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Can Antique Mortars Be Good Oil Well Cements

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Abstract

The model for the composition and preparation of the Roman cements has proven its efficiency over the centuries. The reliability of mortars prepared on this basis, used in building some constructions in salt sea water (the harbours on the Mediterranean) or in sweet water (Traian's bridge over the Danube) has made us think that similar recipes may be successfully used in cementing oil wells.
The special qualities of these binders used in Antiquity are due to the presence in their composition of certain products of Pozzolanic type. Through this study we have attempted to identify the chemical and structural properties of the modern Pozzolanic materials, as well as the manner and proportions in which they can be used to improve the characteristics of the oil well cements.

Key words: *puzzolana, slag, metakaolin, silica fume, fly ashes, compressive strength, permeability*

Introduction

The Roman architect and engineer Pollio Virtuvius, in his famous work „De Architectura", described in the 1st century B.C. "a powder that through its nature produces wonderful results. It is found nearby the place named Baiae (next to the town Puzzoli)… and when it is mixed with lime (calx) and chippings (caementum), not only does it give strength to other brickwork, but when the pillars are built in the sea, they harden under the water"(V II.6.1). The Romans named this material pulvis puteolanis (powder from Puteoli, the Latin name for Puzzoli). In its turn, the name of this material has created the name of pozzolan, having a wide application to all the mixtures conferring hydraulic properties upon binders.[1]

Vitruvius' books have facilitated the understanding of the fact that the special properties of the Roman concrete came from the use of some artificial pozzolan - a baked kaolinic clay named in Latin testa and a baked volcanic stone named carbunculus, as well as a natural puzzolan of volcanic origin named harena fossicia. The ingredients testa, carbunculus and harena fossicia were used in the terrestrial Roman constructions, whereas pulvis Puteoli was used to make pillars in the sea and for the foundations of the bridges.[1]

The strength in time and the quality of Roman mortars prepared on this basis, used in building some constructions in salt sea water (the harbours on the Mediterranean) or in sweet water (Traian's bridge over the Danube) has made us think that similar recipes may be successfully used in cementing oil wells.

Through this study we have attempted to identify the chemical and structural properties of the modern Pozzolanic materials, as well as the manner and proportions in which they can be used to improve the characteristics of the oil well cements.

Pozzolanic Materials and Their Properties

The Pozzolanic materials are "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementing property, but will in a finely divided form - and in the presence of moisture - chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" [2].

This slow reaction between a pozzolanic material and calcium hydroxide (lime) leading to the formation of some hydrate calcium silicates and some hydrate calcium aluminates has been named pozzolanic reaction:

$$CH + pozzolan + H \longrightarrow C\text{-}S\text{-}H + C\text{-}A\text{-}H \quad (1)$$

Table 1. Reactivity of Pozzolanic Materials (Chappelle Test) [3]

Material	Pozzolanic Reactivity mg $Ca(OH)_2$ per g
Blast furnace slag	40
Calcined paper waste	300
Microsilica, fume silica	427
Calcined bauxite	534
Pulverised fuel ash	875
High Reactivity Metakaolin	1050

As the pozzolan are low in calcium oxide, this component must be added in a stoechiometric proportion [4]. CH may be added either as hydrated lime, or, like in the case of cements with mixture, it may come from the calcium hydroxide formed during hydration. The process of lime consumption, followed by the precipitation of minerals in the hydrated cement, with a lower density, is very efficient in filling the space of the capillary pores of the matrix thus formed and leads to increasing the strength, the impermeability, the durability and the chemical strength of cements with pozzolanic mixtures [5].

The Pozzolanic materials have been classified into two main groups – natural products and artificial products, the latter being, in general, secondary industrial products (waste). [8]

Researchers from NewChem-Switzerland have analysed the effect of high-reactivity metakaolin (MHR) on the consumption of calcium hydroxide, during the hardening of certain pastes made of mixtures in which the Portland cement has been replaced with 10%, respectively 20% baked clay. The results are presented in Figure 1. [3].

Takeshi Yamamoto [6] has made detailed studies on the pozzolanic reaction to the hardening of cement with mixture by fly ash. He has shown that there are 2 layers of pozzolanic reaction phases surrounding the fly ash particles. They grow in time, filling a micropore (capillary porosity) of a few tens or hundreds of nanometres, generated after mixing the cement. The decrease of the distance between the hydrates, resulting from this process, improves the attraction force, leading to the hardening of the cement

Yet in the analysis of mixtures, one must make a difference between the Pozzolanic materials and the latent hydraulic materials. The latter comprise an important amount of calcium, laying at the basis of the development of their self-cementing properties, after an alkaline activation. The granulated furnace slags are a typical example of hydraulic latent material. [7].

