Gaseous helium storage in salt caverns: influence of physical properties

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Introduction

There is an intention to develop four large gas-condensate fields in Eastern Siberia in the upcoming decades. The ultimate reserves of these fields with high concentration of helium 0.25-0.58% exceed 4 trn. m^3. The helium reserves outrange 5 bln. m^3. However, world demand for Russian reserves of helium is expected in the 2030s. One of the prospects for helium storage in the first decades of gas recovery in Eastern Siberia is the usage of salt caverns which are constructed in rock salt by drilling.

The main advantages of helium storage in salt caverns are:

- caverns high impermeability
- the preservations of helium properties/market standards during the entire period of storage and the absence of necessity to reclean helium before shipping
- caverns sequential starting in accordance with helium volumes of extraction
- almost unlimited rate of helium recovery and injection under conditions of limited number of operating wells
- salt caverns availability for some other products storage and for the industrial wastes conservation after full recovery of helium.

There is no any foreign experience of helium storage in salt caverns at the moment.

Inside the US gaseous helium is stored in the Cliffside storage facility (Texas) based on abandoned gas field. It contains about 1 bln.m^3 of the helium concentrate (70% of helium). However – as preliminary estimates have shown – helium storage in salt caverns is more cost-effective for East Siberia conditions.

The principle possibility of helium storage in salt caverns is based on experience in operation of underground helium storage (He > 80%) near Orenburg, Russia, which includes several salt caverns were built at the depth of 1350 – 1470 m.

In general, there are no significant differences in the approach to the problem of underground helium concentrate storage in salt caverns as compared to compressed natural gas storage. However, the analysis of information on underground helium concentrate storage has shown that there are significant gaps in fundamental data, related to helium migratory behavior in rock salts, brines and well spaces. These problems are discussed in the paper.

1. Studies of rock salt and backfill helium and nitrogen permeability

Studies of rock salt sample gas permeability have been held according to standard screen rock permeability testing procedure using the unit equipped with core holders of three standard sizes: standard core holder for testing cylindrical samples 30x50 mm in size (figure 1a) and purpose-made core holders for the samples 35x70 mm (figure 1b) and 50x100 mm in size (figure 1c)

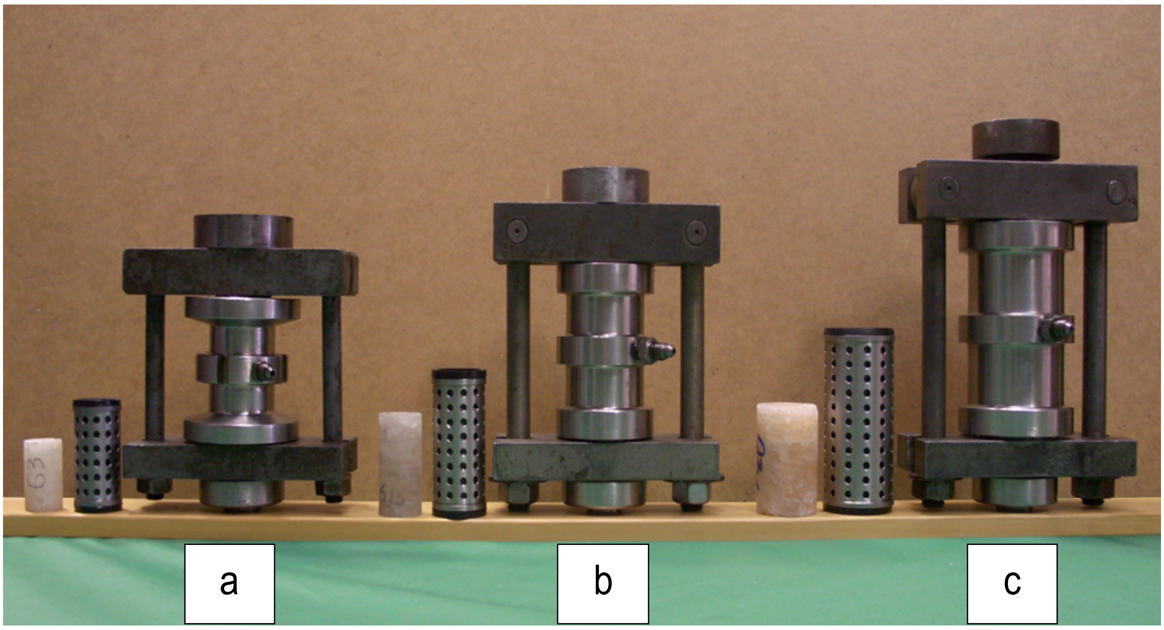


Figure 1 – Standard sizes of core holders:

