

MUD CONTAMINANTS

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Introduction

While drilling the drilling fluids is exposed to many contaminants, each one has different effects and consequences which lead to necessary treatment to minimize and avoid the drilling problems.

1- Solids

In oilfield terminology solids are classified by their density or specific gravity into two basic categories

High Gravity (HGS)

High gravity solids $SG > 4.2$ usually a weighting agent such as barite and hematite.

Low Gravity (LGS)

Low gravity solids $SG 1.6 - 2.9$ usually commercial bentonite and drilled solids with an assumed SG of 2.5.

Source of solids in mud's

High gravity solids are added to the mud to increase fluid density.

Even though they are added deliberately and are essentially non-reactive solids, they still adversely affect fluid rheology, particularly when they degrade by attrition to ultra fine particles.

Low gravity solids are often referred to as drilled solids and are derived from the drilled formation.

Symptoms

Drilled solids are the most common contaminant in drilling mud's.

Any particle of rock that is not removed by the solids removal equipment is re-circulated and reduced in size by attrition.

This process increases the exposed surface area,

More mud is required to wet the surfaces and increased product is required to maintain the desired fluid parameters.

The increase in the number of particles in the mud results in an increase in inter particle action and hence an increase in rheology, particularly plastic viscosity.

The irregular shape and size of drilled solids produces poor filter cake quality which in turn tends to result in an increase in filtrate volume and cake thickness.

Preventative Measures and Remedial Action

The efficient use of the best available solids removal equipment is essential in preventing a build up of undesirable drilled solids.

Primary separation

Primary separation equipment (i.e. **shale shakers**) is by far the most important tool in the control of drilled solids in the mud.

Efficiently operated and correctly screened shale shakers will remove the vast majority of drilled solids before they have the opportunity to degrade significantly.

Modern linear motion shakers will allow the use of screens as fine as 230 mesh, particularly when drilling with an oil mud.

The implications of barite removal must be considered if the use of screens finer than this is contemplated.

Hydro-cyclones

Hydro-cyclones (**de-sanders and de-silters**) should be used with caution.

The action of the centrifugal feed pump can aid in the attrition process and compound any existing problem.

Hydro-cyclones should not be used when drilling with an oil mud as the large volumes of liquid discarded will have adverse effects on the environment and on mud costs.

Centrifuges

Correctly set up centrifuges are effective at removing fine solids however, they are not capable of treating large volumes (**typically 1 – 1.5 bbl/min**) and as such are really only of benefit when using an oil mud where dilution rates are low or when drilling small diameter hole.

Dilution

Eventually solids will degrade to so small a diameter that they cannot be removed even with the use of a high speed centrifuge.

In such circumstances some dilution method must be employed. The addition of base fluid (**water or oil**) may help in the short term by increasing the liquid phase of the mud, hence increasing the separation and therefore inter-particle action of the solids.

However this approach does not actually remove any solids from the system and the solids attrition process and mud property degradation continues. The ultra fine solids can only be removed from the system by removing a portion of the mud from the circulating system.

In the case of water based mud's "whole mud dilution" should be used. This process involves dumping large volumes of solids laden mud (**less than 500 bbls will have little effect on an average circulating system**) and replacing it with newly formulated clean mud. This process is not viable with oil mud's or synthetic oil mud's.

When this type of mud becomes laden with ultra fine solids it must be returned to the shore based mud plant for treatment. Fortunately, as oil mud's tend to maintain the integrity of cuttings, thus allowing effective removal by the shale shakers, this requirement for this action is rare.

When using a dispersed mud, the addition of chemical thinners (.e.g. **lignosulphonate, Drill-Thin etc.**) can be used to treat the symptoms of increasing solids content. However, the cause is still present and dilution will ultimately be required.

2- Calcium and Magnesium

Either of these divalent ions may, even at low concentrations, have adverse effects on some water based mud's particularly when these mud's have a high solids content.

Very high concentrations of either of these ions may have adverse effects on the performance of polymers in water-based mud's and on the emulsification packages of some oil based mud's.

