

## Special Plugging Compositions for Low-Temperature Wells on the Basis of Secondary Soda Resources

A. A. SHATOV and M. A. DRYAMINA

Soda Company,  
Ul. Babushkina 7, Sterlitamak 453122 (Russia)

E-mail: ntc@sodastr.bashnet.ru

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### Abstract

A new formula of the plugging solution of gypsum-free binder containing clinker and calcium oxide (a waste product of soda production, 10 % of the amount of clinker) nitrylmethylenephosphonic acid (0.10–0.13 %) and soda ash  $\text{Na}_2\text{CO}_3$  (3.8–5.0 %) is proposed for cementation of wells in frozen rocks of the deposits of the Far North. It is shown that all the essential characteristics of the stone formed from the indicated plugging solution are 2–4 better than those of binding compositions based on Portland cement with  $\text{CaCl}_2$  (10 %) added.

Intense formation of cavities, underlift of plugging solution to the mouth, leakage of well support caused by low-quality cementation of casing strings and other specific complications arising in boreholes are due to the presence of bedding periods of permafrost in the geological sections of oil and gas deposits of Far North. Consequences of these complications include behind-the-casting gas flow, griffin formation and open gushers damaging the regional ecology and requiring additional material expenses for their elimination. In order to improve the reliability of hole support, within the range of low positive and negative temperatures of cryolite zone, it is necessary to improve the technology of their fixing and cementing, and to modify the plugging compositions in use.

Borehole cementation, that is, filling the required interval of behind-the-casting space with a suspension of binding materials, is made with mineral binding compositions involving the main plugging materials – Portland cement and cement based on blast-furnace slag. Borehole

fixing should provide reliable disconnection of the uncovered layers and waterproof borehole lining for a long operation time.

The plugging solution used to fasten boreholes in the permafrost zones should get hardened at low temperatures without additional heating, have low freezing temperature of tempering solution ( $-4\dots-5\text{ }^\circ\text{C}$ ), sufficiently long pumpability period (not less than 2 h) with the shortest hardening time, internal erosion stability, low dehydration, high rate of heat evolution at the beginning of tempering with the minimal amount of heat evolved as a total, absence of shrinkage during stone hardening, tight contact with the string and the rock, low permeability (not more than  $2 \cdot 10^{-14}\text{ m}^2$ ), increased crack growth resistance and durability of the cement stone, water and frost resistance.

In addition, plugging solutions should possess low (0.25–0.50 W/(m · K)) heat conductivity to decrease the intensity of heat transfer from the borehole to permafrost and to create favourable conditions by means of heat accumulation for a defect-free stone structure to be formed;

relaxing ability (compressibility) and plugging properties to prevent absorption of the solution and decrease the degree of layer contamination.

Due to availability and high insulating and technological characteristics, cementation of boreholes in the intervals with low positive and negative temperatures is made with plugging Portland cement with cement setting accelerators, cement-gypsum compositions, alumina cement, etc. It is also proposed to use Portland cement with increased  $\text{CaCl}_2$  content (8–10 %) for this purpose [2]. Thus, it was established that hydration and structure formation in calcium silicates is accelerated in the presence of  $\text{CaCl}_2$  without any chemical interaction with the latter, due to a decrease in their metastable solubility. The effect of  $\text{CaCl}_2$  additive on structure formation in calcium aluminates is due to the formation of a new compound, calcium hydrochloroaluminate [3]. A similar situation is observed also for potassium and sodium chlorides.

Accelerators (in particular, calcium chloride) promote a decrease in the concentration of hydroxide ions in solution and cause an increase in the solubility of reactive silicates and aluminates; rapid precipitation of particles occurs as a result. Small amount of  $\text{CaCl}_2$  added causes a braking effect on this process due to the formation of a double complex salt [4–6].

The use of solutions based on Portland cement with reagents added does not improve the quality of cementation because these plugging materials have essential disadvantages: low hydraulic activity, evolution of a large amount of heat, shrinkage and destruction of the cement stone. Rapidly hardening plugging materials are necessary; the solutions based on them should be sedimentation-proof and should expand during hardening.

In permafrost zones, cement stone in behind-the-casting borehole space is formed under the simultaneous action of negative temperature (from the borehole side) and positive one (from the side of the casing). With the appearance of temperature gradient (10–15 °C) between the internal and external layers of the cement stone, non-frozen free water located in the pores starts to migrate to the region of negative temperatures and turns into ice there, while the solid phase is squeezed in the casing and

