IMPROVING CEMENT BOND WITH A FORMULATED SILICATE PREFLUSH

Michael McDonald
PQ Corporation

ABSTRACT

A high quality cement bond between casing and wellbore is an environmental and economic imperative for the duration of a well. A strong cement bond provides zonal isolation and prevents gas migration, gas entrapment and excessive water production. The growing public concern about possible gas migration to fresh water or to the atmosphere has further highlighted the importance of achieving the best possible cement bond.

A chemical preflush prior to primary cementing is an inexpensive and effective method to help ensure a quality primary cement job. Ideally, the chemical preflush should be multi-functional and not only remove drilling fluid residue but also provide other features such as: improve fluid loss control, improve water wetting of surfaces prior to cementing, and prevent or aid in the prevention of cement fallback. To achieve all these features, it is common practice to run a sequence or blend of chemicals to adequately prepare the wellbore for cementing. This paper discusses a single-component product built on sodium silicate that can provide all of the aforementioned benefits. Specific focus is directed towards the interactions between surfactants and sodium silicate in a flush.

INTRODUCTION

The necessary steps for successful primary cementing are well established and have not significantly changed over the decades[1]. A key first step is the proper displacement of the drilling fluid. Chemical flushes play a major role in the proper displacement of a drilling fluid. Along with displacing the drilling fluid, the chemical flush should also provide;

-good filter cake removal
-fluid loss control
-water wetting surfaces
-minimal waste for disposal

Several different classes of chemicals are regularly used in flushes. Major classes of chemicals include; solvents, anionic surfactants, polymers, clays, phosphates and sodium silicate. Selection of the correct chemical additive is based on numerous factors including;

-downhole temperature
-type of drilling fluid, oil-based vs. water based
-volume of spacer used to apply the preflush treatment
-desired rheology
-salt vs. fresh water
-environmental considerations
-probability of loss circulation

The chemistry, application and benefits of sodium silicate flushes have been well documented by numerous service companies. Sodium silicate flushes are effective for wells drilled with water-based drilling fluid. Sodium silicate can also be used in wells drilled with oil-based drilling fluids but usually follow flushes of solvent and surfactant. By pumping a sodium silicate-based flush prior to primary cementing, the wellbore and casing are coated with soluble silica. As the cement slurry comes into contact with the silicate coated surfaces, it rapidly develops gel strength and thus providing the following known benefits:

- -controls downhole fluid loss
- -prevents lost circulation and slurry migration
- -prevents slurry fallback
- -improves cement bonding

SELECTION OF SODIUM SILICATE

The manufacturing of sodium silicate closely resembles the manufacture of other types of commercial and industrial glasses. High purity sand (SiO2) is fused with sodium carbonate (Na2CO3) at 1100-1200°C. By fusing enough alkali onto the sand the resulting glass can be solubilized with steam to produce a clear, slightly viscous solution sometimes referred to as “water-glass”.

The key parameter that determines the chemical properties, reactivity and solubility of soluble silicate solutions is the weight ratio of SiO2:Na2O. The commercially available range of SiO2:Na2O ratios is 1.0 to 3.2. Chemical and physical properties of sodium silicate are primarily determined by ratio. At a molecular level, ratio controls the size and shape of negatively charged silica molecules. Higher ratios will contain proportionately greater levels of condensed, complex species with higher molecular weights. Low ratio silicates contain significant levels of low molecular weight chains and cyclics as well as free monosilicate. These changes in silicate speciation will impact flush properties.

When selecting a base sodium silicate, the two ends of the SiO2:Na2O spectrum offer unique advantages. The high ratio, 3.2 ratio liquid sodium silicate, has been the product of choice as a flush additive. The siliceous nature of the high ratio product favors quick reaction and deposition of silica on the wellbore and casing (assuming oil has been removed). This ratio favors the traditional properties associated with sodium silicate flushes; fluid loss control, loss circulation prevention and slurry fallback. The advantages associated with low ratio sodium silicate is tied to the higher levels of alkalinity which provides greater wetting, emulsification and dispersion of oil-based residue.

The other main consideration was formulated on a liquid or powder sodium silicate. Industry feedback indicated that a powder was the preferred form for a formulated product. The preference for a powder product was most noticeable in regions with subzero temperatures but also favors any regions where it is more difficult or costly to deliver liquid products. As a dissolved glass[2], alkali silicates do not have the same physical properties of a dissolved salt and therefore do not have the same level of aqueous freeze point depression.

Field requirements dictate that any dry product be readily mixable using cold water. The solubility of various powdered sodium silicates are determined by the following characteristics:

-SiO_2: Na_2O ratio
- the hydration level
- particle size distribution, fine powder or granular.

A hydrated silicate dissolves much faster than the corresponding anhydrous glass of the same ratio of SiO_2 to Na_2O. As a rule, the hydration factor outweighs all other aspects that determine dissolution rate. Next in importance is ratio, the lower ratio products exhibiting quicker dissolution because of the increased alkalinity.

