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Silicate Based Drilling Fluids: A Highly Inhibitive Mud System Offering HS&E Benefits Over Traditional Oil Based Muds

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Abstract

The past few years have witnessed a rapid growth in the use of sodium and potassium silicate based drilling fluids. The rise in North American popularity has followed from growing recognition within the oil and gas industry that soluble silicate based drilling fluids offer a combination of superior shale inhibition, cost savings and significant advantages with regard to Health Safety and Environment. A general overview will be presented of silicate chemistry, geographical areas using silicate muds and field performance. However, the focus of the paper will be the Health Safety and Environment implications of using silicate muds. Key areas to be discussed include the role of silicate in the health of marine and terrestrial plants and the corresponding results of toxicity tests on sodium and potassium silicate muds. Disposal options and cost will be discussed under current and future state regulations. Finally, health and safety will be discussed as it pertains to workers in contact with, or exposed to silicate muds

Introduction

Offshore and onland, operators in North America are increasingly having to deal with more stringent standards with regards to the disposal of drilling fluids and cuttings. Some of the regulatory changes in North America include:

- -increased restrictions on disposal of advanced gel chem systems
- -limits on admissible chloride levels
- -more stringent ROC limits on olefinic and ester based drilling fluids
- -oil and grease limits
- -new sediment toxicity test

Likewise, operators and contractors are facing higher standards with regards to employees being exposed to drilling fluids. The concern comes in the form of the effect of :

- -skin contact
- -inhalation of air borne drilling fluids
- -flammability and fire hazard
- -Slippery surfaces and footing

The HS&E issues regarding the use and disposal of drilling fluids and cuttings can become particularly challenging and costly in the pursuit to meet regulatory compliance. Therefore much research has gone into developing environmentally friendly drilling fluids that still meet the performance requirements of:

- -high level of shale inhibition
- -low cost
- -high ROP
- -ease of use
- -low depletion rate

It has been well documented that silicates meet the performance requirements of shale inhibition, low depletion rate and high ROP[1,2,3,4,5]. Until now, less attention has been given to the HS&E aspects of using sodium and potassium silicate drilling fluids.

1.0 Silicate Use in North America:

Silicate based drilling fluids have come full circle in North America. Silicate muds were first used in the 1930's to control "heaving shale" that plagued drillers along the Gulf Coast. These early wells proved that silicate based fluids could give oil-like levels of shale inhibition. Lack of strict environmental regulations meant that there was little economic incentive to develop these early silicate muds. Silicate muds were periodically assessed in subsequent years but did not make a commercial return to North America till 1999[5] . Silicate muds have seen the quickest growth in Western Canada. The growth in popularity can be partly attributed to silicate muds being able to meet the strict guidelines for landspreading of waste mud as outlined in Guide 50[6]. Formulation modifications and the recycling of potassium silicate based muds have further improved both the economics as well as the environmental performance.

In the United States, silicate muds are being used on a commercial scale in Oklahoma and Wyoming. Offshore use of silicate muds in the Gulf of Mexico has been sporadic to date

Potassium silicate muds are now being used in Mexico and are showing the potential to be used as a supplement to traditional oil based systems. More wells are expected to be drilled using silicate muds in 2002.

2.0 Silicate Chemistry

Soluble silicates are manufactured by the fusing of sand (SiO_2) with sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) at 1100-1200°C. The resulting glass is dissolved with high-pressure steam to form a clear, slightly viscous liquid that is sometimes referred to as "waterglass". The most important property of soluble silicates is the weight ratio of SiO_2: K_2O (or Na_2O). For example, a "2.5" ratio potassium silicate has 2.5kgs of SiO_2 for every 1kg of K_2O. Silicates are commercially produced in a variety of ratio ranges. The selection of ratio of silicate to formulate a drilling fluid is based on a number of criteria that include ease of use, stability and shale inhibition. In the case of Western Canada, a high ratio potassium silicate is the ratio of choice.

