

CRYOGELS – A PROMISING MATERIAL FOR UNDERGROUND WORKS IN PERMAFROST

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Abstract: Cryotropic gel-forming systems have been developed at the Institute of Petroleum Chemistry SB RAS in Tomsk, Russia. They are capable of generating gels at 0–20 °C, subsequently converting to cryogels during freeze-thaw cycles which exhibit high elasticity and adhesion to rock. Both laboratory and field experiments are reported here, including 2003–2004 pilot tests conducted to seal a leaking interval at the base of a dam at the Irelyakh hydrosystem, Stock Company “ALROSA”, Yakutia.

Key words: cryogel, permafrost, viscosity, elasticity, sealing, cutoff wall, dam

1. INTRODUCTION

The use of permafrost is considered as one option for CO₂ geological storage. From this view point two issues arise:

– depending on injection depth and site conditions the CO₂ may occur as individual and mixed gas hydrates, mineral and organo-mineral complexes (clathrates and carbonates) or in other forms;

– the long-term existence of underground CO₂ storage implies permafrost conservation and consolidation.

The present paper discusses cryogels – a promising material for underground works in permafrost regions. These are polymer gels generated due to freezing and subsequent thawing of aqueous polymer solutions. The more “freezing – thawing” cycles the cryogel is subjected to the better its mechanical properties: strength and elasticity increase and formation bond intensifies (Lozinsky, 1998, 2002). Cryogels, i.e. cryotropic gels, are

peculiar polymer solutions, with a higher critical solution temperature (Rebinder, 1979; Papkov, 1974). The spatial pattern of cryogels is formed during phase transformation and is stabilized with intermolecular bonds of different nature: covalent, coordination and ionic-electrostatic. This variable bond type generates the cryogel manifold and allows their properties to be varied significantly (Lozinsky, 1998, 2002; Sergeev et al., 1978).

Cryogels based on polyvinyl alcohol (PVA) are of great interest both scientifically and from an applied viewpoint. They are widely used in biotechnology, medicine, food industry and others (Sergeev et al., 1978; Lozinsky, 1998). In many respects this interest results from the excellent mechanical, diffusional and thermophysical properties of PVA cryogels, polymer availability, its non-toxicity and biocompatibility, as well as its relatively simple gelation technique involving freeze-thaw cycling. It is possible to regulate physico-chemical properties of cryogels within wide limits (Sergeev et al., 1978; Lozinsky, 1998) by varying polymer characteristics (molecular mass, chain-length distribution, content of residual *o*-acyl groups, tacticity and PVA concentration in the system), solvent composition, additive nature and cryogenic process conditions (temperature and freezing duration, thawing rate, number of over freezing cycles, etc.). In practice water is used as the basic solvent for PVA. PVA is resistant to oils and fats, aliphatic and aromatic hydrocarbons, weak acids and alkalis. In addition PVA exhibits universal adhesive and bonding properties and is also atmosphere and oxidation-resistant.

2. RESULTS

2.1 Laboratory Experiments

Gelation kinetics and the rheological properties of PVA solutions of different concentrations (from 0.5 to 10 wt%) have been studied in the temperature range from -30 to $+10$ °C. We have also studied PVA solutions containing additives, which affect gelation kinetics and rheological properties of gels and cryogels, as well as their adhesion to rocks, in order to create flow barriers within ground constructions. Viscosity and Young's modulus were chosen as rheological characteristics.

Viscosity was measured using a "Reokinetika" vibration viscosimeter equipped with a tuning-fork gauge. Distilled water was used as a calibration liquid.

Modulus of elasticity for gels was determined based on "tension – deformation" diagrams, obtained during quasi-elastic cylindrical-sample compression using in-house developed equipment based on a micrometer

and electronic scales. The modulus of elasticity was calculated as the angle of slope of the initial linear segment, where Hooke's law is observed, relative to the compression – deformation curve.

