization stage and it corresponded to the nucleation and crystallization process of phase separated particles with a transfer of components decreasing the viscosity of glass (fluorine, potassium) from matrix to crystallizing phases.

The third region had a nucleation character again without a significant viscosity change. In the fourth region the crystallization of pyroxene with structure similar to diopside  $\text{CaMgSi}_2\text{O}_6$  and an unknown crystalline phase in matrix occurred and the viscosity increased even above the working range of the instrument. The third and fourth region represented the 2<sup>nd</sup> crystallization stage and corresponded to the nucleation and crystallization process of matrix. With increasing measuring temperature the time of duration of individual regions shortened quickly and processes confluent.

The results obtained enabled to determine the activation energies of processes connected with both stages of crystallization. For the 1<sup>st</sup> and 2<sup>nd</sup> crystallization stage the values of activation energy  $469 \text{ kJ mol}^{-1}$  and  $233$  or  $203 \text{ kJ mol}^{-1}$ , respectively, have been calculated [7].

### **Fused basalts**

The penetration viscometer showed to be very suitable for the study of processes connected with a recrystallization of industrially fused basalts from Slapany and Nová Baňa. Both basalt glasses have been prepared by melting of natural raw materials at  $1500 \text{ }^\circ\text{C}$  and quenched. The changes of viscosity with time (for examples of obtained dependence see Fig. 6) have been observed on samples at selected temperatures. In the connection with electron microscopy and X-ray diffraction it was possible to observe the principle of proceeding processes [8]. In Fig. 7 a summary of experimental results of temperature dependence of viscosity of basalt from Slapany with time isolines, is given. The dependence of both basalt glasses was similar, only the curves were slightly shifted on the time and temperature axes.

Four consequent characteristic regions were recognisable on the detected time-temperature dependence of viscosity of both basalt glasses. In the first region the viscosity did not change, the glasses were amorphous and the phase separation was not detected by electron microscopy. In this region only the nucleation of the following phase separation has proceeded.

In the following second region characterized by viscosity increase by 0.3 to 0.7 order, the phase separation proceeded in the form of spherical particles which successively reached the size about  $1 \text{ }\mu\text{m}$  [8]. However, the samples were still X-ray amorphous according to the X-ray diffraction.

In the third region characterized by an unchanging viscosity, the formation of magnetite was confirmed by X-ray diffraction. In micrographs from the transmission electron microscope the appearance of its small crystals in the interphase boundary phase separated particles/matrix, was well recognisable.

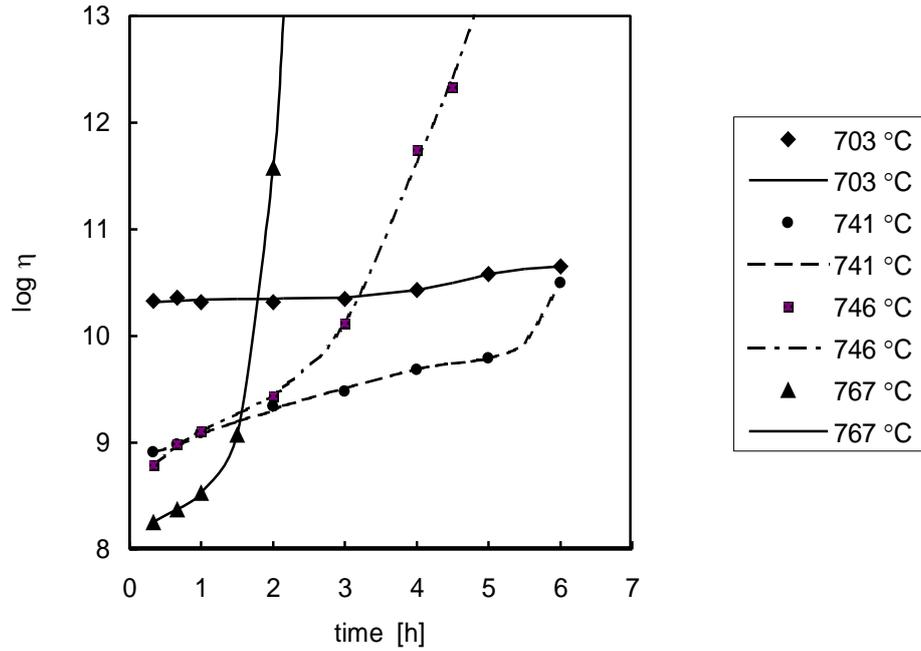


Fig. 6 Examples of isothermal time dependence of viscosity of the fused basalt from Nová Baňa