Sodium (or potassium) silicates are unique in that they can undergo four very distinct types of chemical reactions[7]. These reactions have been defined as:

- -gelation/polymerization
- -precipitation
- -hydration/de-hydration
- -surface charge modification

The gelation and ppt reaction has been discussed as it pertains to shale inhibition but these reactions can be used to help in the disposal of silicate drilling fluids or more particularly cuttings covered with silicate drilling fluids.

3.0 Health and Safety Benefits

Soluble silicates are well-established industrial chemicals that have been used in a variety of environmentally sensitive and health sensitive applications such as water treatment, soil remediation, manufacturing of soap and the latter discussed application of agriculture. Silicates have been classified as GRAS or Generally Recognized As Safe by the FDA. It is the designation given to substances that are considered safe for direct or indirect additives to foods and in many industries is considered a blanket statement of the harmless and nontoxic nature of a substance.

The main hazard associated with soluble silicates derives from their alkalinity. Both sodium and potassium silicate products can range from moderately to strongly alkaline. A similar level of safety and handling precautions should be exercised when working with silicates as with any other alkaline chemicals. Silicate may cause mild skin and eye irritation depending on the degree of alkalinity. It is recommended that personal protective equipment (PPE) and protective clothing be worn based on the degree of alkalinity of the silicate being handled. The inherent alkalinity of silicate drilling fluids has meant that biocides are generally not added to the drilling fluid. Furthermore, soluble silicates are established corrosion inhibitors thus eliminating the need to add corrosion inhibitors to the drilling fluid. The removal of biocides and corrosion inhibitors contributes to a reduction in mud costs and complements the health, safety and environmental benefits.

Soluble silicates are odorless, inorganic chemicals that produce no unpleasant fumes or VOC emissions. Because of this silicate based drilling fluids do not exhibit the distinctive odor associated with petroleum and synthetic drilling fluids. Silicate drilling fluids are also not as slick as oil muds. This helps to reduce slipping and falling hazards on an operating rig. The non-flammable nature of silicates further reduces the safety concerns associated with some drilling muds and makes silicate fluids less of a hazard to work with.

4.0 Agricultural

The use of soluble silicates in the agricultural industry provides data that supports the contention that silicates are not only benign but can be beneficial when applied directly to crops or to cultivated and natural lands supporting vegetation.

Therefore, the most effective and inexpensive disposal option for a drilling fluid is to discard at sea or to land spread. The soluble silica found in a silicate drilling fluid is identical to the material used in agriculture applications and delivers the same growth benefits.

Potassium silicate is an approved fertilizer in many countries including the USA. Crops primarily benefiting from the application of potassium silicate include; rice, grasses, wheat, barley, sugar cane, melons, grapes, beans, apples and other pome fruits, cucurbits, and ornamental plants. The application of potassium silicate is based on the need of plants for potassium but also the need for soluble silica, which is an essential micronutrient. Some of the benefits sited for soluble silica includes the following :[8,9,10,11]

1. Improves the structural strength of cell walls
2. Improves resistance to water stress
3. Improves resistance to fungal and other diseases
4. Higher tolerance to metals such as manganese, iron, phosphorous and aluminum (sequestration)
5. Increases plant growth rate and yield

Sodium silicate is used as a fertilizer in marine applications to help increase the growth of diatoms in seawater. The nutritional value of silica was established recently in North Sea region in a number of "sea harvesting" projects which involved addition of silicates for blue mussels, scallops and cod farming. MARICULT[12] a large-scale "marine cultivation" research and optimization program was funded by both, European Union and The Research Council of Norway. This program, implemented in 1996, has also recognized silica's nutritional value. . Similiar programs have been initiated in the USA (Oceanic Farming) and Japan (Marino Forum 21). High natural levels of silica can already be found in marine sediments. Dissolved silica from commercial soluble silicates is virtually indistinguishable from natural dissolved silica.

5.0 Disposal

Worldwide, various methods have been utilized for silicate drilling waste disposal including land spreading, land farming, solidification and burying for onshore disposal. In offshore drilling, spent silicate mud and associated cuttings have been typically discharged to the sea. The UK and Norwegian governments have awarded silicate the highest environmental rating of class E. Class E material such as silicates can be discharged to the sea at a maximum rate of 4750 tonnes/year/installation.

