Composite Binders for Fastening High Temperature Wells

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Abstract. The article deals with the hydration of oil-well cement, intended for cementing high-temperature wells. At high temperatures and pressures (150°C, P = 30 MPa) Portland cement stone does not have the necessary density and resistance to high temperatures due to the formation of hydrated calcium silicates rich in lime during the hydration of Portland cement, therefore, the work was carried out primarily to find appropriate additives to Portland cement, providing the necessary properties of oil-well cement. From a number of additives to ensure the durability of service were selected reprocessing waste of titanium ores (titanomagnetite concentrate) and blast furnace slag. In addition, to improve the crack resistance of cement stone, the possibility of using expansive additives to oil-well cement was investigated. For these purposes, sulfoaluminate, sulfoferrite clinkers and alumina slag were used. It has been established that during hydration of calcium sulfoferrite ferrous ettringite is formed, which is more stable at elevated temperatures than ettringite formed at hydration of sulfoaluminate clinker and alumina slag. In the presence of sulfated phases and silica, at elevated temperatures and pressures, low-base calcium silicates hydrates and iron contained garnet hydrates are formed.

1. Introduction

Reliability and durability of seam separation are determined by leakproofness, impermeability of cement stone and its contacts with casing pipes, rocks of the trunk walls, a mudcake, as well as corrosion and thermal resistance of cement stone with temperature fluctuations and exposure to aggressive media at specific deposits. A large variety of conditions for the occurrence of oil and gas required the creation of special oil-well cements.

Grouting high-temperature wells required cements, which meet a number of requirements, including:
- heat resistance and durability of cement stone in hydrothermal conditions,
- resistance of cement stone in corrosive environments,
- regulation of the density of cement slurry,
- the ability of cement stone to expansion, etc.

These problems have received much attention from many researchers. Particular attention is paid to cementing wells with abnormally high seam pressures, when, along with high seampresses, the...
The temperature of the cement stone increases [1-5]. Under these conditions, the use of known types of cements often leads to behind-the-column gas manifestation, interlayer overflows. The cause of behind-the-casing emissions after well cement Practice shows that wells with abnormally high pressures (AHP) should be grouted with weighted oil-well slurry with a density of 2-2.3 g/cm$^3$ [6]. As a weighting to oil-well cement used barite, hematite, and waste of chemical plants with a density of 3.7-4.7 g/cm$^3$, etc. [7-9].

In [2], it is noted that under conditions of high-temperature wells, after they are cemented, water-gas manifestation arises due to the formation of channels at the contact, the casing pipe — cement stone — well wall. It was noted that at high down hole temperatures in the resistance. The fact is that the hardening of most oil-well cements at high temperatures is accompanied by phase transformations of cement hydration products, their recrystallization, leading to a decrease in the strength of cement stone and an increase in its permeability [10].

It should also be noted that ordinary oil-well cement is not durable with long-term hardening at elevated temperatures due to recrystallization calcium hydroxides, leading to a decrease in strength and an increase in the permeability of cement stone. The probability of formation of hydrated calcium silicates type is determined by the ratio of CaO and SiO$_2$ in the cement stone. When the CaO / SiO$_2$ ratio is < 1.5, hydrated calcium silicates of tobermorite group are formed, which ensure the long-term stability of the stone [11-13]. Therefore, to control the formation of the necessary phases, many researchers have proposed to introduce sand, ash, slag and other silica-containing additives into the cement composition [8]. However, even the introduction of these materials does not exclude recrystallization processes due to their low reactivity.

In [3], an overview of varieties of cements used for cementing oil, gas and gas condensate wells is given. As a result of numerous studies summarized in [4], weighted cements with a dense cement-water suspension of 1.9-2.1 g / cm$^3$ were proposed. Barite and hematite are used as weighting agents for oil-well cement. However, such cements are sedimentary unstable [14]. In the course of the research, in order to increase the homogeneity of the cement-water slurry, prevent its separation, improve the contact of the cement stone with the casing pipe and the cement components, along with weighting agents, an expansive component was added to cement slurries [15-17]. Currently, as an expansive component, oxides of magnesium, calcium or alumina slag are proposed together with gypsum [16]. The use of these components does not always provide the required quality of well grouting due to the fact that magnesium and calcium oxides during storage for more than one month lose their properties due to carbonization that occurs in the existing conditions of storage of cement materials [3].

