WETTABILITY AND PREDICTION OF OIL RECOVERY FROM RESERVOIRS DEVELOPED WITH MODERN DRILLING AND COMPLETION FLUIDS

Semiannual Report

1 October 2001 through March 31, 2002

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June 2002

DE-FC26-01BC15164

Submitted by:

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Project Objectives

The objectives of this project are:

(1) to improve understanding of the wettability alteration of mixed-wet rocks that results from contact with the components of synthetic oil-based drilling and completion fluids formulated to meet the needs of arctic drilling;

(2) to investigate cleaning methods to reverse the wettability alteration of mixed-wet cores caused by contact with these SBM components; and

(3) to develop new approaches to restoration of wetting that will permit the use of cores drilled with SBM formulations for valid studies of reservoir properties.

Abstract

This first semiannual report covers efforts to select the materials that will be used in this project. Discussions of crude oils, rocks, smooth mineral surfaces, and drilling mud additives are included in this report.

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Review of Potential Wetting Effects of Synthetic Oil-Based Muds

Surfactants in porous media

The oil industry has experience with surfactants in a variety of applications. Processes developed and tested for enhanced oil recovery suffered from surfactant loss as the additives intended to reduce interfacial tension or to stabilize foams were adsorbed onto rock surfaces. Similar phenomena can occur when surfactants, included in drilling fluids to serve a wide variety of functions, encounter mineral surfaces in the reservoir, in the pores of cuttings, and in cores recovered during the drilling process. In the reservoir, the concentration of surface active material is likely minimized by filtration through the filter cake. Cuttings are exposed to the full strength drilling fluid, less material that has adsorbed onto solids in the mud itself. Cores may experience levels of surfactants between these two extremes; the exact levels of surface-active material that invade cores may be difficult to predict or to duplicate precisely in laboratory studies. An alternative is to examine a range of concentrations spanning the maximum to minimum expected values.

How exposure to surfactants will affect the wetting condition in cores is not obvious. In most cases, existing wetting is mixed, with a pattern of more and less water-wet surfaces that depend on the placement of water and oil in the pore space: more water-wet in corners and in the smallest pores, less water-wet or even oil-wet in larger pores (Salathiel, 1973; Morrow, 1990). Crude oil components are adsorbed or otherwise deposited on mineral surfaces to make those surfaces, in most cases, less water-wet than they would have been originally (Anderson, 1986; Buckley, 2001; Buckley and Lord, 2002). How tightly they are bound to the surface varies from case to case. The impact of surfactants from the drilling fluid might range from no effect to wettability reversal from water-wet to oil-wet or even wettability reversal from oil-wet to water-wet. The core would become more oil-wet if surfactants adsorbed in the water-wet small pores and corners. Replacement of weakly bound oil components with more strongly adsorbed surfactants is possible. Specific circumstances where surfactants make surfaces more water-wet, either by removing adsorbed oil components through formation of ion pairs or by adsorbing over oil components, increasing the hydrophilicity of the exposed outer layer of adsorbed material have been demonstrated to occur in chalk (Standnes and Austad, 2000).

Components of SBM with potential to affect wettability

Synthetic oil-based muds have been developed mainly to solve environmental problems. The work reported in the literature on their formulation and testing is primarily intended to show that they fulfill all the normal drilling and completion requirements while at the same time reducing adverse environmental impact. Wettability issues are not considered in these evaluations beyond maintaining oil-wet conditions for cuttings transport. The potential for damage to well productivity due to creation of more oil-wet conditions near the wellbore is a problem that has received little attention. The work on OBM wetting effects suggests that wettability problems can be expected in cores recovered with SBM. The extent of damage and potential for wettability restoration in either cores or in the near wellbore region are the focus of this project.

Base oil

The base fluids now in use include a wide variety of synthetic oleic materials (Friedheim and Conn, 1996; Patel, 1998). Aromatic compounds are rigorously excluded because of their biotoxicity. In general, low temperature viscosities are higher for SBM than traditional OBM, but there is also a greater decrease in viscosity with increasing temperature. At reservoir temperatures the new and old formulations are more comparable. Pour points of the SBM base oils are generally lower than those used in traditional OBM formulations—an important consideration in arctic and sea-floor conditions. Flash points are higher—an important safety consideration. Some of these materials can act as destabilizing agents for asphaltenes, which would have implications for wettability alteration, although no consideration about the potential for asphaltene destabilization appears in published evaluations of SBM base muds.

Some synthetic base oils

Esters have been favored from the standpoint of biodegradation, but the same ester linkage that promotes biological breakdown lacks needed stability, especially at elevated pH and temperature (Patel, 1999) and the byproducts (fatty acids and alcohols) may be more toxic than the original ester. Other oxygenated base oils used are ethers and acetals. Olefins, e.g., linear alpha-olefins (LAO), internal olefins (IO), and poly-alpha-olefins (PAO), are more stable, but still have greater rates of biodegradation and lower viscosities than their saturated analogs.

