RESEARCH AND DEVELOPMENT OF CORROSION RESISTANT OIL WELL CEMENTS

Dorovskikh I.V., Zhivaeva V.V.
Samara State Technical University, Samara, Russia

At present enormous value is given to improving of fastening, reliability and longevity of oil and gas wells. The accomplishment of these objectives is complicated by a useful increase of depths of wells, by the complication of mining and geological conditions, by an increase of requirements for the insulation complex of wells with respect to its reliability and longevity. Especially great difficulties are encountered during fastening of gas and gas-condensate wells with the anomalously high seam pressures and the aggressive formation fluids. These difficulties lead to annulus flows and cross-flows, to the mixing of formation fluids, to the loss of reservoir energy, to pollution of the environment due to the corrosion damage of plugging material. They can be the reason for the premature liquidation of petroleum and gas wells. In spite of the research engineering in the improving of fastening of wells under complex mining geological conditions is conducted constantly, at present it is not possible to name this problem solved. Therefore the creation of the reliable insulation complex of wells is the vital problem of well construction, without this problem solving the more complete extraction of hydrocarbon raw material is impossible, and solution of questions of ecology, conservation of mineral resources and preservation of the environment are impossible too.
Traditional technologies and materials for fastening of wells under these conditions ensure the creation of the reliable and long-lived dissociative bridge in the hole annuity to the smallest degree. This problem can be solved by the application of special inexpensive materials for well construction.

The insufficient effectiveness of the technology of fastening of wells under the conditions of corrosiveness required to develop special corrosion-resistant backfill compositions. Improvement of the quality of many backfill compositions (increase of sedimentation stability and gel-forming ability of solution, obtaining noshrinking cement stone with the low permeability, increased strength and the minimum degree of destruction) is limited by the need of conservation of flow characteristics - pumpability of solution before the completion of well cementing process. Starting from the fundamental ideas of the physicochemical mechanics of dispersed structures, the creation of the self-organizing structure of backfill stone with prevention of erosive leakage and channeling is the most effective direction of improvement of corrosion resistance.

The structure of plugging material is formed as a result of the hydration process and under the action of reagents, belonging to its composition.

Each of the reagents, belonging to the complex for processing of backfill suspension, acts with its inherent mechanism; it has an independent effect on the processes of structurization. It is possible to summarize the action of reagents and in such a way to form purposely the structure of cement stone and to obtain plugging materials with the high service properties.

It was noted in the process of experimental investigations and analysis of trade material that not all reagents behave equally.

Decrease of water-to-cement ratio is set as an object; plasticizers and supersplasticizer are used. Their nature is different; therefore the mechanism of action to the cement particles is various. Thus, the plasticizer NTP (nitrilotrimethylphosphonic acid), that is traditionally and widely used decreases the viscous characteristics of suspension effectively, but according to the results of the realized analysis it acts negatively on the stability of system, on the degree of dehydration. But it means that the undesirable processes take place as a result of interaction of reagent and basic components of cement. Application of reagents - plasticizers of another type, for example, of organic nature - CSAG (sulphide alcohol grain), lignosulphonates, ROP-U (reagent for oil production universal) does not lead to such sharp reduction of the sedimentation stability of system, it increases the dispersity of solid phase, that leads to improving of the solidified cement stone.

On the other hand, it is necessary to use reagents - stabilizers, mainly of polymeric type (CMC, CMOEC, TYLOSE, OEC and others) for increasing stability of system and decreasing filtering degree. But, as it is known, when stabilizing suspensions, even the small concentrations of polymers cause a sharp increase of system viscosity, that in its turn hampers the process of delivery of grouting mortar into the well.

The third aspect of task is application of the highly mineralized backfill suspensions. It might be necessary for cementing salt layers. In the ideal case it is necessary that the components of sealing liquid would not be mutually exclusive and they would go well together, creating favorable conditions for forming the firm low-porosity structure of plugging material.

Unfortunately, not all versions of combination "plasticizer - stabilizer" make it possible to reach positive effect. For example, according to the experimental data it is established that there is no effect of reduction of filtering degree and solution stabilization, when NTP and CMC are used together. It means that the stabilizing effect of polymer is annulled in the presence of a plasticizer. The complexes of organic plasticizers of ROP-U type and fusion cake of salt have distinctions in kind with polymeric stabilizers. In this case there is effect of sharp reduction of filtering degree till values commensurable with the water loss of drilling mud and at the same time there is retention of high degree of freedom with the minimum content of dispersion medium. It speaks in favor of this type of complexes. They make it possible to obtain highly mobile backfill systems with low content of liquid phase and maximum sedimentation stability. And all these characteristics say that from this suspension the firm low-permeability microcellular stone with good functional qualities will be formed. Not all complexes of reagents behave positively in the presence of salts of the type of sodium chloride or potassium chloride also. A question of reagents compatibility in the complex will also take place here. The positive effect of sodium chloride on the complex "organic plasticizer - stabilizer" and the negative effect of salt on the complex "NTP - stabilizer" are noted in practice.

