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Macromolecular and aromatic character influence of SBR on the rheological properties of oil well cement slurries

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Abstract

Ensuring the rheological properties of the latex-based cement slurries in steam EOR is indispensable. $Ca(OH)_2$ is produced after cement/water reaction and the macromolecules tend to disturb the hydration process, after the latex demulsification, by covering the cement particles. The free water decreases due to the high hydrophilicity of demulsified SBR, where final gel values increased up to 67%. The slump diameter was decreased exponentially by increasing the latex content limiting the workability. SBR-modified slurries presented a Pseudoplastic non-Newtonian flow behavior and the plastic viscosity decreases gradually, while the yield stress values registered a progressive increment by adding SBR till 10%.

Influência do caráter macromolecular e aromático da SBR nas propriedades reológicas de pastas de cimento para poços petrolíferos

Informações

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Palavras-chave
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Resumo

Assegurar as propriedades reológicas das pastas de cimento à base de látex no sistema de EOR via steaming é muito importante. O $Ca(OH)_2$ é produzido após a reação cimento/água e as macromoléculas tendem a atrapalhar o processo de hidratação, após a demulsificação do látex, por recobrir as partículas de cimento anídro. A água livre diminui devido à alta afinidade com água do SBR demulsificado, onde os valores finais do gel aumentaram até 67%. O diâmetro de abatimento diminuiu exponencialmente com o aumento do teor de látex, limitando a trabalhabilidade. As pastas modificadas com SBR apresentaram comportamento de fluxo Pseudoplástico não Newtoniano e a viscosidade plástica diminui gradativamente, enquanto os valores de tensão de escoamento registraram incremento progressivo com a adição de SBR até 10%.

Influencia del carácter macromolecular y aromático del SBR en las propiedades reológicas de pastas de cemento para pozos de petróleo

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Resumen

Es muy importante garantizar las propiedades reológicas de las pastas de cemento a base de látex en el sistema EOR mediante vaporización. El $Ca(OH)_2$ se produce después de la reacción cemento / agua y las macromoléculas tienden a dificultar el proceso de hidratación, después de la demulsificación del látex, al cubrir las partículas de cemento anhidro. El agua libre disminuye debido a la alta afinidad con el agua del SBR demulsionado, donde los valores finales del gel aumentaron hasta un 67%. El diámetro de sacrificio disminuyó exponencialmente con el aumento del contenido de látex, lo que limitó la trabajabilidad. Las pastas modificadas con SBR mostraron un comportamiento de flujo pseudoplástico no newtoniano y la viscosidad plástica disminuyó gradualmente, mientras que los valores de límite elástico registraron un aumento progresivo con la adición de SBR hasta un 10%.

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1. Introduction

After the contact between cement powder and water, an immediate exothermic reaction happens and the pH of the suspension rapidly reaches high values due to the presence of calcium hydroxide as one of the main hydration products. The way the cement pastes aggregate indicates their rheological behavior (TAYLOR, 1997). Lots of models were set to describe the aggregation of the suspensions especially at the very early ages of hydration (CHHABRA; RICHARDSON, 2008; CHOUGNET et al., 2008). Polymeric admixtures can be added to cement slurries to improve the behavior of well cement sheath exposed to high-temperature processing and the consequent thermal gradients (ABOELKHEIR et al., 2018; OHAMA, 1998). Styrene Butadiene copolymer (SBR) and polyacrylate (PA) latex systems (emulsion systems) tend to be unstable in alkaline medium. Thus, an immediate demulsification occurs by the contact with the hydrated cement suspension, and this phenomenon even affects the hydration kinetics (ABOELKHEIR et al., 2018; HONGYAN; YE; ZONGJIN, 2011).

The cement slurry is pumped through the casing and placed in the annulus between the casing and the borehole wall displacing the previous fluid in the annulus (PAIVA et al., 2018; SMITH, 1990). Precise rheological characterization of cement slurries is performed to ensure the processing parameters such as slurry's pumpability, the pressure-depth relationship during and after placement, the return rate when free fall is occurring, etc. Non-Newtonian rheological models like the power law and the Bingham plastic are widely applied to describe the well cement slurries flow (GUILLOT, 1990).

