TECHNOLOGICAL ALTERNATIVE FOR USING ASH FROM COAL COMBUSTION IN PECÉM/CEARÁ/ BRAZIL THERMOELECTRIC PLANTS: EVALUATION OF PASTES FOR CEMENTING OIL WELLS

ALTERNATIVA TECNOLÓGICA PARA USO DE CINZAS DA COMBUSTÃO DE CARVÃO EM USINAS TERMELÉTRICAS DE PECÉM/CEARÁ/BRASIL: AVALIAÇÃO DE PASTAS PARA CIMENTAÇÃO DE POÇOS DE PETRÓLEO

ALTERNATIVA TECNOLÓGICA PARA EL USO DE CENIZAS DE LA COMBUSTIÓN DEL CARBÓN EN CENTRALES TERMOELÉCTRICAS DE PECÉM/CEARÁ/BRASIL: EVALUACIÓN DE PASTAS PARA LA CEMENTACIÓN DE POZOS PETROLEROS

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ABSTRACT
In Brazil, cements such as CPP Class G and CPP Class Especial are widely used in the cementing of oil wells due to greater quality control and lower logistics costs compared to common cements. However, cement pastes intended for civil construction do not meet the requirements of NBR 9831/2020, especially regarding compressive strength. To improve this characteristic, the microstructure of the pastes can be modified with mineral additions, such as ash from the combustion of coal, an industrial waste abundant in Ceará. This study evaluates the feasibility of using Portland CPV cement pastes with partial replacement of fly ash and bottom ash for the cementing of oil wells. Replacements of 5% and 10% of ash were tested, varying the water/binder ratio between 0.597 and 0.634. The materials were analyzed for chemical composition, grain shape, granulometry, and the ash for pozzolanic activity. The formulated pastes were evaluated according to ABNT NBR 9831/2020, API SPEC 10/2009 and API RP 10B/2003 standards. The results indicate that these pastes are viable for well cementing, with emphasis on the formulations with 10% ash replacement.

KEYWORDS
Cementing of oil wells; coal ash; Portland cement pastes.

RESUMO
No Brasil, cimentos como o CPP Classe G e o CPP Classe Especial são amplamente utilizados na cimentação de poços de petróleo devido ao maior controle de qualidade e menores custos logísticos em comparação com cimentos comuns. No entanto, pastas de cimentos voltadas para a construção civil não atendem aos requisitos da NBR 9831/2020, especialmente em relação à resistência à compressão. Para melhorar essa característica, a microestrutura das pastas pode ser modificada com adições minerais, como cinzas da combustão de carvão mineral, um resíduo industrial abundante no

Ceará. Este estudo avalia a viabilidade de usar pastas de cimento Portland CPV com substituição parcial de cinzas leves e de fundo para a cimentação de poços de petróleo. Foram testadas substituições de 5% e 10% de cinzas, variando a relação água/aglomerante entre 0,597 e 0,634. Os materiais foram analisados quanto à composição química, forma dos grãos, granulometria, e as cinzas, quanto à atividade pozolânica. As pastas formuladas foram avaliadas de acordo com as normas ABNT NBR 9831/2020, API SPEC 10/2009 e API RP 10B/2003. Os resultados indicam que essas pastas são viáveis para cimentação de poços, com destaque para as formulações com 10% de substituição de cinzas.

PALAVRAS-CHAVE
Cimentação de poços de petróleo; Cinzas de carvão mineral; Pastas de cimento Portland.

RESUMEN
En Brasil, cementos como el CPP Clase G y el CPP Clase Especial se utilizan ampliamente en la cementación de pozos petroleros debido a un mayor control de calidad y a menores costos logísticos en comparación con los cementos comunes. Sin embargo, las pastas de cemento destinadas a la construcción civil no cumplen con los requisitos de la norma NBR 9831/2020, especialmente en lo que respecta a la resistencia a la compresión. Para mejorar esta característica, la microestructura de las pastas puede modificarse mediante adiciones minerales, como las cenizas provenientes de la combustión del carbón, un residuo industrial abundante en Ceará. Este estudio evalúa la viabilidad del uso de pastas de cemento Portland CPV con reemplazo parcial de ceniza volante y ceniza de fondo para la cementación de pozos petroleros. Se probaron reemplazos del 5% y 10% de ceniza, variando la relación agua/aglutinante entre 0,597 y 0,634. Los materiales fueron analizados en cuanto a composición química, forma de grano, granulometría y actividad puzolánica de las cenizas. Las pastas formuladas se evaluaron conforme a las normas ABNT NBR 9831/2020, API SPEC 10/2009 y API RP 10B/2003. Los resultados indican que estas pastas son viables para la cementación de pozos, destacándose las formulaciones con un reemplazo del 10% de ceniza.

PALABRAS CLAVE
Cementación de pozos petroleros; Ceniza de carbón; Pastas de cemento Portland.

1. INTRODUCTION

In the environmental context, the combustion of coal generates significant environmental problems due to the production of waste and polluting emissions. Ash, which can represent 10% to 30% of the burned coal, often contains heavy metals such as arsenic and mercury, which, if poorly managed, contaminate soil and water. In addition, the process emits large amounts of carbon dioxide (CO_2) into the atmosphere, contributing to climate change, and air pollutants such as sulfur dioxide (SO_2) and nitrogen oxides (NO_X), which worsen air pollution and affect public health.

Another challenge is the storage of solid waste, which requires large areas and can cause environmental accidents. The leaching of toxic compounds from ash contaminates water resources, harming ecosystems and communities (SILVA, 2020). In view of this, it is essential to adopt sustainable management strategies, such as the reuse of ash in industrial applications, reducing environmental impact and promoting the circular economy.

Oil exploration faces several environmental and technical challenges. During drilling, there is a risk of soil and groundwater contamination due to fluid and waste leakage. In addition, the emission of gases such as methane and carbon dioxide contributes to global warming.

In the cementing process, which is essential to ensure the stability of the well and prevent leaks, problems such as failures in the adhesion of the cement to the well walls or the use of inappropriate materials can compromise the sealing. This increases the risk of fluid infiltration between the subsoil layers, with potential impacts on the environment and the safety of operations. Therefore, the use of high-quality materials and strict monitoring are essential to minimize impacts. Special types of Portland Cement are used for oil well cementing operations.

Portland cement is the main material used in the cementing of oil wells, applied in the form of pastes that are pumped through the metal casing to fill the annular space between the rock formation and the casing (COOK et al., 2006; THOMAS et al., 2001).

