

The Phenomenology of the Autogenous Contraction which is Manifesting During and after the Hardening of the Slurries Used to Well Cementation

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Abstract

The operation of wells cementing has as purpose the sealing of the space between the casing-string and the well wall for the solving of some technical and environment problems, meaning that fluids migration from the depth in less deep layers or on the surface must be prevented. During the slurry transformation in stone are taking place some phenomena which can have as a result a poor sealing of the circle well space. A deep knowledgement of the causes of these undesired effects will allow us to find the most appropriate solutions as receipes and/or cementing procedures.

Key words: *hydrating, chemical shrinkage, autogenous shrinkage, adherence.*

Introduction

The goal of a cementation operation is to place in a certain space in the well a volume of cement paste, that through hardening seals that space from the flowing fluids' point of view and constitute a supplemental mechanical support for the well's wall or for the casing strings between which is placed. The complex phenomena that are taking place in the hardening of the slurry have major consequences on the success of the cementation process.

Depending on the conditions of utilization of the cement paste and of the cement's quality of preparation, the resulted stone can go in time, in its interior, through diverse dimensional variation and remodeling that can influence its qualities. When a reduction in volume takes place there is the weakening risk of the adherence of the cement stone on the wall and the casing or the apparition of the fissures in the stone's mass, the sealing of the annular space could be compromised.

This is why we proposed to analyze diverse processes that take place during the hardening of the cement paste, as well of the causes that have the effect of volume reduction of the solid phase.

For an easier understanding of these aspects, we will expose briefly the main phenomenon that takes place during paste formation and of the cement stone. In the larger process of hydration, the water is acting on the cement dust through more physico-chemical mechanisms that lead to the apparition of the amorphous hydrating and crystal products. These mechanisms takes place concomitantly, complementary and successively, with variable rhythms. We can distinguish in this way: the absorption, dissociation, hydrolysis, and crystallization.

Even if the transformation of the slurry in stone is an physico-chemical continuous process, complex and time consuming, because from technical point of view, the main bulk of the reactions are taking place in about 8 ours. We try to simplify its presentation in form of three successive stages: hydration, structure formation, and hardening.

The Hydration

We will make reference to the main aspects of the cement hydration and to cement stone's formation, taking in consideration only the case of the most reactive components of the clincher and specifically tricalcic silicate-C3S, and tricalcic aluminum-C3A. We will use consecrated abbreviations from the specialty literature: C represents CaO, S=SiO₂, A= Al₂O₃, F=Fe₂O₃, H=H₂O, S= SO₃⁻.

The components of bicalcic silicate and tetracalcic feroaluminate are hydrated in the same manner as their own correspondents, the only exception is that they do it following more slowly kinetics and have a smaller weight in the first hours of stone hardening.

Tricalcic Silicate

Tricalcic silicate through hydration forms hydrated calcium silicates -of the kind of C-S-H in diverse structural types (alpha, beta, gamma), depending on the increase of the value of the rapport of C/S from 1 to 2 or of increase in C concentration in solution- and portlandit (calcium hydroxide) symbolized C-H, that can exist in solution both in a crystal and amorphous form. If the portlandit has a lamellar form being formed through edges to edge bonding in the same plan of the dioctahedron of calcium, the C-S-H microcrystal have a more complex structure, from here the capacity to fix more water.

A C-S-H microcrystal of alpha type is formed from 2-4 parallel lamellas, spiralled together to form a tubular structure. A lamella is similar with that of montmorillonit- is triple stratified: a layer of calcium dioctahedron is placed between 2 layers of tetrahedron of silica, with the tops directed towards octahedron and the planes of bases towards exterior.

The water is found in 4 forms in their relation to the C-S-H micro crystals and specifically intercrystalline free water; water fixated on the extern surfaces of the crystals on the layers of the tetrahedrons, structured in hexagonal network-accordingly with the tetrahedron's distribution- oxidrilic or polar bonded in several parallel layers; water intracrystalline fixated polar between lamellas; water intracrystallinal fixated oxidrilic on a lamellae.