a) for testing of the samples 30 mm in diameter and 50 mm high
b) for testing of the samples 35 mm in diameter and 70 mm high
c) for testing of the samples 50 mm in diameter and 100 mm high

Core holders enable determination of the filtered fluid flow rate under the conditions of pre-set uniform and non-uniform volume compression of samples.

Each sample has been nitrogen and helium tested and constant hydrocrimp and fluid pressure conditions. Nitrogen or helium swap sequencing was being changed in order to negate experimental errors.

The tests were performed at room temperature as rock temperature at expected helium reservoir location depth in East Siberia ranges from 18 to 27 ^{0}C .

Gas permeability coefficient (K, m^2) was calculated by the following formula:

$$K = \frac{2 \cdot Q \cdot P_б \cdot \mu \cdot L \cdot 1000}{(P_1 + P_2 + 2P_б) \cdot F \cdot \Delta P}$$

where, $Q = \frac{V}{t}$ is the gas flow rate measured at the sample outlet, m^3/s;

V - the volume of the gas passing through the sample, m^3;
t - filtration time, s;
μ - gas viscosity, MPa·s;
L - sample length, m;
F - sample filtering surface area, m^2;
$P_б$ - barometric pressure, MPa;
$\Delta P = P_1 - P_2$, MPa;
P_1 – gas pressure at the sample inlet, MPa;
P_2 - gas pressure at the sample outlet, MPa.

Permeability measurement net inaccuracy falls in the range of $7.9\% \geq \frac{\Delta K}{K} \geq 4.8\%$.

Rock salt is virtually impermeable in natural rock mass. Primary values of salt sample permeability obtained at laboratory conditions are determined by structure microdefects emerging due to mechanical effects during core extraction and sampling. Samples made from the species distinguished by high instantaneous strength (23 MPa and more) are usually almost impermeable (10^{-21} m^2 and less). After primary tests samples were deformed under the loads close to long-term strength, i.e. at conditions close to the loads existing in the vicinity of the cavern after its construction for the purpose of obtaining statistically representative samples in the wide range of nitrogen and helium permeability.

39 rock salt samples of different sizes have been tested altogether. Not less than 4 permeability tests have been carried out for all the samples which survived stressing for the purpose of achieving steady helium and nitrogen filtration before and after stressing.

The findings demonstrate that helium permeability values are slightly higher than those of nitrogen permeability in almost all the cases except for the samples which were not exposed to helium or nitrogen filtration. Figures 2 and 3 show all permeability values measured before and after stressing. Sample numbers on the figures: “a” index is added to samples before deforming, “b” index – after deforming.