For this application, Portland Cements for Oil Wells (CPP) are used, with the CPP Special Class and CPP Class G being common in Brazil. These cements differ from the usual cements used in civil construction due to the strict quality control in their production, which results in less variability in their properties, resulting in different proportions of the main components of the cement such as alite, belite, celite and ferrite (BEZERRA, 2006).

Based on the production processes, cements are produced with greater uniformity, in addition to greater stability of physical and chemical properties, which allows longer storage time and use of additives, being designed to withstand high pressures and temperatures, with low permeability and high compressive strength, ensuring the durability and insulation of wells (OLIVEIRA et al., 2012).

Thus, the production of CPP cement implies increased costs and reduced availability of this type of cement on the market, due to changes in the manufacturing configurations required for its production and increased logistics costs (OLIVEIRA et al., 2012). Such factors justify the possibility of studies on the use of cements commonly used in construction for application in cementing oil wells.

Therefore, in the studies by Belém (2011), there is an indication of the possibility of using Portland Cements commonly used in civil construction such as CPII F and CPV to replace Class G and Special Class Portland cements, for cementing oil wells, with paste formulation with densities of less than 15.6 lb / gal, for application in shallow cementing.

CPP cements and CPV Portland Cement can be added with additives (chemical or mineral additions) to adapt their properties according to environmental requirements, such as density control and setting time.

In the formulation of cement pastes for shallow oil well cementing operations, up to 200 m deep, paste densities of up to 15.6 lb /gal are used. Under these conditions, to maintain the paste density and allow efficient pumping of the paste through the annular space, the pastes are formulated with a lower water/cement ratio, which can cause defects in the paste and compromise mechanical resistance, reducing the useful life and safety in the operation of oil wells (NELSON, 1990).

Therefore, to reduce the possibility of problems occurring in the cement sheath, the formulated pastes must maintain their consistency until setting, not present separation of free water or decantation of solids and must remain adhered to the rock formation and the metal coating and improve the mechanical properties (BALTHAR, 2010), making chemical additives or additions of pozzolanic materials necessary.

Taking the same idea into account, mineral additives can be used in pastes formulated with CPV, seeking to analyze the required properties of cement pastes. Thus, there is a need to investigate the characteristics and properties compatible with the requirements cited in the standards NBR 9831/2020 (ABNT, 2020) and API SPEC 10 A/2009 (API, 209), allowing formulated cement pastes to form an isolation zone between the rock formation and the metal casing, seal the permeable zones and the production zone, prevent intercommunication between the zones and the penetration of high and low pressure fluids, in addition to preventing the loss of circulation and protection against corrosive fluids, forming a hydraulic seal (FREITAS, 2007). In addition to the support functions of the well structure, consisting of the casing and the equipment necessary for prospecting that rests on it, it is necessary to ensure protection against impact loads (BOURGOYNE et al., 1991, BASSIONI et al., 22013, CHOOLAEI et al., 2012, LIU et al., 2016).

This article proposes the study of a system composed of Portland cement CPV and mineral additions – CCCM (ash from the combustion of mineral coal – light and bottom), according to the method of partial replacement of cement by mineral addition.

CCCMs are defined as an industrial byproduct resulting from the burning of coal in thermoelectric plants for the generation of electrical energy. They consist of silicoaluminous materials capable of reacting with calcium hydroxide (CH), forming hydrated calcium silicate (CSH) in cement matrices, known as pozzolanic activity. They do not leach toxic or dangerous products, have lower permeability and greater resistance to reactions with alkalis and sulfates (SABEDOT. et al., 2011) in addition to serving as hydration nuclei, and for materials that do not react, they can act through refinement, filling the spaces between grains through the filler effect and presenting predominantly glassy forms (HUI et al., 2014, LEVANDOWSKI and KALKREUTH, 2009, COOK et al., 2006).

Light and bottom coal ash differ in terms of morphology, particle size fraction, density, chemical composition, moisture content, mineralogical characteristics and proportions and types of inorganic residues (SABEDOT et al., 2011).

As for the chemical composition, both ashes formed have compositions like ceramic materials, composed of phases based on silica, aluminum, iron and calcium, totaling about ninety percent of the material. The remaining composition has proportions of magnesium, sodium, potassium, titanium and sulfur, in addition to non-volatile residues (BASSIONI et al., 2013).

In the state of Ceará, specifically in the Pecém port complex, located in the municipality of São Gonçalo do Amarante/CE, there are two thermoelectric plants, Pecém I and Pecém II, which meet the energy demand of the Pecém steel mill. According to data from the master plan of the Pecém port terminal, to meet the demand of the Pecém steel mill, approximately 1,042,325 tons of coal were imported from Colombia, in 2013 which generates an average of 80 tons of ash per day (light and bottom).

The use of ash from the Pecém thermoelectric plant in the cementing of oil wells is justified by its potential for waste recovery and alignment with the principles of the circular economy. This byproduct, widely available in the region, has pozzolanic properties that can improve the performance of cement pastes used in cementing, contributing to greater stability, resistance to high pressures and temperatures, and durability in aggressive environments. In addition, its application reduces dependence on conventional raw materials, promoting a sustainable solution for the use of waste generated by thermoelectric activity.

2. MATERIALS AND METHODS

This section presents the materials and evaluation methods for Portland Cement, coal combustion ash and formulated pastes, including the characterization of anhydrous materials, paste formulation and evaluation of the consistency and mechanical strength properties of the formulated pastes.

2. 1. Material Characterization: CPV and coal combustion ash

For this work, Portland cement CP V was used, which has smaller amounts of mineral additions in its composition. Table 01 presents the results and normative references regarding the characterization of Portland cement CP V and Figure 01 and 02 shows the granulometric distribution and micrograph of the cement.

Characteristic assessed	Regulatory Reference	Results
Chemical composition of CP V cement	ABNT NBR 14656 (ABNT, 2023)	Compatible with the requirements prescribed in ABNT NBR 16697 (ABNT, 2018)

Insoluble waste (%)	ABNT NBR NM 15 (ABNT, 2012)	1.03
Loss on ignition (%)	ABNT NBR NM 18 (ABNT, 2012)	3.49
Free lime oxide content (%)	ABNT NBR NM 12 (ABNT, 2017)	2.27
Specific mass (g/cm^3)	ABNT NBR 16605 (ABNT, 2017)	3.14
Granulometric characterization (µm)	Laser granulometry	0.1 to 100

Table 1: Characterization of Portland cement CP V.
Source: The Authors.

