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Cement slurries used in drilling – types, properties, application

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ABSTRACT

The cement slurry is formed by mixing water with Portland cement or with a mixture of cement containingf various additives. The most important goal of cementing boreholes is to counter the inflow of water into productive levels of rocks with oil and gas. Physico-chemical conditions in borehole have a major effect on the properties of the grouts (bonding, hardening and durability). The most important of these are increased temperature and pressure as well as the presence of reservoir waters, drilling mud and gas migration. The article specifies the requirements for cement grouts used in drilling. The formation process and various types of cement have been characterized due to their phase composition and chemical and mineralogical composition. The treatment methods for the cements of drilling cements are also given. Finally, examples of drilling in the Polish Lowlands are illustrated as a sample of many factors affecting the type, properties and application of cement.

***Keywords*:** cement slurry, cement grout, drilling, chemical composition, cementing

1. INTRODUCTION

Cement mix is formed by mixing water with portland cement or with cement containing various additives. The most important purpose of cementing is to prevent the inflow of water into productive levels of petroleum rock. Cementing is also performed to regulate the size of the gas index and water-oil quotient, for reconstruction in boreholes and for various technological operations of casing columns. During all operations, the cement grout is pumping into the annular space between the casing pipes and the borehole. After pumping into the annular space and breaking the circulation, the process of thickening and bonding of the cement grout begins, followed by hardening of the cement stone. In this way, a solid barrier for the fluid flow is formed in the annular space of the borehole. This type of cementing of casing pipes plays a decisive role in counteracting the movement of water, brine, oil and natural gas towards the opening of the borehole through the space outside the pipe. Cement slurries with various additives are also used to remove the escape of drilling mud or to stop lost its circulation in the hole and in many other special cases.

2. CHARACTERISTIC OF BOREHOLE ENVIRONMENT

The conditions that are present in the borehole have a major impact on the differentiation of physicochemical properties that effect of the slurry (bonding, hardening and durability). Portland cement applied for cementing of wells must meet completely different conditions than those used by their inventor, and the conditions of modern drilling can be considered extreme compared to the conditions of architecture.

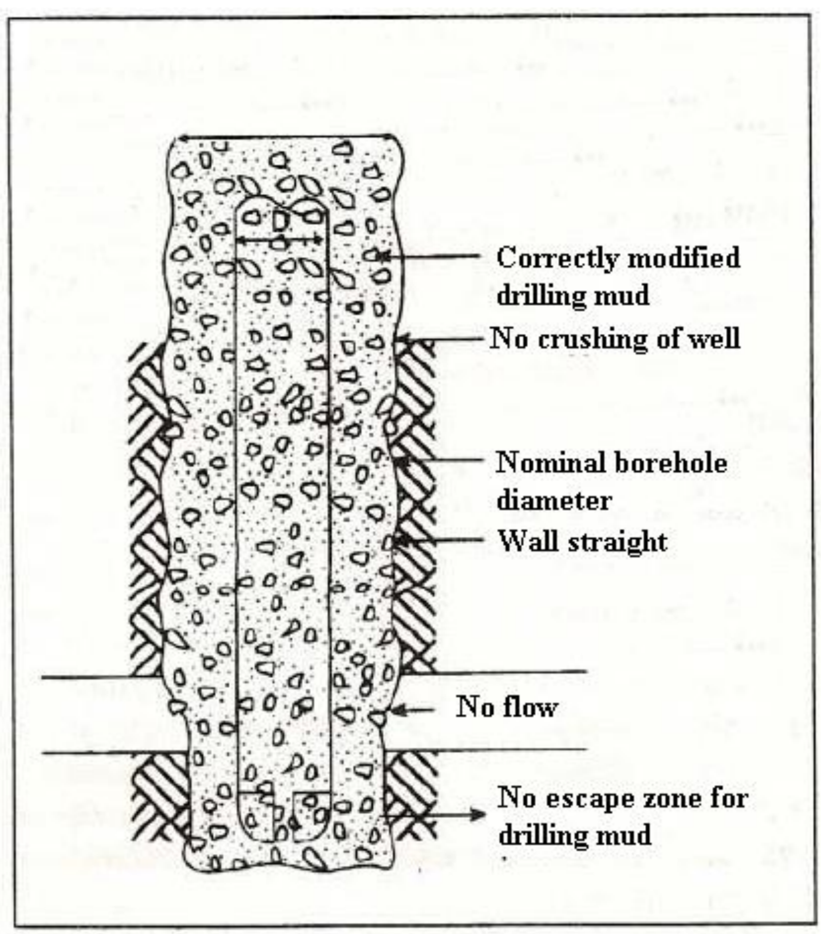

Figure 1. Ideal borehole conditions required during cementing [8].

