Prospects of applying formation water and heavy brines derived therefrom in oil production and national economy

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Abstract. In recent years, the amount of minerals recovered from the earth interior exceeds their production over the entire past human history. The reserves of some rare elements have been significantly reduced and the demand for them has increased dramatically through the use of new techniques and technologies. The task of developing new types of mineral raw materials from formation waters has become ever more relevant. In the process of formation water preparation during the production of table salt the fluids and heavy brines are obtained, which are suitable for their further use in oil production. The fluid obtained through deferrization of formation water has reduced content of magnesium ions. The use of this fluid makes it possible to increase the mechanical strength of the cement stone, the tightness of the “column-cement stone” contact zone, and to reduce magnesia corrosion.

1. Introduction

The strength enhancement of cement stone is achieved by combined use of calcium and sodium chlorides of formation water of an oil field in tempering fluid with simultaneous reduction of magnesium ion concentration by 10 and more times (up to 0.15 \%) \textsuperscript{[1]}. The magnesium chloride content in the formation water reaches 1.76 \%. The most typical values of basic salts in formation waters of the Devonian horizon are given in Table 1.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
n/n & CaCl\textsubscript{2} & MgCl\textsubscript{2} & NaCl & Total \\
\hline
1 & 5.48 & 1.57 & 16.42 & 23.70 \\
2 & 5.29 & 1.76 & 16.41 & 23.69 \\
3 & 5.40 & 1.45 & 16.80 & 23.88 \\
4 & 5.32 & 1.57 & 16.75 & 23.87 \\
\hline
\end{tabular}
\caption{Typical values of basic salts in formation waters of the Devonian horizon}
\end{table}
2. Methods and materials
Magnesium ions are substituted with calcium ions in crystal lattice nodes of the cement stone. Magnesium ions have smaller radius $(0.78 \cdot 10^{-10} \text{ m})$ compared to calcium ions $(1.06 \cdot 10^{-10} \text{ m})$, and the substitution of calcium ions with magnesium ions weakens the crystal lattice. Besides, if non-magnesium-purified water is used as the tempering fluid, magnesium chloride reacts with calcium hydroxide thus forming slightly soluble magnesium hydroxide. The solubility of $\text{Mg(OH)}_2$ is almost one hundred times less than that of $\text{Ca(OH)}_2$: $0.018 \text{ g/L}$ and $1.6 \text{ g/L}$, respectively, so the reaction proceeds towards the formation of magnesium hydroxide. The binding of hydroxyl groups into magnesium hydroxide is accompanied by pH reduction of the pore fluid (up to pH=10), which creates favorable conditions for gradual dissolution and hydrolysis of hydrate neoplasms in cement stone, which in turn leads to the development of magnesia corrosion [2–4].

3. Method description and its evaluation
The density of the cement stone contact to rock on one side, and on the other side—to a casing string determines the tightness of the annular space, reliability of separation of gas, oil and water-containing formations. In this respect, the main criteria of suitability of consolidated cement slurry is impermeability, good adhesion of stone to pipes and rocks [1]. The effect of sodium chloride additives on the adhesion strength of cement stone with metal and clay rock is shown in Table 2.

| n/h | NaCl concentration in tempering fluid, % | Adhesion strength, MPa |
|-----|----------------------------------------|------------------------|
|     | Separation from metal                  | Separation from rock   |
| 1   | 0                                      | 0.3                    | 0.05                   |
| 2   | 6                                      | 1.0                    | 0.10                   |
| 3   | 10                                     | 1.0                    | 0.20                   |

Osmotic phenomena that cause fluids to flow through the cement stone cause cracks in the stone and thus contacting rocks. As a result of osmosis the formation fluid water gets into the well. Reverse flows directed towards the formation contaminate productive horizons and can cause reduction of oil recovery. Significant reduction of cement stone impermeability is achieved by the addition of $5–10\%$ sodium chloride to the fluid [5].

Thus, the increase in the strength of the cement stone is achieved by the combined use of a predetermined ratio of calcium and sodium salts of the formation water in the tempering fluid while reducing the magnesium ion concentration by 10 times (from 1.7 to 0.15%). Besides, the use of the specified amounts of formation water salts of the oil field in the tempering fluid provides an additional positive result: increased impermeability, adhesion to casing and well wall, reduced magnesia corrosion of cement stone [5].

