

A review of the main mineral additions applied to the oil well cementing.

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ABSTRACT: Primary cementing is one of the most important operations performed in a oil well. The cement must support and protect the casing and provide adequate zonal isolation. These requirements make the primary cementing essential for ensuring safety and high productivity throughout the life of the well. Recent researches have focused on the use of several mineral additions in cement slurries for oil wells, in order to improve the properties of the slurries and promote more effective cementing job. The use of mineral additives in cement slurries for wells also results in environmental gains, since most of these materials are industrial or agroindustrial wastes which are often inappropriately disposed in the environment. The studies found in the literature indicate that the main properties increased with the use of mineral additions are the compressive strength, corrosion resistance, durability, rheological properties, porosity, permeability and free water of the slurries. In this context, the present paper aims to review the literature, collecting information about the main materials that have been used in the oil well cementing. This study also highlights the most benefited properties of the slurries through the use of additions, and the form of action of these materials in the cement slurry.

KEYWORDS: Mineral additions; primary cementing; oil well.

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I. INTRODUCTION

The first oil well was drilled in 1859 in Pennsylvania, and had a depth of only 21 meters. With the advancement of technologies and the growing search for oil, the number of wells and their depths have grown exponentially [1].

In 1903 the first well was cemented, located at the Lompoc Oil Field, California. The cementation was performed with the objective of avoiding the inflow of water from the formation to the well [2]. Currently the cementing operation is considered one of the most critical operations performed in the well. Inadequate cementation can lead to a reduction in well production potential, undesirable fluid production, and loss of reservoir control, causing environmental problems and even loss of the well in more extreme cases. [3-5].

The drilling of an oil well is done in several phases. After drilling of each phase, the casing is run into the well, and the cement is placed in the annulus between the casing and the formation surface. The cement must support and protect the casing and prevent the migration of fluids between the various permeable zones located behind the casing [1, 6].

The increasing use of cement in the oil industry has led to the search for alternatives to reduce costs in well cementing operations and increase the slurries performance. Researches in recent years have focused on the study of the properties of cement slurries for wells with different materials, evaluating how these materials influence the properties of the slurries in the fresh state and after hardening.

These materials, called mineral additions, were evaluated as partial replacement of Portland cement or as an addition in oil well cement slurries. Among the most studied materials are metakaolin [7], nanosilica [8-11], rice husk ash [12,13] and sugarcane biomass waste [14,15].

Mineral additions act on the cement matrix through chemical reactions or through physical effects, depending on the nature of the material used. The studies found in the literature indicate that the use of mineral additions led to improvements in properties such as compressive strength, resistance to acid attacks, durability and impermeability of the slurries.

The use of these additions besides promoting technological and economic benefits can also contribute to the reduction of environmental impact, since most of the mineral additions studied in cement materials are industrial and agroindustrial wastes. In the case of additions used as partial replacement of the cement, the environmental benefits are even greater due to the reduction of the cement use. It is estimated that is generated more than 800 kg of CO₂/tonne of clinker during the cement production [16], therefore, the reduction in the use of this material has a very positive environmental impact.

The increased performance of cementitious materials, coupled with sustainable development, makes the use of mineral additions an excellent alternative. In this context, the objective of this review is to gather and present the most recent researches on the study of mineral additions used as additives or cement replacers for oil well cementing operations, relating the main materials used and the improved properties through the use of each of them.

II. MINERAL ADDITIONS

The mineral additions are mainly composed of finely milled silicate or aluminosilicate minerals. These materials are used in concrete, mortar or cement slurries as a way of increasing their properties [13]. The mineral additions can be ground together with the clinker and gypsum in the cement manufacturing process or mixed with the Portland cement at the time of its use [17]. According to Alves [18], the mineral additions can be classified into three groups, according to their physicochemical action:

- Pozzolan material;
- Cementitious material;
- Filler.

The pozzolan material is defined according to NBR 12.653 [19] as a silicious or siliceous and aluminous material which possess by themselves little or no cementitious properties, but in the presence of moisture and in finely divided form it is able to react with calcium hydroxide to form compounds with cementitious properties. During this process the pozzolan reacts with the calcium hydroxide produced by the hydration of the Portland cement, giving rise to calcium silicate hydrates. This reaction can be described by Equation 1 [20].