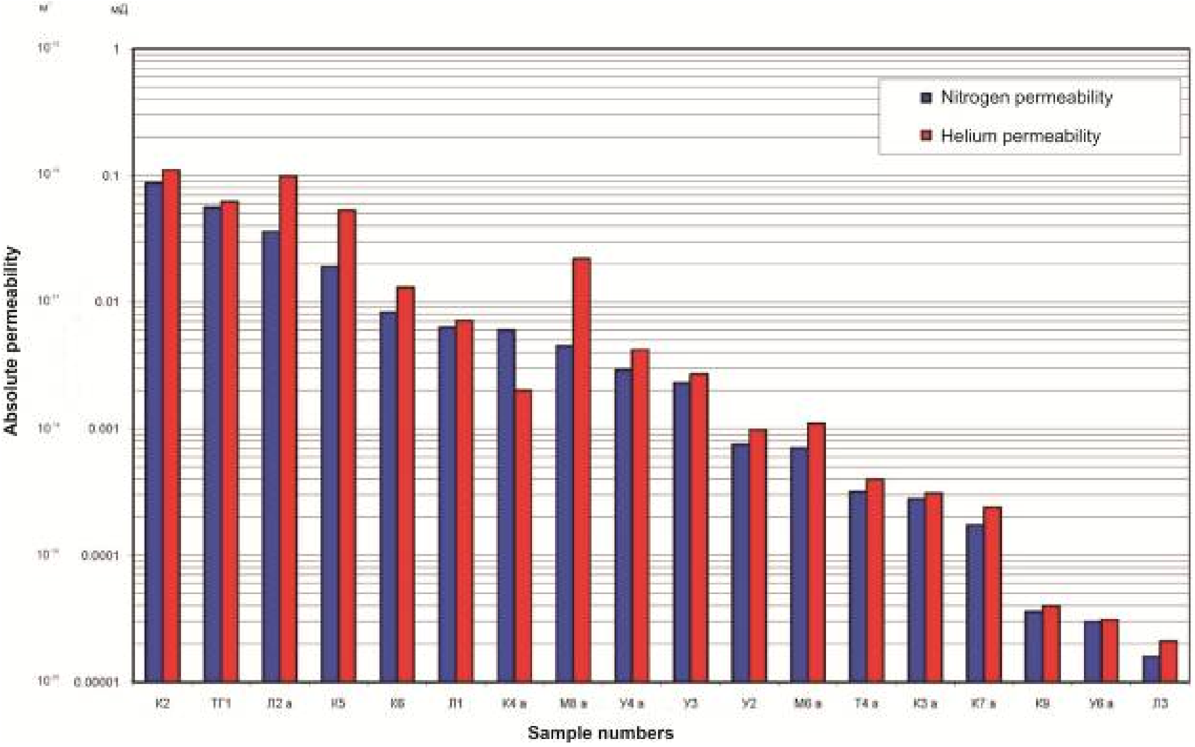


Figure 2 – Absolute permeability of rock salt samples before deforming

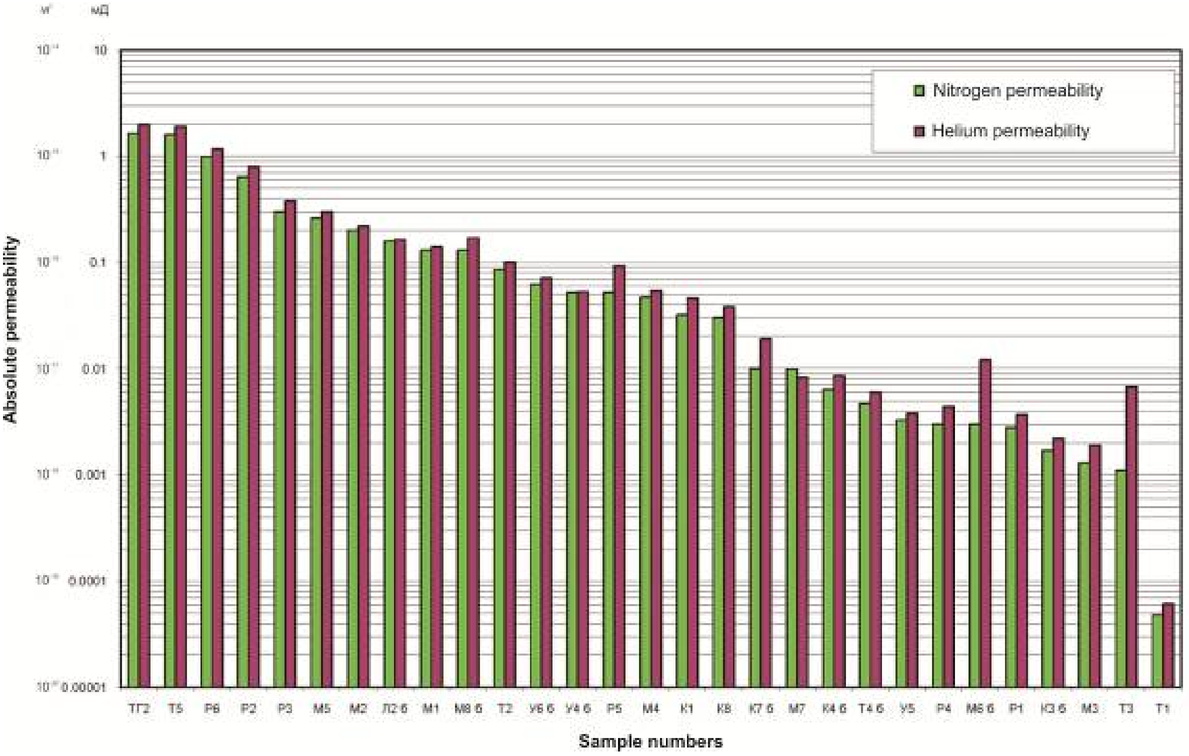


Figure 3 – Absolute permeability of rock salt samples after deforming

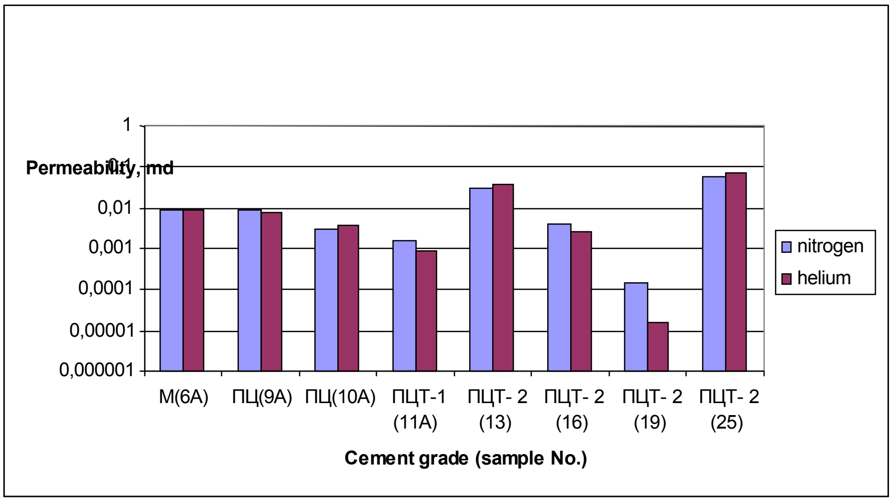
Permeability reduction during transition into dilatancy phase is determined by the threshold channel size enlargement ratio. This process is illustrated dramatically by the mercury injection data. This method is based on the pore size – mercury capillary pressure relationship.

Two pieces with permeability difference of two orders were taken out of rock salt samples for testing. Pore-size distribution was defined in each of the pieces. Resulting porograms show that the contents of large filtrating pores located on the right-hand side of porograms serves as permeability increase determinant. The mechanism of gas transfer in such pores seems to be determined by viscous