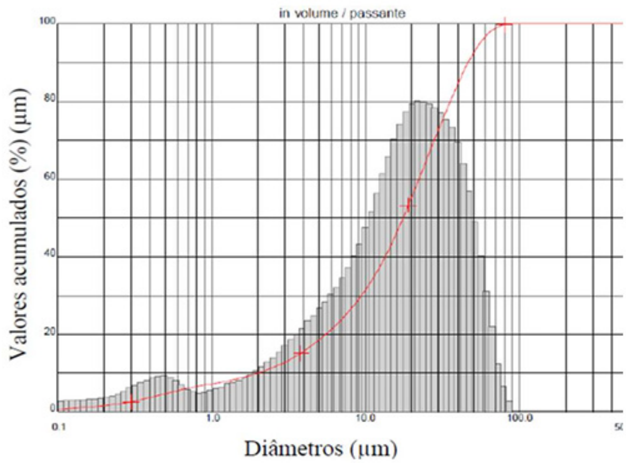

Figure 1: CPV particle size distribution.
Source: The Authors.

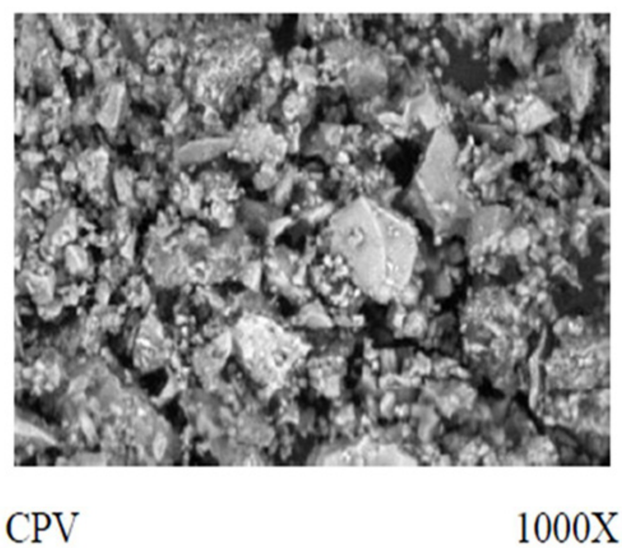

Figure 2: CPV micrograph.
Source: The Authors.

Portland CPV cement has chemical and physical properties compatible with the normative requirements for this cement. The granulometric properties stand out, with a fraction ranging from 0.1 µm to 100 µm and good material uniformity, irregular and slightly angular morphology, in addition to presenting an average particle diameter of 17.56 µm.

The coal combustion ash used in the research comes from the Energia Pecém Thermoelectric Plant, located in the municipality of São Gonçalo do Amarante, Ceará, Brazil. The coal combustion ash in this work is called CV1 for light (fly ash) and CP2 bottom ash. Table 2 and 3 presents the results of the chemical characterization of ash CV1 and CP2. To complement the results of the granulometric characterization, Figure 4 shows the micrograph of coal ash CP2 and CV1.

Characteristic	Regulatory reference	CV1	CP2
Insoluble waste (%)	ABNT NBR NM 15 (ABNT, 2012)	88.72	57.90
Loss on ignition (%)	ABNT NBR NM 18 (ABNT, 2012)	1.83	6.57
Free lime oxide content (%)	ABNT NBR NM 12 (ABNT, 2017)	0.10	4.04
Moisture content (%)	ABNT NBR NM 24 (ABNT, 2003)	0.35	0.88
Specific mass (g/cm^3)	ABNT NBR 16605 (ABNT, 2017)	2.33	2.36

Table 2: Chemical characterization of CV1 and CP2 ashes.
Source: The Authors.

Sample	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
CV1 Gray	50.33	18.62	14.96	1.25	1.64
CP2 Gray	29.97	10.96	11.05	1.00	10.77
Sample	**Na_2O**	**K2O**	**TiO_2**	**CaO**	**Others**
CV1 Gray	1.37	2.27	1.40	6.76	1.40
CP2 Gray	0.75	1.32	1.10	31.06	2.02

Table 3: Chemical characterization of cv1 and cp2 ashes – Xray Fluorescence (XRF) ABNT NBR 14656.
Source: The Authors.

Figures 03, 04 and 05 shows the micrographs taken by Scanning Electron Microscopy and the particle size distribution of CV1 and CP2 ashes determined by laser particle size measurement.

The granulometric characterization of the ash indicates that the CV1 ash has a greater inclination than the CP2, which represents a smaller granulometric distribution of the grains with a greater concentration of grains for the same diameters.

Regarding the average diameters, the particles of coal ash CP2, with a variation between 0.15 µm and 200 µm, and CV1 with a diameter varying between 0.20 µm and 5.00 µm, present a granulometry of less than 63 µm, indicated as the expected average diameter of coal ash particles (HENDRICKS, 2000).

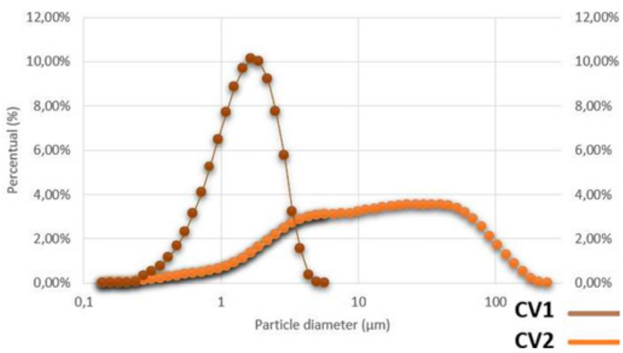

Figure 3: Distribution particle size of CV1 and CV2 ashes.
Source: The Authors.

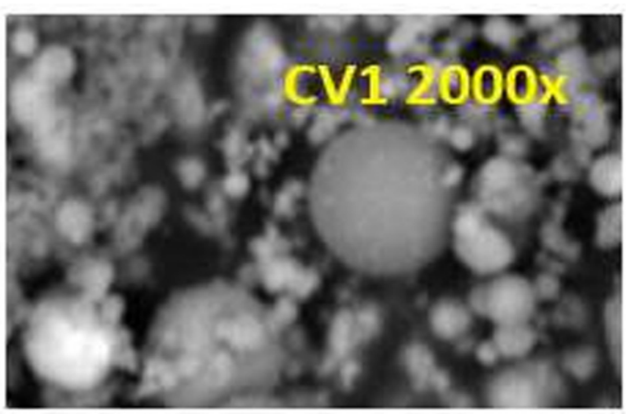

Figure 4: Micrograph of ash CV1.
Source: The Authors.