Source

Both calcium and magnesium can be present in make up water (particularly sea water), formation water and mixed salt evaporite formations.

Calcium is encountered in greatest quantity when drilling cement or anhydrite.

Magnesium often accumulates in the mud when drilling in magnesium rich shales (e.g. **North and Central North Sea**) or mixed salt formations (e.g. **the Zechstein evaporites of the southern North Sea**).

Symptoms

Magnesium

The major effect of **magnesium** is to react with hydroxyls in the mud system thus depleting mud alkalinity and pH. This can in turn allow the undesirable carbonate and bicarbonate components of alkalinity to become dominant.

Calcium

Calcium ions flocculate bentonite based mud's and other water based mud's containing reactive clays giving rise to changes in rheology (decrease in plastic viscosity and increase in yield point and gels) and loss of filtration control. The presence of increased calcium levels can be verified from chemical analysis of the filtrate. The combination of high calcium levels and high pH will precipitate most common polymers used in water based mud's – loss of rheology and filtrate control will result.

Preventative Measures and Remedial Action

Magnesium

Small quantities of magnesium such as those present in seawater can be readily removed with additions of caustic soda.

Magnesium hydroxide is precipitated at a pH of approximately 10.5.

When large quantities of magnesium are encountered (**magnesium shales, evaporites or brine flows**) it is not practical to treat out the contaminant.

Large scale gelatinous precipitation of magnesium hydroxide will adversely effect rheology, increasing gel strengths in particular.

The large surface area of this precipitate consumes huge quantities of mud chemicals. This is particularly problematic in oil mud's where surfactants are effectively stripped from the mud and can cause the whole system to "flip". In these cases no attempt should be made to adjust the alkalinity until clear of the source of magnesium.

Modern surfactant packages do not generally require a big excess of lime so oil mud performance should not be compromised.

A low pH in a water based mud could promote corrosion of drill pipe so consider the application of oxygen scavengers and filming amines until the pH can be restored.

Calcium

Small quantities of calcium (<400 mg/lit) are acceptable, even desirable, in most water based mud's. A background level of calcium acts as a buffer against the presence of undesirable carbonate alkalinity.

High concentrations of calcium can, however, have major adverse effects on water based mud's. The major sources of large quantities of calcium are discussed below:

Cement

The chemistry of cement is complex. However, from the mud contamination point of view, it can be considered to be lime, Ca(OH)₂. The major contaminant is calcium but in some circumstances, the hydroxide ion will compound the problem. At high temperatures (> 250°F)

severely contaminated bentonite based mud's can solidify.

When it is planned to drill cement, particularly when it is not completely hard, some precautions can be made to minimise the potential effects of the contamination.

- If viable, drill out as much cement as possible with seawater before displacing to mud.
 - Minimise caustic soda additions during operations, including the mixing of new mud, preceding the drilling of cement.
 - Pre-treat with small amounts of sodium bicarbonate – 0.25 lb/bbl is usually sufficient, perhaps twice this if green cement is anticipated. Avoid over treatment, as an excess of bicarbonate in the mud system can flocculate mud solids and adversely affect rheology and filtration control.
 - Closely monitor pH and Pf while drilling the cement and adjust treatments as required to prevent polymer precipitation (**keep pH below 11.0**) and clay flocculation. Sodium bicarbonate will reduce calcium and pH. Any acid, conventionally citric acid, will reduce pH as will SAPP, Lignosulphonate and lignite.
 - When it is known that large amounts of green or soft cement are to be drilled consideration should be given to converting the mud to a lime system, which is tolerant of cement contamination. Large amounts of a suitable dispersant (e.g. Lignox) must be available to successfully accomplish this conversion.

Oil based and synthetic oil based mud's are largely unaffected by cement. However, the water fraction of green cement may reduce oil water ratios.

Whenever possible drill out cement with seawater or water based mud, prior to displacing to oil based mud.

Anhydrite

Anhydrite (CaSO₄) is the anhydrous form of gypsum and is sufficiently soluble to provide calcium ions for clay flocculation. The calcium effects will be as for cement, but gypsum contamination generally has no direct effect on the pH of the mud.