In Western Canada, a growing number of operators have chosen potassium silicate based drilling fluids over other water based drilling technologies.

In view of 1996 Guide 50 Drilling Waste Management Guidelines issued by the Alberta Energy and Utility Board (AEUB), a significant amount of study concerning environmentally sound disposal options for silicate based drilling fluids has been completed to date. The results of these studies have confirmed potassium silicate drilling wastes meet current requirements for safe disposal. One of the recommended on-site disposal methods for silicate drilling wastes is Mix-Bury-Cover, where drilling waste is incorporated into the subsoil in a ratio of at least three parts subsoil to one part drilling wastes. From the off-site disposal methods, clear fluids pump off and Mix-Bury-Cover method for disposal of drill solids and cuttings, is a viable and cost effective disposal option. Frequently, the choice of one disposal method over the other is determined by the method's suitability at the particular site.

As mentioned earlier in this paper, more stringent standards in regards to disposal have been imposed on all Advanced Gel Chem. Systems. As a result of tighter regulations, disposal approvals are mandatory for any land application involving these fluids. At present, operators are successfully obtaining approvals for disposal of potassium silicate drilling wastes.

Disposal practices for silicate based drilling wastes in US are comparable to the previously discussed practices. Drilling wastes can be disposed by landfarming, landspreading, roadspreading, solidification and burying activities. Primary agencies with jurisdiction over drilling wastes disposal vary with each state. Disposal regulations also differ from state to state.

6.0 Toxicity Testing of Soluble Silicate Muds

Although there is an extensive body of work on the toxicity limits of potassium silicate and sodium silicate, it is important to measure the toxicity effects of silicate based drilling fluids in order to establish safe disposal options. Based on drilling waste management guidelines set out by the Alberta Energy Utility Board (AEUB) and American guidelines set out by the American Society for Testing and Materials (ASTM), the Environmental Protection Agency (EPA) and the Rail Road Commision (RRC) the following tests have been performed on soluble silicate muds:

- seed germination and root elongation (barley and cucumber)
- earthworm survival.
- Microtox
- Mysid shrimp testing

Figures 1,2,3 give a summary of the test results. At the concentrations tested, waste potassium silicate drilling fluids had no negative impact on either seed germination or earthworm survival. Root elongation testing for cucumbers showed an improvement in root length of cucumber at a dilution up to 25% with a negative impact at higher levels.

One of the essential criteria that must be satisfied prior to any drilling waste disposal is that the drilling waste has to pass a toxicity evaluation. In Western Canada, the evaluation of potential mud toxicity was conducted on marine luminescent groups of bacterium, *Photobacterium Phosphoreum*. Soluble Silicates and silicate drilling fluid waste have been rated as non-toxic and successfully passed the Microtox bioassay, the established drilling industry standard test for defining potential mud toxicity in Western Canada. The Microtox results correlate to LC50 concentrations. Table 1 contains Mircotox test results and protocol for the tested silicate drilling fluids.

In the Gulf of Mexico, Mysid shrimp toxicity is a critical parameter. Mysid shrimp are known to be extremely sensitive to free potassium ions so there are some concerns surrounding the use of potassium silicate mud in this ecosystem. Growth, fecundity and survival tests run on *Mysidopsis Bahia* (EPA Method 1007.0) indicates that a neat solution of potassium silicate has an LC50 of 41,000 ppm. Since drilling fluids normally contain only about 10% silicate, the LC50 concentration should be approximately ten times higher for the drilling fluid itself if there were no other factors contributing to toxicity. This would be well above the EPA allowable concentration of 30,000 ppm and more than double the level of 200,000 ppm that most operators set as a minimum to avoid compliance problems.

To test this assumption, two generic mud formulations were prepared using potassium silicate and tested on Mysid shrimp. Both muds were designed to match common formulations currently used in the Gulf of Mexico. Table 2 contains the 96-hour LC50 Bioassay Test results for both muds. Detailed mud formulations are presented in Table 3.