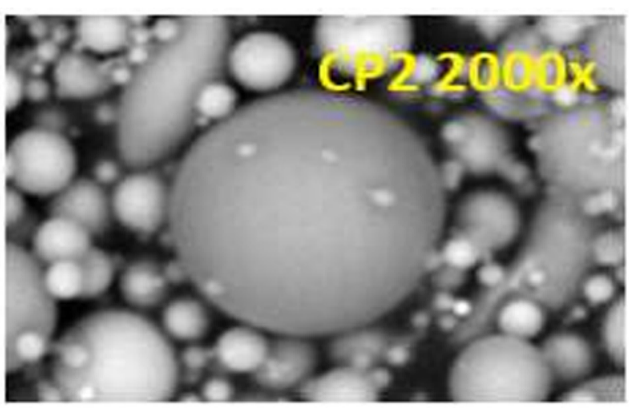

Figure 5: Micrograph of ash CP2.
Source: The Authors.

Regarding the micrograph of the ash from the combustion of mineral coal, spherical shapes are observed. Due to the spherical shape, there is a tendency for the grains to slide, which may imply greater fluidity of the pastes in cement pastes (HENDRICKS, F; A NIJKERK, A; VAN KOPPEN, 2007).

The ashes were also evaluated for pozzolanic activity according to ABNT NBR 12653/2014 (ABNT, 2014) for chemical and physical parameters, where the results are presented in Table 04.

Chemical Properties	Regulatory Requirement	CV1	CP2
$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	≥ 70.0	84.03	52.00
SO_3 (%)	≤ 5.0	1.64	10.77
Loss on ignition (%)	≤ 3.0	0.35	0.88
Moisture content (%)	≤ 6.0	1.83	6.57
Alkalis (Na_2O) (%)	≤ 1.5	1.35	0.75
Physical Properties	**Regulatory Requirement**	**CV1**	**CP2**
Material retained on the 45 µm sieve	< 20.0 %	1.26 %	13.18 %
Performance with Portland cement at 28 dayys of curing	≥ 90.0% of the strength of the reference cement – Value observed for the reference cement 26.76 MPa	28.31 MPa	26.90 MPa
Pozzolanic activity with lime at 7 days	≥ 6.0 MPa	7.6 MPa	6.6 Mpa

Table 4: Pozzolanic activity of CV1 and CP2 ashes.
Source: The Authors.

Pozzolanic activity results indicate that CV1 ash is compatible with fly ash, meeting the chemical, particle size distribution and grain shape requirements. It also meets all the parameters evaluated according to the normative requirements ABNT NBR 12653/2014 (ABNT, 2014) and ASTM C 618 – 12a/2012 (ASTM, 2012), and can be classified as class C pozzolan, with proven pozzolanic activity.

CP2 ash does not meet the pozzolanicity requirements. Result arising from the process used in the generation of electrical energy at the Pecém thermoelectric plant, known as lewanlew. CP2, about the high percentage of sulfur oxide, with 1.64% for CV1 and 10.77% for CP2, may have a reaction to the FGD process, which inserts calcium carbonate (CaCO3) to reduce the emission of SOx gases into the atmosphere (JUNIOR ROCHA, 2012).

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2. 2. Formulation of Portland cement pastes

Based on the data obtained, it was possible to determine the mass of the components of the Portland cement pastes, carried out based on the BWOC – By Weight Of Cement, referring to the mass of cement. The procedure for calculating the folders was carried out in accordance with the American standard API RP 10B (API, 2019).

Thus, Table 05 presents the formulations and percentages of partial replacement of Portland cement CPV by coal combustion ash, where CV1 corresponds to light coal ash (fly) and CP2 to bottom coal ash (heavy).

Formulations	Percentage of replacement	Cement mass (g)	Water mass (g)	Ash Mass (g)	Water/ Cement Ratio
CPV	0	652.77	389.72	0.00	59.70
CPIIF5CV1	5	628.32	384.79	31,32	61.43
CPIIF10CV1	10	602.21	380.23	60.21	63.16
CPIIF5CP2	5	628.32	384.79	31,32	61.43
CPIIF10CP2	10	602.21	380.23	60.21	63.16

Table 5: Portland cement paste formulations.
Source: The Authors.

It is worth noting that the water/cement ratio becomes variable depending on the density of the cement pastes, in this case adopted at 14.5 lb / gal (1.74 g/cm³), compatible with shallow wells.

To prepare the Portland cement pastes, the mixing and homogenization procedures were followed according to NBR 9831/2020 (ABNT, 2020) and API SPEC 10 A/2022 (API, 2022). For this purpose, a Chandler model 80-60 mixer and a Chandler model 120 atmospheric consistometer were used to mix the cement pastes.

Figure 6: Pressurized consistometer.
Source: The Authors.

2. 3. Evaluation of consistency and compressive strength properties of Portland cement pastes

After the preparation of the pastes, API technological tests were performed for free water content, consistometry for maximum paste consistency in the 15 to 30-minute test period, pumpability time (50Uc) and thickening time (100Uc), using the Chandler brand pressurized consistometer equipment, model 7716, shown in Figure 06 (only for the CPV, CPV10CV1 and CPV10CP2 formulations , due to operating costs.

The determination of the free water content is determined by the volume of free water observed, over the course of two hours, multiplied by the density of the cement paste, then divided by the mass of Portland cement paste inserted in the Erlenmeyer flask, according to Equation (1): Volume of free water (Val); mass of the cement slurry inserted into the Erlenmeyer flask (mp); and the density of the cement slurry (ρ). For this research, the density is 14.5 lb/gal (1.74 g/cm³).

$$\% AL = \frac{Vol\,.\rho}{Mp}\,.100 \qquad (1)$$

For compressive strength, the pastes formulated for ages of 8 hours, 24 hours, 7 days and 28 days were evaluated. NBR 9831/2020 (ABNT, 2020, indicates as a requirement for acceptance of cements a curing age of 8 hours with a curing temperature of 38°C; however, it was decided to evaluate compressive strength for ages of 24 hours, 7 days and 28 days, a fact associated with the observation of the mechanical behavior of the pastes at important ages for the cementing of oil wells.

The compressive strength test was performed on specimens made in cubic metal molds with internal dimensions of 50 ± 5 mm (Figure 07) and prepared by applying lithium soap-based grease to the metal-to-metal contact, the internal faces of the molds and the edges, to prevent water loss. Then, the prepared and homogenized pastes were poured into the molds in two layers, with approximately equal heights. For each layer, the cement paste was stirred with a glass rod with 25 constant circular movements in a clockwise and counterclockwise direction, to remove air bubbles.