hardens under the low water-to-cement ratio [7]. As a result of migration, the walls of capillaries and pores get destroyed, permeability of the cement stone increases by a factor of several tens. Especially substantial structural disturbance is observed at the hardening temperature –2 and –5 °C. Substantial amount of water freezes at a temperature of 0...–2 °C, which is accompanied by volume expansion and causes the rise of crystallization pressure. According to the data reported in [8], this value varies from 17 to 57 MPa, depending on environmental temperature (within the range –2...–6 °C). In some cases this pressure is 3–10 times higher than the critical collapse load characteristic of the tubes of the most widespread standard sizes used in conductors, intermediate and production strings; so, it may cause string collapse. This is confirmed by the data on the analysis of string discontinuity in the deposits of the north of the Tyumen Region. It was established that about 60 % of collapse cases occur only with production strings; other (intermediate) strings got collapsed more rarely (22 %); together with production strings – 17 %. Discontinuity sites in strings were observed in the majority of cases within cementation intervals from 3 to 230 m. Temperature of the surrounding rocks during the collapse was –3...–5 °C.

The stability of lining to the action of collapse pressure is determined by the structure of pore space and by the strength of the cement stone framework, which are to a large extent dependent on the hydraulic activity of the binder. Analysis of the balance of mass and structure of the porous space of the formed cement stone showed that with the water-to-cement ratio equal to 0.32–0.40 the possibility of phase transitions of water into ice decreases substantially. Because of this, we assume that the necessary condition for cementation within the negative temperature range is the use of plugging solutions with decreased water content.

At negative temperature, dissolution processes and transition of aluminate components of Portland cement into solution slow down; so does hydrolysis of the regions of clinker grains with increased surface energy. A decrease in the activity of aluminate components and

therefore a decrease in their effect on the formation of cement stone structure are explained by their interaction with calcium sulphate. The latter compound interacts with calcium aluminates to form calcium hydrosulphoaluminates which get adsorbed on the grains of di- and tricalcium silicates with the formation of a screen limiting the access of water. In addition, trivalent ions are untimely removed from solution, which slows down coagulation and hence hardening of the plugging solution. The heat of calcium aluminate hydration is not abstracted, which also results in a decrease in the hardening activity of plugging solutions based on Portland cement. In this connection, it is necessary to solve the problem of removing calcium sulphate from the composition of Portland cement and to develop the composition of a gypsum-free binder to prepare the cement solution with decreased water content meeting the requirements of permafrost disconnection. The application of a solution based only on Portland cement clinker for borehole cementation is limited due to stone shrinkage and poor pumpability of the solution.

In order to eliminate shrinkage appearing when gypsum is removed, it is necessary to use other expanding additives. It is known that such additives can be the substances containing calcium oxide [9, 10]. Theoretically, an annealed solid waste material of soda production or fine liming wastes (FLW) can be used for this purpose because these materials contain  $\text{CaO}_{\text{act}}$ ,  $\text{CaO}_{\text{free}}$ ,  $\text{MgO}$ . It may be assumed on the basis of chemical and mineralogical composition of the solid waste product that thermal treatment (annealing at a temperature of 700–1100 °C) would cause dissociation of calcium carbonate with the formation of  $\text{CaO}$ ,  $\text{CO}_2$ . Then calcium oxide will interact with silica, both present in the solid residue itself and introduced additionally, which will result in the formation of calcium silicate (most probably, dicalcium silicate). An excess of calcium oxide will promote volume expansion of the hardening system, an increase in its sedimentation stability, while an excess of dicalcium silicate and silica will cause an increase in the thermal stability of the stone under formation. Annealing temperature should not exceed 950 °C, because the growth of calcium oxide crystals, accompanied by a decrease

is specific surface, and a decrease in hydraulic activity occur at higher temperature.

The most important factor affecting the strength of the stone in the case of early freezing is the water-to-cement ratio. It was established [7] that an increase in the water-to-cement ratio (from 0.44 to 0.82) accompanying freezing of the solution causes a sharp increase in the intensity of formation of ice veins (from 0.68 to 28.3 mm<sup>2</sup> per 1 cm<sup>2</sup> of the sample). It was shown [11–13] that for the water-to-cement ratio 0.40 and complete hydration of the binder, the formation of ice in the structure of cement stone is excluded. Since, as a rule, in order to provide pumpability of plugging solutions, the water-to-cement ratio is accepted to be 0.50, capillary pores will be formed in the cement stone, a part of free water in these pores will be sorbed on the surface of the solid phase, while the rest part will be present in the free form and will be able to transform into ice. The less is water content, the less (with the lower hydration degree) is capillary porosity of the formed structure. At the same time, a decrease in the water content of plugging solution results in a decrease in its mobility.

