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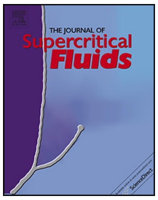

Removal of contaminants from polluted drilling mud using supercritical carbon dioxide extraction

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ABSTRACT

Liquid drilling fluid is often called drilling mud is heavy, viscous fluid mixtures use to carry rock cuttings to the surface and lubricate and cool the drill bit. During carrying cuttings they contaminated which not only reduce their functionality but also make them a hazardous and dangerous wastes which cannot be discharged anywhere without treatment. Due to this fact, in the present study, supercritical extraction process was used to remove contaminants from the drilling mud. Regarding this, effect of different parameters including extraction temperature (313–338 K) and pressure (100–200 bar), flow rate of CO_2 (0.05–0.36 cm^3/s) and static time (20–130 min) on the removal of contaminations from drilling mud was examined using the design of experiment of changing one factor at a time. The obtained results revealed that the optimum operational conditions that lead to the highest removal degree of contaminations are temperature and pressure of 333 K and 180 bar, respectively, flow rate of lower than 0.1 cm^3/s and the static time of 110 min. In addition, to examine the effect of the supercritical extraction on the crystalline structure modification and removal contaminations X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses were performed which confirmed the successful removal of contaminations from the drilling mud without significant crystalline modification.

1. Introduction

Drilling fluid – mud – is usually a mixture of water, clay, and a few chemicals. Sometimes, oil may be used instead of water, or oil added to water to give mud certain desirable properties. World oil's annual classification of fluid systems lists different categories of drilling fluids, including fresh-water systems, salt-water systems, oil-or synthetic-based systems, pneumatic (air, mist, foam, gas) "fluid" systems [1–3].

Among the above drilling fluid categories, water-based fluids (WBFs) are the most widely used systems which are less expensive than oil-based fluids (OBFs) or synthetic-based fluids (SBFs). Water-based fluids (WBFs) are used to drill approximately 80% of all wells [4]. The base fluid may consist of fresh water, seawater, brine, saturated brine, or formation brine. The type of selected fluid depends on the anticipated well conditions or on the specific interval of the well being drilled [5,6].

Regardless of drilling mud categories, drilling fluids are used to raise the cuttings made by the bit and to lift them to the surface for disposal. In other words, as the drill bit grinds the rocks into drill cuttings, these cuttings will be entrained in the mud flow and then carried to the surface. In order to return the mud to the recirculation mud system and to make contaminations easier to handle, contaminations must be separated from the mud. In more details, from 1993 discharges of cuttings containing more than 1% oil were prohibited in several regions due to environmental reasons. For some period, oil-based fluid was common to be replaced by organic fluids such as esters, ethers and olefins, but the operational discharges of cuttings with residues of oil or synthetic base fluids ceased it around 1995. In practice, operational discharges in drilling mud only take place by using water-based drilling fluid. All cuttings which contain oil exceeding one percent by weight must either be re-injected or taken ashore for treatment. Generally, there are several kinds of compounds in the contaminated drilling mud which make it a dangerous waste in the case of being released into the environment without any purification and treatment [7,8].

During the past years, several treating processes have been proposed such as steam stripping, dehalogenation, chemical reduction/oxidation, ultraviolet (UV) oxidation and etc. [2,9,10]. Although these kinds of processes are efficient to some extent, all

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these techniques suffer from safety, complexity or high-energy use problems [11]. On the other hand, one of the consequences of the treatment of these wastes is the generation of residual solids or concentrated brines that are separated from the treated water. In some cases, these residual wastes consisted of high concentrations of salts and metals that are themselves landfilled, or sent for underground injection. Unfortunately, the disposal of residual waste in landfills raises the concern that landfill personnel and environmental quality may be at risk. In this regard, to overcome the limitations of current drilling waste treatment and disposal options, alternative technologies are being investigated for the treatment of oil-contaminated drill cuttings which are not only energy consuming but also are green and environmentally benign. In general, it has been reported that there are several kinds of contaminates can occupy the active sites of the drilling mud such as sulfur, chlorine and hydrocarbons mostly with carbon number of C_{10}–C_{28} [11]. In this regard, several authors have been tried to find if supercritical carbon dioxide is able to remove these contaminants from the polluted drilling mud [11–13]. For example, Goodarznia and Esmaeilzadeh [11] have been reported that using SC-CO_2 by changing the temperature and pressure in the range of 328–352.5 K and 160–220 bar respectively, leads to removal of 22.4% contaminant from the polluted drilling mud.