The hydrating reactions take place quickly enough and in several minutes the calcium anions passing in the solution leads to the increase of the value of the C/S rapport to 2, a fact that transforms C-S-H (alpha) in C-H-S(beta) much richer in calcium anions fixated to the lamellas' surfaces and then in 2-3 hrs in C-S-H(gamma), when on the tetrahedron's surfaces the small crystals fixes, then bigger and bigger of C-H.

Tricalcic Aluminates

Tricalcic aluminates hydrates with very big speed producing diverse forms of C-A-H (aluminates of hydrated calcium), which crystallises in the shape of hexagonal plates (C₄AH₁₄), which fixes more C-H and very much water and passes through a cubical form, more stable – C₃AH₆. But as in the solution we have also calcium sulphate (added to the clincher grinding), appear quickly in accicular structure, hexagonal in section the etringit, a sulfoaluminate of hydrated calcium, at the beginning in a trisulfo aluminates C₆ AS₃ H₃₂ shape, and after the

exhaustion of the gypsum in the form of monosulfoaluminate C_4ASH_{12} , and hydroaluminate C_4AH_{14} , in hexagonal form, which induce the growing bind [1,2,3].

Increasing the concentration of C and S, besides the acicular etringit, monosulfoaluminate of calcium hydrated is modified also in the shape of hexagonal crystals and it forms solid solution with the hydroaluminate. The volume of the solid etringit increases in time through fixation of water determined by more mechanisms such as osmotic pressure at the hydration's interface, crystallization pressure etc [4].

The Structuring

In a couple of ours interval since preparation, the cement paste is placed in the destined space in the well and remain unmoving. In the next 3 – 4 ours it is taking place what we call the structuring which needs as more time as bigger water – cement factor is.

The structuring is a complex physical-chemical phenomena through which appearing a putting-together of the free solid particles or weak bond particles, in the intimacy of the larger cadre of the hydration products and in them expansion, which produce the apparition and growing of the number of contacts between them.

During this process, in the mass of the paste is formed through the contacts between the solid products, a structure with an increasing mechanical consistency, structure which adheres also to the space's borders in which the paste is placed. In the beginning of the process this structure is weak, so it can be destroy by moving and it needs repaus to be restarts again. When 20-30 percents of cement mass is captured in these hydration products, slurry becomes stiffness [5,6].

If before the formation of this structure, the paste is exercising on the space's borders a pressure that is proportional with its density, so it is in a hydrostatic state, after the formation of these structures, the pressure on the same limits is exercised only by the free water- with a certain electrolyte concentration-which is in the paste's mass and which pressure, is of course much smaller than that exercised by the paste in the initial period of placement.

This modification of the value of the pressure exercised by the paste has major consequences in achieving the goal of the cementation operation/procedure.

The Hardening

In the next 2 – 3 hours, depending on the nature and proportion of the components and also of the environment's conditions, the paste is transformed in stone. This transformation takes place gradually, through continual increase of the volume of the solid products of the hydration reactions.

These ones has a proper and big porosity – nearly 0.3, formed by micropores with dimensions less than 2.5 nm. These products are forming and inside of unhydrated granules clogging up capillary pore system which has dimensions up to 10000 nm, and interrupting most of part the connections of this system [4].

The growing of this hydration products leads to the apparition of the more frequent interactions on the bigger and bigger surfaces. The resistance to compression is at the beginning much bigger that that at the traction, because it is a result of the frictions that takes place in the contact zones.

The contacts/interactions are taking place through films and menisci of liquids, but also solid-solid of the same or different mineralogical nature. Other forces that contribute to increase the stone's resistance are in ascendant order of size [5]:

-the van der Waals forces, which are manifested at the contact through liquids and are generated by the electrical charges of the anions from the solution;

-oxidrilic forces (hydrogen bridges);

-valence forces.