Figure 7: Mixing the pastes in the molds 5cm x 5cm x 5cm.
Source: The Authors.

The paste was added until it exceeded the top of the mold, which was then covered with a glass plate, also greased, and secured with elastic bands. A total of 3 test specimens were prepared per formulation, resulting in 9 test specimens for each age of compressive strength assessment.

The molds were cured in a Nova Ética thermostatic bath, model 500/3DE, at a temperature of 38°C for 8 hours, 24 hours, 7 days and 28 days. After the necessary curing time for the tests, the specimens were removed from the thermal bath, unmolded and placed in a cooling bath for 35 minutes. The specimens were then dried with absorbent paper and measured with a caliper to observe possible variations in dimensions.

Shimadzu Universal Testing Machine was used to break the test specimens. Autograph of the AG-I model, which is controlled by the TRAPEZIUM 2 software, with an application rate and load of 6.9 Mpa/min (1000psi/min), according to ABNT NBR 9831 (2020).

Finally, the evaluation of the microstructural characteristics of the formulated pastes was carried out after the rupture of the test specimens, using XRD and SEM, using the Shimadzu X-ray Diffractometer - model 7000 and the Shimadzu equipment model EDX -820, for the SEM. Based on the results obtained, the materials were compared with each other and with the available literature for pastes formulated with the same density evaluated in the study, for CPP Special Class and CPP Class G cements, specific for use in oil well cementing operations.

3. RESULTS AND DISCUSSIONS

3. 1. Free water content

The free water content refers to the percentage quantification of the supernatant water volume, corresponding to the water that will not participate in the chemical hydration reactions. Figure 08 presents the results for the free water content.

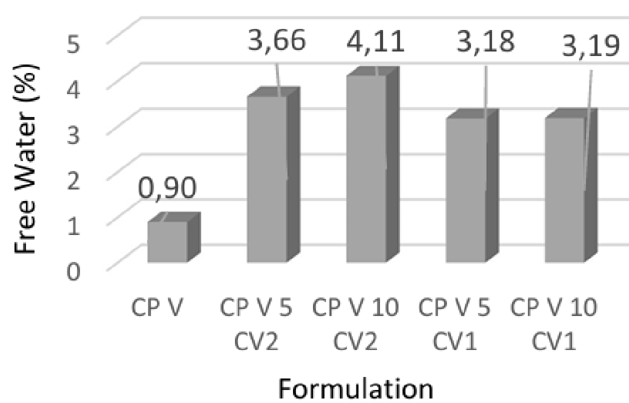

Figure 8: Percentage of free water.
Source: The Authors.

The results observed, for all samples, are lower than the value of 5.90% established in ABNT NBR 9831/2020 (ABNT, 2020) and in API SPEC 10 A/2022 (API, 2022), however, they do not prevent the use of the pastes.

The CPV formulation presented the lowest percentage of free water among the samples analyzed, and the formulations with the highest percentage of CCCM presented the highest percentage of supernatant water. This fact may be related to the higher percentage of fine materials (such as limestone filler and mineral additions) and the lower proportion of cement, which may reduce the hydration reactions of the cement pastes, especially for the 2-hour test time.

Comparing the pastes formulated according to the type of CCCM, the formulations containing CP2 ash presented higher percentages of free water when compared to the mixtures formulated with CV1 ash. A possible explanation for this behavior is due to the larger average diameter of the CP2 ash particles, as observed in figure 2, thus having a smaller surface area, which implies a lower water demand, allowing a higher percentage of free water.

According to the results by Belém (2011), which evaluated pastes with the same density, the percentage of free water content for the paste formulated with CPP Class G was 17.22% and for CPP Special Class it was 14.75%. Therefore, all the formulated pastes presented lower percentages of free water in relation to CPP Class G and CPP Special Class

3. 2. Assessment of paste consistometry

The Figure 09, 10 and 11 shows the graphs of the consistometry test, which evaluates the gain in resistance of the pastes over the test time, where the environmental conditions where the pastes will be used are simulated.

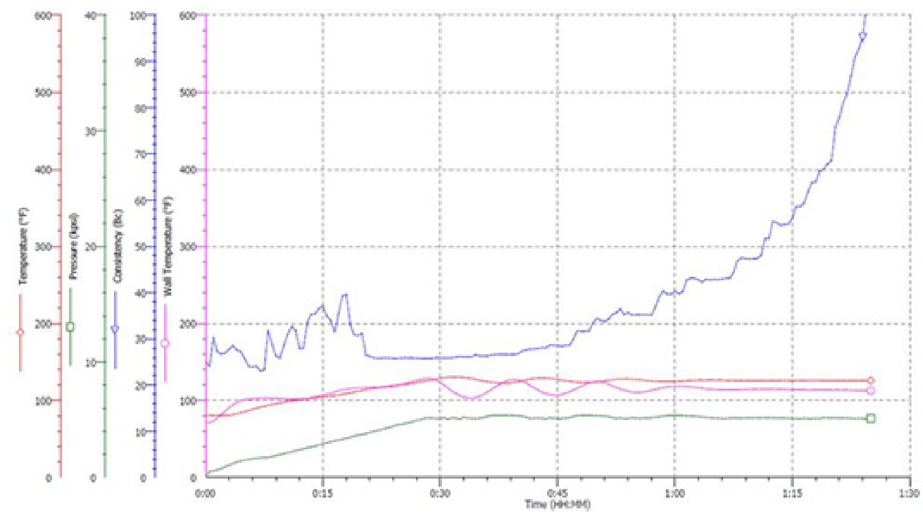

Figure 9: Paste consistometry CPV Formulation.
Source: The Authors.

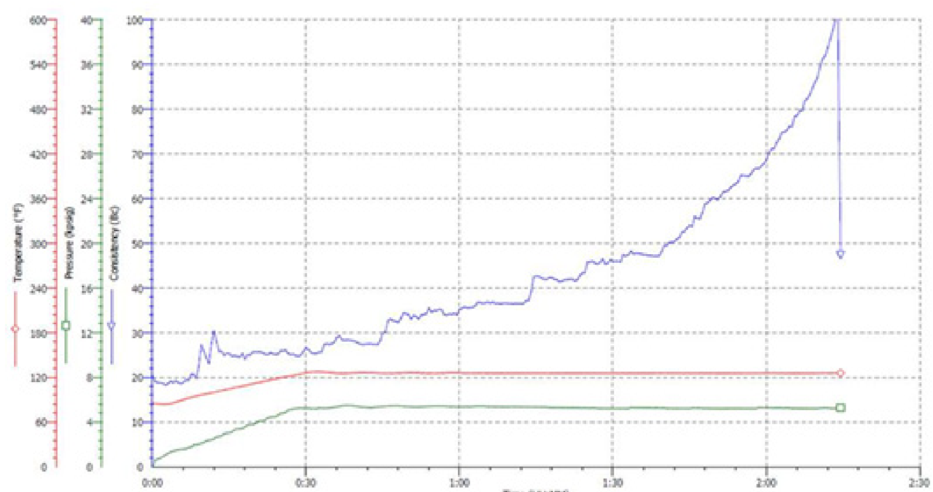

Figure 10: Paste consistometry CPV10CV1 Formulation.
Source: The Authors.