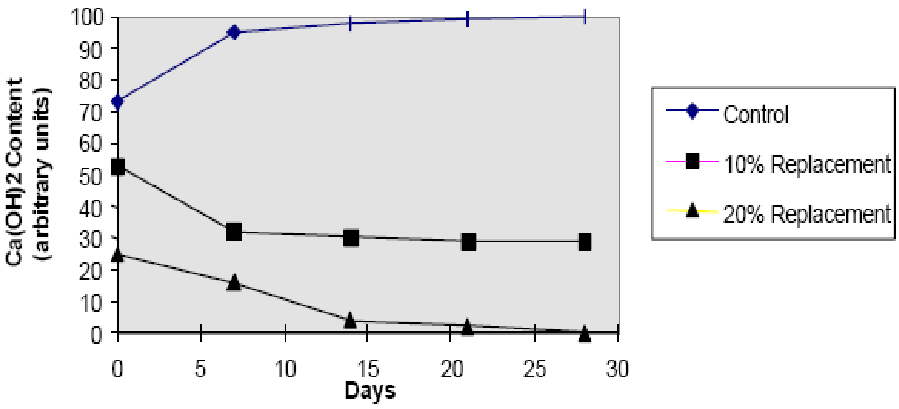

Fig.1. Effect of metakaolin on the Ca(OH) content during the hardening of cement [3]

Table 2. Classification of pozzolanic materials [9], [10].

Nature of Material	Pozzolanic material	Active components
natural	Volcanic tufa	Vitreous aluminosilicates, zeolites, clayey minerals
natural	Rocks of meteoric impact	Vitreous aluminosilicates, zeolites, clayey minerals
natural	Diatomeic soils	Remainders of skeletons finely granulated by diatomee
natural	Bauxite	Aluminium hydroxides
artificial	Baked clays up to the melting point	Unstable products of dehydroxylation of clayey minerals
artificial	Fly ash with low contents of calcium	Vitreous compounds, baked silicates
artificial	Condensed silica fume	Vitreous silica
artificial	Rice straw ashes	Vitreous silica

From the point of view of researching the properties of cements with mixture of pozzolanic materials, this classification is not very useful, because all the products described above give similar products at the hydration of the mixture with cement. Yet it is necessary to underline the difference existing with respect to the main reaction of formation of C-S-H, in the case of

Portland cement and in the case of mixing the Portland cement with pozzolanic material, in order to understand why differences occur in the behaviour of the pasta achieved with each of them. [11]

$$C_3S + H \xrightarrow[quickly]{} C\text{-}S\text{-}H + CH \quad (2)$$

Formation of C-S-H by hydrating Portland cement

$$Pozzolan + CH + H \xrightarrow[slow]{} C\text{-}S\text{-}H \quad (3)$$

Formation of C-S-H of the mixture of Portland cement + pozzolanic material

Cements with Mixture of Pozzolanic Materials

Portland Cements with Mixture of Volcanic Ashes or Fire Clays (Pozzolan)

The baking of clayey minerals at high temperatures, comprised between 250^0C - 800^0C, produces the loss of the hydroxylic water from the structure of the crystal (dehydroxylation), the reaction going together with a structural reorganization of the material. The further growth of the temperature determines the destruction of the crystalline structure and the formation of some metastable phases of transition which show special pozzolanic reactivity both due to their great area and to their amorphous nature. [2],[10] A typical representative of this metastable phase, successfully used during the last years in the cements industry, is the *metakaolin* [7].
The dehydroxylation of kaolin and the formation of metakaolin can be expressed through the following equation:

$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_5(OH)_x\, O_{2-x} + (2-x/2)H_2O \qquad (4)$$

Metakaolin typically has an average particle size of about 1.5 μm in diameter, which is between silica fume (0.1 to 0.12 μm) and Portland cement (15 to 20 μm). [12]
The cements with mixture of puzzolans used worldwide have a variable content of 15-40% baked clay in weight, out of the total mass of the mixture.

Portland Cements with Mixture of Fly Ashes

Thermal power plant ashes (fly ashes) are residues coming from the burning of coals and bass. In the burning rooms, the sterile, very finely grinded, undergoes a baking process and, driven by the burning gas (wherefrom the name of „fly ashes" comes) is retained on the special construction filters or in the water screens. The main chemical compounds the ashes contain are SiO_2 (40-50%), Al_2O_3(20-37%), Fe_2O_3 (8-15%), CaO (3-13%), but next to them there are also other substances, in small amounts, not burnt carboniferous or bituminous materials, alkalis up to 1,5% and SO_3 up to 5%.