Mud formulation A was found to have an LC50 of 166,000 ppm. While this result is a slightly lower LC50 concentration than expected based on the neat silicate numbers it is explained by the presence of KOH in the formula. KOH contributed additional potassium ions to the system thereby slightly increasing the impact on Mysid shrimp. Mud formulation B, which contained no additional sources of potassium, had an LC50 concentration of approximately 600,000ppm, which was more in line with the anticipated results. Both potassium silicate drilling fluids tested exceed the EPA requirement by a substantial margin and as such would be acceptable for use in the Gulf of Mexico.

Conclusions

Oil based muds offer excellent shale inhibition but at an ever increasing HS&E cost. Silicate based muds offer the same degree of shale inhibition as oil based systems but with numerous HS&E advantages. Some of the key HS&E properties of silicate muds are as follows:

- -soluble silicate can be disposed with negligible environmental impact
- -soluble silicates are safe, non-toxic and have a GRAS rating
- -silicates are non-volatile and contain no organics
- -soluble silicates have agricultural applications including the use of potassium silicate as a fertilizer
- -numerous environmentally sound disposal options exist for silicate based muds

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Figure1 – Response of Barley Seeds to Increasing Levels of Waste Potassium Silicate Drilling Fluid

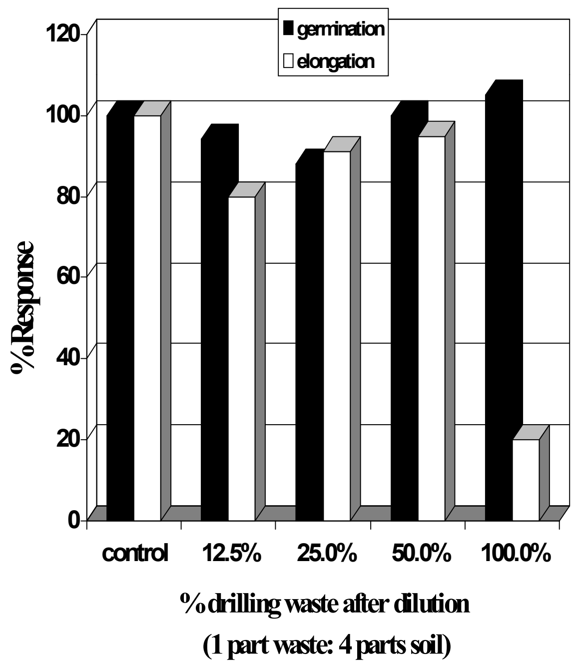


Figure 2 – Response of Cucumber Seeds to Increasing Levels of Waste Potassium Silicate Drilling Fluid

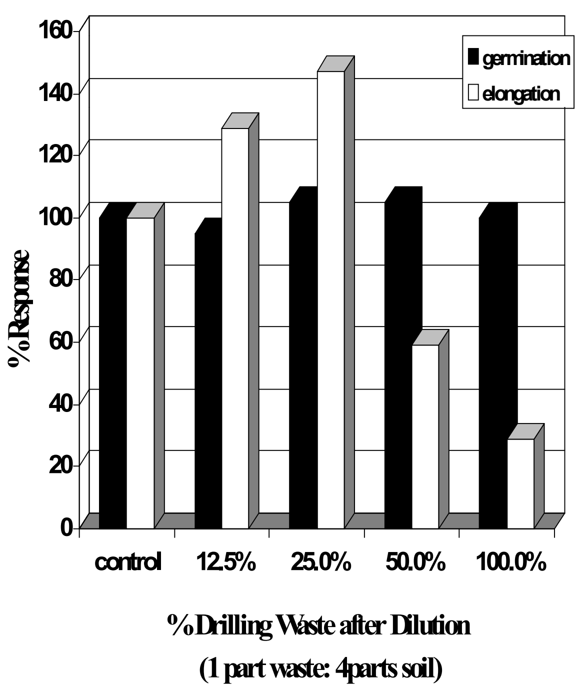
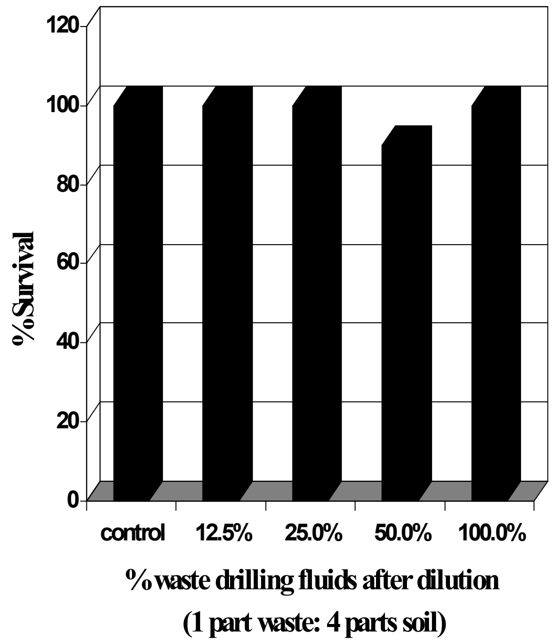