In reviewing all of the various desirable characteristics for a single component flush, a granular, hydrated, low ratio sodium silicate was chosen as the base product.

SURFACTANT SELECTION & DOSAGE

Anionic surfactants are the primary class of surfactants used in flushes. These surfactants remove oil-based residue but require large volumes and turbulent flow. Standard surfactant solutions can only solubilize a small amount of oil[3]. The blending of sodium silicate with anionic surfactants provides an environment that optimizes surfactant efficiency while reducing surfactant consumption. This synergy is well known in the detergent industry where sodium silicate has a long history as a builder[4].

Hardness (Ca+2, Mg+2) can complex with anionic surfactants making them less reactive or unstable. The silica anions minimizes these unwanted charges by sequestering the metals via a precipitation reaction. The silica anion also competes for active, positively-charged sites on the casing[4] and wellbore[5] thereby reversing their surface charge and repelling surfactants.

Surfactant efficiency is increased by the sodium silicate acting as pH buffer and keeping the pH at a high and constant level during the flush process (i.e. similar to the pH of the cement used). The combination of soluble silica and alkali reduces the interfacial tension between oil and water. Silicate ions are very hydrophilic and help promote partition between the oil and water phases. This translates into higher performance from the surfactants and oil-based residue is more easily removed. This also contributes to the wetting action.

Anionic surfactants remained the primary class of surfactants/co-surfactants that would be formulated with the base sodium silicate. Several surfactants were considered for blending. List of candidate surfactants was narrowed based on the following criteria;

-cost
-potential wet-ability alteration
-temperature stability
-efficiency
-environmental performance

Given that sodium silicate is an environmentally friendly product it followed that any surfactants used in conjunction with sodium silicate in this application should likewise have good environmental performance. This consideration was also important given the trend to disclose chemical compositions and in order to meet increasing environmental regulations.

SOLVENT SELECTION

Displacement efficiency is enhanced by reducing the ratio of the viscosities of the oil-based residue and the flush . The solvent further reduces the oil /fluid interfacial tension. Aromatic solvents such as xylene are highly effective at “cutting” oil-based drilling fluids. The disadvantages of such solvents include; cost , flammability and toxicity. Safer and less toxic alternatives are terpene-based solvents. The chief disadvantage associated with these natural products is cost. A small amount of a terpene-based solvent was blended into the granular silicate to further enhance the removal of oil-mud residue.

EXPERIMENTAL MATERIALS & PROCEDURES

A wide range of oil-based drilling fluids were obtained from different drill sites. These mud samples were supplied by several different service companies. This allowed surfactant screening and efficacy testing to be conducted on a broad cross section of base-oils, emulsifiers, mud weights and drill solid levels.

Standard dosage of flush material was set at 50 lbs per barrel. This dosage represented an easy concentration to work with in the field. Once dissolved, the single component silicate system would yield a concentration within the range of liquid sodium silicate currently used in a flush. Surfactant loading from the formulated silicate would be ~5 to 10 x’s less than the surfactant concentration used in a anionic flush. Viscosity of the dissolved system was less than 5 centipoises at room temperature. This low viscosity would allow the flush to go into turbulent flow at low pump rates.

Lab testing focused on 3 areas, cleaning efficiency, volume efficiency and water wetting.
The efficiency of a single component product was compared against surfactant(s) without silicate and sodium silicate without surfactants. Cleaning efficiency was determined by coating the surface of a beaker with oil-based mud. A fixed volume of flush material was stirred under mild agitation for 5 minutes. (see appendix for details). Testing was conducted at room temperature. For most drilling fluids (photo 1), it was easy to visually distinguish the controls from the single component product. For certain oil-based drilling fluids, the difference in percent of mud removal was minimal between the single component flush and anionic flush. However, the glass surface washed with the anionic surfactant flush would have a thin film of oil making the surface oil-wet.

Volume Efficiency was measured using a simple field procedure used to gauge the volume, chemical compatibility and concentration of additives to add to a flush . The procedure measures the volume of flush material required to clean a glass jar coated with oil mud (see appendix). For most of the tested oil-based drilling fluids, the anionic surfactants required 3 flushes while the single component product required 2 flushes (photo 2). Similar to the previous test, the surfactant flush usually left the surface beading water.

CONCLUSION

This paper has highlighted many of the factors that affect design of a single component chemical flush. The results of the oil mud displacement studies show the synergistic effect between anionic surfactants with sodium silicate. Such a single component system reduces surfactant loading and promotes a higher level of water wetting. These results are not surprising considering the extensive use of sodium silicate as a detergent builder, particularly low ratio sodium silicates used in this application. Retained in this single component system are the traditional benefits associated with sodium silicate.