The most important physical and chemical factors in the occurrence of boreholes include:

- temperature increased and changed during the procedure,
- pressure increase in the hole (additionally pumping pressure),
- presence of salt water (brines) and their influence on the change of the chemistry of slurries,
- presence of high pressure and often also high chemical activity gases - methane and hydrogen sulphide,
- variety of borehole rocks (high variability of the sectional volume and wall profile),
- presence of drilling mud, its chemical impact.

All of mentioned factors create a highly varied and extremely complex environment in the borehole for cement slurry. Therefore, the choice of type of cement, the correct formulation of the grout and the technology of its production and injection are complex and extremely important [2,4,8,11,13,18-24].

3. REQUIREMENTS FOR CEMENT SLURRIES

Cement slurries, whose role is to isolate, seal and stabilize the rock mass in drilling, should meet the following requirements:

a. The density of the cement grout should be dependent on the geological conditions that exist - the density can be adjusted from the pressure equating the reservoir pressure to just below the fracture pressure.
b. The continuous and long-lasting flow of the slurry with a relatively high intensity of movement should characterize certain rheological properties: on the one hand, it enables it to be pumped to its destination (relatively low flow resistances providing the greatest radius of flow in the sealed medium) and, on the other hand, effective liquid displacement from the well.
c. The consistency and time of pumping possibility of the slurry after mixing will guarantee failure-free overflow to the selected medium under conditions existing in well.
d. The grout composition should allow for both start and finish of bonding adjustment within a fairly wide range (hole conditions).
e. "Break time" for the bonding should last as short as possible - the grout after the pumping down should quickly bind.
f. The cement slurry should be characterized by low separation of water and low filtration, so that after pumping down it retains its homogeneity (stability of the slurry).
g. Resistance of the slurry to erosive / aggressive action of reservoir waters.
h. The amount of heat generated during the bonding reaction should be limited (different coefficients of the warm expansion of steel and hard cement - the possibility of leakage).
i. The resulting cement stone is characterized by suitable strength parameters, corrosion resistance and co-operation with rock formations and casing columns (applies also to grout). The size of the crush strength of 3.5 MPa is considered and the minimum

tensile strength (required to maintain the suspension of the casing tube) is 0.56 MPa, which corresponds to a crushing strength of 0.7 MPa.

j. The components of the cement grout should meet the ecologic and economic criteria, for example the possibility of making grout in industrial conditions due to the simple technology, relatively low unit cost of the grout, the non-flammability and non-toxicity of the components and no harmful interactions with the environment.

In conclusion, several criteria are used to ensure the reliability of the work being performed for the cement slurry. The first is the condition of physicochemical compatibility with the environment. The second is due to the leaktightness of the cement slurry - it is realized through appropriate adjustment of the rheological model and rheological parameters of the cement slurry, and these make it possible to determine the resistance of the slurry in the injection system. The third criterion is the appropriate strength and durability of the cement stone - the recipe of the slurry should be composed in such a way that the resulting solid has a similar nature to the natural rock properties of the mechanical properties. The fourth condition determines the aforementioned economic and ecological factor.

Based on the above considerations, it can say that the choice of suitable sealing slurry can not be accidental or not fully confirmed. On the contrary, it requires a comprehensive examination and an optimal fit. Many authors consider the cementing process to be one of the most important, if not the main treatment that determines the success of the entire drilling process, so detailed research remains justified [3,4,6,8,12].

4. DRILLING CEMENTS - TYPES AND CLASSIFICATION

Portland cement is used in drilling as a basic material for making cement grout in virtually every borehole.

4. 1. Process of formation and composition

The basic raw material for cementing operations is Portland cement. It is characterized by a certain percentage of clinker, which is obtained by the appropriate selection of raw materials: limestone (or chalk) - providing calcium oxide and clay particles (clay, shale) - introducing into the composition of silica and alumina. Sometimes a marguer is also used as a rock constituting a mixture of limestone and clay materials. The technological process of cement production is quite complicated, which is related to the high requirements of its properties (proper grinding, specific surface area, etc.). The first stage is the preparation of raw materials, which is understood by preliminary fragmentation of raw materials (by jaw and/or ball breaker) and preparation of the batches (the dry method is to obtain the meal, while the wet is the sludge). The next step involves firing: the powdered mixture is directed to a special rotary kiln, where a clinker with an average particle diameter of 3-25 mm is obtained at 1450 °C. The quality of the clinker and the cement itself is a function of the rate and intensity of cooling. The best clinker is obtained by slow cooling to about 1250 °C, followed by a sudden cooling of 18-20 °C / min [8]. Subsequent grinding of clinker and addition of gypsum in the amount of 3-5%. It fulfills the role of regulator of bonding time.