Pseudoplastic or shear-thinning is a time-independent non-Newtonian fluid behavior in which the apparent viscosity is inversely proportional to the shear rate. In general, the larger the enclosed area of thixotropy, stronger is the time-dependent behavior of the materials. So, no hysteresis loop is observed for time-independent fluids (CHHABRA; RICHARDSON, 2008).

The consistency of SBR-modified cement mortar depends on both water-to-cement ratio (W/C) and percentage of latex. Latex content influences yield stress and apparent viscosity. Thus, the mortars present shear thinning behavior at low W/C (ALLAN, 1997; BARLUENGA; HERNÁNDEZ-OLIVARES, 2004). Polymers in latex and surfactants tend to decrease the viscosity of cement pastes due to a plasticizing effect (BARLUENGA; HERNÁNDEZ-OLIVARES, 2004). Polycarboxylate superplasticizers can decrease the yield stress and apparent viscosity of cement admixtures due to adsorption mechanisms that change the zeta potential (PENG et al., 2015). In the presence of superplasticizer, attractive depletion forces induced by non-adsorbing polymers can be noticed and can contribute to the flocculation of the suspension (BESSAIES-BEY et al., 2018). SBR latex can enhance the workability of fresh state mortar and retard nucleation and growth of hydration products(UKRAINCZYK; ROGINA, 2013).

Flexible cement sheath can eliminate the formation of cracks caused by the thermal recovery in the steam-based EOR methods, thus innovative solutions such as designing cement slurries with high deformation capacities are essential. In this paper, SBR latex was used in different contents to prepare ductile polymer-modified cement specimens. The corresponding influence of the latex on the workability through the slump test and on the rheological parameters (viscosity and yield stress) of the slurries was given priority and the results are reported.

2. Experimental

2.1. Materials

The cement slurries consisted of cement CPP G class from Holcim-Brazil, silica filler mesh 325, SBR emulsion from Nitriflex S/A, Hormitec superplasticizer third generation additive from Anchortec company, and deionized water. The chemical composition of the dry materials is presented in Table 1. All the materials were used as received.

2.2. Mix design

Two different methods are applied to add

Table 1. Chemical composition of cement CPP G class and Silica mesh 325.

Oxide	Content in Cement (%)	Content in silica (%)
CaO	67.95	0.057
SiO_2	16.35	98.49
Fe_2O_3	5.49	-
SO_3	3.89	1.427
Al_2O_3	3.64	-
Sc_2O_3	1.61	-
K_2O	0.52	-

polymers to cement composites: a) keeping constant the water-to-cement ratio (W/C) to obtain similar hydration of the cement paste and b) fitting the consistency of the composite adjusting the W/C or the plasticizers content (BUREAU et al., 2001). According to TGA analysis (see Fig. 1), the latex lost almost 70% of its mass (aqueous phase) at 100°C. Thus, only 30% of the mass is from the polymer. This material was later decomposed and the decomposing temperature of SBR was registered, W/C was fixed to 0.53 and the aqueous phase of the latex after its demulsification was taken into consideration and was subtracted from the total W/C.

The Compressible Packing Model (CPM) of Larrard was adopted to design the reference slurry composition as a high-performance material (LARRARD, 1999). The software MEC, COPPE 1.0 was used to calculate the packing of granular phases. Cement CPP G Class and silica 325# were added in the quantity of 100% and 37% respectively. SBR latex was added to the reference slurry by 6%, 10% and 13% through a volume-in-volume substitution (V/V) forming the groups of slurries A6, A10, and A13, respectively. The dry materials (after dry mixing) were added to the liquid phase already in Chandler mixer model 30-60. The mixing speed was adapted to avoid the formation of clusters of SBR, so the applied speed was 2970 rpm for 10 minutes for a 600 ml volume of slurry. Further details about this item are available in a previous paper from our group (ABOELKHEIR et al., 2018).