BIBLIOGRAPHY

1. R. Crook et al., « Eight Steps Ensure Successful Cement Jobs”, Oil & Gas Journal, volume 99, issue 27
2. PQ Technical Bulletin, 36-02, “Reduced Salinity of EcoDrill® Potassium Silicate-Based Drilling Fluids”
3. R. van Zanten et al., “Surfactant Nanotechnology Offers New Method for Removing Oil-Based Mud Resdidue to Acieve Fast, Effective Wellbore Cleaning and Remediation” , SPE paper 127884 SPE/IADC Formation Damage Conference, LaFayette, LA, March 2010
4. Chester L. Baker, Detergent Value of Sodium Metasilicate *Ind. Eng. Chem.*, 1931, *23* (9), pp 1025–1032
5. M. McDonald et al., "Use of Silicate-Based Fluids to Mitigate Corrosion”, SPE 100599, 2007 SPE International Symposium on Oilfield Chemicals, Woodlands, TX, March 2007
6. E. van Oort et al., “Silicate-Based Drilling Fluids: Competent, Cost-effective and Benign Solutions to Wellbore Stability Problems” , SPE paper 35059 presented at SPE/IADC Drilling Conference, New Orleans, LA, March 1996

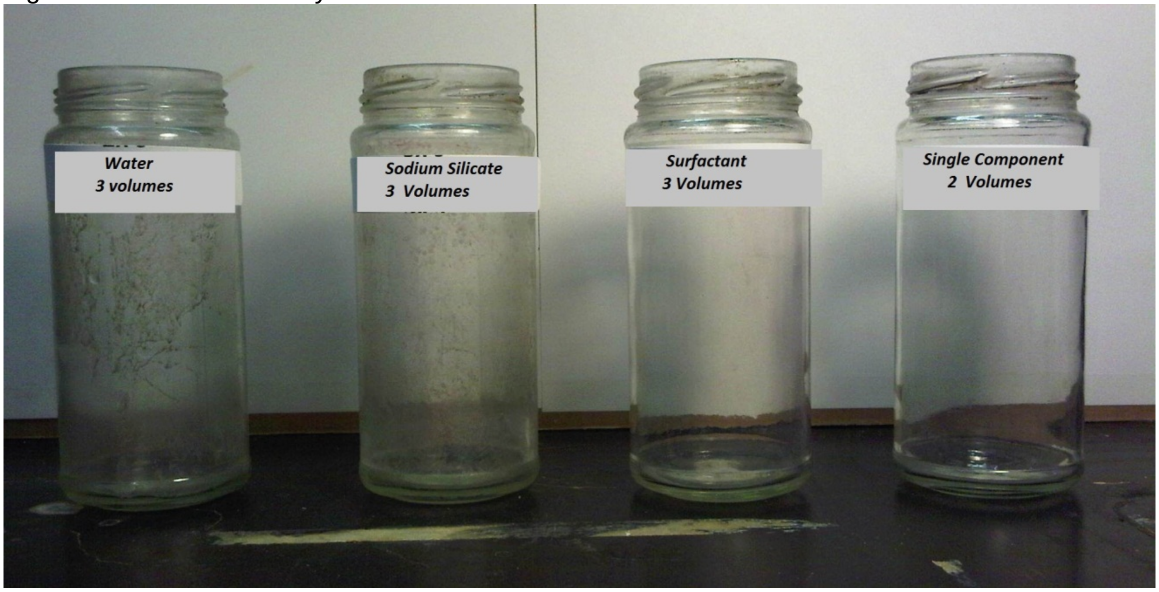
ACKNOWLEDGMENTS

Thanks to PQ Corporation for permission to publish this paper. Special thanks to Xianglian Li of National Silicates for conducting the necessary lab work and contributing to development of this product. Also to Brett Cramer of PQ Corporation for sharing his expertise on surfactant technology.

Appendix

Photo 1: Cleaning Efficiency

Figure 2: Volume Efficiency



Cleaning Efficacy

300 mL glass beaker was used in the test.

First, the clean beaker was weighed, and then fills it up with oil based mud and set for 5 minutes. After 5 minutes, mud was pouring out from beaker and the beaker was re-weighed, the weight of mud residue (coated in the beaker) was set as mud residue (A).

Second, the 300 mL of flush was added into the beaker, the beaker was placed under a stirrer and mixed with flush at 600 rpm for 5 minutes. After 5 minutes washing, the flush was pour out from the beaker, the beaker was re-weighed and the weight of mud residue (B) was ascertained by difference.

Finally, the beaker was placed upside down and let the free water to drop for 5 minutes. After 5 minutes, the beaker was re-weighed and the weight of mud residue (C) was ascertained by difference.

% of removed mud residue was calculated as below:

After pour out flush: % of removed mud residue=(A-B)/Ax100
After 5 min dropping: % of removed mud residue=(A-C)/Ax100

Jar Test Procedures

-250 mL glass beaker was used in the test.
 - the clean jar was filled with oil based mud and set for 5 minutes. After 5 minutes, mud was pouring out from jar.
-25 mL of flush was added into the jar, the beaker was shaken by hand for 15s and the flush was pour out from the jar
-repeat till the jar is clean.
-after the last flush, flush with 25 ml water
-observe jar, look to see if glass surface has beading