The kinetics of cryotropic gelation of 5 and 10 % PVA solutions was studied at - 32 and - 18 °C by using the modulus of elasticity as the principle monitoring parameter. Solutions were maintained at sub-zero temperatures for a pre-determined time and then they were subjected to thawing at 2 and 18 °C. The mode of thawing is a factor which significantly affects visco-elastic properties of cryogels. Slow thawing promotes generation of cryogels exhibiting high viscosity and modulus of elasticity, and thus the lower the freezing temperature the stronger the cryogels (Figs. 1 and 2). At higher thawing rates the effect of freezing temperature on the visco-elastic properties of cryogels decreases.

The effect of the number of "freeze-thaw" cycles on the properties of cryogels, prepared from aqueous PVA solutions, has been studied. The cryogels were frozen at - 18 and - 32 °C and then thawed at 18 and 6 °C. The results obtained in the study indicate that the modulus of elasticity increases with the number of "freeze-thaw" cycles and it does not depend on the thawing rate (Fig. 3). The greatest increase in elasticity was observed after 2 – 4 freeze-thaw cycles.

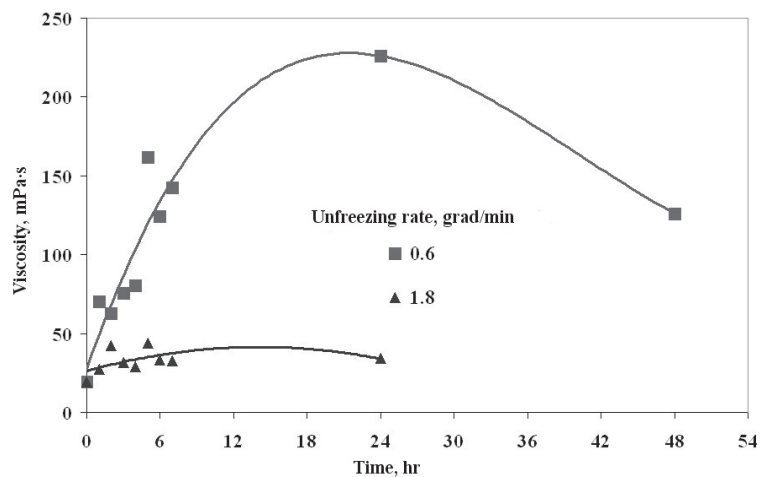


Figure 1. Viscosity change of 5 % PVA solution after thermostating at -32 °C and thawing at different rates.

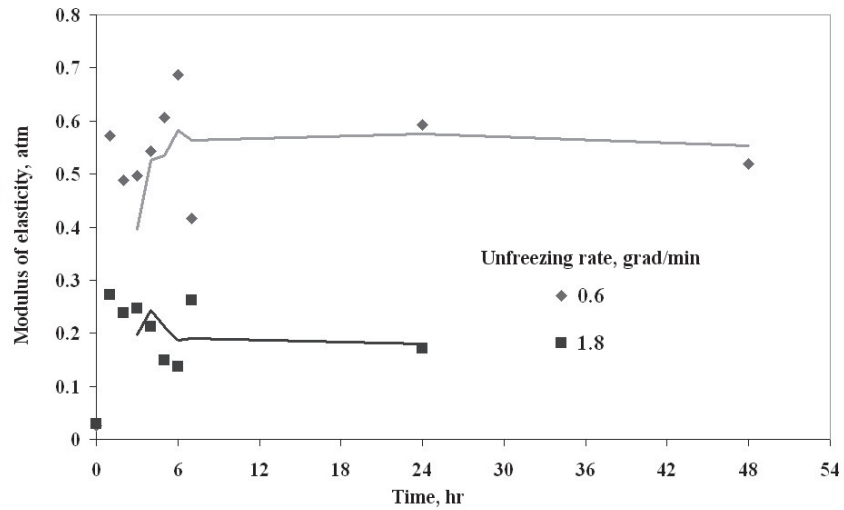


Figure 2. Elasticity changes of 5 % PVA solution after thermostating at -32°C and thawing at different rates.