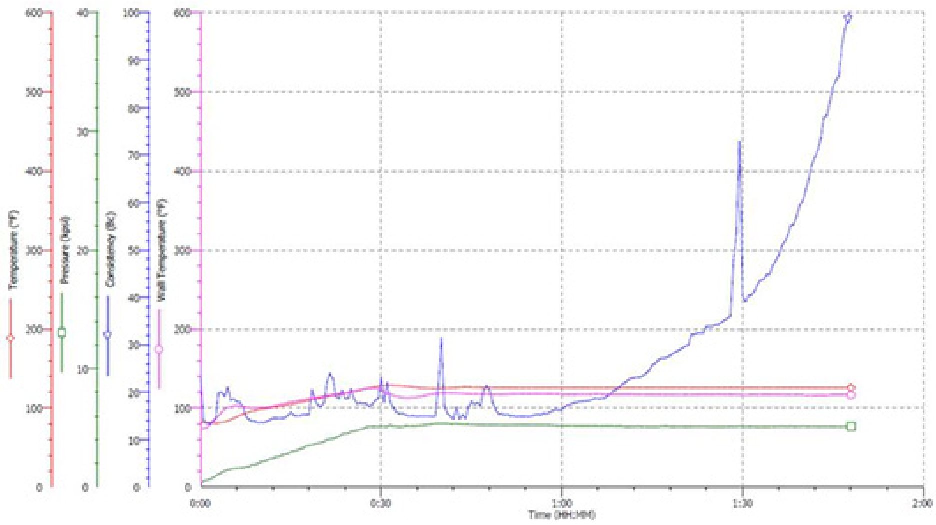

Figure 11: Paste consistometry CPV10CP2 Formulation.
Source: The Authors.

Table 06 presents data relating to the parameters of pumpability time, thickening and maximum consistency between 15 and 30 minutes, which are fundamental for real cementing operations.

Thickening time refers to the setting time of cement pastes under certain temperature conditions and represents the time it takes for the spaste to reach m100 Uc (Consistency Units). In practical terms, it indicates the time the cement paste remains in a fluid state.

Formulations	Pumpability time 50 Uc - (minutes)	Thickening time 100 Uc - (minutes)	Maximum consistency between 15 and 30 min. (Uc)
CPV	87	97	13
CPV10CV1	101	130	26
CPV10CP2	111	151	33
Limit values stipulated by ABNT NBR 9831 (ABNT, 2020)			
CPP Class G	-	90 to 120 minutes	30 Uc
CPP Special Class	-	90 to 120 minutes	30 Uc

Table 6: Pumpability time, thickening time and maximum consistency between 15 and 30 minutes.
Source: The Authors.

Comparing the observed values, the CPV formulation presented results within the range stipulated by ABNT NBR 9831 (ABNT, 2020), as acceptable values. For the other formulations, values higher than the normative limit of 90 to 120 minutes were observed.

This behavior can be related to the water/cement factor of 0.631, referring to the CPV10CV1 and CPV10CP2 formulations, where there is a reduction in the setting time of the pastes (Sing et al., 2000). This value was obtained using the BWOC methodology to calculate the formulations, where the density of 14.5 lb /gal was fixed. By reducing the solids content, the setting time increases, with the spacing between the cement particles and thus, the intertwining speed of the ettringite crystals and hydrated calcium silicate is reduced (FORMAGINI, TOLEDO-FILHO and FAIRBAIRN, 2005).

For the formulation CPV10CP2, the thickening time was 151 minutes, a higher value than that observed for the CPV10CV1 formulation with 131 minutes. This result may be due to a larger surface area for the formulation with CCCM CV1 ash (compatible with the Blaine fineness result of 8220) and the particle size distribution varying between 0.2 µm and 5.0 µm.

The consistency of the CPV10CP2 pastes, around 25 Uc, indicating a possible false setting, also called calcium sulfate setting (Neville, 2016). This fact is possibly related to a higher percentage of SO 3 for the CP2 ash, in the order of 10.77% against 1.64% for the CV1 ash. The increase in the SO 3 content may indicate the reaction of C 3 A (Aluminate Phase of Portland cement) with calcium sulfate ($CaSO_4$), accelerating the setting, as observed by the high initial consistency of the paste (Sing et al., 2000). The CPV and CPV10CV1 formulations presented values within the normative limits and CPV10CP2, with 33 Uc, presented a value slightly higher than that referenced in ABNT NBR 9831 (ABNT, 2020).

The pumpability time corresponds to the time required for the cement paste to reach a consistency of 50 Uc, representing a limit value at which the paste can be pumped (Nelson, 1990). It is worth noting that this parameter is not contemplated by ABNT NBR 9831 (ABNT, 2020) as an acceptance or rejection parameter, but rather as a relevant operational parameter.

Since this is a non-normative parameter, the results observed were compared with the time for the paste to reach 50 Uc, which should be greater than 75% of the total test time (SING et al., 2000). Thus, the CPV and CPV10CV1 pastes presented a time greater than 75%, respectively with 89% and 77% of the test time, and the CPV10CP2 paste with 73% of the test time, was slightly lower than recommended.

Consistometry test the results indicate good acceptance parameters, even for pastes that presented parameters lower than those stipulated by ABNT NBR 9831 (ABNT, 2020) and observed by Belém (2011), since this parameter can be modified with the inclusion of chemical additives.

3. 3. Evaluation of the compressive strength of the pastes

The Table 07 shows: Compressive strength for ages of 8 hours, 24 hours, 7 days and 28 days of the formulated pastes.

Formulation	8 hours (MPa)	24 hours (Mpa)	7 days (MPa)	28 days (MPa)
CPV	5.17	12.58	20.45	22.16
CPV5CV1	4.92	12.20	23.44	26.13
CPV10CV1	5.32	12.61	23.35	30.78
CPV5CP2	3.72	12.39	24.00	28.22
CPV10CP2	3.30	10.70	25.18	29.62

Table 7: Compressive strength for ages of 8 hours, 24 hours, 7 days and 28 days of the formulated pastes.
Source: The Authors.