Formation water of the Devonian horizon was used to prepare the tempering fluid with the specified ratio of sodium, calcium and magnesium salts. The construction lime (GOST 9179-77) was used to remove $\text{MgCl}_2$ from the formation water of the oil field in the form of $\text{Mg(OH)}_2$. Since the solubility of $\text{Mg(OH)}_2$ (0.018 g/L) is significantly lower than $\text{Ca(OH)}_2$ (1.6 g/L), the reaction proceeds towards the formation of $\text{Mg(OH)}_2$:

$$\text{MgCl}_2 + \text{Ca(OH)}_2 = \text{CaCl}_2 + \text{Mg(OH)}_2.$$  

When calculated 14 g/l of lime is added to the formation water, the amount of magnesium chloride is reduced to only 0.78 %, which does not provide an acceptable reduction of magnesia corrosion. As indicated in [5], all calcium hydroxide will be consumed at 0.259 % magnesium sulfate concentration. Therefore, lime is introduced in excess for more complete settlement of magnesium chloride. The introduction of 20 g/l of construction lime into formation water reduced magnesium chloride up to 0.30 %. By further diluting the formation water to prepare the tempering fluid 2 times or more, the magnesium chloride content is reduced to 0.15 % and less. This concentration is taken as the upper limit of the magnesium chloride content of the tempering fluid.
In order to determine the effect of salts (CaCl₂, MgCl₂ and NaCl in different combinations) on the main characteristics of the cement slurry and cement stone for the preparation of cement slurry with constant water-cement ratio of 0.5, the initial formation water with the density of 1.189 g/cm³, fresh tap water and calcium chloride solutions were used as the tempering fluid. The density of purified and diluted formation water prior to calcium chloride content of 5, 4, 3 and 2% was 1.147, 1.102, 1.072 and 1.051 g/cm³, respectively.

The results of the laboratory tests are shown in Table 3. The table shows that the concentration of low salt solution does not significantly increase the mechanical strength of the cement stone. The use of formation water, diluted to 2% sodium chloride and 1% calcium chloride as tempering fluid if compared to fresh water results in only a slight increase in strength properties after 2 days of solidification. The bending strength was 26 MPa for fresh water and 30 MPa for salted water, and the compression strength was 6.1 and 8.2 MPa, respectively. The strength properties of cement stone increase considerably with the content of 3% calcium chloride and 6% sodium chloride in fluid. Bending and compression strengths were 4.8 and 11.8 MPa, but the flow of the cement slurry was reduced. When 5% calcium chloride and 10% sodium chloride was contained in the tempering fluid, the flow rate made 14 cm. The cement slurry with such flow rate retains mobility only for 30 minutes after tempering, then it thickens. Using standard tempering techniques, it is almost impossible to pump and pour cement slurry into the well during this time. Thus, the use of refined Devonian formation water will allow increasing the strength properties of cement stone, accelerating the hardening of cement slurry and eliminating the purchase of imported calcium chloride by using local raw materials [6].

During repair and insulation works at oil wells the well killing operation is a standard technological procedure, which is necessary to prevent the discharge of process liquids. This process includes the balance of the formation pressure with the pressure of the hydrostatic fluid column at a given density. Such solutions are prepared on the basis of imported calcium chloride, zinc bromide, etc. [7–9].

The volumes of calcium chloride-based killing fluid with a density of 1300 kg/m³ used in various oil companies are presented below in tons (data derived from requests from company process departments):

- PJSC Tatneft – 10000;
- OAO Samaranef – 15000;
- OAO Udmurtneft – 1000;
- OAO Bashneft – 2500;
- OAO Orenburgneft – 3500.

In order to prepare such solutions, it is necessary to purchase technical calcium chloride dissolved in fresh water. This, firstly, is too expensive, secondly, the iron impurities contained in the technical calcium chloride lead to blockage of productive formations and reduction of oil recovery. Therefore, we propose to use associated heavy brines obtained during formation water evaporation as the killing fluid [10–12].