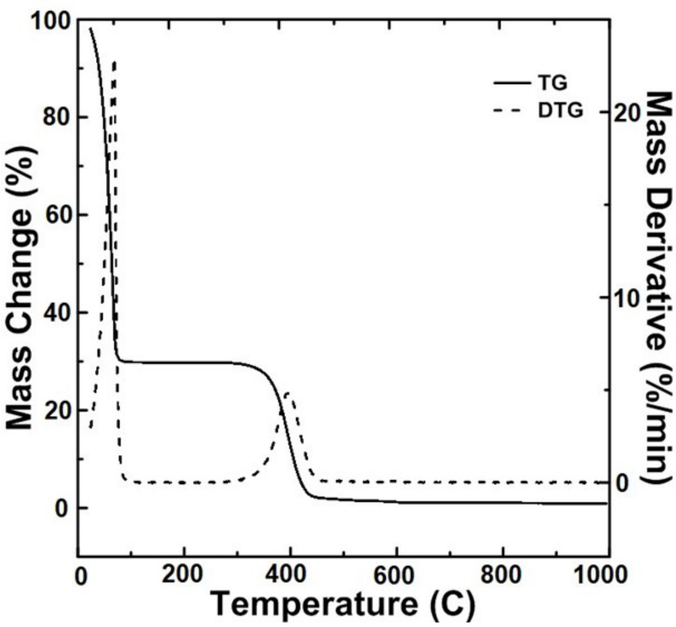

Fig. 1. TG/DTG curves of SBR emulsion.

2.3. Thermogravimetric analysis (TGA)

TGA analyses were carried out using SDT device, model Q 600. The analyses conditions included heating rate of 10 °C/min from 30 to 1000 °C, under nitrogen atmosphere with a gas flow rate of 100 mL/min using a platinum crucible as a sample holder. Each sample was tested two times.

2.4. Free Fluid Content

This test was performed as described in ABNT NBR 9831 standard (2006). A quantity of 760 g of the slurry were placed into a conical flask and placed into stationary state for 2 h. After this period, the supernatant fluid was collected. Eq.1 was applied to calculate the free fluid content of the cement slurry.

$$FF = 100.(V_{ff}.\rho)/m \qquad (1)$$

where FF is the percentage of free fluid content in the slurry; V_{ff} is the volume of supernatant fluid collected in mL; m is the initial weight in g; and ρ is the theoretical density in g/cm^3.

2.5. Mini-Slump Test

This test aims to evaluate the fluidity and workability of the material by determining the average diameter of the slurry after pouring it into a funnel which is raised slowly to let the slurry flow on a plane surface, as recommended by a commercially used method. Finally, three diameters are measured of all the slurries to take the average.

2.6. Rheological Parameters

The rheological properties of the slurries were determined as recommended by a commercially used method at 27°C. The yield stress and plastic viscosity were determined according to the rheological model of Bingham. The test was performed using the coaxial cylinder direct readings viscometer of Chandler, model 3506. This equipment has rotor factor R1 with a diameter of 3.68 cm and an effective length of 5.84 cm, while Bob factor B1 with a diameter of 3.45 cm and an effective length of 3.80 cm. The distance between the walls of the rotor and Bob (gap) is 1.17 mm. The deflection readings were taken applying ascending/descending rotational speeds in this order; 3, 6, 30, 60, 100, 200, 300, 200, 100, 60, 30, 6 and 3 rpm at time intervals set by the method. Then, a rotational speed of 600 rpm was applied for 60 seconds, and the motor was then turned off for 10 seconds and then switched on again at a speed of 3 rpm. Maximum observed deflection was noted to determine the initial gel value. The engine was turned off again, and after 10 minutes of motionlessness, the engine was turned on at a speed of 3 rpm. The maximum deflection was recorded in order to determine the final gel value. At least three tests were performed to take the average reading. The temperature was registered in the start and the end of each test.