When only small stringers are anticipated the excess calcium can be treated out with soda ash (sodium carbonate).

Care should be taken to avoid over treatment, as the adverse effects of carbonate contamination are equally as bad as those of calcium.

Small additions of a deflocculant such as Lignosulphonate will smooth out the rheology during treatment.

If massive anhydrite is prognosed and a water-based mud is being used, consideration should be given to converting the mud to a gypsum system which is tolerant of calcium contamination.

Oil based mud's are unaffected by anhydrite contamination.

3- Carbonates and Bicarbonates

There are three species of contaminant in the “carbonate system”

1. 1. **carbonic acid (H₂CO₃),**
2. 2. **bicarbonate (HCO₃)**
3. 3. **and carbonate (CO₃).**

Figure 1 shows the equilibrium levels of these species at varying pH levels.

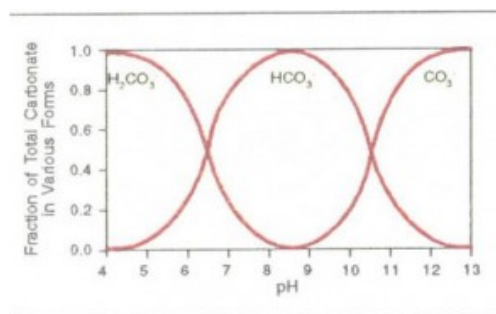


FIGURE 1

Figure 1: Equilibrium levels of carbonates and bicarbonates

Source

There are four common sources of carbonate system contaminants:

1. **1.** Carbon dioxide from formation gases. *E.g. Over treatment when removing calcium from the mud i.e. excess use of soda ash and sodium bicarbonate.*
2. **2.** Thermal degradation of organic mud products (e.g. *FCL, lignite and starch*).
 1. Contaminated barite, particularly when drilling HTHP wells with water based mud's. It is essential that QA/QC procedures are applied to all batches of barite prior to shipment to such wells.
 2. Contaminated bentonite.

Symptoms

Characterised by general increases in rheology, particularly yield point and gel strengths, and increases in filtrate.

Typically these effects are worse in high solids mud's and in high temperature applications.

The symptoms will not respond to chemical deflocculation such as Lignosulphonate treatment.

Preventative Measures and Remedial Action

Prior to treatment the situation should be assessed with all available data – over treatment with the calcium ion must be avoided. Several mud testing options are available to the mud engineer none of which, however, render definitive information in the field.

· **pH, Pf and Mf** are determined by pH meter and by titration. The ratio and relationship between these values will, in theory, allow carbonate species to be determined.

Table 1: Ph, Pf, & Mf, Alkalinity concentration mg/lt

Criteria	OH-	CO₃²⁻	HCO₃
Pf = 0	0	0	1220 Mf
2Pf > Mf	0	1200 Pf	1220 (Mf – Pf)
2Pf = Mf	0	1200 Pf	0
2Pf < Mf	340 (2Pf – Mf)	1200 (Pf – Mf)	0
Pf = Mf	340 Mf	0	0

· **P1 and P2** is another titration method which generally gives more reliable results than the Pf, Mf method.

Table 2: P1, & P2, Alkalinity concentration mg/lt

· The **Garrett Gas Train** is another method that uses weak acid to convert all carbonate species to CO₂ which is then measured in a Drager Tube. A conversion factor is then used to determine the carbonate concentration.

Experienced mud engineers place little faith in the results of these tests when determining the required treatment. There are a number of reasons for this.

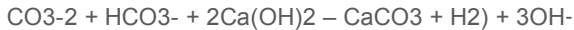
Primarily the titration methods and end points are notoriously subject to error and secondly, by the time the analysis has been completed, changes in mud chemistry will have already occurred. A combination of judgement and pilot testing usually corrects the problem.

In cases where the system does not respond to treatment or where continuous CO₂ influxes occur, consideration should be given to

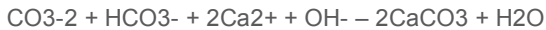
converting the mud to a lime system.