The resulting blend is called Portland cement and contains chemical bonds between the compounds listed in Table 1.

Table 1. Typical portland cement composition (G or H class according to API) [13].

Ingredient (Oxide) Name	Formula	Content (%)
Silicon oxide	SiO_2	22,43
Calcium oxide	CaO	64,77
Iron oxide	Fe_2O_3	4,10
Aluminum oxide	Al_2O_3	4,76
Magnesium oxide	MgO	1,14
Sulfur trioxide	SO_3	1,67
Potassium oxide	K_2O	0,08
Other ingredients	-	0,54

Portland cement must comply with certain chemical and physical standards, depending on their purpose. The principal distinguishing feature of Portland cement in terms of chemistry is the relative distribution of the main clinker phases, called the phase composition [8,13]. Therefore, four basic compounds are included in the basic mineralogical constituents of Portland [9]:

- Tricalcium silicate $3CaO \cdot SiO_2$ - alite - the most important component of Portland clinker; is responsible for early cement bonding [7]. Reactivity of alite in relation to water determines the course of hardening of the slurry and the properties of the cement stone - it regulates the period of durability development and is responsible for the strength of the cement. Cements containing increased amounts of tricalcium silicate exhibit higher calorific value, heat of hardening, also rapid build-up of strength and high endurance, but also characterized by high shrinkage and high hydration heat.
- Dicalcium silicate $2CaO \cdot SiO_2$ - belite, larnite - is responsible for late binding of cement. Its slow release (medium active) affects the bonding time and the final strength of the cement stone. Low caloric, gives the cement a high endurance strength with a slow increase in strength.
- Tricalcium aluminate $3CaO \cdot Al_2O_3$ - celite - high caloric, corrodent component that affects the bonding speed (accelerating bonding). Its main function is to provide a large amount of heat and provide the start of bonding of slurry. It is easily soluble in water (with high heat output), especially sulphated, which results in its limited contribution to cements with high sulphate resistance.
- Tetracalcium alluminoferrite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ - brownmillerite - affects the increase in strength over time with significant calorific value. Exits a small amount of heat during hydration, only slightly affects the properties of the cement stone.

Table 2. Portland cement chemical compounds [13].

Formula	Standard designation
$3CaO \cdot SiO_2$	C_3S
$2CaO \cdot SiO_2$	C_2S
$3CaO \cdot Al_2O_3$	C_3A
$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF

Table 3. Typical percentage composition of API classification of cements [8].

Class	C_3S	C_2S	C_3A	C_4AF
A	53	24	8	8
B	47	32	5	12
C	58	16	8	8
D, E	26	54	2	12
G, H	50	30	5	12

Main components of the cement - specially selected inorganic materials with more than 5% [13]:

- Portland clinker (K).
- Granulated blast furnace slag (S) - material with latent hydraulic properties, for instance, exhibits hydraulic properties by appropriate activation. It is produced by the rapid cooling of the liquid slag of the appropriate composition obtained by smelting the iron ore in the blast furnace.
- Natural pozzolans (P - volcanic / sedimentary rocks) and natural firing (Q - thermally activated clays / slates) - silicate or aluminosilicate materials; they do not harden but finely ground and in the presence of water they react at normal temperature with calcium hydroxide (portlantide), forming compounds with hydraulic properties (hydrated silicates and calcium aluminates).
- Fly ashes: (V) - siliceous - pozzolanic properties and (W) - calcareous - hydraulic and pozzolanic properties. Fly ash is obtained by mechanical/electrostatic deposition of dusty particulate flue gases from coal-fired furnace burners.

- Slate (T) - in particular bituminous slate fired at 8000C.
- Limestone (L, LL)
- Silica dust (D) - consists of very fine, spherical particles with an amorphous silica content. It is produced during the reduction of high purity quartz with carbon in electric blast furnaces for the production of silicon or ferroalloys.

Secondary components - specially selected inorganic materials with less than 5% share - mineral inorganic and clinker mineral materials and main components, if less than 5%.

It is also common to use various additives to improve the production or properties of cement (usually less than 1%) [7-9,11,13].

4. 2. Cement classification

In accordance with EN 197-1, cement is designated as CEM and is a hydraulic binder, for example a finely ground inorganic material which, when mixed with water, forms lees, binds and hardens by reaction and hydration, after hardening remains strong and durable. Also in the aquatic environment. According to the above standards, the cement, properly measured and mixed with water, should create a mortar that will retain the ability to be pumped long enough and after a certain period of time it should achieve a fixed level of strength and should maintain a constant volume. Hydraulic hardening of CEM is mainly due to the hydration of calcium silicate (CSH - tobermothite phase) as well as other chemical compounds (for example aluminate - ettryngite). The sum of reactive shares: calcium oxide and silicon dioxide in cement should be at least 50% by weight.