The goal of our research was to establish the possibility of using various weighting materials and sulfated clinkers as expansive components in the production of oil-well cements for high temperature wells.

2. Materials and research methods

2.1. Materials

Portland cement and weighting materials were used in the work: cinder, flue dust of a metallurgical plant, titanium magnetite concentrate (TMK) - apatite production waste. Sulfoaluminate (SAC) and sulfoferrite clinker (SFC), alumina slag and gypsum were used as an expansive component. The chemical composition of the materials is given in table 1.
Table 1. Chemical compositions of raw materials.

| Material                        | Содержание оксидов, % |
|---------------------------------|-----------------------|
|                                 | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | other |
| Portland cement clinker         | 21.60 | 5.15  | 4.85  | 65.40 | 0.30 | 2.60 | 0.25  |
| Pyrite cinder                   | 12.73 | 3.52  | 71.73 | 4.30 | 3.00 | 2.83 | 1.90  |
| Furnace dust                    | 9.76  | 5.85  | 70.33 | 4.47 | 2.81 | 2.40 | 4.31  |
| Titan-magnetite concentrate     | 2.30  | 2.70  | 81.00 | 1.30 | 1.60 | 10.80* | 0.25  |
| SAC                             | 10.90 | 22.9  | 4.22  | 56.53 | 1.67 | 3.23 | 0.55  |
| SFC                             | 4.95  | 1.50  | 37.44 | 4.47 | 2.81 | 2.40 | 4.31  |
| Alumina slag                    | 9.49  | 46.82 | 0.80  | 37.60 | 2.15 | 0.54 | 2.20  |
| Gypsum                          | 2.80  | 0.50  | 0.40  | 32.20 | 1.50 | 40.50 | 22.60  |

* content TiO₂

The clinker for Portland cement is represented (in %): C₃S = 60; C₂S = 15; C₃A = 7; C₄AF = 14.

Sulfoaluminate clinker (SAH) contained in its composition (%): calcium sulfoaluminate Ca₃Al₅S [(3CaO·3Al₂O₃·CaSO₄) - 40.6; C₃S - 29.4; C₁₂A₇ - 10.0; CaSO₄ - 6.8; C₄AF - 13.2. The mineralogical composition of sulfoferrite clinker (SFK) was presented (%): C₃S -35.4; calcium sulfoferrites and aluminoferites - 62.1; CaSO₄ - 2.5.

All cements were obtained by joint grinding of the components in a laboratory mill to a specific surface area S = 350 m²/kg.

2.2. Methods
Tests: spreadability, thickenability, density of cement slurry, water separation, strength and expansion were determined according to the national standard GOST 1581-91 at normal temperature, and in hydrothermal conditions at 150° C and pressure 30 MPa strength and expansive was determined.

For cement hydration known methods of XR- diffraction, DTA, IR, optical and electron microscopy were used.

3. Experimental results and discussion
The optimization of the composition of the weighted oil-well cement was carried out according to the following criteria: spreadability, density of the cement slurry and strength of the cement stone. The quantity of weighting additives in all samples was 30 wt.%. Results are in Table 2.

Table 2. Test results for cement.

| No | Type of weighting agent | Density, g/cm³ | Flowability, mm | Water separation, % | Setting, h min | Bending strength after 2 days, MPa |
|----|-------------------------|----------------|-----------------|---------------------|----------------|-----------------------------------|
| 1  | Pyrite cinder           | 1.92           | 200             | 3.4                 | 5-40           | 7-15                             | 1.80                              |
| 2  | Furnace dust            | 1.90           | 195             | 2.9                 | 5-20           | 6-50                             | 2.00                              |
| 3  | Titan-magnetite concentrate | 2.00           | 205             | 3.5                 | 6-40           | 8-00                             | 1.93                              |

For further research, a cement containing TMC was chosen as a weighting component for the production of oil-well cement.