In order to evaluate the possibility of using heavy brine as killing fluid, the model tests were carried out on tubular formation models. The purpose of the studies was to identify the effect of heavy brines on the reservoir properties. For this purpose, the formation model of one-meter-long and 27 cm diameter was packed with quartz sand, after which the initial formation water was passed through it. Heavy brine was then pushed through the model and left alone for 24 hours, after which the initial formation water was passed through. At the same time for models with permeability of 0.2; 0.7; 1.0; 1.5; 2.0 μm² the filtration attenuation was not observed at pressure gradients corresponding to formation pressure. Similar studies were carried out with oil-saturated models, which also did not show a decrease in filtration.

Thus, the model tests show that there is no deterioration of reservoir properties of productive formations when they are in contact with heavy brine and the possibility of using such brine as killing fluid.
The works of Zaripova L.P., Shakirov Sh.K. show the huge role of food preservatives in feeding farm animals. They lay the foundations for the use of formation waters and their processing products for the preparation of food preservatives. The scope of food preservatives includes the improvement of silo quality, which now, for example in Tatarstan, makes about 4 million tons per year and the preservation of fodder grain – up to 300000 tons from 1000000 tons of fodder grain required in the republic, which are used as additives in animal diet to fill the deficiency of table salt, as well as salts of calcium, magnesium, iodine, iron, selenium.

Major problems in the use of preservatives:
- relative cost of traditionally industrialized green feed preservatives;
- need to bring them from other countries and regions of the Russian Federation;
- narrow spectrum of action compared to available and widely used preservatives, limited to inhibition of fermentation and not providing for compensation of deficient nutritional additives in the form of macro- and microelements.

The expediency of forage grain preservation is based on the following:
- possibility of preserving grain with high humidity, which is particularly important in high yields and unfavorable weather conditions;
- possibility of storing preserved fodder grain in concreted trenches and burrows;
- lower degree of exposure of preserved fodder grains to rodent eating.

The need for feed supplements is dictated by the following reasons:
- additives of table salt, iodine salts should be added to the nutrition of all animals and birds;
- there is a deficiency of calcium salts and microelements in the diet of pigs and birds.

In order to solve these problems in the Republic of Tatarstan, it is proposed to produce and introduce into feed production a new cheap food preservatives based on highly concentrated multicomponent water salt brine formed through processing of formation waters of the Devonian horizons.

The analysis of the composition of formation waters of the Devonian horizon produced along with oil in Leninogorsksneft oil-and-gas production department shows that there are large amounts of salts extremely important for livestock and poultry production – sodium chloride and calcium chloride. In particular, the formation water of wells 9187 and 23556 of D2 horizon has the following composition (wt %): calcium chloride – 5.48, sodium chloride – 16.42, magnesium chloride – 1.60, potassium chloride – 76.27.

| Table 3. Laboratory test results | Tempering fluid | Cement slurry characteristics | Setting time | Bending/compression strength, kg/cm² | Sample storage period in formation water |
|-------------------------------|-----------------|-------------------------------|--------------|----------------------------------------|----------------------------------------|
| n/n Type of tempering fluid | CaCl₂ | MgCl₂ | NaCl | Spreadability, cm³ | Density, g/cm³ | Water return, cm/30 min | beginning | end | 2 days | 7 days | 28 days | 3 months | 6 months |
| 1 Fresh water | – | – | 21.5 | 1.81 | 189.6 | 8-00 | 9-40 | 26/61.3 | 28/64 | 39/68.4 | 70/75.4 | 87/95 |
| 2 Initial formation water | 2 | 0.5 | 5.5 | 21 | 1.85 | 139.0 | 6-30 | 7-40 | 36/110 | 38/115 | 44/120 | 72/124 | 90/129 |
| Magnesium chloride-free | 1 | 0.04 | 2 | 21 | 1.83 | 142.4 | 7-30 | 8-10 | 30/82 | 33/96 | 49/100 | 84/116 | 109/120 |
| 3 formation water | 2 | 0.08 | 4 | 20.5 | 1.85 | 149.2 | 6-00 | 6-40 | 38/116 | 58/126 | 70/123 | 92/129 | 114/134 |
| Calcium chloride brine | 3 | 0.12 | 6 | 19 | 1.87 | 140.0 | 5-45 | 6-05 | 48/118 | 64/120 | 80/125 | 103/138 | 119/146 |
| 4 | 4 | 0.15 | 8 | 18 | 1.89 | 137.6 | 5-30 | 6-00 | 48/120 | 69/123 | 89/126 | 108/130 | 117/138 |
| 5 | 0.20 | 10 | 14.5 | 1.90 | 130.0 | 2-30 | 3-10 | 47/119 | 63/121 | 84/120 | 100/129 | 115/131 |
| 6 | 2 | 0 | 0 | 18 | 1.86 | 158.0 | 6-03 | 7-35 | 37/112 | 43.5/11 | 58.4/11 | 66/119 | 97/123 |
| 7 | 0 | 0 | 18 | 1.86 | 154.7 | 4-55 | 5-30 | 40/116 | 47/118 | 60/121 | 65/123 | 75/124 |
Thus, 92.29% of salts are of great value and are actually imported into Tatarstan. This formation water can be used directly as extracted from the subsoil. However, to achieve high efficiency while compensating for salt deficiency and to avoid overdose, it is necessary to separate salts for each diet of each species of animals and birds.