As calcium hydroxide contributes little to the cement slurries resistance and among the hydration products it is the first to be leached and solubilized by water [21], its consumption with C-S-H generation provides a chemical and mechanically stronger structure. In addition, the products generated by the pozzolan reaction act by filling the pores in the hydrated cement, thus reducing its permeability, with consequent increase of its durability [20].

The cementitious materials are those that do not require calcium hydroxide to form products with cementitious properties, but their hydration is usually slow, and the amount of cementitious products formed is insufficient for these materials to be used alone for structural purposes. However, when used as partial replacement of Portland cement or as an addition in the cement slurry, the presence of gypsum and calcium hydroxide accelerates its hydration, making its use possible [18]. The blast furnace slag is an example of cementitious material [20].

The fillers are finely ground materials with particle diameter close to the cement, which contribute to the improvement of the cement matrix due to its physical effect, without chemical activity [21,22]. According to Petrucci [23], the particles of the fillers have dimensions between 5 μm and 75 μm. The particles of the additions act by filling the pores left by the hydration products or by the non-hydration of the cement. This effect is called the filler effect and has as a consequence the pore size refinement, with consequent reduction of permeability [24, 25].

III. MINERAL ADDITIONS USED IN OIL WELL CEMENTING

A large part of the recent research in the area of well cementing has evaluated the use of mineral additions in cement slurries applied to wells. These studies sought to improve the properties of the slurries in the fresh state and after hardened, through the use of the additions.

In addition to the benefits observed in slurries properties, the use of the additions can also bring economic and environmental benefits. The economic benefits are associated with the reduction in raw material costs due to the reduction in the use of cement. And the environmental benefits are due to the application of wastes in the cement matrix, avoiding their inappropriate disposal.

Among the mineral additions that have been studied for oil well cementing are: nanosilica, sugarcane biomass, rice husk ash and metakaolin. All these materials are rich in silica, which allows them to act as pozzolans in the cement matrix, improving properties such as compressive strength, porosity, impermeability and durability of the slurries.

Choolaei et al. [8] presented a study on the effect of nanosilica on the physical and rheological properties of oil well cement. The experimental results showed that the nanosilica improved cement properties, producing an increase in compressive strengths (from 3217 kPa to 26808.39 kPa in the slurries cured for 24 h at 87.7 °C) and a reduction in the porosities and permeabilities of the samples. The increase in the development of compressive strength of the slurries was attributed to the pozzolanic reactions between the nanosilica and the cement. Nanosilica is considered more effective in pozzolanic reactions than other types of silica due to the fact that the rate of pozzolanic reaction is proportional to the surface area of the material. In addition, the nanosilica particles fill the pores between the particles of the C-S-H gel, producing smaller pores (filler effect). In the rheological properties, all the slurries containing nanosilica presented a thixotropic behavior.

Quercia et al. [9] presented results observed from the use of a nanosilica obtained by the dissolution of olivine, called Olivine nanosilica (OnS). It was observed a improvement of 16% and 119% in the compressive strength, after 12 hours of cure, in the slurries with addition of 0.5% and 5.0% OnS, respectively, compared to the reference slurry (without addition). The acceleration of the compressive strength development allows drilling operation to resume quickly, reducing the wait for the cement to harden and, in consequence, reducing operational cost. The addition of 0.5% of OnS also led to improvement in the rheological properties of the slurries, with reduction of the plastic viscosity (from 33 cP to 29 cP) and the yield point (from 0.88 Pa to 0.76 Pa), compared to the reference Class G slurry. At higher concentrations, the nanosilica increased the rheological properties and the gelling capacity of the slurries.

El-Gamal et al. [10] and Li et al. [11] investigated the effects of different curing temperatures on the properties and hydration of slurries admixed with nanosilica. El-Gamal et al. [10] used a nanosilica obtained from the rice husk at concentrations of 1% and 2% by weight of cement (BWOC). The compressive strength tests were performed at room temperature and at 90 °C. It was observed that the compressive strength values were higher for the samples cured at 90 °C when compared to those cured at room temperature, it can be attributed to a higher hydration degree and a subsequent more condensed structure caused by the high temperature.