Asphaltene stability

Asphaltenes are the material in crude oils that is insoluble in low molecular weight paraffins. As oil from the formation mixes with the drilling fluid, the potential exists for asphaltenes to be destabilized. When that happens, the asphaltenes exhibit an increased tendency to adsorb on mineral surfaces and to alter their wetting properties (Al-Maamari and Buckley, 2000). While the stability of asphaltenes as a function of oil composition has been studied for alkanes (Buckley and Wang, 2002), little is known about stability or instability in the synthetic base oils now being used in drilling fluids.

Surfactants

With the development of synthetic base oils has come new surfactants and surfactant mixtures. Fewer chemical details are available about the surfactant packages, as the identity of the surfactants used is usually considered to be proprietary. However, it is possible to learn generally about the families of compounds in use.

Drilling mud studies inevitably face problems because of the complexity of the whole mud. Filtrate compositions are highly dependent on the filtration process. For systematic studies, representative surfactants at known concentrations are preferable to complex mixtures. For surfactants that form micelles, interactions with surfaces can be quite different above and below the CMC. Mixtures of surfactants introduce additional complexity. Relating the results of systematic studies to more realistic mud conditions is a significant problem.

The surface active materials likely to occur in an SBM formulation include the primary emulsifiers and oil-wetting agents, as well as additives that might be used to modify low-shear rate rheology, and the surfactants used to make fluid loss materials oil-wet.

An empirical scale, known as the hydrophile-lipophile balance or HLB, developed to assist in emulsion formulation, is often used to rank surfactants. Lower numbers (less than 9) indicate greater hydrophobicity; higher numbers (greater than 11) are assigned to surfactants with greater hydrophilicity. Surfactants that stabilize water-in-oil emulsions with crude oils rank about six or less on the HLB scale. Lipophilic surfactants between an HLB of 6 and 10 are referred to as wetting agents. Information about chemical structures and HLB requirements can be combined to make reasonable estimates of surfactant species that might be representative of components in drilling fluids.

Fatty acids and alcohols

Whether a fatty acid is classified as an emulsifier or a wetting agent depends on the length of the hydrocarbon chain, which affects the behavior of these and related compounds at interfaces (oil/air, oil/water, oil/solid). The calcium salts of fatty acids are made by mixing the acid with lime (CaO) in the base oil. Oleic acid, an unsaturated fatty acid, has been used to form dimers or trimers to adjust the low-shear viscosity of drilling fluids (ref). Saturated and unsaturated fatty acids are readily available in a range of molecular weights. As acids, the fatty acids themselves should interact most strongly with carbonate minerals. Their impact on clean sandstones should be less than in limestone, dolomite, or chalk cores unless carbonate cements are significant. If cationic crude oil components are adsorbed, however, there is the possibility that fatty acids, especially in their ionized form, might form ion-pairs with the adsorbed species, removing them from the surface.

Derivatives of fatty acid are sometimes added as viscosifiers. These might be related to 12 hydroxystearic acid which can form a gel in mineral or synthetic oil. Either the monomer or polymer might exhibit surface activity.

Alcohols, which can partition between oil and water, have some interfacial activity as well.

Amines and other nitrogen compounds

Amines are likely to adsorb on silicate mineral surfaces, and are used as wetting agents for that reason. Clays are treated with amines to enhance their dispersal in the base oil to increase the oil phase viscosity; some free amine might occur if the clay coating material is removed from the clay, although this is unlikely to be as large a source of surface-active material as the emulsifiers and wetting agents themselves. Primary amine analogs of the fatty acids are available up to about C_{18}, as are a wide variety of secondary and tertiary amines.

Another potential source of amines is the amine-treated lignite used to control fluid loss. Like the clays, this is likely a minor source of amines, compared to the primary and secondary emulsifiers.

In addition to the amines, there are polyamines and amides used as emulsifiers. Sources of these chemicals are still being sought. Derivatives of imidazolines are also used as emulsifiers. Members of this class of compounds are also used as corrosion inhibitors because of their ability to adsorb on and protect steel surfaces. Adsorption on mineral surfaces must also be considered.

Asphalt derivatives

Asphaltic material from the heavy ends of a crude oil is sometimes used as a viscosifier. In crude oils, these are among the materials that adsorb on mineral surfaces and alter wetting, especially near the onset of asphaltene instability. Although they are poorly defined and may vary significantly from one source to another, they are interfacially active and should be included in the overall consideration of potential effects of drilling mud components on wetting.