As the number of interaction increases, weight of these forces becomes bigger. The hydration, progressive structuring and the hardening as stages which are generated and induced successive, are presented schematically in No 1 figure, in which we have:

a)-the suspension period - the solid granules are isolated in the liquid phase, and the increase in the volume of the solids is complementary with a decrease of the total volume;

b)-the structuring period - the development of the hydrates around the anhydrous cement granules determines the successive apparition of the menisci between the granules;

c)-the hardening period - appears a progressive silting of the capillaries through the increase of the hydrating products, which have their own porosity [6]. Through the consumption of water the menisci radius is reduced, the capillary tension increases, the volume of the solid and liquid phase is reduced; the voids or gaseous phase appears in the pores [7].

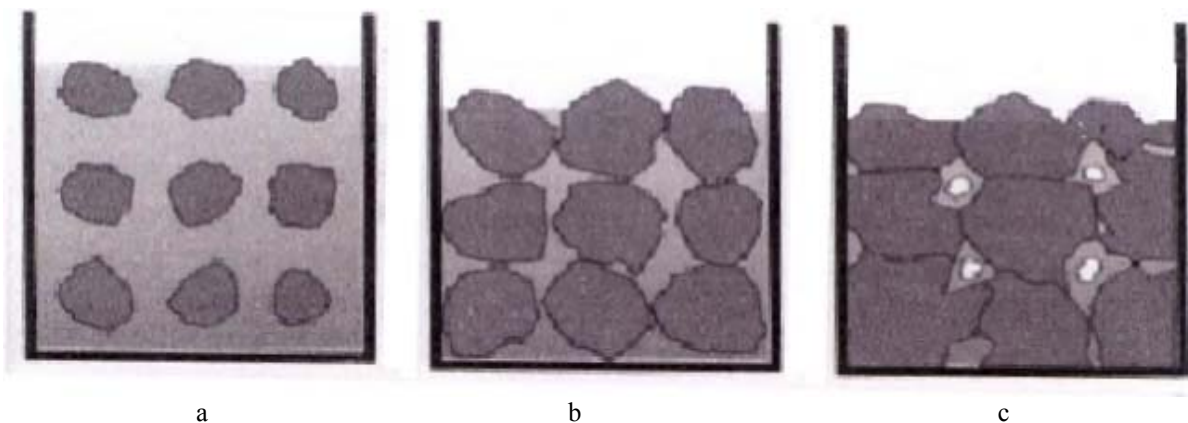


Fig. 1 – Cement hardening phases

Contraction

It is considered that during the hardening of the cement stone the volume reduction is manifested in 4 types:

- Dehydration contraction
- Thermal contraction
- Carbonatation contraction
- Chemical contraction

These 4 types of contraction which are manifested in the stone's matrix have very different kinetics, but are cumulative [9].

The weight of them is sustain by chemical contraction.

The causes of this contraction, are induced mainly by water 's action on the cement, which following the advanced hydration, dispersion and structuring of water at the surface contact, solution's passage mainly of the calcium and sulphate ions, favourites the production of chemical reactions, whose products have a smaller volume than of the compounds that enter in the reaction. This phenomenon is expressed in the relation:

$$V_h = V_c + V_a - DV \tag{1}$$

where:

- V_h** = the volume of the hydrated resulted products;
- V_c** = the volume of anhydrous cement;
- V_a** = the volume of used water;
- DV** = the volume difference.

To establish the volume reduction produced by the hydration chemical reactions Le Chatellier calculated the contractions of the chemical nature for the basic compounds of the cement. Therefore, the chemical contractions at the tricalcic silicate's hydration is described as:

	$2C_3S$	+	$6H_2O$	\longrightarrow	$C_3S_2H_3$	+	$3Ca(OH)_2$
Mass	456,6		108,1		342,5		222,3
Density	3,15		1		2,71		2,24
Volume	145,0		108,1		126,4		99,0
	253,1				225,6		

$$\text{The chemical contraction} = \frac{(253,1 - 225,6)}{253,1} \times 100 = 10,87\% \tag{2}$$

The total contraction of the cement paste in every moment of the reaction, was after that calculated through summing up of the calculation of each individual compound which reacted. Also the hydrating chemical reactions can lead to a dehydration of the paste, if there is not a source of water in contact with water, a fact that will provoke a retraction of the water from the bigger pores, a reduction of the capillaries' radius-so an increase of the capillary tension that could be followed by a reduction of the apparent volume or by the apparition of internal fissure.