As the facts were available, the attempt to determine the mechanism of interaction of reagents in the complex was made. The complex was prepared as the sealing liquid of backfill suspension.

An experiment for the investigation of the mutual influence of reagents forming part of mixing water for the cement mortar was made. Organic reagents are combined with the stabilizers well; they form the structure "in each other" during the formation of backfill stone, and thus they contribute to an improvement of the service properties of cement cover. But other reagents are not combined with each other at all, they do not improve properties but on the contrary they sometimes worsen them. The influence of corroding agents on backfill compositions in the suspensions and the sections prepared from the formed backfill stones was also noted.

To realize the experimental work we have taken two types of plasticizers (NTP (nitrilotrimethylphosphonic acid) and developed by us and produced by industry ROP-U) and also stabilizer (water-soluble polymer CMC (carboxymethyl cellulose)) as the most commonly used in practice for the treatment of oil-well cement. The oil-well cement of brand PCT II-SS-100 was used as the binding component. The oil-well cement of brand PCT II-SS-100 was prepared according to Government Standard 1581-96. Temperature of tests was 20-220 ^{o} C.

To study we have taken plugging materials obtained as a result of the hardening of cement paste that had been processed by the solution of the following chemical reagents:

1. PCT II-SS-100 is fresh
2. PCT II-SS-100 is salt
3. PCT II-SS-100 + 5 % ROP-U is fresh
4. PCT II-SS-100 + 5 % ROP-U is salt
5. PCT II-SS-100 + 0,5% CMC + 5 % ROP-U is fresh

6. PCT II-SS-100 + 0,5% CMC + 5 % ROP-U is salt
7. PCT II-SS-100 +0,03% NTP is fresh
8. PCT II-SS-100 + 0,03% NTP + 0,5% CMC is fresh
9. PCT II-SS-100 + 0,5% phosphates is fresh
10. PCT II-SS-100 + 0,5% phosphates + 0,5% CMC

Water-to-cement ratio of all suspensions is 0,5.

The formation water of well №303 of the field Podgornenskoe was used as salt mixing water. The ionic composition of water is represented in table 1.

Table 1. The ionic composition of water

Specific gravity, d_4^{20}	Mineralization, g/l	Ionic composition, g/l					
		HCO_3^-	Cl^-	SO_4^{-2}	Ca^{+2}	Mg^{+2}	K^++Na^+
1,178	255,2463	0,3794	152,8208	2,7883	2,6448	1,0579	95,5551

Tests were conducted according to the International Standard NACE TM0177-96. The sections of different composition of two day's, ten day's and monthly period of storage were prepared as the reference patterns. Models of the same composition were placed into the corrosive environment. Test solution consisted of 5% NaCl and 0,5% of crystalline acetic acid dissolved in the distilled water. Then solution in the desiccator was saturated with hydrogen sulfide till concentration 3000 mg/l. pH of medium was 2,8. Such aggressive medium was created to see in a short space of time how the prepared sections of cement stone, which had been subjected by the action of it, would behave. Then reference patterns subjected to action of aggressive medium were analyzed and described with the observation under a 100-power electron microscope "Philips". The X-ray spectrum analysis of models was also conducted.

All microscopical analyses were conducted with thin sections prepared from the hardened compositions; all models were sprayed with graphite. Porosity, fissuring and structure of units served as a criterion for changing the structural state of cement stone that had been subjected by sulfurated hydrogen corrosion.

As can be seen from the given photomicrographs (fig. 1, 3, and 5) it is possible to observe sufficiently distinctly the processes of focal corrosion development, crack formation over the entire surface (model №1 that was not subjected to treatment by reagents (fig. 3)). The reference pattern of the same composition is represented in the figure 1. Composition №5 (Fig. 5) proved itself to be the most stable of all enumerated compositions to the aggressive medium. It can be explained by means of synthesizing the organic-mineral microdispersed phase in the cement mortar and then in the cement stone. Analyzing data of X-ray spectrum analysis (fig .2) we can draw the following conclusions: judging by the results of X-ray spectrum analysis, model №1 (Fig. 3) endured a qualitative and quantitative change of composition to the utmost. The fact of corrosion damage confirms it (fig. 2, 4). In the presence of ROP-U and CMC (fig. 6) corrosion damage is not considerable, in products of hydration part of water-soluble salts subjected to erosive leakage is reduced in several times.