3. Results and Discussions

The cement slurry (composed only by cement and water) was characterized using the coaxial cylinder viscometer, and the Bingham model was applied to describe its rheological behavior (see Fig. 2).

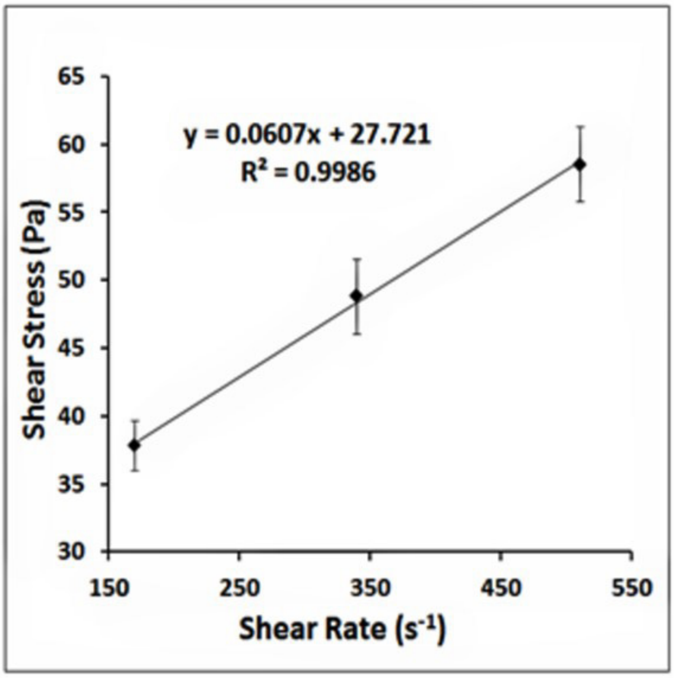

Fig. 2. Flow curve of cement CPP G class.

Table 2 shows the different contents of the free fluid of all the studied slurries. The REF slurry has a free fluid content of 1.89% and it was decreased gradually by increasing the polymer content, indicating a higher affinity with water molecules.

The slump behavior is highly depending on the free water content in the fresh slurry. The chemical nature of SBR is the decisive factor in determining the real quantity of free water and the consistency of the modified slurries. The large polarizability of the aromatic rings, coming from styrene portion of SBR, leads to the formation of different van der Waals interactions with water if compared to another aliphatic polymer as proven by the hydration thermodynamic techniques (GRAZIANO, 2004). SBR presents high water affinity leading to a decrease in the quantity of the free water in the system, as shown in the demulsification test and free fluid content tests. The diameter of the slurry in the mini-slump test is decreased as well (see Fig. 3-a). The slurries registered 175, 120, 114 and 110 mm of diameter for the slurries REF, A6, A10, and A13, respectively. The optimum polymer content to reach a stable spreading diameter equals to 7.92% according to the proceedings, adopted from ISO 11358, applied to the exponential regression model with R^2 = 0.998. (see Fig. 3-b).

Table 2. Free fluid content of SBR-modified slurries.