The next stage of research involved the study of the effect of the expansive component on cement hardening under conditions of elevated temperatures. For this purpose three oil-well cement were prepared using Portland cement clinker, gypsum, blast furnace slag, titan-magnetite concentrate, an expansive component. The composition of the cements is given in Table 3. Cements differed by type of expansive component.
Properties of cements during hardening under standard conditions are presented in Table 4. Cement stone achieves the greatest strength and expansion during cement hardening using SAC as an expansive component. According to the results given in Table 4, cement 2 has the required thickening.

A study of hydration of these cement cements showed that when cement 1 hydrates at ordinary temperature, after one day hexagonal hydrates SAH$_{10}$, C$_2$AH$_8$, aluminum hydroxide and ettringite formate, along with which, by 3 days, calcium monosulfate appears. The content of gypsum in hydrated cement is constantly decreasing and by 7 days its full binding is fixed.

**Table 3.** The composition and density of non-shrinking weighted cement.

| No | Portland cement clinker | Gypsum | Expanding additive $^*$ | Granulated blast furnace slag | Titan-magnetite concentrate | W/C | Flowability, mm | Density, g/cm$^3$ |
|----|-------------------------|--------|-------------------------|-------------------------------|----------------------------|-----|----------------|------------------|
| 1  | 30                      | 8      | 10                      | 22                           | 30                         | 0.57| 180            | 1.87             |
| 2  | 30                      | 8      | 10                      | 22                           | 30                         | 0.50| 195            | 2.00             |
| 3  | 30                      | 8      | 10                      | 22                           | 30                         | 0.54| 190            | 1.90             |

* Expansive component in 1 – SAC, 2 – SFC, 3 – AS

**Table 4.** Strength and expansion of weighted cement.

| No | Setting, h-min | Bending strength after days, MPa | Expansion, %, after day | Thickening, min |
|----|----------------|----------------------------------|-------------------------|-----------------|
|    | Initial        | Final                            | 2                       | 7               | 2               | 7               |
| 1  | 0-55           | 1-35                             | 1.5                     | 8.8             | 0.3             | 0.40            | 60               |
| 2  | 2-45           | 5-05                             | 1.0                     | 6.8             | 0.1             | 0.21            | 97               |
| 3  | 1-20           | 3-22                             | 1.0                     | 6.7             | 0.2             | 0.35            | 80               |

In the samples of hydrothermal hardening, according to XRD data (Figure 1), during the first two days, along with ettringite calcium monosulphate is formed. Beside them boehmite (d = 0.616; 0.316; 0.233nm), tobermorite, detected by the lines d = 1.13;0,546; 0.298 nm, xonotlite (d = 0.706; 0.425; 0.364 nm) and hydrated calcium garnets (d =0.310; 0.272; 0.198 nm) are formed.

**Figure 1.** The change in the intensity of the analytical lines hydrate compounds in samples (SAC) hydrothermal hardening: 1 – C$_4$A$_3$S; 2 – C$_3$S; 3 – C$_3$AC$_8$S$_{12}$; 4 – C$_5$S; 5 – C$_5$S$_6$H$_5$; 6 – C$_3$AS$_n$H$_m$. 
According to DTA, samples hardened under hydrothermal conditions are characterized by an extended area of the endothermic effect in the temperature ranges 200–300°C, 500–530°C, 680–700°C and the presence of an exothermic effect at 840–860°C which indicates the presence of garnets, tobermorite and xonotlite in the sample. The composition of hydrated calcium garnets changes during cement hydration. After two days of hydration, according to X-ray diffraction data, they are represented by a low-silica type $\text{C}_3\text{AS}_{0.5}\text{H}_{5.2}$ ($d = 0.509; 0.311; 0.265$ nm). After 7 days, diffraction lines with $d = 0.505; 0.309; 0.263$ nm are observed, which indicate the presence of $\text{C}_3\text{ASH}_4$ hydrogarnets in the samples, and after 28 days the high silica hydrogarnets $\text{C}_3\text{AS}_{1.6}\text{H}_{2.8}$ ($d = 0.500; 0.306; 0.261$ nm) crystallize.

SEM examination have shown the presence of needle crystals of ettringite and the gel-like mass of hydrated calcium silicates and aluminum hydroxide in the samples that hardened in usual conditions. According to SEM data hydrothermal hardening samples is represented mainly by octahedral crystals of calcium hydrogarnets, fibrous crystals of calcium hydrosilicates and boehmite scaled plates among which small needle crystals of ettringite and calcium monosulphoaluminate twins are seen (Figure 2).