According to the standard cements are divided into five categories:

CEM I - Portland cement
CEM II - multi-component Portland cement
CEM III - metallurgical cement
CEM IV - pozzolanic cement
CEM V - multi-component cement

Due to the amount (concentration) of mineral additives in their composition, among them we distinguish categories A, B and C. The strength classes determine the compressive strength after 28 days: 32.5; 42.5; 52.5 [MPa]. For each class of strength, there are two types of early strength: normal (N) and high (R).

Classification according to API standards.

In API RP 10B, nine classes of sealing cements are classified:

Table 4. Scope of application of cement classes according to API [4,11].

Class of cement	Depth of application [m]	Temperature [°C]
A	0-1830	44-94
B	0-1830	44-94
C	0-1830	44-94

D	1830-3050	94-144
E	1830-4270	94-144
F	3050-4880	127-167
G	0-2440	44-111
H	0-2440	44-111

These cements addition to Class A are produced with normal and high resistance to sulphates.

However, in the foreseeable future, the main G and H cements will still be produced in the highest quantities. The most important type of cement used in the world is HSR class G cements and does not seem to be able to be replaced much more widely in common cementating of wells by other types of cement. The superiority of using G and H grades is due to the stricter requirements for these cements compared to architectonic cements.

4. 3. Control of the properties of drilling cements

Slurry based of Portland cement may be modified by the introduction of various regulating additives:

- rheological parameters of the cement slurry (density, viscosity, effluent, filtration, amount of separated water and time of cement slurry density);
- start and end of bonding of cement grout depending on the technical conditions (borehole temperature and pressure, casing liner type, hole depth, occurrence of aggressive waters, crude oil, natural gas and drilling fluids);
- strength parameters of cement stone (crush and bend strength, permeability, adhesion of cement stone to casing pipes and rock forming the borehole wall);
- resistance of cement stone to sulphate corrosion and the aggressiveness of reservoir waters.

Additives are called various chemicals mixed with cement to improve cementation efficiency and sealing efficiency of reservoir rocks. All possible additives for cement or cement slurry are divided into:

- accelerating time of bonding or thickening of cement slurry;
- binding retarders and dispersants;
- additives - density reducing fillers;
- load materials;
- additives used in the elimination of leakage of drilling mud or cement grout;
- additives for special cements (tar, gypsum, latex, puzzolanic cement, cement mixture with diesel oil and cements for high temperatures);
- anti-pollution additives for cement slurry;
- additions to the pre-washing liquid and buffer overrun liquid.

5. CHARACTERISTICS OF THE DIFFERENT TYPES OF CEMENT

Portland cement (symbol: CEM I) - also called "pure", because it contains no mineral additives, consists entirely of portland clinker; it is practically inaccessible on the Polish market, manufacturers are inclined towards mixed Portland cement.

Multiple Portland cement (CEM II/A and CEM II/B) commonly called "mixed", besides Portland clinker, contains additives in the form of slag, ash, silica or lime; the content of additives is 6% to 20% (CEM II/A) or 21% to 35% (CEM II/B). Because of the great variety of cements in this group, each of them can have different characteristics. In most cases, they are lowered hydration heat, slower increase in strength, increased resistance to chemical aggression.

Metallurgical cement (symbol: CEM III/A or CEM III/B or CEM III/C) - contains Portland cement clinker blended with blast furnace slag and so slag content from 36% to 65% is CEM III/A, 66% to 80% % CEM III/B, 81% to 95% CEM III/C; the metallurgical cement is more resistant to sulphate than other Portland cements, it also has a slower increase in strength over time and less heat of hydration than Portland cement. Widely used in conditions of increased corrosion danger.
We can stand out [16]:

- CEM III / A metallurgical cement - contains clinker with the addition of 36-65% slag
- CEM III / B metallurgical cement - contains clinker with the addition of 66-80% slag
- CEM III / C metallurgical cement - contains clinker with an additive of 81-95% slag

A pozzolan cement (symbol: CEM IV/A or CEM IV/B) - its composition is most commonly portland clinker, pozzolana and gypsum. (Pucolana is a dust or very fine ash, once of volcanic origin, also recovered from coal-fired power exhaust fumes today). Its main ingredient is pure silica in the form of very fine rounded grains.

Important feature of pozzola is the ability to bind calcium also under water. It is currently used as an additive for concrete mortars to increase their water resistance. Pozzolan cement has properties similar to metallurgical cement, it is highly resistant to the negative effects of chemical aggression (for example sulphate).