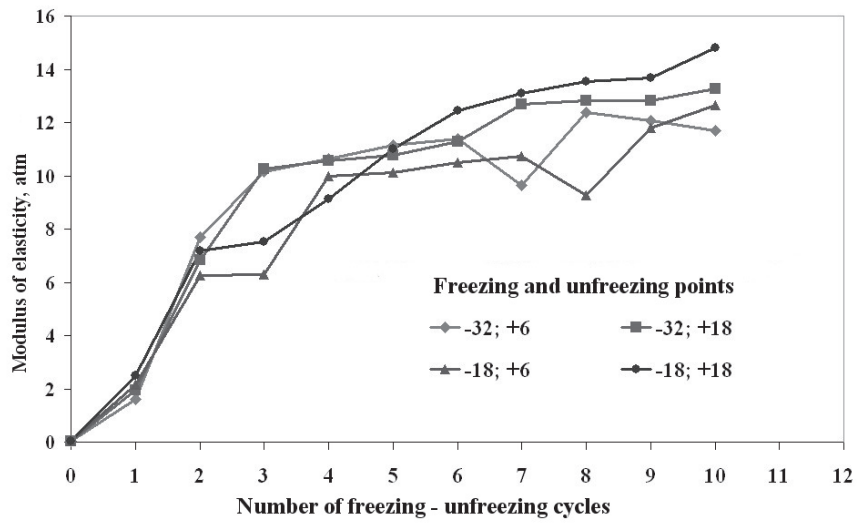


Figure 3. Dependence of the modulus of elasticity (for cryogels obtained from 10% PVA solution and which were frozen at -32 and -18°C), on the number of freeze-thaw cycles at 18 and 6°C .

We studied gelation kinetics of a 5 % PVA solution at +2 °C and compared the visco-elastic properties of the prepared gel with those of cryogels obtained from the same solution during freezing at –18 and –32 °C, followed by thawing at +18 °C. The study showed a significant increase in gel viscosity and modulus of elasticity at the lower freezing temperature (Fig. 4).

The viscoelastic properties of gels prepared from 5 and 7 % PVA solutions at –5, 0, +2 and +22 °C have also been studied. The gels contained electrolytes as additives, which affected gelation kinetics and the rheological properties of gels and cryogels, as well as their adhesion to rocks. Gelation kinetic studies of PVA solutions containing electrolytes as additives already showed that the gels were formed in several hours at 0 – 18 °C.

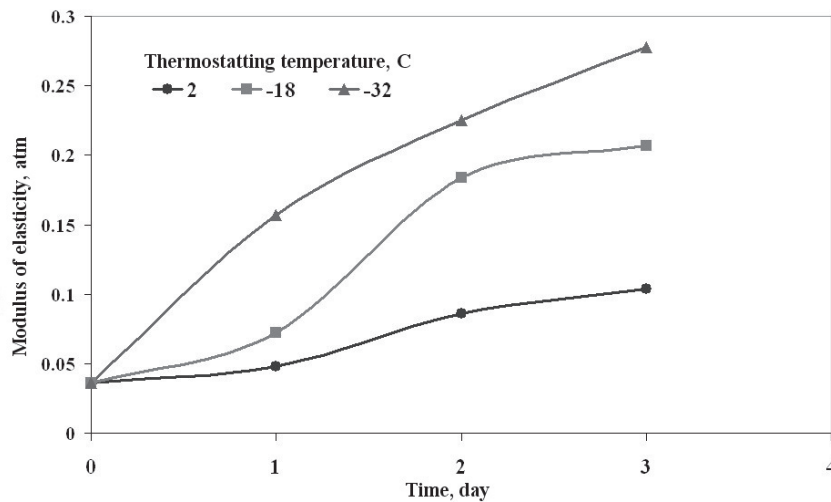


Figure 4. Dynamics of modulus of elasticity for 5 % PVA solution thermostated at different temperatures.