During the last years, out of economic and environmental considerations, the use of fly ashes as substitute has been stimulated. Starting with 1985, the term of cement with „a high volume of fly ashes" (HVFA) has been introduced, as proposed by V.M.Malhotra at CANMET (Canadian Centre for Mineral and Energy Technology) [13]. These cements require a low volume of water and at least 50% of the Portland cement in the mass is replaced by fly ashes. They have a low hydration heat, an adequate initial hardening and a very good final hardening, a low dry contraction and an excellent durability. [14]

A team of researchers in Serbia and Montenegro, led by Ljubica Ćojbašić, has studied the influence of the composition of fly ashes (FA) on the hydration mechanism of the mixture of

Portland cement (PC) with fly ashes having low content of CaO (FAL). They have chosen this type of material because it has clear pozzolanic properties, unlike the ashes with high contents of CaO that simultaneously develop both pozzolanic properties and their own binding characteristics.[15]

The hydration process of the mixture can be divided into several stages of development:

$$2SiO_2 + 3Ca(OH)_2 = 2CaO.\ 2SiO_2.\ 3H_2O(C_3S_2H_3) \quad (5)$$

$$Al_2O_3 + CaSO_4.2H_2O + 3Ca(OH)_2 + 7H_2O = 4CaO.\ Al_2O_3.SO_3.12\ H_2O(C_4A\hat{S}H_{12}) \quad (6)$$

$$Al_2O_3 + 4Ca(OH)_2 + 9H_2O = 4CaO.\ Al_2O_3.13\ H_2O\ (C_4AH_{13}) \quad (7)$$

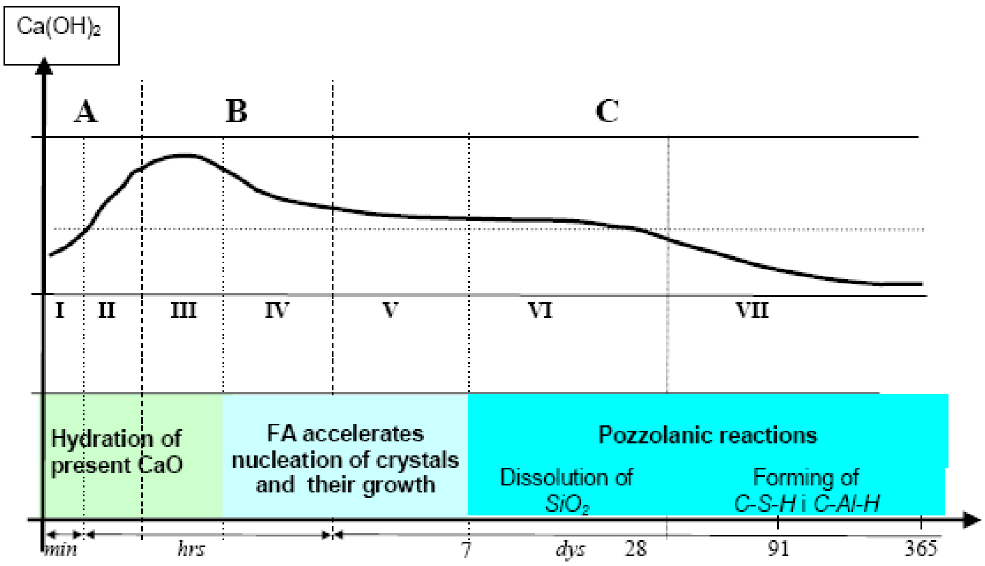

Fig.2. Stages of hydrating cement mixture with fly ashes with a low content of CaO [15].

A. Early stage
1) Preinduction – hydration of Portland cement and creation of C-S-H, C-A-H and CH products.
2) Induction – rest period

B. Medium stage
3) Acceleration phase
4) Formation phase of the crystallisation germs

C. Late stage
5) Growth of crystals
6) Dissolution of amorphous SiO_2
7) Pozzolanic reactions

Due to the growth of the concentration of ions $(OH)^-$, as a consequence of the occurrence of $Ca(OH)_2$, the environment becomes more and more alkaline. Fly ashes activated in this early stage have a neglectable extension and behave like an inert material, accelerating the hardening of the grout, acting like some sedimentation nucleus of C-S-H and C-A-H, as well as of $Ca(OH)_2$ created after the cement hydration.