There are two types of pozzolanic cement.

The first type is CEM IVA. This type of pozzolanic additives, natural pozzolana, naturaly baked and silica fly ash are 11 to 35%, and the addition of silica dust can not exceed 10%. CEM IV components should be between 36% and 55%, and silica dust should not exceed 10%.

Comparing Portland cements with pozzolanic cements, it is noted that pozzolanic cements are characterized by slower hardenieng rates, which are due to initially low speed, slower pozzolanic reaction, greater resistance to aggressive chemical factors, and longer bonding times relative to Portland cements. By physical, thermal or chemical activation, we can accelerate the rate of hardening of pozzolanic cement. Shredding more cement grains and hydrothermal treatment will accelerate the pozzolanic reaction. Often, the rate of hardening of pozzolanic cement depends primarily on its grain size.

Also, the introduction of adequate amounts of fly ash shapes the properties of pozzolanic cement. The optimum content of fly ash in pozzolanic cement is 30 to 45%. We can obtain pozzolanic cement within the range of 3400-4000 cm2 / g and thus (if we meet the quality requirements for clinkers and ashes) we will obtain brand cement from 32.5 ÷ 42.5.

Ensuring adequate environmental humidity in the initial cementation hardening period can contribute to a suitable cement hardening process, to provide better strength and to provide resistance to aggressive agents.

One of the disadvantages of pozzolanic cement is that it is less durable in dry weather than Portland cement. Air-dry conditions aggravate the course of the pozzolanic reaction. Decreasing the rate of hardening of pozzolanic cement may result from lowering of temperature. However, in this respect it is better than metallurgical cement. wastewater. There are different types of CEM IV cements.

Characteristic features:

- good dynamic of strength increase in longer hardening periods,
- extended bonding time,
- mprovement the tightness of cement stone,
- good pumping rate of the slurry,
- moderate amount of heat released during bonding,
- Increased resistance to aggressive environments,
- low shink.

Multicomponent cement (symbol: CEM V/A or CEM V/B) - we do not call it Portland, because the content of additives is higher than 35% and CEM V / A is 36% to 60% and CEM V / B is 60% up to 80% (EN ISO 10426-1, EN ISO 10426-2).

Slag cement - has properties and applications similar to metallurgical cement (and high early strength). The group of slag cements include:

• clinkerless slag cement - produced by grinding blast furnace slag with gypsum, anhydrite, dolomite fired at temperature 900 °C and hydrated lime. Cement slag is dark green.

• slag-gypsum cement - produced by grinding blast furnace slags, gypsum and Portland clinker. It is more resistant to sulphates and acidic waters. It is not used in drilling because it corrodes steel.

Slag-alkaline cement - compared to fly ash, the slag-alkaline grout is used to a lesser degree. There are several examples of effective use of it, for instance for the work of chink up the rock mass in Wieliczka Salt Mine. Because of its high water stability and favorable mechanical properties, ash and slags are suitable for use in geoengineering, hydrotechnical drilling and mining.

Granulated blast furnace slag, properly ground and water-treated, has the ability to bind and harden. The slag hydraulic properties are primarily related to the hyaline phase. Polish granulated blast furnace slags belong to the weakly alkaline and less active hydraulic group. In spite of this, it is possible to obtain positive results from the use of slags as hydraulic binders in the selection of suitable activators and other stimulatory factors. The slag hydraulic activity can be increased by adding chemical activators, increasing the temperature and ripeness pressure, or increasing the fineness of the slag. As chemical additives that activate the slag bonding process, non-silicic salts of the weak metals of the first group of the periodic table (Na_2CO_3), water glass of various silicate modules and alkaline alkalis are used. In general, the following raw materials are used to produce slag-alkaline slurries: ground

granulated metallurgical slags, chemical activators, mineral additives (fillers) - modifying technological parameters. The type of activator used depends on the chemical composition of the slag. The amount of added activator should be determined experimentally and is primarily dependent on the alkali, the vitrification degree, and the degree of fragmentation of the slag.
The resulting hydrates of the slag-alkaline slurries exhibit significantly lower solubility compared to typical Portland cement hydration products, which causes corrosion processes to be significantly reduced. These slurries are characterized by a very compact microstructure, have a lower total porosity, and a smaller pore size compared to Portland cement grout. Slag-alkaline slurries have a wide range of technological and mechanical parameters. They are characterized by very good rheological properties, achieving satisfactory pumping ability at a water/cement ratio of about 0.4, and very good at w/c from 0.5 to 0.55. Good rheological properties of slag-alkaline slurries are associated among other, with the classifying effect of alkaline activators. The bending strength and compression values of the hardened slag-alkaline slurry are comparable to those of the hardened Portland cement slurry. Due to the high degree of hydration of the slag slurry, the hardened ore is practically insoluble. An important advantage of these slurries is also low shrinkage, as well as the ability to obtain materials with expansive properties, characterized by very good adhesion. Slag-alkaline slurry is much more resistant to the effects of various types of aggressive environments than portland cement grout and less costly to execute [5,10].