flowing. Different gas transfer mechanisms (viscous and molecular flows) act simultaneously in void space. Gas flowing in small pores comparable to gas molecules in size would occur according to the Knudsen law. It can be expected that higher values of helium permeability in comparison with nitrogen permeability have been obtained due to this particular component of the total gas flow as helium molecular weight is lower which makes it more fluent. The differences in rock salt helium permeability and nitrogen permeability obtained during tests range within the same order and have no vital importance for practical use. It means that past relationships based on rock salt nitrogen permeability can be used in calculations connected with helium storage development.

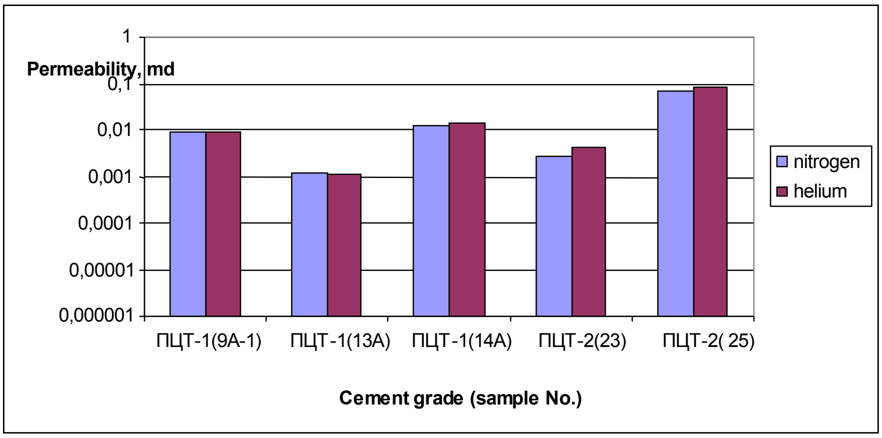
Experimental studies of backfill helium and nitrogen permeability were carried out in much the same way as those of rock salt permeability.