This total volume diminution of the cement paste is no representative for the external apparent variation of the volume. The volume difference comes from the enlargement of big pores by internal contraction of the matrix followed by appearance of certain voids in the capillary pores that initially, were filled with water.

It is necessary to tell that there are two conditions of hydration of the cement in the well: a situation where the mixture is isolated, as it is in the first hours after paste's placement and a situation in which the material is in continual contact with the water from the well's wall. In the second situation, gaps' formation which could be determined by contraction is impeded due to the constant provision of water from outside towards capillary pores, which compensates the volume reduction due to hydration, even allows an increase of the volume of the cement paste.

This mechanism is limited in time because, once with the paste hydration, the permeability of this decreases and the acceptance of water from exterior is made more and more difficult [10].

We consider useful, for understanding of these aspects to start from the distinction made by Le Chatellier on the volume of the paste or of the cement stone. He considered that we deal with an *absolute volume* and an *apparent volume*.

Absolute volume is the volume of the solid matrix of the paste which hydrates or of the stone. The modifications of the absolute volume which are taking place during hydration as well as after the stone formed, following the hydration physic-chemical reactions which take place in the mass of the paste and of the stone.

Apparent volume is the volume occupied in a vessel by a paste or by the formed cement stone.

The modifications of the apparent volume are taking place generally up to formation of the stone and in a smaller proportion, in large periods of time, after the stone is formed.

In drilling activity we pay attention to this one. The weight of this volume changes are done in its reduction direction - are contractions and are named *autogenous contractions* - depending only by the reactions from the system. The term autogenic is meaning from a theoretical point of view, that the paste is isolated from the surrounding environment, so doesn't exchange substance or heat with this.

As the well is not a perfectly closed space from the heat and mass exchange point of view, we consider that the changes of autogenic volume take place on the basis of the changes induced by the exchanges with the surrounding environment, and we will refer here to the loss of the free water through filtration during paste's placement and in the first hours after that and to the heat loss after hardening. To sum up, the autogenous contraction is the result of the following causes:

- water loss through dehydration during and after paste's placement
- chemical reactions that took place before and during the hardening, whose solid compounds have a smaller volume than of the components entered in the reaction.
- pores' dehydration, provoked by the chemical reactions, that lead to reduction of the radius of the contact menisci, followed by a capillary decompression which increase the tensions of the internal traction, provoking the apparition of internal fissure and the apparent volume reduction (figure 2).