The standard deviation observed for the average of the three specimens tested, by age, was less than 10%, which indicates that the results are reliable and can be used.

Based on the results, it can be observed that, for the curing age of 8 hours, the compressive strength values are higher than those indicated as a minimum, which is at least 2.1 MPa (ABNT NBR 9831, 2020). The CPV pastes and those formulated with CCCM CV1 stand out, indicating the filler and nucleation effect, related to the smaller granulometry of the CV1 ash, as previously observed in the Figure 12.

It is worth noting that, at the age of 24 hours, a slightly significant difference was observed between the compressive strength values between the pastes, with a variation of 3.25%. The exception was the CPV10CP2 formulation, with a variation of 15.15%, which may be related to the larger granulometric fraction of CP2 ash, which is associated with a lower proportion of cement in the mixture.

Regarding the curing age of 7 days, it was observed that the CPV paste presented the lowest compressive strength value, with a variation of around 18.78%, in relation to the formulation with the highest observed value, the CPV10CP2 paste (a result in contrast to that observed for the age of 24 hours).

In general, the results indicate that the ash from the combustion of mineral coal improved the compressive strength properties of the pastes, being higher than 25.18% compared to the CPV10CP2 folder and, 28.00%, for the CPV10CV1 folder, both in relation to CPV.

Therefore, it can be inferred that the filler effect (elated to the granulometry of CV1 ash) and the pozzolanic activity indicate good results regarding compressive strength, especially at 28 days. As for CP2 ash, even though it does not present pozzolanic activity, in relation to chemical properties, there are indications of improvement in physical properties, due to greater compactness of the cement matrix.

3. 4. Microscopy and diffractometry of formulated pastes

Scanning electron microscopy seeks the morphological characterization of the hydrated and cured cement pastes at 28 days. The micrographs of the formulated pastes are presented in the Figures 12, 13 and 14. In the micrographs, it is possible to observe ettringite (E) crystals intertwined with portlandite (CH) crystals and the occurrence of hydrated calcium silicate (CSH) with low evidence of voids.

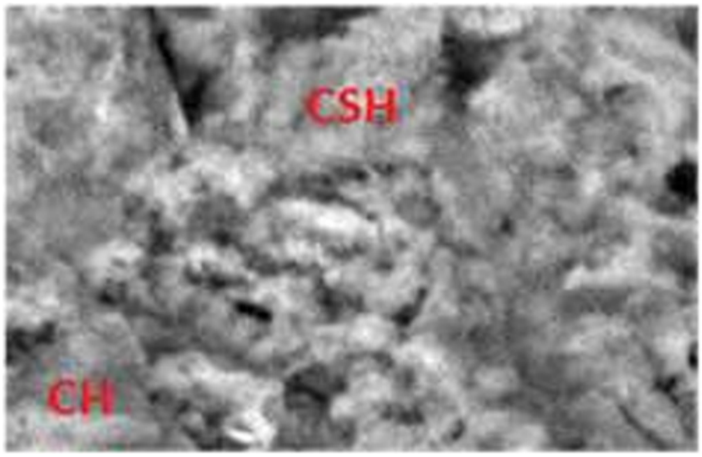

Figure 12: The micrographs of CPV.
Source: The Authors.

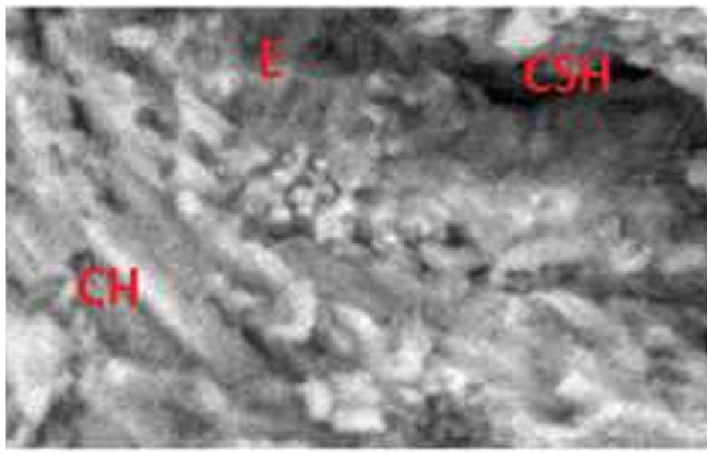

Figure 13: The micrographs of CPV10CV1.
Source: The Authors.

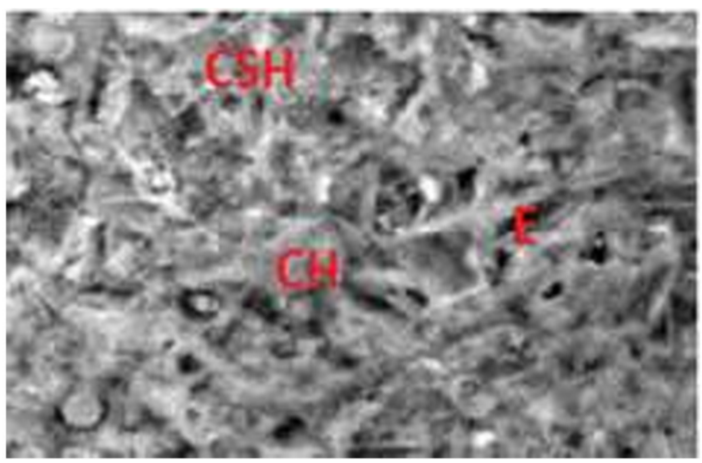

Figure 14: The micrographs of CPV10CV2.
Source: The Authors.

The X-ray Diffraction test was used to identify the crystalline phases present in Portland cement pastes. They are observed in the diffractograms of the formulated pastes (Figures 15, 16 and 17), where the peaks refer to the main hydrated phases for the curing age of 28 days.