Oil-well cement hydrated in saturated NaCl brine is used for well casing and packing in soluble saliferous rocks. Portland cements to be applied are tested for quality and properties compliance with corresponding specifications before cementing.

Figure 4 shows the results of cement sample nitrogen- and helium-permeability determination for oil-well cements from different manufacturers. The tests were carried out in 7, 14 and 28 days.



b)



c)

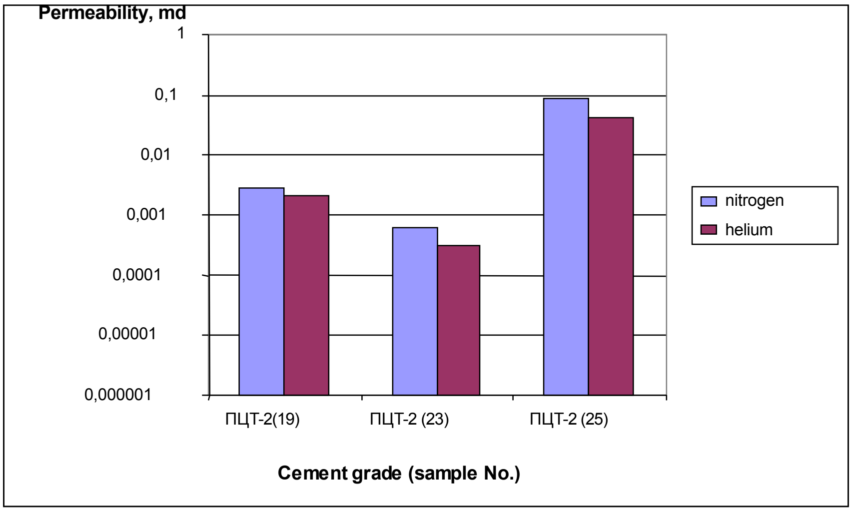


Figure 4 – Cement sample nitrogen permeability and helium permeability
a) in 7 days; b) in 14 days; c) in 28 days

Comparative evaluation of nitrogen and helium permeability for metal core-free cement samples with different compositions demonstrated that permeability characteristics are virtually identical. The same is registered for backfill samples containing metal core. On the whole, the analysis of experimental data presented shows that helium and nitrogen permeability of backfill samples as well as that of the "rock salt - cement stone" system and "rock salt – cement stone – metal core" system is virtually identical.

2. Helium diffusion in rock salt

Solving a problem of possibility of long-term helium storage in rock salt caverns requires thorough investigation of the processes of its expansion into salt deposits. Analysis of literary data performed in the paper [1] shows that helium travel by way of diffusion in either defect-free or defect (dislocation and grain boundaries) crystal lattice can be excluded from consideration in evaluation of permeability in unbroken layer zones as corresponding diffusion coefficients fall in the area of negligible values. However natural salt occurrence means inevitable existence of brine inclusions in the form of intergranular layers persistent at the boundaries of substantially misoriented grains with high specific surface energy (> 80 – 100 mJ/m^2) [2].

Theoretical calculations and laboratory-based experiments with sodium chloride [3], as well as natural rock salt analysis [4] give similar results: subject to NaCl contact existing water is capable of wetting 30 – 35% of all grain boundaries. According to percolation theory [5] it means that percolation threshold in NaCl – H_2O system is far exceeded which corresponds to stable occurrence of long continuous network of wetted boundaries. It follows there from that only cohesive network of liquid intergranular layers can serve as the only one effective route of helium diffusion expansion in unbroken rock salt mass as the coefficient of helium diffusion in water solutions D is approximately 15 orders higher than that in NaCl crystals [6].