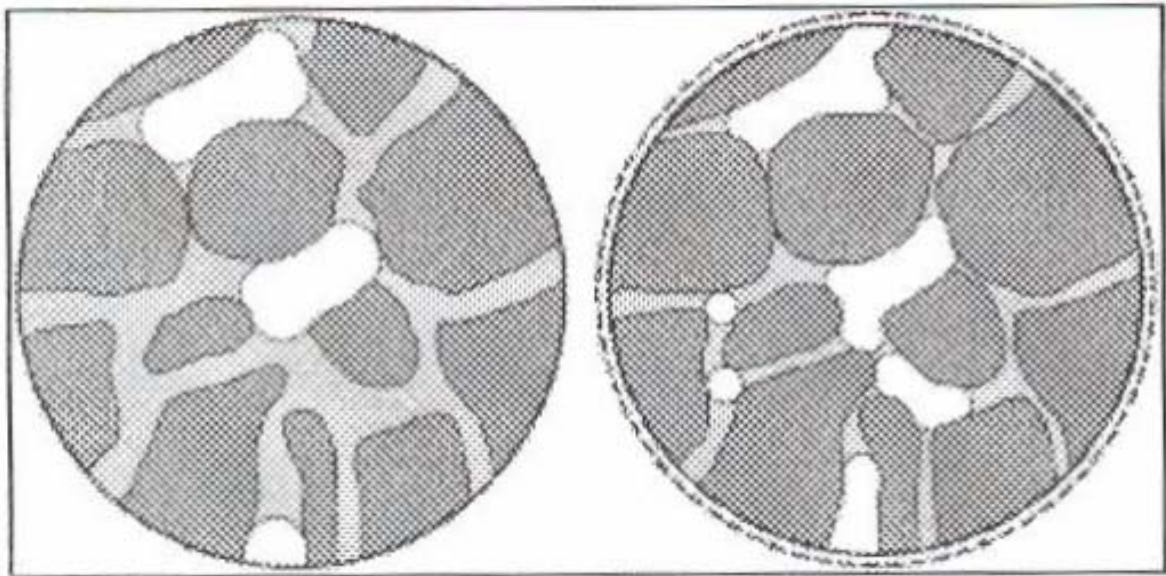


Fig. 2. The scheme of autogenous contraction [11]

In the figure are presented cement particles colored dark gray, intergranular and capillary water - light gray, and voids - white. In the right circle we can see the consuming of water from the big pores by hydration, and water from small capillaries is delimited by small radius of curvature menisci, which lead to decompression of water and autogenous shrinkage - dot line circle.

In oil and gas industry autogenous shrinkage is important, from technical point of view, because it can lead to the weakening risk of the adherence of the cement stone on the wall and the casing or the apparition of the fissures in the stone's mass, the sealing of the annular space could be compromised.

Factors which influences autogenous contraction. The autogenic contraction is influenced by the rapport water-cement, by the nature of the cement (mineralogical composition of the cement), by the presence of mineral addition and used additives. We will exemplify the influence of two of these factors.

The Influence of the Cement Nature on the Autogenous Contraction.

The cement nature influences the auto dehydration phenomenon both through the mineralogical composition and through its morphology [9]. The mineralogical composition of a cement and especially of its content of C3A and in a smaller proportion of C4AF, influences auto dehydration [11,12]. This fact is reflected by the graphics from the Figure 3 which refer to the cementations from the table 1.

Table 1 Mineralogical composition of two cements

Mineralogical composition	Cement 1	Cement 2
C ₃ S %	61.66	55.23
C ₂ S %	13.37	20.57
C ₃ A %	10.10	2.82
C ₄ AF %	5.74	11.85
CaSO ₄	5.81	5.76
CaCO ₃ %	4.02	0.68
CaO (free) %	0	0.6
Na ₂ O %	0.41	0.31
CO ₂ %	1.77	0.30

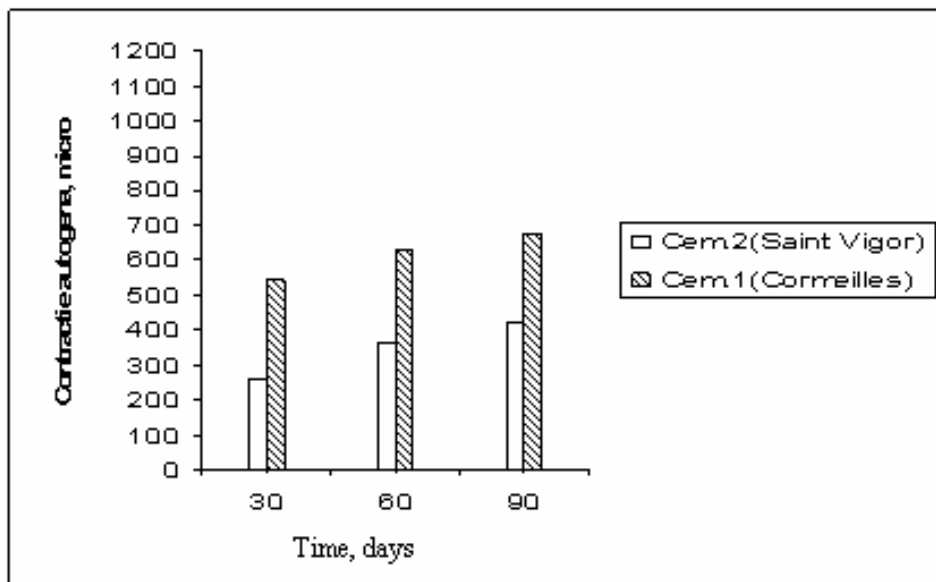


Fig. 3. The dependence of autogenous contraction on the cement type (table 1)