Moreover subsequent thermostating or freezing – thawing of the gels improved their strength. It has been determined that viscosity and elasticity of the solutions increased 3–5 times when a cross-linking agent was added to the PVA aqueous solutions, depending on agent concentration and thermostating time (1 to 8 days) at +2 °C

Strength changes occurring in cryogels with different fine-filling agents were also studied, such as crushed carbonate rock (fraction 0.16 – 0.5 mm), sand and crushed core material having sandstone / argillite ratios of 2:1; 1:1 and 1:2. The highest modulus of elasticity was observed with the filling

agents in a 1:1 ratio and cryogel prepared from a PVA solution with a cross-linking agent and filled with crushed carbonate rock and core material. Moreover the modulus of elasticity of the cryogel also increased with an increase in PVA and cross-linking agent concentrations. The addition of electrolyte and a cross-linking agent to the PVA solution significantly increased the modulus of elasticity in all PVA solutions – crushed carbonate rock ratios (Fig. 5).

The filtration characteristics of gel-forming systems were studied under thermobaric conditions simulating water filtration through anti-filtration barriers in constructions in the northern climatic zone. Experiments consisted of water filtration at a constant discharge rate through a laboratory model of a filtering medium.

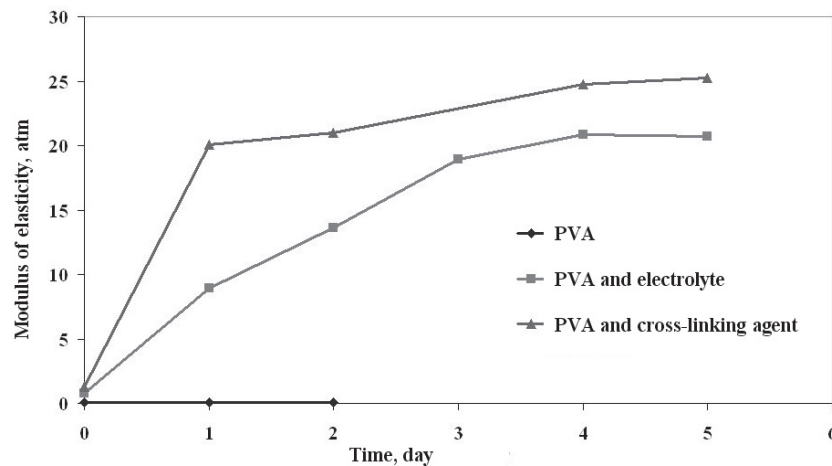


Figure 5. Increase in modulus of elasticity for PVA solutions with added electrolyte and cross-linking agents after thermostating with crushed carbonate rock at a ratio of 1:2 at +2 °C.

The model was packed with crushed carbonate rock (fraction 0.16-0.5 mm), with permeability varying from 9.78 to 87 μm^2 . A gel-forming solution containing 3 % PVA and a cross-linking agent (Fig. 6) was injected into a model consisting of crushed carbonate rock with a permeability of 87 μm^2 at 6 °C at lower pressure values (from 0.3 to 2.25 atm/m). The model was subsequently held at 6°C for 5 hours to form the gel, and then once again water infiltration experiments were continued. At pressure increases up to 50 atm/m no water infiltration was observed (Fig. 6).

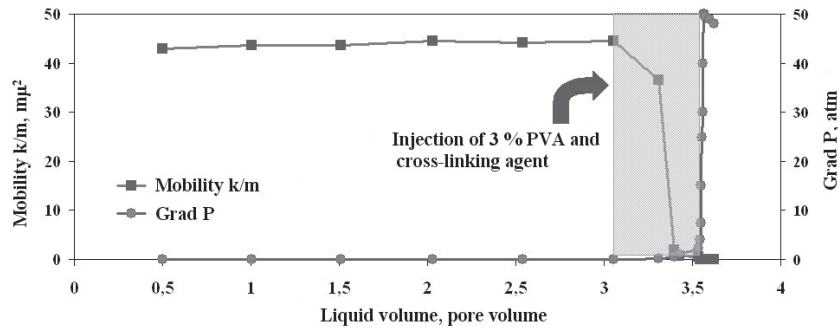


Figure 6. Creation of a cutoff wall via injection of a gel-forming solution (3 % PVA and a cross-linking agent) into a crushed carbonate rock model with permeability of $87 \mu\text{m}^2$ at 6°C .