The strength of cement stone after 7 days of hardening reaches 7 MPa, an expansion of 0.08%.

**Figure 2.** Microstructure of hydrated samples with SAC (2 days): a – normal conditions of hardening; b – in hydrothermal conditions, SEM, magnification, x 2000.

The study of hydration of cement 2, containing sulfoferrite clinker as an expansive component, showed that ferrite contained ettringite is formed in the composition of hydration products at elevated temperature ($d = 9.85; 7.46; 2.46$Å).

Hydrogarnate $\text{C}_3\text{F}_{\text{SH}_4}$ ($d = 0.302; 0.272; 0.199$ nm), xonotlite ($d = 0.362; 0.307; 0.198$ nm), tobermorite ($d = 1.13; 0.307; 0.298$ and 0.246 nm), cubic calcium hydroferrite $\text{C}_3\text{FH}_6$ and goethite are observed.

Judging by the change in the intensity of the diffraction lines of the above compounds on X-ray spectra, the degree of cement hydration gradually increases.

The formation of the hydrogarnet proceeds in steps: initially the hydrogarnate is unsaturated with $\text{SiO}_2$ oxide, and then for up to 7 days it is gradually saturated to the ratio $\text{Fe}_2\text{O}_3: \text{SiO}_2 = 1: 1$, as indicated by X-ray powder diffraction data. According to XRD hydrothermal hardening samples after 2 days have diffraction lines with $d = 0.509; 0.312; 0.267$ nm, and by 7 days the diffraction lines are shifted to large angles, which indicates a distortion of the crystal lattice of the crystalline hydrate.

It is noted that the amount of ferrous ettringite increases with increasing time of hardening. Along with calcium hydrogarnets and calcium hydroferrites, the formation of low calcium hydrosilicates is observed in the sample. Apparently, calcium hydroxide released during hydration is used to the formation of ferrous ettringite. The absence of an excess of $\text{Ca(OH)}_2$ causes the formation of low calcium hydrosilicates $\text{CSH}$. Their presence in the composition of the hydrating sample is fixed on the DTA curve by the peculiar exothermic effect in the temperature range of 820–880 °C, corresponding to the transition of the dehydration product into wollastonite. Electron microscopic
studies have established that the hydrothermal hardening stone structure is formed by fibrous calcium hydrosilicates (Figure 3), elongated prismatic crystals of ferrous ettringite in combination with cubic and octahedral crystals of hydroferrites and hydrogarnates.

Figure 3. Microstructure of cement stone, SEM, magnification, x 1500 (a), 3000 (b).

Strength characteristics of cement stone of weighted cement based on sulfoferrite clinker after 7 days of hardening in hydrothermal ones are relatively high, reaching 9.4 MPa in bending and 85.5 MPa in compression, which is due to the more dense structure of cement stone. Expansion of cement stone in all periods of hardening is in the range of 0.12–0.24 %.

At hydration of oil-well cement, containing alumina slag as an expansive component, under normal conditions, after one day hexagonal hydrates CAH_{10} are formed, which can be detected by diffraction lines with d=1.41; 0.71; 0.37;0.354 nm, and C_{2}AH_{8} (d = 1.07nm). After 2 days, the intensity of lines CAH_{10} and C_{2}AH_{8} increases, and after 7 days on X-ray pattern of the hydrated samples, there are clearly visible lines with d = 1.07; 0.536; 0.51;0.485; 0.43 and 0.33nm, characteristics of C_{2}AH_{8}, AH_{3} and C_{3}AH_{6}, which are observed up to 28 days.

These data correlate well with the DTA results. In the initial period, on the DTA curves, endo-effects are observed at 150 and 200°C, and then the exo-effect at 310–320°C, which is characteristic of the transition of AH_{3} into boehmite AlOOH. Gelenite contained in an alumina slag does not change the composition of hydration products, since it does not react with water at ordinary temperature.