Experiments were aimed at direct measuring of change in helium diffusion speed through polycrystal sodium chloride samples. Resulting values of diffusion coefficients were compared to permeability coefficients and average values of thickness of liquid intergranular layers in these samples measured in parallel.

The amount of helium passing through the sodium chloride polycrystal was determined by means of commercial mass spectrometer for isotope analysis. Refusal from vacuum processing impossible due to presence of water layers in samples is peculiar feature of this system as compared to the systems described in literature. Original isobaric version enabling helium amount registration according to its partial pressure was used instead.

The sample was put into metal tube; sodium chloride-powder compacts were prepared directly in the tube; they were attached to the tube with picein during operations with polycrystals. Helium inlet pressure amounted to some portions of kPa. Helium diffused through the sample entered the mass spectrometer puffing system subject to opening of the three-way vacuum valve and was adjusted by proportioning needle valve. Ar+ ionic current which was set almost identical for every measurement and served as gas flow measure was also determined additionally in order to control puffing amount. The valve was being closed between the measurement cycles. Device calibration was performed by the three-way valve opening to the bottle filled with a standard air-helium mixture, the proportion being known. Calibration was performed in the course of the test on ionic currents He+/Ar+ proportion in the air mixture with a known helium addition existing in a closed vessel during evaporation of water containing certain amount of dissolved helium (maximum solubility at standard conditions amounts to about 8 ml He in 1 l of saturated NaCL water solution). Helium amount was determined at ionizing electron energy of 95 eV and emission current of 1 mA.

System configuration allows to dinstinguish the mode of helium diffusion through the sample from helium flowing (in the phase form) in the presence of large cracks the solution can squeeze through in case of pressure drop. Should the crack be present in the sample pressure increase leads to jump in helium amount in the puffing system due to pressure balancing through the leak.

Accumulation kinetics for helium passing through the sample in pseudo-steady state (Q flow) has been studied. 2-3 measurements have been taken for each sample type (polycrystals or sodium chloride compacts).

Effective diffusion coefficients were calculated by Fick equation in the linear approximation $dc/dL \rightarrow c/L$.

$$Q = D_{eff} \cdot \frac{\Delta c}{\Delta L} \cdot S$$

The values of effective diffusion coefficients are presented in the table 1.

Table 1 – Calculated values of effective diffusion coefficients D_{eff}

Sample type	D_{eff}, m^2/s
Compacts, d = 100–250 μm	$(2.0\pm0.8)\cdot10^{-12}$
Polycrystals, d = 2–3 mm	$(1.4\pm0.7)\cdot10^{-12}$

Effective section area of mass transfer S_{eff} has been calculated following the measurement results with provision for known values of the coefficient of helium diffusion in water (10^{-8} m^2/s). In polycrystals this value turned out to be about 0.01 % of the sample section which corresponds – the average grain size being about 2.5 mm - to much the same thickness of the layers (~ 130-140 nm), determined in the intergranular layer volume tests and permeability coefficient tests .

Obtained values of effective diffusion coefficients characterizing the speed of helium mass transfer through intergranular water layers in sodium chloride exceed the values of the coefficients of helium diffusion through dry grain boundaries of any polycrystal solids by some orders whereas the latter exceed the coefficients of diffusion through the grain body by far.

The fact that total water content localized in pores has no significant influence upon either effective diffusion coefficient or sample permeability coefficient appears to be an essential finding. Measured D_{eff} values for compacts with about 20% of pores filled with water and for compact polycrystals where the water content does not exceed 0.5% turned out to be of the same order of magnitude; the same applies to permeability coefficients K. It follows therefrom that phase water flowing speed and helium diffusion speed are limited by a “bottle neck” – the presence of thin intergranular brine layers.

Findings show that the speed of frontal advance in unbroken salt deposit cannot exceed some centimetres per year.

3. Helium solubility and diffusion in NaCl water solutions

The analysis of available numerical data on helium solubility in water and NaCL solutions at high and low pressure demonstrated insufficiency of accurate and reliable information in this field as large portions of data on helium solubility in water even at a standard pressure $p^{\varnothing}$ = 0.1 MPa are often far different not only in the absolute value but also in the behaviour of solubility with variations in temperature.