The basic treatment for carbonate contamination is to precipitate the carbonate with the calcium ion derived from either lime (Ca OH₂) or gypsum (CaSO₄). The addition of calcium will, however, have effect on bicarbonates. These must first be converted to carbonates by the addition of hydroxyls. Conventionally this would be achieved either with caustic soda or with lime. Bicarbonate cannot exist in the presence of hydroxyls. Under normal conditions bicarbonates begin to convert to carbonates at a pH above 9.5. The basic reactions that take place during the treatment are:

Lime



Gypsum + Lime or Gypsum + Caustic Soda



A gypsum/caustic combination tends to be the preferred treatment in polymer mud's as good control of pH is possible. The combination of calcium and high pH in lime can be detrimental to polymer performance. The use of large amounts of gypsum should be avoided in clay-based fluids as the sulphate ion can itself cause severe flocculation.

4- Salts Formations and Brine Flows

By far the most commonly encountered salt in the drilling industry is sodium chloride. Potassium chloride, calcium chloride and magnesium chloride are however, sometimes drilled in complex evaporite sequences.

Source

Various chlorides are found in seawater, brine flows, salt domes, salt stringers and massive complex evaporite formations.

Symptoms

Water Based Mud's

The extend of the effects of contamination depends largely upon the mud type and the concentration and type of contaminating salt. Divalent salts (calcium and magnesium) will have a greater contaminating effect on water-based mud's than mono-valent salts (sodium and potassium). Freshwater bentonite mud or low salinity mud with active drilled solids will be flocculated by high chlorides or by divalent ions in the salt. Viscosity will initially increase but at very high chloride levels may decrease due to collapse of the clay structure. Low solids polymer mud's exhibit good resistance to salt contamination.

Oil Based (and Synthetic Oil Based) Mud's

Oil based mud's are largely unaffected by drilled salts although the water phase of the mud will increase in salinity and may well reach saturation if massive salt is drilled. Large brine flows can adversely affect oil mud's. The mud tends to take on a grainy appearance, rheology tends to increase as oil/water ratio decreases due to the water content of the brine flow. Chloride content can show marked changes depending upon the salt content of the brine flow. In extreme cases saturated brine flows can result in re-crystallisation of the brine phase of the mud. This can result in removal of crystals at the shakers and a corresponding loss of surfactant. If rapid remedial action is not taken (i.e. **replacement of surfactants water wetting of solids will occur and phase separation will result**). This can be disastrous in terms of borehole stability and well control. Similar problems can occur if the brine flow contains magnesium chloride **–this reacts with lime in the mud and the resulting precipitation of magnesium hydroxide will strip surfactants from the system.**

Preventative Measures and Remedial Action

The use of the correct mud weight will minimise brine flows into the system and adjustment of mud weight must be the initial step in the prevention of further influx. Early detection of a brine flow will minimise the volume and hence the effects of the brine influx.

Water Based Mud's

Chloride levels cannot practically be reduced by chemical precipitation. Dilution with freshwater may reduce chlorides to tolerable levels but this is only feasible in low density mud's – the additions of barite required to maintain mud weight in a high weight mud would be prohibitive in terms of time and cost. When using a bentonite system, pre-hydration of the clay in drill water prior to addition to the active system will provide some short term viscosity and filtration control. For longer term stability it will be necessary to substitute salt resistant polymers (e.g. **PAC, XC and Starch**) for the bentonite.

Oil Based (and Synthetic Oil Based) Mud's

The symptoms detailed above must be addressed as soon as they are recognised.

· When magnesium salts are present, from drilled formation or from brine flows, addition of lime to the mud should cease.

When a brine flow is encountered, oil-wetting surfactants must be added steadily until any hint of water wetting is removed.

There is an API test for water wetting but an experienced mud engineer will be aware of the problem and begin treatment before the test is underway.

**** Any trace of water or emulsion in the HTHP filtrate must be eradicated by the addition of an appropriate combination of primary and secondary emulsifiers.***