Alumina cement - characteristic for it is the rapid increase of strength in the first days after use, increased resistance to higher temperatures. Can be used during winter work.

Special cements

Standard PN-B-19707 includes the following types of special cements:

• **HSR** (High Sulphate Resistant) cement, whose linear expansion after holding for 52 weeks in Na_2SO_4 solution should be less than 0.5%
• very low heat **VLH** (Very Low Heat), which should exhibit heat less than 220 J/g in the semiadistatic method after 41h and in the case of CEM IV and V the same size after 7 days,
• low alkali (sodium and potassium) cement (**NA**), where for CEM I, II, IV and V $Na_2O_e \leq 0.60\%$ and for metallurgical cements it increases from 0.95% to 1.10% to 2% for CEM II / B and CEM III / A and B, C (PN-85 G-02320, PN-EN 197-1).

Kurdowski and Sorrentino belong to special cements whose properties are not specified in the standard requirements and have special applications. They are often produced in an unconventional way or from atypical raw materials.

Foamed cement slurry with a density of 1080 kg/m^3, after bonding has the same strength as cement slurry with a density of 1440 kg/m^3. Foaming of cement grout is most often done with nitrogen or compressed air. These slurries are used for cementing reservoir levels if the hydraulic fracturing of the rock is at a relatively low pressure.

Quick-setting cements - these are lightweight cement slurries used to control liquid circulation loss at depths up to 1220 m. These binds at temperatures of 26.7 to 35°C within 30 minutes, permitting sealing of the circulation loss zones. Quick-setting cements can not be used in depths of more than 1,220 m. They are highly viscous in comparison to normal ones.

Tar slurry - it is a mixture of liquid tar and Portland cement with high initial strength. It is recommended for making cement plug in the open hole, for cementing the casing line of the hole through perforation channels under pressure through the perforation channels and cementing the casing columns. It is a material that adequately isolates oil, water or gas reservoirs when conventional methods fail.

Gypsum cement - these cement have adjustable setting time. When mixed with water, the binding starts after 50 to 60 minutes at temperatures up to 60 °C. The gypsum cement during expansion is approximately 0.3% and its compressive strength after 1 hour is about 17.5 MPa.

Cements used for small diameter boreholes - cementing small diameter boreholes is difficult but it is important. Cements used to obtain zone isolation in small diameter boreholes include good quality G and H drilling cements, slag and pozzolanic cement and polymer cements, all of which are composed of small particles. Small amounts of liquid additives and retarders should also be used in small quantities. Drilling and cementing small diameter wells is much cheaper than traditional drilling and cementing wells, and much better for the environment. Cementing small diameter wells is important for reopening abandoned wells to resume oil and gas extraction, and may be useful in future to place carbon dioxide through boreholes. The importance of cementing small diameter wells with good quality cement is increasing, but it is more complex than traditional cementation with drilling cements.

Plastic cement mixtures - flexible cements. Elasticity for drilling cements is defined as the ability to take over hardened cements of such shape to fill the annular space outside the wellbore, without the effect of long-term shrinkage and the resulting fluid migration. Such problems can occur when cured shrinkage and microdeposited cracks occur in the hardened cement coating, with the cured coating being disturbed from the casing or rock formation. Zone isolation is therefore a key feature required of a hardened cementing coating in the annular space.

The high elasticity of the hardened slurry can prevent cracking and shrinkage - which is necessary to eliminate the migration of gases and the penetration of reservoir fluids that can destroy the cement coating. The main plastic cement mixes used in the world include:

- flexible cement slurries with designed grain distribution, containing suitable solid fillers (crushed rubber, metal or polymer fibers),
- latex sluries with high plasticity,
- swelling blends, containing a positive additive volumetric additive at the time of binding,
- blends based on a drilling mud with a filler such as ground granulated blast furnace slag, fly ash and others,
- cement mixtures based on aluminum cement and phosphate cement compositions. Plastic cement mixtures (so-called "flexible cements") may contain fibers or crushed gum and be "reinforced" simultaneously - for example by adding latex and a swelling factor. Flexible cements can be used both for conventional columns of casing pipes or lost columns as well as intended for underground gas storage.