Sample	Fluid content (%)
REF	1.89 ± 0.04
A3	0.28 ± 0.01
A6	0.050 ± 0.001
A10	0

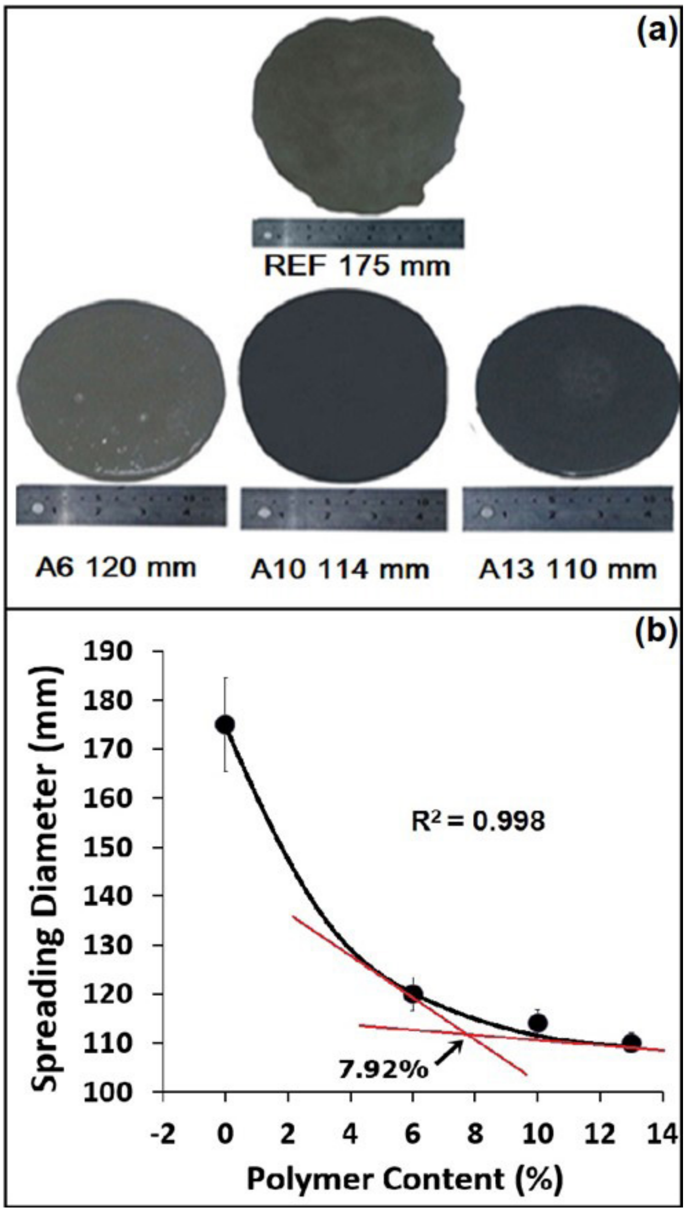

Fig. 3. Influence of SBR latex content on the spread diameter of SBR-modified slurries in mini-slump test: a) mini-slump diameters and b) exponential regression model of the results.

