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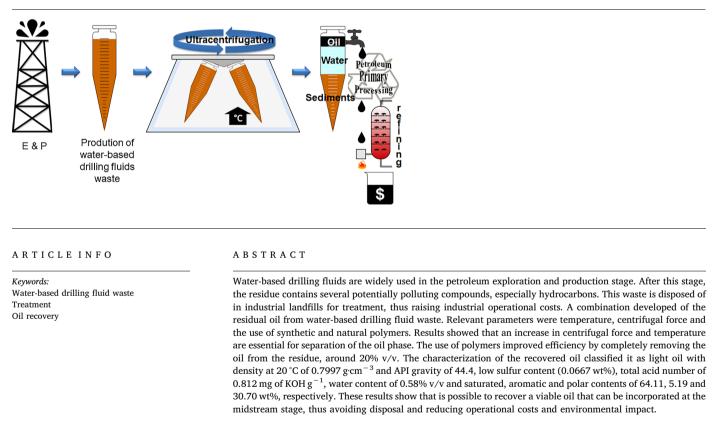
Oil recovery from water-based drilling fluid waste

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G R A P H I C A L A B S T R A C T



1. Introduction

Drilling fluids are complex homogeneous mixtures, chemically stable, of natural or synthetic compounds used in the petroleum exploration and production (E & P) stage [1]. These are classified according to their base, which may be aqueous (usually fresh or salt water), oily (generally water-in-oil type emulsions), synthetic (composed of esters, poly alpha olefins and acetates) or pneumatic fluids,

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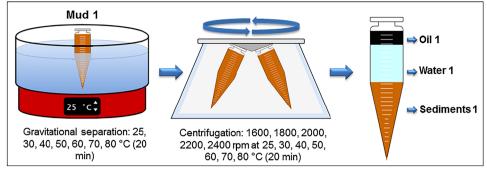


Fig. 1. Oil separation process of Mud 1 by the physical method.

which can be based on air, gas or foam [1]. They are responsible for carrying the perforated rock fragments to the surface and keeping those fragments suspended when circulation is interrupted. Furthermore, they work in several ways: in the cooling and lubrification of drills, reducing corrosion, hydraulically supporting the well walls and maintaining the optimum density levels, and avoiding the disorderly movement of oil and gas to the surface, among others [2].

Nowadays, water-based drilling fluids are widely used (approximately 80% of drillings) due to low cost and biodegradability [3]. In these fluids substances such as polymers (carboxymethylcellulose), clays (bentonites) and salts are incorporated, composing a solid/liquid system, with the purpose of improving the function [1].

Drilling fluids are circulated from the well to the platform several times during the drilling an oil well. As a result, the residue has several compounds potentially pollutants, being especially contaminated by hydrocarbons from the oil reservoir [4]. The *Associação Brasileira de Normas Técnicas* identifies it as Class 1 waste (dangerous) by NBR 10,004 (2004) because it has high toxicity, corrosivity and reactivity [5].

The Petrobras sustainability report (2016) reported that 132,000 tonnes of solid waste were generated in 2016, with 28,000 tonnes corresponding to contaminated drilling fluids and cuttings, commonly called oily residues or drilling mud wastes [6].

Usually, petroleum industries dispose of drilling waste mud by reinjecting it into the well or placing it into industrial landfills for later treatment; a lower cost final destination. However, factors such as assessing the groundwater contamination risk, knowledge of the chemical composition and waste reactivity should be considerated to determine the environmental risk [7,8]. Waste treatments are carried out by physical and chemical methods, such as heat treatment [7], chemical stabilisation and solidification [9], solid–liquid separation using cationic flocculants [10], the use of supercritical carbon dioxide [3] and use of microorganisms to remove or destroy the contaminants [11].

However, the study of physical methods such as gravitational sedimentation and centrifugation, and low-cost chemical methods (using natural and synthetic polymers), which aim mainly at the separation of the oil associated to the waste, have become interesting, in view of the amount of waste generated. Furthermore, to verify the oil evaluation in the E & P stage, usually the characterization of physicochemical properties is carried out, highlighting the water content, density, API gravity, pour point, viscosity, total acid number (TAN), total sulfur content and saturated, aromatic and polar (SAP) content [12,13]. Such properties are relevant in defining the oil quality and enabling its incorporation into production stage, minimising the environmental impact caused by hydrocarbons. In this regard, the present work has as its objective the study of physical and chemical methods for the waste treatment of water-based drilling fluids, aiming at oil reuse.

2. Methodology

For the study, a sample of water-based drilling fluid waste

designated as Mud 1 from E & P activities was used.

Two samples of natural polymers were tested, designated as Polymer A (a solid vegetal extract obtained from the bark of black wattle (*Acacia mearnsii de Wild*), provided by the company TANAC S. A.), and Polymer B (a product based on the extract obtained from black wattle with 5% limonene extracted from orange peel), together with a synthetic polymer designated as Polymer C (a commercial demulsifier containing surfactants based on polyethylene oxide and polypropylene oxide copolymers (PEO–PPO) with different molar ratios of EO/PO). For addition to Mud 1 an aqueous solution of each polymer was made (50% w/v).

2.1. Rheological behaviour of the water-based drilling fluid waste

To evaluate the rheological properties of Mud 1 (dynamic viscosity, shear stress and shear rate) the sample was analysed on a rotational rheometer (Anton Paar – Rheolab QC model), with a Couette geometry (CC27) coupled to a thermostatic bath (Julabo – F25-MC model), according to ASTM D4402 [14]. Generated data were recorded in Rheoplus V 2.66. In total, 100 measurements of dynamic viscosity with shear rates ranging from 100 to 600 s^{-1} at temperatures of 50, 60, 70 and 80 °C were collected. The mean of the 100 measured values was reported as the sample dynamic viscosity.

2.2. Physical method

2.2.1. Oil/water/sediment separation of Mud 1

The physical process of oil separation from Mud 1 is shown in Fig. 1. To separate oil, water and sediments from the waste, physical tests were performed at 25, 30, 40, 50, 60, 70 and 80 °C. For this, 25 mL of sample was placed in an oil centrifuge tube. After 20 min, the separated oil/ water/sediment volumes were recorded. The samples were naturally cooled to 25 °C and then centrifuged for 20 min using each of the following rotations: 1600, 1800, 2000, 2200 and 2400 rpm at the same temperatures as above. The oil phase, designated as Oil 1, was separated for physicochemical characterization: water content, density, API gravity, dynamic and kinematic viscosity, TAN, total sulfur content, pour point and SAP content. In addition, the characterization of the water phase (Water 1) was analysed in terms of pH, conductivity, total chlorides, turbidity, and total, fixed and volatile solids, and the sediments phase (Sediment 1) was analysed in terms of total, fixed and volatile solids. X-ray diffraction and fluorescence analyses of the fixed solids obtained from the water and sediment samples were performed.

2.3. Chemical method

2.3.1. Oil/water/sediment separation of Mud 1 using natural and synthetic polymers

The chemical process of oil separation from Mud 1 is shown in Fig. 2. For the chemical tests the same oil/water/sediment separation procedure was carried out (Section 2.2.1.). However, to each sample

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