Figure 7 presents the results of the creation of a cutoff barrier in a model consisting of crushed carbonate rock having a permeability of $10.254 \mu\text{m}^2$ at 20°C . Injection of a gel-forming solution containing 10 % PVA and electrolyte was performed at a pressure gradient of 3.5–4 atm/m. The model was subsequently held for 12 hours at 20°C to form the gel, after which water infiltration was once again initiated. No water infiltration was observed at pressure increases up to 140-160 atm/m (Fig. 7).

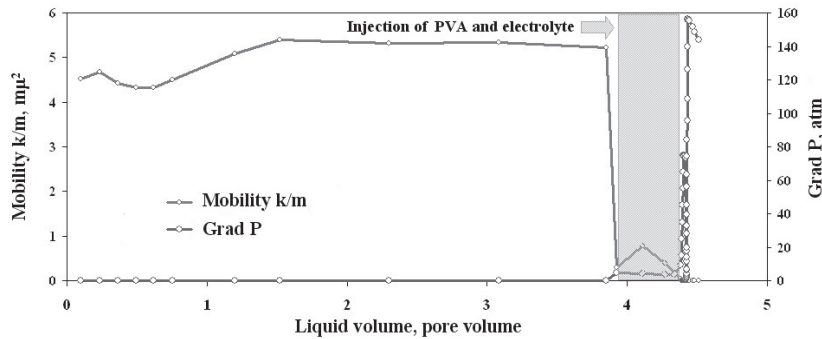


Figure 7. Creation of cutoff screen via injection of gel-forming system: 10 % PVA and electrolyte into a model of carbonate rock with permeability of $10.254 \mu\text{m}^2$ at 20°C .

Thus, PVA-based gel-forming solutions with a cross-linking agent and electrolyte as additives are capable of creating reliable cutoff barriers in carbonate rocks. The study of infiltration characteristics of soils with PVA-based gel-forming solutions under thermobaric conditions demonstrated that after gelation one could observe a sharp decrease in water mobility, even up to pressure differences higher than 100 atm/m.

2.2 Field Experiments

In order to seal a leaking interval at the base of a dam at the Irelyakh hydrosystem in Mirny City, Sakha Republic (Yakutia) we have developed the CRYOGEL-1 system based on PVA and a cross-linking agent. The system is capable of forming gels at 0–20 °C during several hours and then cryogels during the freeze-thaw process. In August-September of 2003, 51 tons of cryogel-forming solution were injected into 5 holes at the base of the dam. This injection formed a cryogel barrier that is 15m in length, 3 m thick and covers an area of about 430 m² at a depth ranging from 16 to 45 m. The barrier created a cutoff wall which decreased water infiltration by 150 times. The results of geophysical studies and hydrodynamic investigations in a test hole, drilled between the third and the fourth holes into which the cryogel was injected, show that the average specific water absorbing was 0.15 L/(min·m·m water column) up to 40 m deep, highlighting the positive results of the research.

In 2004 the work at the Irelyakh hydrosystem dam was continued. Based on the regulations of IPC SB RAS Stock Company, “Korona-TEK” designed and made equipment for the preparation and injection of cryogel-forming solutions. In September-November of 2004 starboard plugging of the dam, where the filtration was the strongest, was successfully carried out. A total of 70 tons of cryogel-forming solution was injected into 13 holes to create a cryogel barrier at a depth ranging from 13 to 43 meters.

In 2005 cryogel-forming solutions will be injected into more than 100 holes to create a cutoff wall along the full length of the Irelyakh hydrosystem dam.

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