Figure 3 – Survival Rate of Earthworms in Soil Mixed with Waste Potassium Silicate Drilling Fluid



Testing Protocols

For Seed Germination, artificial soil was mixed with the appropriate sample dilution at a ratio of 1 part waste: 4 parts artificial soil. 30 grams of soil and sample were placed in a petri dish. Twenty seeds were added to the soil and covered by a 30g sand cap. Soil was hydrated with 7.5ml of de-ionized reverse osmosis water. Test was scored on the 5th day

For root elongation, a Whatman #3 filter paper was placed in a plastic petri dishes. The filter paper was hydrated with 3.5ml of the appropriate sample dilution after centrifugation. The controls were hydrated with deionized reverse osmosis water. The root lengths were scored on the 5th day.

For the survival rate of earth worms, 200g of artificial soil was placed in a 474 ml plastic cup. Ten worms were randomly added to the soil. The soil was hydrated with 40 ml of the appropriate dilution of sample. The organisms were scored on day 7 and 14. Day 14 results are reported

Note: All tests were conducted at 23C with 16hrs of light followed by 8hrs of darkness

Table 1- Microtox® Test Results

	Potassium Silicate concentration % by vol.	EC50(15) %
Potassium silicate drilling fluid waste(1)	12	>91
Potassium silicate drilling fluid waste(2)	10	100% with charcoal

The Microtox test is based on monitoring changes in the level of light emission from *Photobacterium Phosphoreum* bacterium cultures when challenged with a toxic substance or sample containing toxic materials. The Microtox endpoint is measured as the effective or inhibitory concentration of a test sample that reduces light emission under defined conditions of time and temperature. Normally, it is expressed as EC50 (15), which is effective concentration of a sample that reduces light emission of the test organism by 50% over a 15-minute test period at 15ºC.

Table 2 – 96 hour LC50 Definitive Bioassay Test Results on *Mysidopsis bahia;*
EPA, "Drilling Fluids Toxicity Test", 40 CFR; Part 435, Subpart A, Appendix 7

Drilling Fluid	Drilling Fluid Type	96 hour LC50	Pass or Fail
A	Silicate with 10% by vol Ecodrill 317	166,280 ppm	Pass
B	Generic 7 with 10% by vol Ecodrill 317	604,590 ppm	Pass

Table 3- Drilling Fluid Formulations

Additive	Drilling Fluid **A**	Drilling Fluid **B**
Seawater, bbl	0.79	-
Freshwater,bbl	-	0.79
Bentonite, ppb	-	20
Soda Ash, ppb	0.5	1
Lignosulfonate,ppb	-	4
Lignite,ppb	-	4
KOH, ppb	1.6	-
Caustic Soda, ppb	-	2
Xanthan Gum,ppb	0.75	-
PAC LV, ppb	5	0.5
Ecodrill 317,ppb	10% by vol	10% by vol
Barite, ppb	157.8	150