The TatNIPIneft Institute of PJSC Tatneft developed a design plant for complex processing of formation waters, which will be located in the village of Karabash of the Bugulminsky district of the Republic of Tatarstan (Leninogorskneft oil-and-gas production department). The project implies the processing of these waters in order to obtain food table salt (30,000 tons per year, which fully meets the needs of Tatarstan for table salt) and concentrated salt solution (concentration of salts – 43%, of which more than two thirds of calcium chloride), which can be used in the oil production industry as heavy killing fluid with a density of 1300 kg/m$^3$. The planned volume of production of the killing fluid is 40,000 tons per year.

The brine composition after sodium chloride isolation and dilution with fresh water to a density of 1300 kg/m$^3$ has the following composition:

- calcium chloride – 25%;
- sodium chloride – 2.5%;
- magnesium chloride – 7.2%;
- potassium chloride – 1.0%;
- water – 64.3%.

The analysis of properties and composition of the resulting heavy killing fluid (acid properties pH = 2.4 and high concentration of calcium salts, presence of sodium chloride, iron salts – 797 mg/l, iodine – 23.5 mg/l and other biogenic elements) shows that it can be used as an effective food preservative. Some adjustment of the composition of this solution will make it possible to use it through preserved silo mass, preserved forage or by direct addition to food to fully compensate for the deficiency of a number of vital elements in animal diets. The planned volume of production of this saline solution can fully cover the need of the Republic of Tatarstan for silage preservatives.

The need for livestock and poultry farming of Tatarstan in feed salt is about 40,000 tons per year, the amount of food preservatives with a composition close to the above is also about 40,000 tons per year. Thus, if the first salt plant covers the needs of Tatarstan in food table salt and the needs of oilmen in the killing fluid, for the needs of agriculture it will be necessary to build a second plant with the productivity of not less than the first.

The proposed food preservatives replace the known preservatives with very high cost and do not have the ability to enrich feed with elements, the acute deficiency of which is relevant for the animals in the territory of the republic. On the basis of concentrated salt solutions, by adding some deficient components, more efficient compositions of food preservatives can be prepared to compensate for the deficiency of nitrogen, phosphorus and other elements not contained in the brine under consideration.

Due to the shortage of feed salt at the first stage, the use of both formation water and heavy fluid presents the greatest practical interest. Since in the first case the ratio of calcium chloride to sodium chloride is 1:3 and in the second – 10:1, the different quantitative ratio can satisfy any requirements of a wide variety of animal and poultry diets.

4. Conclusion

The use of the proposed cheap food preservatives not so much saves by not importing expensive preservatives, but rather, in the face of a shortage of working capital for agricultural enterprises, creates a prerequisite for the widespread use of food preservatives. This will fundamentally improve the quality of feed, its balance in biogenic elements and, ultimately, the productivity of animals. On the basis of the above, in order to produce food preservatives in solid form it is recommended to convert the excess heavy fluid with a density of 1400 kg/m$^3$ obtained by additional evaporation into a fluid with a density of 1500–1600 kg/m$^3$, which after cooling crystallizes into a solid. Thus, using another evaporation step, it is possible to obtain food preservatives in granular solid form. This will make it possible to eliminate additional transportation costs when carrying unnecessary water in food preservatives to agricultural
objects. The studies show that the formation water and its processing products are promising reagents that will be used in oil production and agriculture.

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