At elevated temperatures (75 °C) and under hydrothermal conditions (150 °C and pressure of 30 MPa), the CA hydration of alumina slag is accompanied by the formation of boehmite, gibbsite and cubic calcium hydroaluminate C_{3}AH_{6}, and the hydration of gehlenite forms gehlenite hydrate C_{2}ASH_{8}. In this case, the rate of hydration increases significantly. Using the XRD for the determination of changing the intensity of the CA line with d = 0.295nm, it was found that under normal conditions the degree of mineral hydration is 50, 62, 72 % after 1, 2 and 7 days respectively, at 75 °C at the same time the degree of hydration is 60, 75 and 95 %, and at 150 °C and P = 30 MPa the degree of hydration of CA is 65, 80, 100 %, respectively, that is, by 7 days the full hydration of CA occurs. The cubic calcium hydroaluminate C_{3}AH_{6} in the X-ray spectra of the samples is detected by diffraction lines (d = 0.36; 0.230 nm), boehmite along the lines with d = 0.610; 0.317; 0.186 nm, gehlenite hydrate C_{2}ASH_{8} − d = 1.23; 0.418; 0.287nm. In addition to these crystalline hydrates, hydrogehlenite C_{2}ASH_{8}, high-silica calcium hydrogarnate C_{6}ASH_{4}, calcium monosulfate and boehmite are formed in the composition of hardening weighted oil-well cement based on alumina slag under hydrothermal conditions.

Determination of the properties of the samples showed a relatively their high strength, both under normal and hydrothermal hardening, while the values of expansion at elevated temperatures and under hydrothermal conditions are significantly lower than during normal hardening (Table 5).

Microscopic studies have revealed (Figure 4) that during hydrothermal hardening in cement stone samples, the morphology of crystals is characteristic of low calcium hydrosilicates twisted into fibers...
or bundled, among which calcium octahedron of calcium hydrogarnates and finely dispersed boehmite scales are traced.

| Temperature, °C | Strength, MPa, after, days | Expansion, %, after, days |
|----------------|-----------------------------|--------------------------|
|                | bending | compressive | 2 | 7 | 2 | 7 | 2 | 7 |
| 20             | 2,30    | 5,00       | 5,0 | 23,0 | 0,26 | 0,37 |
| 75             | 2,70    | 5,20       | 5,7 | 26,2 | 0,08 | 0,03 |
| 150 (P = 50 MPa) | 2,83 | 5,45       | 5,9 | 28,3 | 0,06 | 0,01 |

**Table 5.** Strength and expansion of cement stone depending on temperature.

**Figure 4.** The microstructure of hydrated images of cement 3 under conditions of elevated temperatures through: a - 2 days; b - 7 days. SEM, magnification, x3000.

The similar structure of a stone formed by finely dispersed crystals in combination with fibrous crystals with inclusions of cubic hydrates causes a high density and strength of the cement stone. In this case, its expansion is reduced. The results show that weighted oil-well cements with sulfoaluminate clinker and alumina slag on the first day of hydration have high degrees of hydration of the expanding component (55 and 53%, respectively). This is associated with the rapid formation of crystalline hydrates, which leads to the rapid structuring of the cement slurry, causing it to thicken.

**4. Conclusion**

At hydration of the expanding components based on sulfoaluminate and calcium aluminate (alumina slag + gypsum) at elevated temperatures and during hydrothermal processing, calcium monsulfoaluminate and hemihydrate gypsum is formed.

When the expanding component based on calcium ferrite (sulfoferrite clinker + gypsum) hydrates ferrous ettringite is formed, which is stable under hydrothermal conditions.

Under conditions of elevated temperature and pressure, hydrated garnets are formed during hydration of weighted cements, whose composition depends on the initial sulfated compound in the cement composition: on basis of calcium sulfoferrite ferrous hydrogarnates $C_3$FS$_n$H$_m$ crystallize; on the basis of calcium sulfoaluminate aluminate hydrogarnates $C_3$AS$_n$H$_m$ crystallize.

It has been established that the hydrogarnates crystallize in the form of octahedra and rhombic dodecahedrons forming intergrowths, the gaps between which are filled with acicular or lamellar crystals of ferrous ettringite, which creates a tobermorite crystals, prismatic dense structure of cement stone, reaching relatively high strength.

The presence of ferrous ettringite in the structure of the weighted cement stone compensates its shrinkage deformation.
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