Brine-based slurry - slurries prepared for injection work in salt rock are prepared using a saturated brine solution as a working liquid. Hydrolysis and hydration of mineral binders in the presence of saturated brine solution are distinctive, which results in their phase composition, product morphology and microporosity, and especially the structure of the pores, differ significantly from the classical hardened cement slurries. The phase composition and microstructure of hardened brine salts have a major impact on their operating properties, especially their durability [14].

Cement slurry used in borehole heat exchangers. When making borehole heat exchangers, it is very important to use a suitable sealing slurry when the exchanger pipes are lowered. The use of a suitable cement grout is primarily intended to isolate the various aquifers so that groundwater is not polluted. The basic requirement for cement grout is their greatest durability and least permeability after hardening in the hole. A particularly desirable feature in the case of sealing bore heat exchangers is as high a capacity as possible for the conduction of heat energy. This feature allows efficient transfer of heat from the heat exchanger to the rock mass while the heat exchanger is heated and in the opposite case - the heat absorption from the hole. The third important factor for sealing slurries is their pre-hardening parameters. To ensure that the groove is as easy to be pumped into the hole, it should have the appropriate properties. Getting a cement grout meeting all these requirements is extremely difficult. Graphite is used as a thermal conductivity. In addition to improving the thermal contact with the rock formate, it also affects other parameters of the slurry (lowers the density, pourability and viscosity) [15].

Chloride, sulphate and magnesium corrosion resistant cement slurries.

- Effect of acids on cement grout:

Portland cement, which is a highly alkaline material, is not resistant to strong acids or compounds that can turn into acids. Generally, chemical aggression on the slurry takes place through the decomposition of hydration products and the formation of new ingredients which, if soluble, can be flushed out and, when not soluble, may break down at the site of formation. $Ca(OH)_2$, which is most susceptible to chemical factors, can also be affected by the C-S-H phase and calcium hydrolysates. Limestone is also susceptible to aggressive elements.

- Corrosion by Ions Cl^-

Concentrated chlorine solutions cause very rapid progressive corrosion of cement slurries leading to their destruction. The few exceptions include gehlenite glass and alumina cement. Both types of slurries do not contain calcium hydroxide, the first one consists of gehlenite hydrate and the other contains calcium aluminates CAH_{10} and C_2AH_8. Particular durability in chloride solutions is due to the very low porosity and lack of calcium hydroxide.

- Sulphate corrosion

In response to the destructive effect of sulphates, internal hardening of hardened slurries and concretes for sulphate corrosion has been developed, which involves adding a sufficient amount of dicalcium silicate containing a variable amount of barium in solid solution to the mixture. Bar creates solid solutions with dicalcium silicate in a wide range of compositions.

The solid solution of dicalcium silicate added to the slurry does not react with water during pre-maturation and autoclave treatment. The reactivity of this silicate is activated after the water has migrated into the interior of the cement stone during use.

- Magnesium corrosion

As shown by the tests of resistance to sulfate-magnesium corrosion, the highest resistance, irrespective of the w/c ratio, is found on CEM III A 32.5 NA. The CEM II A-V 32.5 R ash cements as well as CEM I 52.5 R hardeners are significantly lower in durability.

Sulfate-magnesium corrosion is a typical example of corrosion-destroying microstructure of a hardened cement grout. It consists of the reaction of the double ion exchange between magnesium and calcium cations:

$$Ca(OH)_2 + MgSO_4 = Mg(OH)_2 + CaSO_4 \cdot 2H_2O$$

As there are many years of practical experience, two solutions are possible in the selection of hardened cement grout for sulphate-magnesium corrosion. The first is the minimum C_3A content in cement, for example the use of sulfate resistant cements. The second is the reduction of the $Ca(OH)_2$ content in the hydrated cement slurry by the use of portland slag cements, smelting cements, slag-alkaline cements and pozzolanic cements.

Geopolymer slurries - cement grouts based on geopolymers are based exclusively on components of inorganic origin. They are obtained by modifying the composition of suitably prepared slurries prepared on base of multi-component cements of general use or ground granulated blast furnace slags with pozzolanic additives[1].

6. AN EXAMPLE OF MANY FACTORS AFFECTING THE TYPE, PROPERTIES AND APPLICATION OF CEMENT - DRILLING IN THE POLISH LOWLANDS

In order to use cement slurry under conditions of Lowland Poland, it must contain a number of components. In addition to the necessity of using suitable cement, the slurry used to seal the of exploitation column in the Polish Lowlands should be made with 10% NaCl (relative to the weight of the water). This is due to the presence in the section of the drill hole of the salt formations. The high depth of foundation of the exploitation tube columns (usually 3000 - 3500 meters), the high temperature and the pressure at the bottom of the hole make it necessary to use a variety of modifiers for the sealing grooves. These include:

- dehumidifiers (reduce the amount of air contained in the slurry),
- liquefying, for example decreasing the viscosity of the grout (regulates the rheological-structural parameters),
- lowering the filtration and de-watering (protection by loss of water from the slurry),
- lengthening of the dense start time (delays the binding process).