At the early stage, as expected, there are no traces of pozzolanic reactions. At the formation stage of the crystallisation germs, the final structure of the grout is formed. At the late stage, the grout is solidified, and the pH value, affecting the dissolution of the amorphous SiO_2 molecules, grows in the pores of the grout. During the growth of the pH value, also grows the dissolution of the amorphous phase.[16] After 28 days the particles of ashes are crossed and surrounded by hydration products, but still keep their spherical stage. When the pozzolanic reactions start developing, the particles of ashes lose their spherical form and start being covered with a layer of product. After a period of 6 months they maintain the same aspect.

The technical importance of cements with mixture of pozzolanic materials (as well as that of the slag cements) mainly derives from the 3 main particularities of the pozzolanic reaction.

- The reaction is slow, therefore the speed of heat release and the hardening development shall be slower.
- The reaction consumes calcium hydroxide product for the entire duration of the hydration reaction, which has an important impact on the strength to the aggression in acid environment of the grout.
- The reaction products efficiently fill the large capillary spaces, thus increasing the compressive strength and the impermeability of the system.

Researches on the Effect of the Mixtures of Pozzolanic Materials on the Physico-Chemical Properties of the Pastes

The Hydration Heat

Due to the fact that the pozzolanic reactions are slow, the partial replacement of the Portland cement with pozzolanic materials results in a slower release of heat, for a longer period in time. Thus, the temperature of the cement stone remains lower, because the heat is dissipated while it is produced.[17] It has been estimated for instance that the participation of the fly ashes in generating the heat, at the initial stage, is only 15-30% from the one of an equivalent mass of Portland cement [18].

The Evolution of Hardening

P.K. Mehta and P.J.M. Monteiro [11] have made a comparative study on the behaviour at hardening of the cements with mixture of slags or pozzolans and the properties of the Portland cement. They have noticed that in the first days the pozzolanic cements harden slower than the ones with furnace slag. The mixtures of Portland cement -slags show a significant strength after 7 days, and the mixtures of Portland cement –pozzolans have a special strength in the period between 7-28 days. When they are used in moderate proportions (for instance 15-30% pozzolans or 25-50% furnace slags) and the humidity is assured for a long period, the final strengths of the Portland cement –slag and Portland cement –pozzolans mixtures are greater than the strengths of the Portland cements used for composition, prepared separately.

Compressive Strength

The Chinese researchers Ding J.T. and Li Z.J [19] have studied a series of concrete samples where they replaced the cement with 5%, 10% and 15% metakaolin or silica fume and noticed that both mixtures lead to an effective growth of the compressive strength after 14 days. The mixture of metakaolin produces an almost linear growth of the strength during the first 28 days of hardening, then the rhythm slows down, so that up to 65 days the measured value was only 6-8% greater than the one found at 28 days.

At 365 days, according to other researches [20] the samples prepared, using a W/C ratio of 0.40, with mixture of 5% metakaolin, have shown the greatest values of strength (11,35 ksi), followed by the samples with 10% metakaolin, 10% silica fume and 5% silica fume (9,21 ksi), and the control samples, made only out of cement, had lower values at all analysed ages. Investigations have been made also on some samples made with 10% metakaolin and simple Portland cement or Portland cement mixed with ultrafine slag [21] and it has been noticed that the latter have shown the greatest strength at 28 days.

Similar results have been reported by Wild S. and his team too [22], who tested the strength of some concretes prepared with various proportions of metakaolin, using a W/C ratio of 0.45, within the interval 1 day – 90 days. The results are presented in Table 3.

It is noticed that, in the first day, the pastes where the cement was replaced with metakaolin in proportion of 5%-20% have compressive strength values similar to the simple cement. The values recorded from the 7th hardening day on, are higher in all mixtures of cement with metakaolin 5%-30%, as compared to the control sample made only out of cement.

Table 3. Compressive strength of concretes with metakaolin mixture [22]

MK (%)	Density (kg/m^3)	Compressive strength (N/mm^2)				
		1 day	7 days	14 days	28 days	90 days
0	2490	19.07	50.23	57.10	62.60	72.43
5	2440	21.50	53.80	58.97	63.50	71.63
10	2460	22.43	62.30	69.23	71.00	80.07
15	2470	20.23	64.80	74.67	76.00	83.70
20	2480	19.33	66.47	75.73	82.47	85.13
25	2470	15.73	62.50	69.77	73.93	82.23
30	2480	14.53	60.53	72.33	76.73	81.80