Li et al. [11] studied the effect of nanosilica on the mechanical properties of oil well cement slurries at low temperature (8 °C). The slurries were formulated with additions of nanosilica from 0% to 2.5% BWOC (ranging from 0.5% to 2.5%). The study showed that the initial compression strength of the cement slurries was significantly increased with the addition of nanosilica, also indicating that the nanosilica can be applied as an accelerator when used in cement slurries subjected to low temperatures.

According to El-Gamal et al. [10] the optimal dosage of nanosilica was 1% at both curing temperatures, because at higher dosages (2%) the nanosilica agglomeration occurred, leading to a drop in resistance. For Li et al. [11] the optimal dosage of nanosilica was 1.5%, obtaining with it an increase in the compressive strength of 46% for the cement cured for 7 days, in addition to a reduction of 4.77% in the porosity of the samples, when compared with the reference slurry (without addition of nanosilica). Another benefit observed by the author was the reduction in free water content as the dosage of nanosilica was increased. According to Choolaei et al. the addition of mineral particles with high surface area to the cement mixtures has a direct effect on the amount of water required in the mixture. In these cases, the formulation needs to be adjusted to avoid excessive self-desiccation and microcracks.

The use of biomass ash as a partial replacement of cement has been studied by several researchers, with the aim of promoting sustainable development. These materials are agroindustrial wastes and, if discarded inappropriately, can generate environmental problems. The two most studied sources of biomass are the sugarcane biomass and the rice husk ash. Anjos et al. [14] evaluated the hydration of the cement slurries for oil wells containing sugarcane biomass waste (SBW) from 10% to 40% BWOC. Silica flour (SF), a material commonly used to partially replace the cement in operations above 110 °C, was chosen as control material (40% BWOC). The slurries containing 10% and 20% of sugarcane biomass presented higher compressive strength after 28 days, reaching 35.9 and 38.2 MPa, respectively, while the resistance reached by the slurry without addition (reference slurry) was 32.5 MPa. The increased compressive strength of the slurries containing sugarcane biomass is associated with the reduction of the Ca(OH)₂ content in the cement matrix, in addition to a decrease in the porosity of the slurries with the residue, due to the filler effect caused by the unreacted residue. This demonstrates the applicability of the waste material in the formulation of well cement slurries. The pozzolanic activity of the sugarcane biomass waste (SBW) was confirmed by thermal analysis (TG/DTG) of cement slurries containing SBW.

Santos [15] also demonstrated that sugarcane bagasse ash acts by avoiding the cement strength retrogression when subjected to high temperatures - above 110 °C. The compressive strength retrogression of

the slurries is the process in which C-S-H is converted to the α -C₂SH phase, with high Ca/Si ratio, which has characteristics of low mechanical strength and high permeability. The residue acts avoiding the strength retrogression due to the high concentration of silica present in the material. With the use of the residue, the CaO/SiO₂ ratio is significantly reduced, being close to 1, thus maintaining the C-S-H phase. The slurries containing 40% (BWOC) of sugarcane biomass reached values of compressive strength above 17 MPa. This study demonstrated the applicability of sugarcane biomass ash in HPHT (high pressure and high temperature) wells, such as those subjected to steam injection.

Other similar results were obtained with the use of rice husk ash. Soares et al. [12] studied the use of rice husk ash as pozzolan in addition to cement Portland for oil well cementing. The material was obtained from two different processes: by calcining (RHA) and by washing with hot water (WRHA). The slurries were formulated with additions of 10% and 20% of RHA and WRHA and were cured for 28 days at 58 °C. The washing pretreatment with hot water (WRHA) helped to obtain a more reactive and pure material than the calcining process (RHA). The pozzolanic activity of RHA and WRHA in cement slurry was confirmed by thermal analysis (TGA/DTG), XRD and compressive strength. The slurry with addition of 20% of WRHA showed the best results with a reduction of approximately 73% in the Portlandite phase (calcium hydroxide) at TGA/DTG analysis and a increase of 63.69% in the compressive strength (from 16.69MPa to 27.32 MPa) compared to the standard slurry (water and cement).

Santiago [13] showed that the rice husk ash also acts by avoiding the cement slurries strength retrogression when subjected to high temperatures, if used in concentrations of 30% BWOC. The slurry with addition of 30% of rice husk ash achieved a resistance equivalent to that obtained for the slurry containing 40% of silica flour. The slurries with addition of rice husk ash were prepared with dispersants to ensure better homogenization.

