

Salt Contamination

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The three naturally occurring types of rock salt encountered in drilling operations are halite (NaCl), sylvite (KCl) and carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$); also, see the chapter, "Drilling Salt." These salts are listed in the order of increasing solubility. Two other common salts are magnesium chloride (MgCl_2) and calcium chloride (CaCl_2). These two salts do not occur naturally in the crystalline form due to their extreme solubility. However, both can occur singly, together or with other dissolved salts in connate water.

A saltwater flow can be far more detrimental to flow properties than drilling into rock salt since the salts are already solubilized and react with the clays more rapidly. When a saltwater flow occurs, the mud density must be increased to control the flow before time can be taken to condition mud properties.

The mechanism of contamination in the case of salts is based on cation exchange reactions with the clays, mass action by the predominant cation and sometimes pH. The only systems on which dissolved salts have little or no effect are clear water, brines, oil-base muds and some low-colloid polymer systems. Whether the source of salt is from makeup water, seawater, rock salt or from saltwater flows makes little difference on bentonite-base mud systems. The initial effect is high viscosity, high gel strengths, high fluid loss and a large increase in the chloride content with smaller increases of hardness in the mud filtrate. Salt base-exchanges with the clays to flush the calcium ion from the clay particles, resulting in an increase in hardness. Detecting a chloride increase does not define the problem well enough to know how best to treat the mud since the chloride test does

not indicate what metallic ion(s) are associated with the chlorides.

For a better understanding of these salts and how to treat the contamination in each case, the salts and/or their associated cations are described separately.

HALITE (NaCl)

Halite (common table salt) is the most frequently drilled salt and is the major constituent of most saltwater flows. The initial effect on drilling mud is flocculation of the clays caused by mass action of the sodium ion. The funnel viscosity, yield point, gel strengths and fluid loss will all increase when halite is encountered. The presence of halite can be confirmed by an increase in chlorides. The clays dehydrate with sufficient sodium and time. In doing so, the particle size is decreased due to the reduction in adsorbed water. The released water rejoins the continuous phase of the mud, which may result in a slight reduction in plastic viscosity. But the dehydrated clay particles flocculate, causing a high yield point, high gel strengths and a high fluid loss. The fluid loss will increase in direct proportion to the amount of salt incorporated into the mud.

Treating the mud involves adding enough deflocculant to maintain desirable flow properties and dilution with freshwater to obtain suitable rheology. Chemical treatment must be continued until the clays have been deflocculated. Additional caustic is required to raise the pH. This depends on how much salt is drilled and whether there is a sufficient amount to dehydrate all the clays in the system. If the pH is reduced to less than 9.5, the pH may need to be increased with caustic soda for the acid-base deflocculants to become soluble in order to be effective.

Pure halite has a pH of 7. Therefore, the more halite drilled, the more caustic is required to maintain the pH above 9.5. Halite also has an effect on the instruments used to measure pH. If pH paper is used, the accuracy of this paper is affected by the chloride concentration and will indicate a lower pH as the chlorides increase. If the halite is pure, a pH reduction greater than one unit is not expected up to complete saturation of the mud. However, pure halite is rarely encountered. Associated minerals such as anhydrite are usually present to some extent, which will increase the filtrate calcium. Therefore, some caustic soda will usually have to be added along with the defloculants to maintain the pH in the proper range.

A greater degree of accuracy can be attained if a pH meter is available. The normal probe used in this instrument contains a potassium chloride (KCl) solution and is inaccurate when measuring pH in high-sodium-content solutions. Therefore, a special salt-compensated probe should be used to measure pH in high-salt muds.

The chloride titration is used to indicate the degree of saturation of NaCl solutions, since a quantitative measurement for sodium does not exist for field use. Since neither sodium nor chlorine can be economically precipitated from the mud, there is no alternative but to tolerate the concentration of halite that enters the mud system. Dilution with freshwater is the only economical way to reduce the chloride concentration.