The Influence of the Mineral Adding Over the Autogenous Contraction

In the construction industry there were tried and used in the last decades minerals additions, which replaced the cement, in order to lower the cost, the impact over the environment and the improvement of the pastes properties, the increase of the resistance and the life of the formed stone.

This mineral additions are solid materials, fine milled, which has a chemical reaction with the hydrated cement, creating a modified microstructure of the paste. So we can distinguish materials with *puzzolanic* properties, materials with latency hydraulic property and mixtures.

a.- materials with *puzzolanic* properties, are those siliceous materials, that under the form of finely divided dust and in the presence of the water, reacts with the calcium hydroxide and forms cement components. The *puzzolanele* can be of natural or industrial origin. The natural ones are the *volcanic ashes* and the *diatomeic grounds*. As industrial ones we have the *flying ashes* – inorganic waste from the coal burnings, *silica fume (silicate residue)* – resulted from the gases formed in the making of the silicium

b.- *latent hydraulic* materials, react directly with the water and forms cement component. In this category we can find the *zgurile de furnal*.

Silica fume has the biggest influence over the autogenous contraction (fig. 4)[12]. This is explained by the fact that its presence in the cement matrix leads to the forming of a very fine anhydrous mixture. Decreasing the capillary pores (fig. 5) of the internal structure of the cast generates an internal balance which leads to a decrease of the relative humidity and an increase of the capillary tension. A second effect of the *puzzolanic* reaction – the replace of $\text{Ca}(\text{OH})_2$ with C-S-H – leads to an increase of the specific area of the cast consuming more water for absorption. As a result of the transformation appears a decrease of the free water volume disposable for the cement hydration.

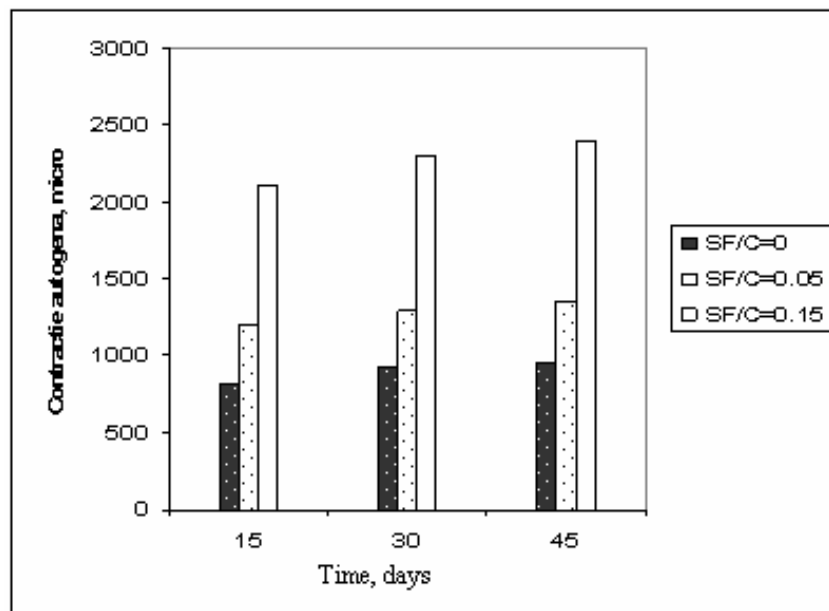


Fig.4. The relation between the content of the silicate residue in cement and the value of the autogenous contraction [12]

The flying ashes [15], decreases the total contraction due to the lack of CaO from the composition and to the fact that there're less reactive than the siliceous waste and the *chlincher* components [9]. The paste that contain *filer* or flying ashes have a bigger solid volume than the paste without the additions, the contact among the particles is bigger which leads to a lower contraction.