Strength in an Aggressive Environment

The research made during the last years has shown that the mixtures of Portland cement –slag and Portland cement –pozzolans have greater strength in acid environments. This behaviour is due to the combined effect of a higher impermeability, in a water/cement ratio and a given hydration degree, as well as the reduction of the calcium hydroxide content in the grout. [11]

The tests made have shown that in a 1-year old grout having a content of 30% in weight of Santorini volcanic ash (Greece), the penetration depth of the water was reduced with almost 50%, as compared to one of Portland cement under similar conditions. Likewise, as compared to the 20% value of calcium hydroxide, present in a 1-year old grout made out of the reference Portland cement, only an amount of 8,4% calcium hydroxide has been found in a grout, similarly hydrated, containing 30% in weight of volcanic ash.

The Portland cements-slag have behaved the same way. In a content of approx. 60% slag, the amount of calcium hydroxide becomes so low that, even in the slags having a high content of reactive alumina, they may be used to make sulphate-resistant cements.

Some slags and fly ashes rich in alumina tend to increase in the grout the amounts of C-A-H and monosulphate products, which are vulnerable to the sulphatic attack. But, as long as great amounts of calcium hydroxide are necessary in the system in order to form the *expansive ettrigite*, the laboratory tests and the experience in the field have shown that the mixtures Portland cement-slag, containing 60-70% slag, are very resistant to the sulphatic attack, irrespective of the content of C_3A in the Portland cement and the content of reactive alumina in the mixture.

Gas Permeability

A series of research made in 2006 at the Teheran University have analysed the effect of high reactivity metakaolin (HRM) on the gas (oxygen) permeability and other physico-chemical properties of high-performance concretes (HPC). [23]

In these experiments metakaolin and Portland cement have been used from 2 classes of compressive strength (70-90 MPa and 50-60 MPa), aggregates with maximum dimension of 25mm and a superplastifier based on polycarboxylate. The W/C ratio for the first class was constant of 0,26, and for the second class the ratio was 0,38. The percentage of cement replaced with metakaolin was 5%, 10% and 15%. The superplastifier dosage was comprised between 1,2-1,6% of the cement weight for the first class and between 0,8-1,2% for the second class.

Table 4. Compressive strength and gas permeability coefficient ($x10^{-16}$) after 28 days [23].

The class of cement used	The sample code	Compressive strength (MPa)	Gas permeability ($x10^{-16}$)m^2
1st class cement	C10	73,7	0,21
	M11 (MK5%)	80,6	0,19
	M12 (MK 10%)	83,7	0,088
	M13 (MK 15%)	88,4	0,063
2nd class cement	C20	50,0	1,2
	M21 (MK 5%)	53,6	1,1
	M22 (MK 10%)	55,0	0,94
	M23 (MK 15%)	59,8	0,75

The research made has shown that:

a. The partial replacement of the cement with metakaolin increases the compressive strength of the cement stone, after 28 days, and reduces its gas permeability.

b. The permeability coefficient of the hardened cements, resulted from the mixtures of Portland cement -metakaolin, is comprised between $6.3x10^{-18} – 1.1x10^{-13}$ m^2. These values range in the middle of the generally expected domain of values for a structural cement.

c. The replacement with metakaolin of 15% of the cement content is the most adequate value to simultaneously ensure a low permeability and a high compressive strength. Using this proportion of 15% metakaolin, the gas permeability of the cement stone decreases almost by 70%. [23]

The results of the researches made so far, briefly presented in this study, entitle us to believe that, through the optimal combination of the cements with pozzolanic materials, based on laboratory tests, improved compositions may be achieved for oil well cementation, which may contribute in the future to the optimization of this operation.

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Pot fi mortarele antice bune cimenturi de sondă

Rezumat

Modelul de compunere şi de preparare a cimenturilor romane şi-a dovedit eficienţa peste secole. Fiabilitatea mortarelor preparate pe această bază, utilizate la realizarea unor construcţii în apă sărată de mare (porturile de la Marea Mediterană) sau în apă dulce (Podul lui Traian de la Dunăre) ne-a făcut să ne gândim că reţete asemănătoare pot fi folosite cu succes şi la cimentarea sondelor.
Calităţile deosebite ale acestor lianţi folosiţi în antichitate se datorează prezenţei în compoziţia lor a unor produşi de tip puzzolanic. Prin acest studiul am căutat să identificăm proprietăţile chimice şi structurale ale materialelor puzzolanice moderne, precum şi modul şi proporţiile în care ele pot fi folosite pentru a îmbunătăţi caracteristicile cimenturilor de sondă.