In order to provide the necessary mobility (flowability) of plugging solution and decrease energy consumption of grinding process, it was proposed to add plasticizers into the raw mixture and into tempering liquid. Taking into account the fact that, as a rule, the latter are surfactants, in order to mitigate by-effects (an increase in hardening time, worsening of strength characteristics) and to decrease the freezing temperature of tempering liquid, we proposed to combine plasticizers with an electrolyte. Analysis of the available information about plasticizers and electrolytes and about their action on the kinetics of hardening, on the properties of the solution and the stone allowed us to propose the LSTM-2 type lignosulphonate as a plasticizer. This substance is obtained by modifying LST with a water-soluble urea-formaldehyde resin of KS35 type. Another plasticizer proposed by us is nityltrimethylene phosphonic acid (NTP). This choice is explained also by the ability of these agents to cause strengthening action on the plugging stone. It is proposed to use soda ash as an electrolyte [12]. This plugging material was called

“Low-temperature sedimentation-stable shrinkage-free cement” (TsNUB). The plugging material and the solution based on it has the following composition:

- clinker of Portland cement (90 %) and annealed solid residue of liming (10 % of clinker content);
- plasticizing additive NTF (0.1–0.13 % the mass of dry mixture);
- electrolyte: soda ash  $\text{Na}_2\text{CO}_3$  (3.8–5 % of the mass of dry mixture).

Physicomechanical properties, X-ray characteristics and thermographic investigations of the developed plugging material of solution and stone showed that in the absence of gypsum component hardening at low positive and negative temperature proceeds more intensively in comparison with the solutions based on Portland cement. The degree of hydration of the samples hardening at  $-5\text{ }^\circ\text{C}$ , at the age of 2, 7 and 28 days, was 12.7, 14.2, 18.5 % for TsNUB, 3.85, 4.10, 4.32 % for Portland cement, respectively.

A more intensive character of TsNUB hardening predetermines its increased strength characteristics. Bending strength for the stone made of gypsum-free binder at the hardening temperature of  $-5\text{ }^\circ\text{C}$  at the age of 2 days is 1.4 MPa and increases to 2.7 MPa after 28 days. For the stone made of plugging Portland cement under the same hardening conditions, strength characteristics are 2–4 times less. Dehydration of the solution based on TsNUB does not exceed 2 % due to low water content and the presence of an annealed solid residue.

The formation of stone at the initial stage of hardening proceeds with the formation of hydroaluminates and hydrocarboaluminates. At later stages, calcium hydrosilicates appear. The structure of the pore space of stone at negative temperatures is represented mainly by pores 0.1–1  $\mu\text{m}$  in size. Total porosity of the samples hardening at  $-5\text{ }^\circ\text{C}$  is  $197 \times 10^3\text{ m}^3/\text{kg}$  after hardening for 2 days and decreases to  $0.154 \times 10^3\text{ m}^3/\text{kg}$  after 28 days, while the same characteristics for the samples of plugging Portland cement are higher by a factor of 1.7 and 1.9, respectively.

Porosity changes only slightly with an increase in hardening temperature and in the

age of samples. Investigation of changes in the structure of pore space depending on temperature and time of hardening revealed that redistribution toward an increase in the number of pores of smaller size occurs. Higher frost resistance of stone in comparison with plugging Portland cement used under these conditions and containing calcium chloride, and in comparison with plugging low-temperature cement (TsNT) is due to the composition of hardening products and the structure of pore space.

It was established that thermal conductivity coefficient of the stone made of plugging solution of the proposed composition is 1.4–1.5 times lower than that of the stone of plugging Portland cement. Heat generation in the solutions is almost the same; the major part of heat is evolved in the former solution at the initial stage of hardening. Hardening of the gypsum-free solution is accompanied by volume expansion up to 0.23 %.

An important parameter of the insulating ability of the material is the density of contact of the cement sheath with the casing string and with rocks. It was established that cohesion of the cement sheath with the casing string after 2 days at the hardening temperature of  $-5\text{ }^\circ\text{C}$  was 0.17 MPa and increased after 28 days to 1.45 MPa, while the shear force for the stone of plugging Portland cement with calcium chloride added (10 %) under the same hardening conditions is absent at the age of 2 days while at the age of 7 and 28 days is only 0.8 and 0.75 MPa, respectively.

Introduction of the plugging TsNUB material was carried out at the industrial association “Arktikmorneftegazrazvedka” at the deposits: Peschanoozerskoye, Rusanovskoye, Shtokmanovskoye, where temperature within the cementation interval (0–600 m) was from  $-2$  to  $+15\text{ }^\circ\text{C}$ . According to the data of acoustic cement-bond logging, the fraction of intervals related to the category of good cohesion of the cement stone with the casing string increased to 50–60 %, against 6–16 % in boreholes cemented with plugging Portland cement containing calcium chloride as an accelerator of cementation.

Thus, results of field tests of gypsum-free plugging materials confirmed their efficiency.

Results of investigation showed that the use of waste products of soda production for the purpose of improving physicomechanical properties of plugging solutions is efficient and reasonable. On this basis, additives to plugging solutions were proposed, their composition was optimized, and the properties of the solution and the stone obtained from it were studied. Advantages of the proposed composition in comparison with conventional ones were shown.

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