If massive salt or frequent salt stringers must be drilled, the mud should be saturated with salt to avoid washout and hole collapse. Whether saturated or not, a fluid-loss-control agent is usually necessary at concentrations greater than 10,000 mg/l. This could be one of several materials such as RESINEX[®], POLY-SAL[™], SP-101[®], MY-LO-JEL[™],

POLYPAC[®] R and prehydrated bentonite. The addition of bentonite is usually recommended regardless of the specific type of salt contamination. Under these circumstances, dry bentonite should not be added directly to the system. The bentonite should be prehydrated and protected with additional chemical before adding it to the active system.

SYLVITE (KCl)

The response of the mud properties to sylvite contamination and the treatment of the mud for sylvite are identical to that for halite. If the mud contains no chlorides other than those obtained from drilling the sylvite salt, the chloride titration value would be an accurate measurement of the potassium ion concentration. However, this is rarely the case. It is not uncommon to find these salts interbedded. The quantitative titration for the potassium ion can be used to identify the salt as either pure sylvite or partially sylvite for geologic purposes.

It is important to know the type of salt to be drilled. Since the solubility of sylvite is slightly greater than halite, a massive sylvite salt section drilled with a saturated halite fluid would still wash out to some extent, although not as severely as if freshwater is used. It is difficult to prepare a saturated KCl fluid with desirable flow properties, fluid-loss control and good suspension characteristics. However, if required (and assuming that hole conditions would permit), a clear, saturated KCl fluid could be used.

CARNALLITE (KMgCl₃•6H₂O)

The complex salt "carnallite" is relatively rare. However, it does occur to some extent in parts of the United States, South America, Europe and the Middle East. The most notable occurrence is in Northern Europe underlying the North Sea drilling area. This is the Zechstein salt that consists of

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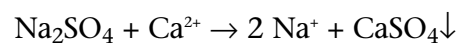
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interbedded halite, sylvite and carnallite. Mud problems associated with carnallite are severe and two-fold:

1. When solubilized, there are two strong cations (calcium and magnesium) acting on the clays to cause flocculation and dehydration. Mud treatment would not be too difficult if this were the only problem.
2. In the presence of hydroxyl ions (OH⁻), the magnesium from the dissolved carnallite precipitates as magnesium hydroxide (Mg(OH)₂). This precipitate (Mg(OH)₂) is a thick jelly-like substance that acts as a viscosifier. At the relatively low pH of 9.9, there are sufficient hydroxyl ions present for the precipitate to have a profound effect on mud viscosity. Magnesium can only be precipitated by caustic. This reaction starts occurring with as little as 0.03 lb/bbl of caustic soda. Therefore, caustic soda should not be used if it can be avoided. A viscosity

increase will occur if magnesium is precipitated by caustic soda.

Most drilling muds are run in an alkaline state to maximize the performance of the clays and other chemicals used to treat drilling fluids. They are also run in the alkaline state to minimize corrosion. Calcium should be removed by raising the pH and treating with soda ash to neutralize the calcium as CaCO₃. Sodium sulfate (Na₂SO₄) is one chemical available to control filtrate calcium in high magnesium content fluids. The chemical reaction is as follows:



This reaction does not affect the potassium or magnesium content. However, it will control filtrate calcium to a maximum of 400 mg/l. This is the equilibrium solubility of CaSO₄, or gypsum, and is indicated by the reversible segment of the above equation.

Saltwater Flows

Connate waters can contain a broad spectrum of salts. The origin of these salts is directly related to the origin of the sediments themselves. Since marine sediments are deposited in seawater, they usually contain salts similar to those found in seawater. However, with most of the water driven off in the compaction process, the salt concentration can be considerably higher.

The solubility of most common salts is directly proportional to temperature. As the temperature of a salt solution increases, the solubility of the salt in that solution increases. A solution saturated with a certain salt at surface temperature is capable of holding more salt in solution at elevated temperatures. In addition, other chemical reactions such as leaching of minerals from sediments by groundwater can enrich connate

waters with additional anions and cations. Many of these can be detrimental to drilling fluids. Those waters highly enriched in calcium and magnesium are the most detrimental.