Statistical data processing has been performed for the purpose of expert data selection and classification using Bunsen absorption coefficient ($a_2^* = \frac{v_2^g(T^{\varnothing}, p^{\varnothing})}{v_1^l(T, p^{\varnothing})}$ where v_2^g is dissolved gas volume and v_1^l - dissolvent volume) as the unit of expressing gas concentration in saturated solution. Experimental determination of helium solubility in water on special units has been performed at a standard pressure and different temperatures in order to verify the accuracy of samples obtained.

The value of relative divergence of Bunsen coefficients calculated by approximate equation from experimentally measured coefficients has been taken as the criterion for selection of the most reliable solubility values. Table 2 shows some results of experimental studies.

Table 2 - a_2^* experimental values at different temperatures and NaCl solution concentrations at a pressure of 20 MPa

Concentration NaCl, %	Temperature, K		
	298.15	328.15	353.15
10	1035; 1042; 1038 a_2^* (average) =1038±9	1099; 1106; 1098 a_2^* (average) =1101±11	1301; 1298; 1306 a_2^* (average) =1301±10
20	701; 708; 709 a_2^* (average) =706±11	772; 770; 767 a_2^* (average) =770±6	969; 969; 974 a_2^* (average) =971±7

Comparison of obtained a_2^* numerical values with experimental data has shown that design Bunsen absorption coefficients are quite accurate. The findings allowed to compile the tables of recommended Bunsen absorption coefficient numerical values at NaCl concentration from zero to 25 % mass., gas partial pressure from 0.1 MPa to 20 MPa and a temperature of 293.15 K – 353.15 K in increments of 5 K.

Helium solubility-temperature function passes through the minimum in the temperature area of 303 K associated with change of the helium dissolution mechanism from void to solvation one. Maximum helium concentration is registered during its dissolution in brines with minimum salt concentration subject to high pressure and temperature.

Helium diffusion in water and NaCl water solutions was studied via computer simulation in a wide range of concentrations, pressure and temperature. Approximation of obtained diffusion coefficients as a function of concentration and pressure gives the following formula for the coefficients of helium diffusion in NaCL water solutions.

$$D = D_0 (1 - 0.01138P)(1 - 0.1808s + 0.028s^2 - 0.0018s^3),$$

where P is pressure in MPa, s – molal concentration.

Figure 5 shows diffusion coefficient at a temperature of 300 К and a pressure from 0.1 to 30 MPa.