In addition to the additives mentioned above, latex (gas exhalation), silica (silica powder), raising the thermal resistance of the cement stone at high temperature, and the loading material (giving the required cementing density) are also introduced. Microcrement (finely ground Portland cement) can also be used to improve the tightness of the matrix. The latex additive inhibits the formation of gas channels during bonding, by combining microcracks into the hardening cement paste. Latex, an aqueous dispersion of butadiene styrene-amide copolymer with added modifiers, is used as a milk suspension in the form of very small, spherical polymer particles. Latex reduces the permeability, reduces shrinkage, and increases the flexibility of the hardened cement grout. Latex modified cement systems form a kind of plastic membrane that surrounds and covers the CSH phase.

Additional advantageous features of slurries modified latex are their very low filtration, extremely favorable rheological parameters and low porosity and gas permeability. Silica powder (silica, microsilica) with a particle size of about 15 mm increases the resistance of the cement stone to high temperatures (added to the cement grout at a temperature of 90 °C). Hematite (Fe_2O_3) is a mineral with an iron content of about 65 ÷ 70%. After proper treatment (grinding) can be used to increase the density of cement slurry.

In order to obtain the lowest porosity of the hardened grout (and hence the low permeability of the cement matrix), it is advisable to use fine material which by packing between the hydrated cement clinker grains will fill voids between the grains. Such a role can play the microcement formed from ground cement (surface area of the microcement - about $1200 m^2/kg$, fractions of dimensions: 16 μm - about 10% [17].

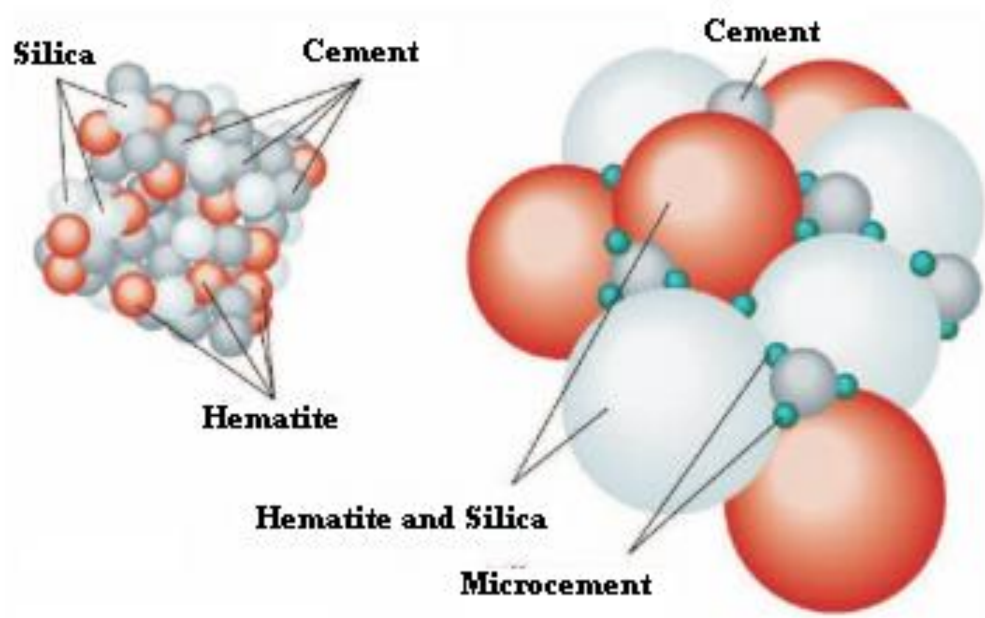

Figure 2. Schematic arrangement of the individual components in the loaded cement slurry [17].

7. CONCLUSIONS

The most important purpose of cementing is to prevent the inflow of water into productive levels of petroleum rock. The article specifies the types of cement grout used for cementing boreholes, both the most common ones and those for special applications. Particular attention has been paid to characterizing, extending and systematizing the knowledge of cement slurries and their varied properties and applications, as industry demand for new solutions continues to grow and the field develops extremely dynamically. Thanks to thorough research of fresh and hardened cement grout and more and more perfect modification of the recipes, the quality of cementing jobs of casing or exploitation columns providing oil, gas, fresh water or heat energy deposits is constantly improving.

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