In the case of high-magnesium-content water, the relationships previously discussed under carnallite apply. The indicators for magnesium are as follows:

1. A rapid pH reduction occurs.
2. Mud thickens with additions of caustic soda or soda ash.
3. Titrate for magnesium ion concentration.

The total hardness titration is reported as soluble calcium in mg/l. However, this titration also detects magnesium. To verify the presence and concentration of magnesium, calcium and magnesium must be titrated separately.

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Indicators for a high-calcium-content water flow, assuming little or no magnesium present would be:

1. A lesser effect on pH.
2. A positive mud response to caustic soda or soda ash additions.
3. Titrate for the true calcium ion concentration.

The terms *high-calcium-* or *high-magnesium-content* connate water is used because sodium salt is nearly always present. This illustrates the point that the chloride determination can be misleading. For instance, observe the variance in the ratio of chloride to the associated metallic ions in the salts previously discussed.

NaCl	- Halite
KCl	- Sylvite
MgCl ₂	- Magnesium chloride
CaCl ₂	- Calcium chloride
KMgCl ₃	- Carnallite

In a pure solution of one salt, that salt can be identified by the chloride content and titrating for the cations (except sodium). However, in mixed-salt solutions the problem becomes complex to the point of becoming an academic exercise. This is especially true since only calcium, potassium and magnesium can be easily identified in the field. The chlorides not associated with the identifiable cations are assumed to be associated with the sodium ions.

Hydrogen Sulfide (H₂S) Contamination

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The most serious and corrosive contaminant discussed in this chapter is hydrogen sulfide (H₂S) gas. This gas is destructive to tubular goods and toxic to human life. The appropriate personal protective equipment and worker safety measures should be taken immediately if H₂S is identified. Hydrogen sulfide gas originates from:

1. Thermal deposits.
2. As a formation gas.
3. Biologic degradation.
4. Breakdown of sulfur containing materials.

Hydrogen sulfide gas can be identified by the:

1. Reduction of pH of the mud.
2. Discoloration of mud (to dark color) due to the formation of FeS from barite.
3. Rotten egg odor.
4. Viscosity and fluid loss increase due to pH reduction.
5. Formation of a black (FeS) scale on steel drill pipe.

Since H₂S is an acid gas, the pH of the mud is quickly reduced by

neutralization of OH⁻. In order to offset the harmful aspects of the H₂S gas, the pH must be increased to at least 11, or a safer level of 12, by adding caustic soda or lime. The following chemical reaction describes the alkaline application to H₂S. This can also be seen in Figure 5.

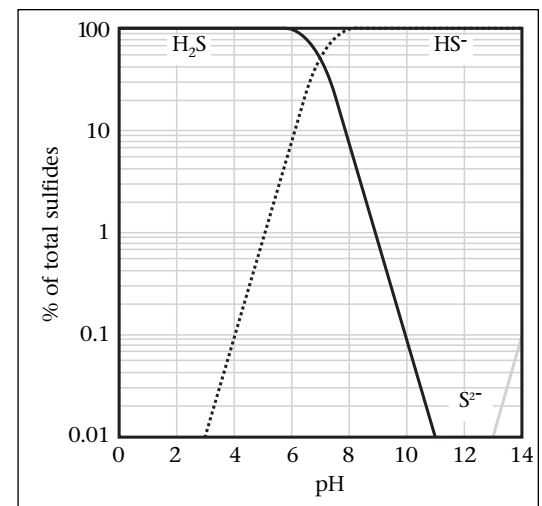
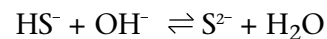
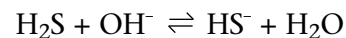
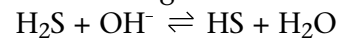


Figure 5: Distribution of sulfides with pH.