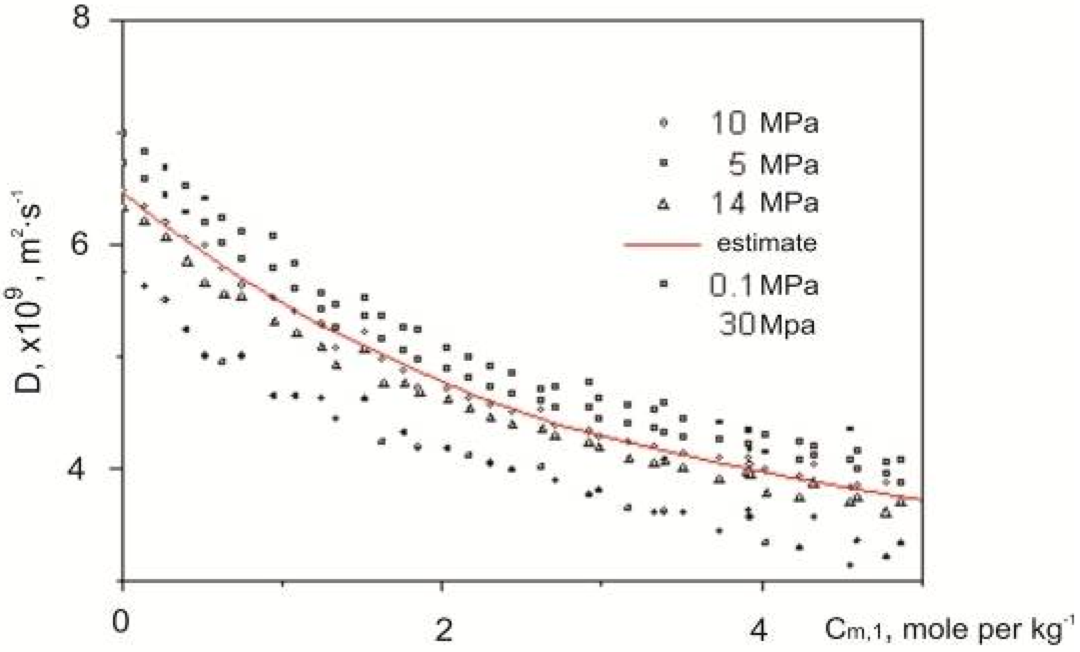


Figure 5. Coefficient of helium diffusion in NaCl water solutions at a temperature of 300 К and a pressure from 0.1 to 30 MPa.

Helium diffusion coefficient – temperature relationship is described by the following equation:

$$D = D\ (T)(1 - 0.01138P)(1 - 0.1808s + 0.028s^2 - 0.0018s^3),$$

where D(T) is the coefficient of helium diffusion in water as the function of temperature.

Figure 6 shows diffusion coefficient-temperature relationship at a pressure of 10 MPa and NaCl concentrations of 1, 2, 3, 4, 5 , mole per kg^{-1} , from top downward respectively.

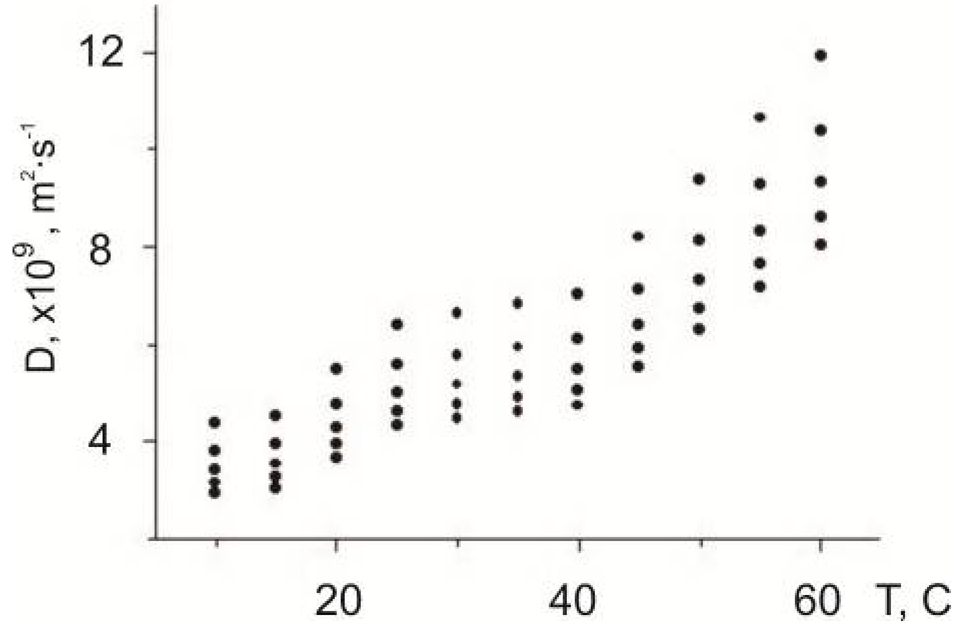


Figure 6. Diffusion coefficient-temperature relationship at a pressure of 10 MPa and NaCl concentrations of 1, 2, 3, 4, 5 , mole per kg^{-1}, from top downward respectively.

Curve bend associated with maximum hydrogen bond network tension is registered in the temperature area of 313 K. The change of diffusion mechanism is also observed in the temperature area of 300-305 K as it was in helium solubility discussion. Such change leads to inflection point emergence.

Conclusion

The research results demonstrate that rock salt is a reliable screen for long-term storage of helium in salt caverns, actually without losses. The gained numerical characteristics of helium migration behaviour could be used in the process of practical calculations when dealing with underground helium storage issue.

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