The nature of the structure of pore space is one of the most important structural parameters of cement stone, determining its filter discrimination. By sight, by means of microphotoarchitecture analysis we can note that in the process of contact with hydrogen sulfide the body of cement stone is destroyed. It is confirmed by change of pore size and configuration, by increase of the porosity, by presence of the elements of dissolution in pores, by crack and channel formation.

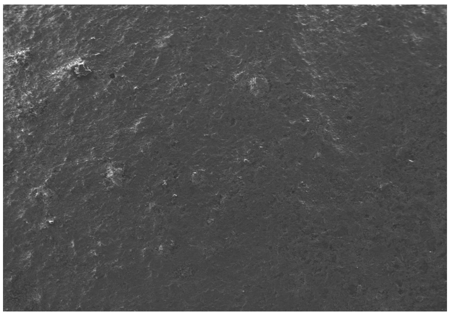

Fig. 1. The surface of reference section (composition №1)

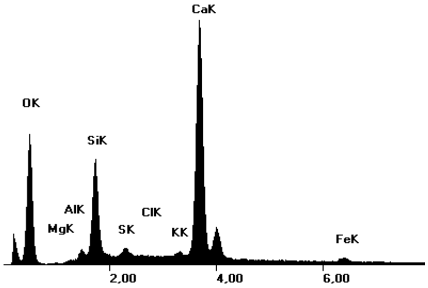

Fig. 2. X-ray spectrum analysis of reference section (composition №1)

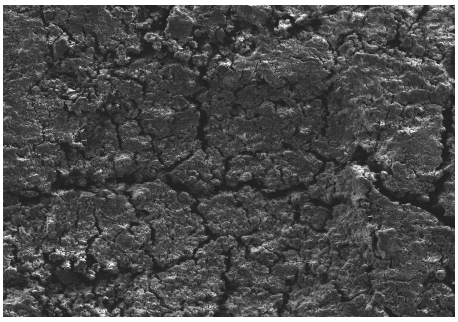

Fig. 3. The section's face subjected to corrosion (composition №1)

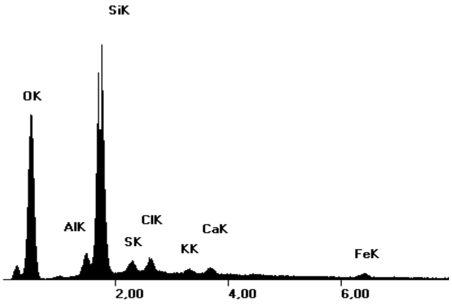

Fig. 4. X-ray spectrum analysis of the section subjected to corrosion (composition №1)

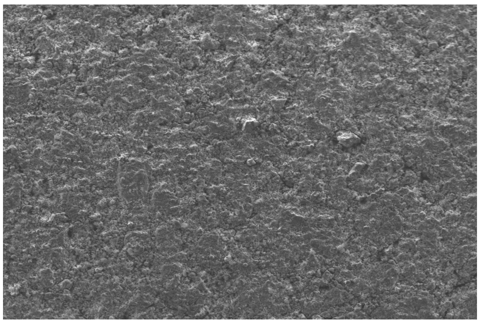

Fig. 5. The section's face subjected to corrosion (composition №5)

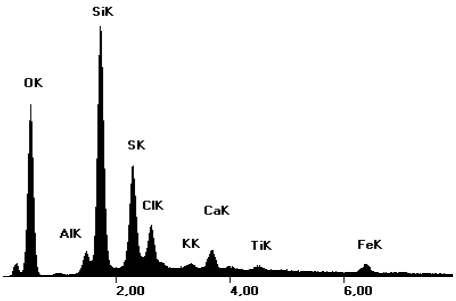

Fig. 6. X-ray spectrum analysis of the section subjected to corrosion (composition №5)

Thus, to increase the life of well, and hence to increase the reliability of disconnection of layers containing corrosion-active medium it is necessary to stabilize backfill suspensions in such a way as to a plugging of interpore space by newly formed organic-mineral substances, which make it possible to decrease the permeability of stone and contact zones till minimum, would be the result of effect of the complex of reagents.