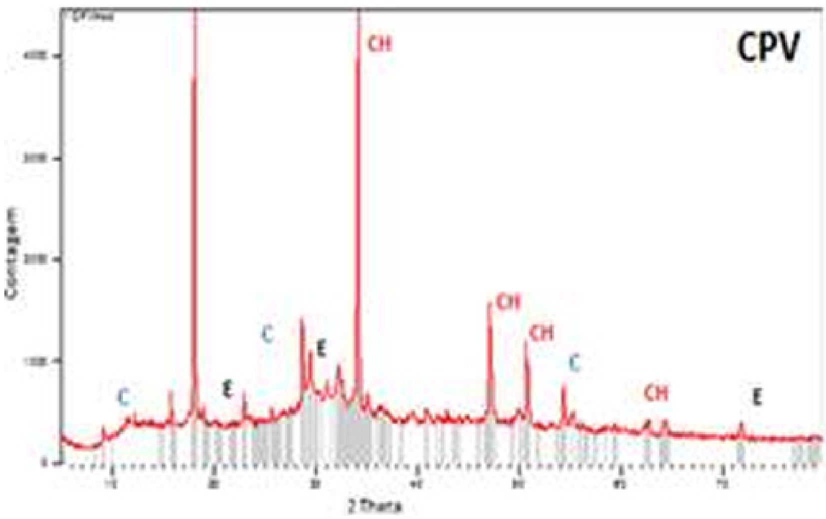

Figure 15: Diffractogram of Portland cement pastes. CPV.
Source: The Authors.

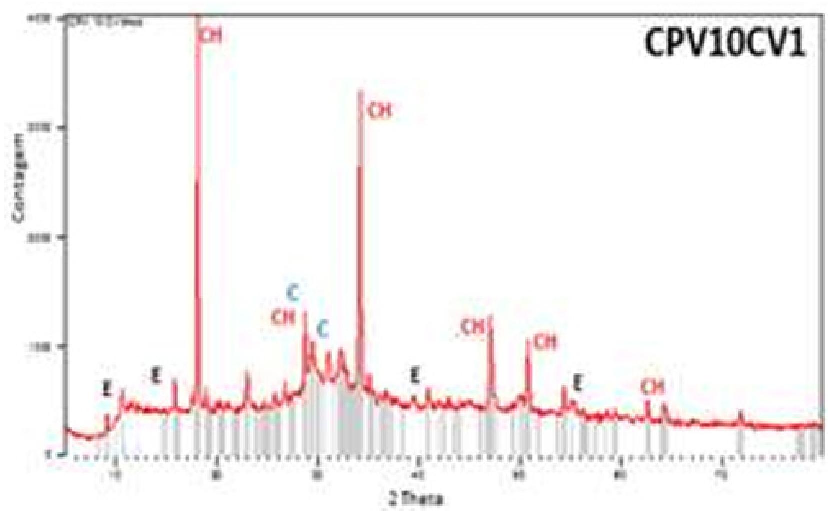

Figure 16: Diffractogram of Portland cement pastes. CPV10CV1.
Source: The Authors.

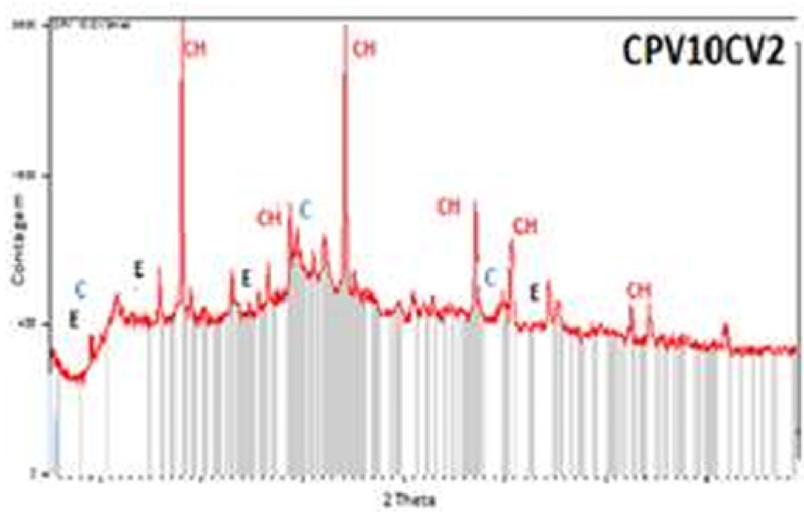

Figure 17: Diffractogram of Portland cement pastes. CPV10CV2.
Source: The Authors.

All formulated pastes present, in the peaks of highest dispersive energies, Portlandite (CH) and ettringite (E), calcium silicates and other non-hydrated compounds such as C 3 S and C 2 S (C), mentioned in the literature (NELSON, 1990 and TAYLOR, 1997).

The observed peaks with the highest intensity and frequency refer to portlandite, which is present in all samples evaluated, and, with lower intensity and frequency, peaks referring to non-hydrated compounds and ettringite, also present in all pastes evaluated. It is worth noting that the pozzolanic reaction occurs between portlandite and silica, so this reaction occurs slowly, observed only at higher hydration ages for the occurrence of new CSH phases that tend not to appear in the hydrated form, for their main phases, because they are materials in the form of amorphous or poor crystalline gel.

4. CONCLUSIONS

In this study it can be concluded that the pastes formulated with partial replacement of Portland Cement CPV by ash from the combustion of light mineral coal (CV1) and bottom (CP2), have potential for use in the cementing of shallow oil wells with pastes formulated with a density of up to 14.5 lb /gal.

The formulations presented good results in terms of free water, remaining below the minimum established as acceptable by the standard. For pumpability time, consistency and thickening time, it is recommended to use formulated pastes, even if they exceed some normative values, since chemical additives that alter the rheological properties of the pastes can be used.

The results for compressive strength indicated that all pastes presented values higher than 2.1 MPa for a curing time of 8 hours at a temperature of 38°C and good resistance evolution up to the curing age of 28 days.

The best results were observed for the formulations with CV1 ash. This result highlights the filler effect and possible chemical action of pozzolanic activity.

CP2 ash, there were low rheological properties, which indicate a low application in shallow oil well cementing operations. However, no losses in mechanical strength were observed.

In addition to the potential for application in oil well cementing operations, the use of ash from coal combustion helps to reduce the amount of waste in thermoelectric plant disposal yards, in addition to the possibility of reducing the costs of the cementing operation.

Therefore, the use of coal ash in the cementing of shallow oil wells represents an important solution from both an environmental and technological point of view. Its application contributes to the proper disposal of industrial waste, avoiding improper disposal and contamination of natural resources. Furthermore, when incorporated into cementing materials, the ash in question can offer beneficial properties, ensuring safety and efficiency in the process, while promoting sustainability and the use of waste in shallow oil well cementing processes.

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MAGC: conceptualization, data curation, formal analysis, investigation, methodology, writing – original draft and writing – review & editing.

AVGB: conceptualization, visualization and writing – original draft, review & editing.

AEBC: supervision and writing – review & editing.

BLD: supervision and writing – review & editing.

JCOF: supervision and writing – review & editing.

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