Metakaolin (MK) is among the most studied materials for use as a partial replacement of the cement. Bu et al. [7] studied the properties of cement slurries with high dosage of metakaolin. The metakaolin was used in the slurries as a partial replacement of the cement, with concentrations from 30% to 60% by weight of cement. In general, at 75 °C, the compressive strength decreased with the increase in the level of metakaolin content. At temperatures above 150 °C, the cement slurries with 40%-60% of metakaolin presented good compressive strength at both early age and long-term curing. In addition, the slurries formulated with metakaolin had a higher corrosion resistance and shorter thickening time when compared to the reference slurry (water and cement only).

Santos [15] also evaluated the compressive strength retrogression of the slurries containing metakaolin under high temperatures in a steam injection simulation. The slurries were cured at 280 °C for 3 days, after initial cure for 28 days at 38 °C. The loss of compressive strength for the slurries with addition of 40% of metakaolin was lower than that observed in the slurries with addition of 40% of silica flour. Silica flour is the material commonly used as anti-retrogression additive by the petroleum industry. This proves the potential of the use of metakaolin as an anti-retrogressive additive in cement slurries subjected to high temperatures.

El-Gamal et al. [10] evaluated the effects generated by the use of nanometakaolin (NMK) in slurries cured at high temperatures (90 °C) and at room temperature. The slurries were formulated with additions of 1% and 2% BWOC of nanometakaolin. At room temperature, slurries containing 2% of nanometakaolin had the highest compressive strength values, attributed to the pozzolanic reaction between nanometakaolin and Portlandite, formed during the hydration of the cement. At 90 °C, the slurries containing only 1% of nanometakaolin were the ones that showed the best results. However, at both temperatures, the slurries containing nanometakaolin presented higher compressive strength values when compared to the reference slurry (without addition).

The studies mentioned in the present review are listed in Table 1, grouped according to the material used as additive or replacement for the cement. The techniques and properties evaluated in each of the studies are also presented.

Table 1. Studies described in the literature with mineral additions applied to the oil well cementing.

MATERIAL	REF.	APPLICATION	ASSESSED PROPERTIES AND ANALYTICAL TECHNIQUES
Nanosilica	[8]	-	Rheology; Compressive strength; Free water content; Thickening time; Porosity and Permeability.
	[9]	Addition from 0.5% to 5% BWOC	Rheology; Compressive strength; Stability; Thickening time; Hydration degree.
	[10]	Addition of 1% and 2% BWOC	Mechanical properties; XRD; TG/DTG; SEM.
	[11]	Addition from 0% to 2.5% BWOC	Stability; Fluid loss; Porosity; Mechanical properties.; XRD; SEM; FTIR.
Rice husk ash	[12]	Addition of 10% and 20% BWOC	Thermogravimetry; XRD; SEM; Compressive strength.
	[13]	Addition of 20% and 30% BWOC	Thermogravimetry; XRD; Compressive strength.
Sugarcane biomass	[14]	Addition from 10% to 40% BWOC	Thermogravimetry; XRD; Compressive strength; Permeability.
	[15]	Addition of 20% and 40% BWOC	Thermogravimetry; XRD; Compressive strength.
Metakaolin	[7]	Replacement of 30% to 60% BWOC	XRD; SEM; Compressive strength; Thickening time; Porosity; Rheology; Corrosive fluid exposure.

IV. CONCLUSION

The oil well cementing operation is extremely critical and important to ensure the well productivity throughout its life. In this way, several researchers have sought for ways to increase the performance of the slurries used in these operations, improving their properties in the fresh state and after hardened. The most recent studies have focused on the use of mineral additions as replacement or additives to Portland cement for application in oil wells. The present work gathered the main studies in this topic, presenting the results obtained by the use of different additions.

The studies presented confirm that, when used in suitable concentrations, the mineral additions generate beneficial effects on the properties of the oil well cement slurries, such as increased compressive and corrosion resistance, improved rheological properties, and reduced porosity, permeability and free water from slurries. The property most benefited by the use of additions was the compressive strength, presenting increases greater than 100% in some of the evaluated studies.

Besides the technological benefits, the use of mineral additions can also lead to cost savings and environmental benefits, since much of the materials used as additions are industrial and agroindustrial waste. The association of these factors makes the use of mineral additions in oil well cement slurries a very promising alternative.

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