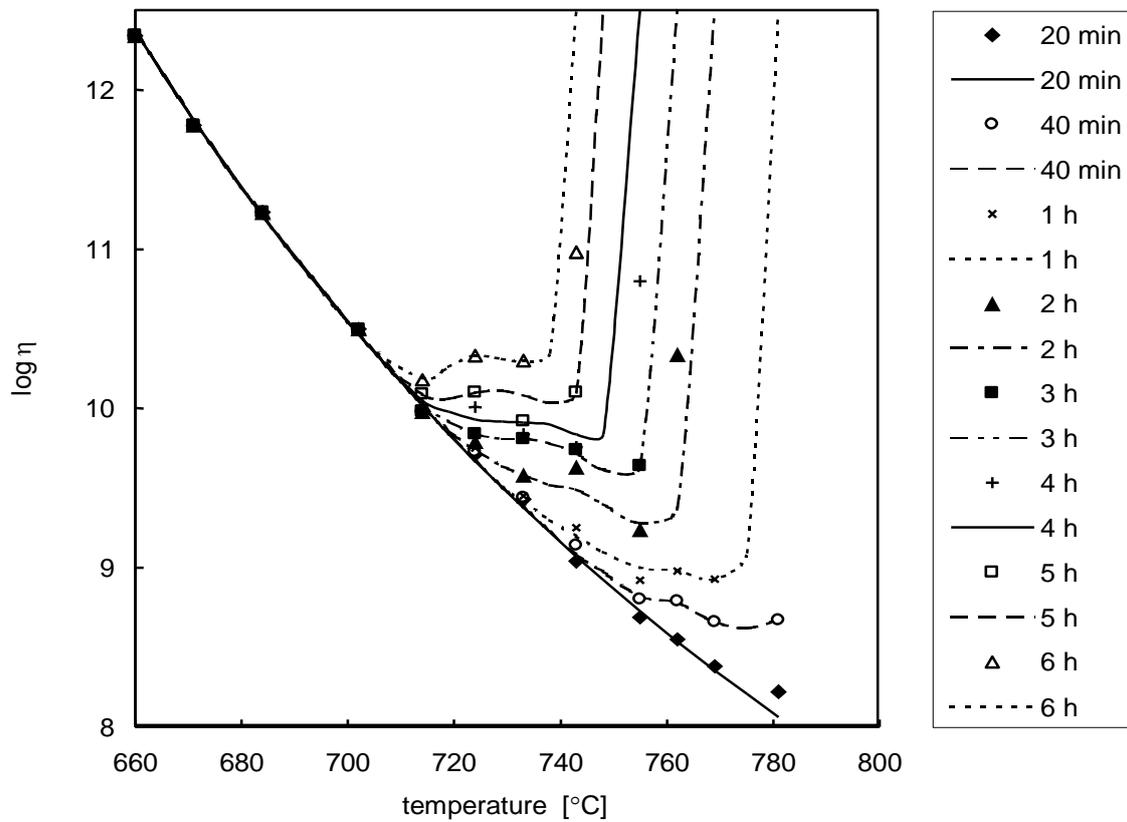


Fig. 7 Temperature dependence of viscosity of the fused basalt from Slapany with time isolines

The fourth region was characteristic by a steep increase of viscosity over the working range of the instrument. This growth was caused by the pyroxene crystallization on the above mentioned magnetite crystals which acted as a nucleator from the interphase boundary to matrix.

#### IV. CONCLUSIONS

The investigation of viscosity changes of glasses by the penetration viscometer is a very sensitive method for observation of phase separation and crystallization of glasses. The results in a number of cases can be used directly for optimization of technological processes in the production of phase separated or glass ceramic materials. In combination with other methods, especially with electron microscopy and X-ray diffraction it can be used for a detailed explanation of proceeding processes.

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