One of the most widely used and studied new techniques for the removal of pollutions from the contaminated matrixes are supercritical fluid based technologies. Supercritical fluids have several desirable properties that make them attractive for certain separation processes, e.g. the product is not contaminated with residual solvent [14–24]. The supercritical fluid extraction (SFE) processes used are environmentally friendly, inert, cheap and are widely available. Supercritical carbon dioxide (SC-CO_2) exhibits excellent solvating characteristics which are easily manipulated to dissolve non-polar compounds like diesel and mineral oils. In details, using supercritical fluids such as carbon dioxide (CO_2) overcomes many drawbacks in connection with the use of liquid organic solvents like liquid hexane. The commonly used solvents undergo the problems of toxicity and residual content after extraction. In addition to toxicity, there is also the dander of security during storage due to flammability [17]. In this context, using SC-CO_2 enjoys many advantages: it is nontoxic, inflammable and CO_2 separation is easily done by a simple depressurization. The other crucial point is that after the processes are finished (remediation, cleaning and removal of contaminates from the polluted matrixes), there is no residual organic solvent trace in the final products.

Among the many investigations conducted using SC-CO_2 for removal of contaminants from the dense matrixes, one can pointed out to cleaning of deactivated catalysts using supercritical carbon dioxide extraction (SCE) [25,26]. In details, Rajaei and his coworkers [25,26] used supercritical carbon dioxide extraction process to remove contaminations and pollutants from R-134 catalyst and Tonsil CO 610 G clay soil which found it successful to remove contaminants from polluted catalysts and regenerate them.

Furthermore, Chen et al. [27] studied the removal of polychlorinated biphenyl (PCB) from soils in a laboratory scale using supercritical fluid extraction (SFE) unit to provide information for soil remediation. The results demonstrated the effectiveness of SFE as a promising technology for the clean-up of PCB contaminated soils/sediments. They have been reported that after 30 min of extraction at 313 K and 100 bar, more than 86% of PCBs in real world Hudson River sediment and 92% in St. Lawrence River sediment were removed.

Based on the best knowledge of the authors, there are a few investigations on the removal of contaminants from the polluted drilling mud performed by co-authors [11] represented possibility of removing contaminants from the polluted drilling mud using supercritical carbon dioxide extraction process.

In this regard, the potential of supercritical carbon dioxide to extract contaminants from drilling mud was investigated by changing extraction pressure from 100 bar to 200 bar, extraction temperature from 313 K to 338 K, flow rate from 0.05 cm^3/s to 0.36 cm^3/s and static time from 20 to 130 min. Finally, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis were performed for more reliable conclusion on the feasibility of supercritical carbon dioxide to remove contaminants from the polluted drilling mud considering the crystalline and morphology modification.

2. Experimental

2.1. Experimental procedure

The used extraction apparatus was designed for maximum pressure and temperature of 400 bar and 373.15 K, respectively (see Fig. 1). The used procedure during this investigation was as follow in brief. Carbon dioxide supplied from a gas cylinder was liquefied through a cooling unit. Then, liquid carbon dioxide was compressed by a high-pressure air driven oil-free reciprocating pump (Haskel, USA). The liquefied high pressure carbon dioxide was dispatched into a surge vessel to dampen the pressure fluctuations generated by the operation of the pump. At the outlet of the surge tank, a bourdon gauge in the range of 0–400 bar by a division of 1 bar was placed to monitor the pressure of the system easily. Then, the pressurized supercritical carbon dioxide entered into the equilibrium cell (180 cm^3). The surge tank and the extraction vessel were surrounded by a regulating hot water jacket to set the temperature of system up to373.15 K. The extraction temperature could be sensed easily by a PT-100 thermocouple with precision of 1 K which controls the temperature of the system using a PID control protocol. The point worthy of mentioning is that during the experiments, the extraction pressure and temperature were held constant in the range of 3% of instrumental full scale by the continuous monitoring of the system operational conditions.

The contaminated drilling mud (about 147 g) which was packed by glass beads and glass wool in a stainless steel basket was placed in the extraction vessel for further processing. The glass beads were used to increase the surface area between the contaminated drilling mud particles and the SCF. Also, the wool glass was used to prevent carrying out the mud particles over the SCF flow. The basket was then placed into an extraction vessel and held in the desired conditions. In this procedure, the difference between the initial and final weight of the V-separator was the amount of the extracted contaminations from the drilling mud. The point must be mentioned is that the extracted contaminants were weighed after 24 h period which the V-separator was heated up to313 K. This heating up was performed to eliminate any possible presence of carbon dioxide and water in the extracted contaminants which may leads to errors in the calculations of extracted contaminants.

In other words, before and after finishing the extraction process, the V-separator was weighted and the difference between the initial and final mass of the V-separator was considered as the amount of the extracted contamination. The mass of extracted contaminations was determined to be 0.1 mg using a Sartorius BA110S Basic series balance. The typical mass of solute for each experiment was greater than 50 mg, giving a potential error due to weighing of 0.2% wt. Finally, the vented carbon dioxide is passed through a wet test meter.

2.2. Materials

Drilling mud from Nar gas field in the neighborhood of Kangan oil field, Jam, Iran was kindly supplied from South Zagros Oil &