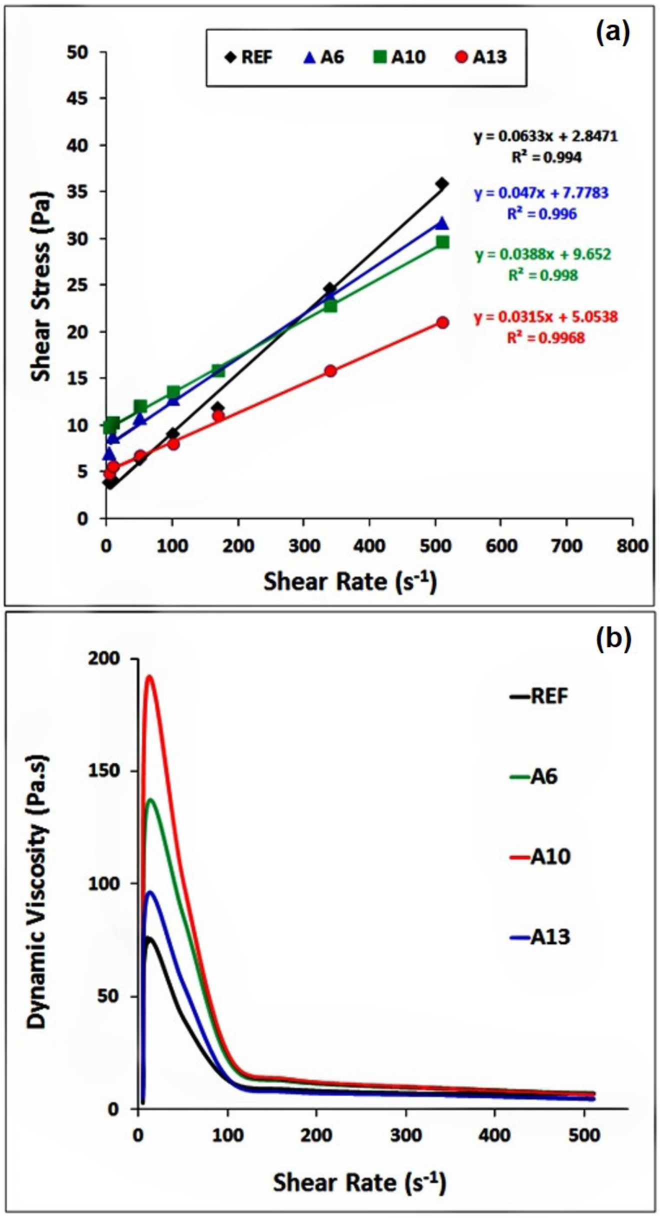

Fig. 4. (a) Flow curve and (b) Dynamic viscosity of SBR-modified slurries.

The flow curve findings indicate that all the slurries show a Pseudoplastic non-Newtonian flow behavior. After applying the Bingham model, one can notice that the REF slurry registered the lowest values of the dynamic viscosity and yield stress (see Fig. 4-a and 4-b) and the highest value of the plastic viscosity (see Fig. 5-a). The plastic viscosity registered 63.3, 47, 38.8 and 31.5 (Pa.s) for the slurries REF, A6, A10, and A13, respectively. All the studied SBR-modified slurries obtained lower plastic viscosity than the REF slurry (see Fig. 5-a). Two factors cause a declination of the plastic viscosity after adding SBR to cement slurries. They are: (i) The increasing possibility of interactions between SBR and water, sucking out the water necessary for the hydration process, and (ii) the demulsification of the SBR latex, which dislodge the polymer from the emulsion micelles, dispersing the polymer into the newly formed cement suspension. These macromolecules can cover the unhydrated cement particles disturbing the formation of the conventional cement hydration products leading to form a less viscous medium(HONGYAN; YE; ZONGJIN, 2011; OHAMA, 1998) leading to form a less viscous medium. Then, the diffused SBR particles start to control the rheological behavior until the end of the induction period.

On the other hand, the yield stress values registered a progressive increment by adding SBR to 10% of substitution. However, all the SBR-modified slurries had higher yield stress than the reference slurry and registered 2.85, 7.78, 9.65 and 5.05 (Pa) for the slurries REF, A6, A10, and A13, respectively (see Fig. 5-b). According to the Bingham model, the yield stress value is related to the plastic viscosity, and both are related to the slope of the adopted linear model. Thus, in the current case of SBR-modified cement system, the plastic viscosity reached lower values, leading to higher yield stress values.

Table 3 shows the Initial and final gel values before and after adding SBR latex to the cement slurries. The values of the initial gel registered a deflection of 8, 7, 8 and 5 units for the slurries REF, A6, A10 and A13, respectively, while the values of the final gel registered a deflection of 45, 58, 67 and 75 units for the slurries REF, A6, A10, and A13, respectively. The correlation Coefficient (R) between the initial and final gels registered -0.70, indicating a big gap between the result tendencies of both phenomena. This result indicates that by increasing the SBR content, in the current case, and after being demulsified and diffused into the system, the values of the final gel are significantly influenced and increased.

4. Conclusions

SBR latex influences the slump behavior and rheological parameters of the slurries. The free fluid content of the slurries is affected by the presence of the demulsified SBR with the high styrene content indicating some interactions with the water as proved by thermodynamics. Thus, the slump behavior is also affected by this phenomenon and the spreading diameter decreases by increasing the polymer content in an exponential way limiting the workability of the slurries. From the flow curve findings, one can conclude that all the SBR-modified slurries presented a Pseudoplastic non-Newtonian flow behavior and obtained lower plastic viscosity and higher yield stress values than the REF slurry. The macromolecules tend to disturb the hydration process after the demulsification happens by covering the unhydrated cement particles, and increase the final gel values up to 67%, as well.