It's been showed that by replacing 7,5% of the cements weight with the hydrophobic ashes based on *silicates* lowers the contraction, the effect is due to the fact that the ashes increase the angle contact among the solid phase and the water from 47,5 to 115,3 degrees in 7 days and from 48,2 to 64,6 degrees in 28 days. The angle increase lowers the *menisci' curvature*, it even changes the direction, phenomenon that reduces the capillary tension and the contraction.

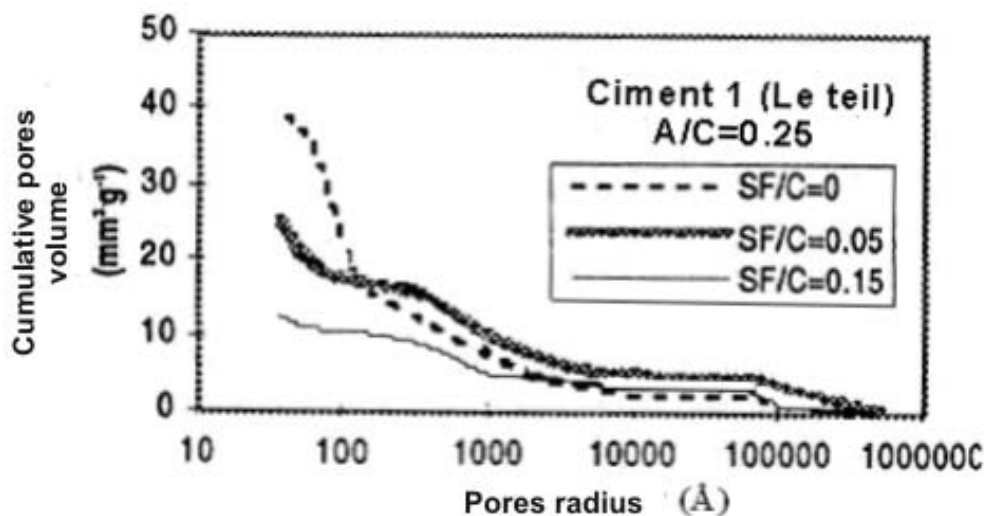


Fig.5. The relation between the content of the silicate residue in the cement and the diameter of the capillary pores in the cement stone [12]

Furnace slag leads to a bigger contraction, and this increases with the increase of the fine milled. The blend of the Portland cement with *Furnace slag* may determine a contraction increase of about 70% [12].

Conclusions

- Autogenous contraction phenomenon starts immediately after the placing of the paste, it continues after the stiffening of the rock but in a slower rhythm and it's influenced, in a big part, by the water properties of absorption or release from the wells wall.
- In the conditions from the oil wells, the continuing of the autogenous contraction in the stiffening period may lead to a decrease adhesion of the cement- flow string and cement-field.
- The autogenous contraction may cause the increase of the pores, sometimes by cracking the cement rock, and even forming a path for the gas flow.
- The autogenous contraction can be controlled by using additions at the cement paste preparation.

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Asupra fenomenologiei contracției autogene ce se manifestă în timpul și după întărirea pastelor folosite la cimentarea sondelor

Rezumat

Prin operația de cimentare a sondelor se urmărește etanșarea spațiului dintre coloana și peretele sondei în vederea rezolvării unor probleme tehnice și de mediu, în sensul că trebuie prevenită migrarea fluidelor de la adâncime în stratele mai puțin adânci sau la suprafață Pe parcursul transformării pastei de ciment

in piatră, se produc unele fenomene care pot avea ca rezultat nerealizarea etanșării spațiului inelar al sondei. Cunoașterea mai aprofundată a cauzelor acestor efecte nedorite, ne va permite găsirea celor mai potrivite soluții, ca rețete și/sau proceduri de cimentare.