Other materials

Samples of crude oils, rock, and smooth mineral surfaces are under consideration for use in the next stages of this project. A meeting of the two institutions involved was held in Socorro on 20 May, 2002. A barrel of asphaltic crude oil from the Minnelusa formation has been acquired. Other oil samples will be selected from supplies on hand. Testing for wetting alteration will begin with mica as the model mineral surface and Berea as the standard sandstone.

Future work

This report summarizes the first stages of this study in which we are identifying materials with which we will be working. A table that identifies materials by their chemical types and applications has been started to facilitate identification of those materials from trade names. Note that we are not proposing to work with these specific materials. Rather this list is being assembled for informational purposes. The current version, to which we will be adding as the project proceeds, is appended to this report.

Surfactants of known structure (fatty acids, amines, etc.) are being ordered. Baseline testing with selected crude oils is underway.

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Appendix - Summary of surfactant groups

Use	Class	Example / def	Comment	Typical concentration	Reference
Surfactant	terpene-derived	Barascrub	Flash point:115 F		
Emulsifiers	fatty acids C16-C18		HLB = 6	Concentration in drilling mud: 9.0-14.0 lbs/bbl--25.7-39.9 kg/m3	
		Omni-Tec	synthetic blend	4-8 lb/bbl	
		Le Mul	Fatty acid blend in synthetic carrier fluid	6-10lb/bbl (in SBF)	
	polyaminated fatty acids	Ez Mul NTE	in ester carrier fluid	6-12 lb/bbl	
		Le Supermul	in synthetic carrier fluid	2-4 lb/bbl	
		Novamul	Primary emul/ with solvent blend	6-10lb/bbl (in SBF)	
	imidazoline	2-phenyl-2-imidazoline	thermal stability		
	amide	R-C(=O)NH2	thermal stability		
	polyamide	Omni-Mul	synthetic blend	8-16 lb/bbl	
		Wellguard 1252	invert mud secondary emulsifier		
		Wellguard 1252HF	invert mud secondary emulsifier for drilling fluids that require high flash point components		
		Wellguard 1252HFD	invert mud secondary emulsifier for drilling fluids that require high flash point components		
	modified polyamide	Wellguard 1764A	invert mud secondary emulsifier that can be used without primary emulsifiers		
		Wellguard 4060	invert mud secondary emulsifier for high emulsification and improved oil wettability of drilling solids		
	polyamides and modified fatty acids	Wellguard 1899	invert mud secondary emulsifier that is often used with primary emulsifiers		
		Wellguard 4042	invert mud primary emulsifier for olefin synthetic muds		
	superamides, and dtaa (diethylene triethylene), and amido-amines	alkanolamides with 18-22 C atoms	fatty acid esters (from vegetable triglycerides) transamidified to make alkanolamides with 18-22 C atoms		

Use	Class	Example / def	Comment	Typical concentration	Reference
Emulsifiers (cont.)	poly-α- olefin mud	CH3-(CH2)n-C ((CH2)p-CH3) =CH-(CH2)m-CH3		5.0 lbs/bbl --14 kgs/m3	
	polyolefin	Omni-Coat	sulfonate blend, good at high temperature		
	sulfonated amido-amine	EMUL-II	secondary oil mud emul, blended with oil wetting agent	1 to 4ppb	
	phospholipids and amino-amines	Wellguard 4093	all-in-one invert mud emulsifier blend for high-weight muds exposed to high temperatures		
	nonionic phenol ethylene oxide	Surf-Act	liquid, high temperature	active C 60%, 25 to 100 gal of surfa per 100bbl of mud	
	oxidized natural oils	Wellguard 4	invert mud primary emulsifier and wetting agent		
		Wellguard 3088	primary emulsifier that improves oil wettability of drilling solids		
		Wellguard 4057	invert mud primary emulsifier for fluid loss control of ester synthetic muds systems		
	oxidized and modified natural oils	Wellguard 2053	invert mud primary emulsifier for fluid loss control		
	oxidized natural oils and fatty acids, modified amido-amines	Wellguard 3087	invert mud primary emulsifier for a wide range of invert drilling fluids		
oil wetting agents	fatty acids	mostly oleic and linoleic acid			
	Ca salts of ddbsa (dodecylbenzene sulfonic acid)		HLB= 4-5		
	imidazoline	Novawet		1-2 lb/bbl (in SBF)	
oil mud thinner	Fatty acid blend	Novathin		0.5-2 lb/bbl (in SBF)	
	petroleum	alkyl benzene sulfonates			
	lecithin				
	hydrocarbon resins	OFLC-400	used to reduce the filtrate and seepage losses to aid in wellbore stability for oil based invert drilling muds.	2.0 to 10.0 ppb	