Table 3. Initial and final gel values before and after the addition of SBR latex to the cement slurries.

Polymer content (%)	Initial gel (°)	Final gel (°)
REF	8.0 ± 0.6	45.0 ± 1.5
A3	7.0 ± 1.0	58.0 ± 2.0
A6	8.0 ± 1.5	67.0 ± 0.6
A10	5.0 ± 1.7	75.0 ± 2.1

References

ABOELKHEIR, M. et al. Influence of Styrene-Butadiene Co-Polymer on the Hydration Kinetics of SBR-Modified Well Cement Slurries. **Macromolecular Symposia,** v. 380, n. 1, p. 1800131, 1 ago. 2018.

ALLAN, M. L. Rheology of latex-modified grouts. **Cement and Concrete Research**, v. 27, n. 12, p. 1875–1884, 1 dez. 1997.

BARLUENGA, G.; HERNÁNDEZ-OLIVARES, F. SBR latex modified mortar rheology and mechanical behaviour. **Cement and Concrete Research**, v. 34, n. 3, p. 527–535, 1 mar. 2004.

BESSAIES-BEY, H. et al. Non-adsorbing polymers and yield stress of cement paste: Effect of depletion forces. **Cement and Concrete Research**, v. 111, p. 209–217, 1 set. 2018.

BUREAU, L. et al. Mechanical characterization of a styrene–butadiene modified mortar. **Materials Science and Engineering: A**, v. 308, n. 1, p. 233–240, 30 jun. 2001.

CHHABRA, R. P.; RICHARDSON, J. F. Chapter 1 - Non-Newtonian Fluid Behaviour. In: CHHABRA, R. P.; RICHARDSON, J. F. (Eds.). **Non-Newtonian Flow and Applied Rheology** (Second Edition). Oxford: Butterworth-Heinemann, 2008. p. 1–55.

CHOUGNET, A. et al. Rheological behaviour of cement and silica suspensions: Particle aggregation modelling. **Cement and Concrete Research**, v. 38, n. 11, p. 1297–1301, 1 nov. 2008.

GRAZIANO, G. Aliphatics vs. aromatics hydration thermodynamics. **Biophysical Chemistry**, v. 110, n.

3, p. 249–258, 1 ago. 2004.

GUILLOT, D. 4 **Rheology of Well Cement Slurries**. In: NELSON, E. B. (Ed.). Developments in Petroleum Science. Well Cementing. Elsevier, 1990. v. 28, p. 4–1.

HONGYAN, M.; YE, T.; ZONGJIN, L. Interactions between Organic and Inorganic Phases in PA- and PU/PA-Modified-Cement-Based Materials. **Journal of Materials in Civil Engineering**, v. 23, n. 10, p. 1412–1421, 1 out. 2011.

LARRARD, F. DE. **Concrete Mixture Proportioning: A Scientific Approach**. London: CRC Press, 1999.

OHAMA, Y. Polymer-based admixtures. **Cement and Concrete Composites**, v. 20, n. 2, p. 189–212, 1 jan. 1998.

PAIVA, M. D. M. et al. A geopolymer cementing system for oil wells subject to steam injection. **Journal of Petroleum Science and Engineering**, v. 169, p. 748–759, 1 out. 2018.

PENG, J. et al. Influence of superplasticizer on the rheology of fresh cement asphalt paste. **Case Studies in Construction Materials**, v. 3, p. 9–18, 1 dez. 2015.

SMITH, D. K. **Cementing**. 2th. ed. Nova York: Henry L. Doherty Memorial Fund of AIME, Society of Petroleum Engineers, 1990. v. 4 SPE monograph series.

TAYLOR, H. F. W. **Cement chemistry**. London: Thomas Telford Publishing, 1997.

UKRAINCZYK, N.; ROGINA, A. Styrene–butadiene latex modified calcium aluminate cement mortar. **Cement and Concrete Composites**, v. 41, p. 16–23, 1 ago. 2013.