Overview of H_2S

Sources of Hydrogen Sulfide:

- Formation fluids that contain Hydrogen Sulfide
- By-product from anaerobic bacterial action on sulfur compounds present in the mud (i.e. Sodium Sulfite)
- Thermal degradation of mud additives containing sulfur (i.e. Lignosulfonates)
- Chemical reactions with tool joint lubricants containing sulfur.

Physical and Chemical properties

Hydrogen Sulfide (H_2S) is a colorless gas with a typical rotten egg odor at low concentration in air. At concentrations greater than 100 ppm, it cannot be smelled any more. It has a specific gravity of 1.18 (S.G. of air is 1.00), hence being heavier tends to settle at ground level and accumulate in lower areas.

H_2S is soluble in water, oil, alcohol and many other solvents.

H_2S is a flammable gas and burns with a blue flame producing Sulfur Dioxide—a very irritating gas.

H_2S is a weak acid that can go through the following 2 stages when dissolved in water or water based mud:

1. $H_2S \leftrightarrow H+ + HS-$
   - both steps (1 and 2) can go back and forth depending on the pH.
2. $HS- + OH- \leftrightarrow S^{=} + H_2O$

The graph on page 2 shows the relative concentrations of sulfide species (H_2S, HS- and $S^{=}$) versus pH in water solutions (including water based muds).

If the pH is less than 6, then hydrogen sulfide is mainly in the H_2S form. When pH increases to 6–8, part of H_2S converts into HS-. So, at pH 6–8 there is a mixture of H_2S and HS-.

For a pH of 8–12 the main ion is HS- but there is still some H_2S (that did not ionize in step1) and some $S^{=}$ (produced from HS- in step 2). Above a pH of 13, $S^{=}$ is the major ion in solution.

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Why is H_2S dangerous?

- It is extremely toxic to life, even in smallest concentrations
- It is highly flammable (more than methane) producing Sulfur Dioxide—a toxic gas.
- It is highly corrosive causing rapid pitting and hydrogen embrittlement of steel.
- Since it is a highly soluble acidic gas, it is also a mud contaminant, especially in Water Based Muds, where it can rapidly reduce the pH and increase mud viscosity and fluid loss.

Detection and determination of H_2S concentration in drilling fluids:

- Hach Kit for H_2S using Lead Acetate paper—for very low concentrations of H_2S: 0–5 ppm
- Garrett Gas Train (GGT) using Drager tubes—for higher concentrations of H_2S of up to 7%vol.

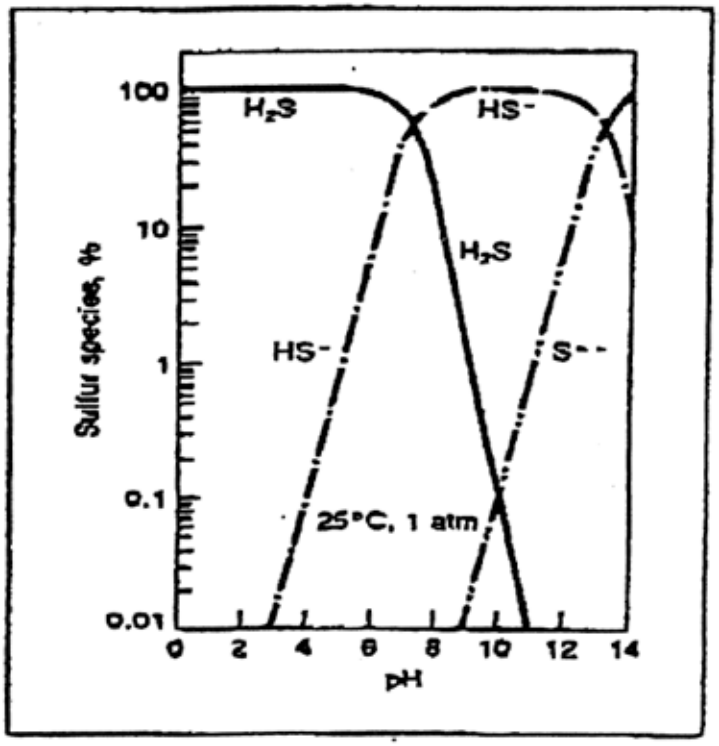

Fig. 3—Relative concentrations of sulfide species vs. pH for aqueous systems.

How to deal with H_2S:

- **The first step is to maintain alkalinity in the mud using Caustic Soda/Lime.**

  The concentration of H_2S that can be neutralized by the mud alkalinity is:
  H_2S (ppm) = 682,000 x Pm / Mud Density where: Pm – mud alkalinity, ml; Mud Density, kg/m^3

  Caustic Soda and Lime can successfully neutralize small amounts of H_2S, however the product of the reaction is Sulfide ($S^=$), which is not stable and will reverse to dangerous HS^- and H_2S when the pH drops. The Sulfide ($S^=$) should be removed by treatment with Zinc Carbonate or Zinc Chelate.

- **Use H_2S scavengers such as Zinc Carbonate, Zinc Chelate or Amines (HSO 600, HSW 705)**
  The Zinc ions provided by Zinc Carbonate or Zinc Chelate will react with the Sulfide ions forming insoluble Zinc Sulfide (solid in water) as follows:

  $Zn^{++} + S^= \rightarrow ZnS\downarrow$ - this ZnS is a stable form of sulfide

Zinc Carbonate is used in WBM. It has a limited solubility in fluids with pH 8–11.5 so the level of Zinc ions available to react is low.

- Maintain pH 10.5–11.0 when treating with Zinc Carbonate, start treatment rate at 3–9 kg/m^3.
- 3 kg/m^3 Zinc Carbonate will remove 500 ppm Sulfide. Determine the concentration of Sulfides with the GGT and add the required concentration of Zinc Carbonate to the mud.
- Disadvantages: it may lead to increase in YP, Gel Strength and Fluid Loss and may flocculate clays. Having a specific gravity of 3.5, it may settle in fluids that have low carrying capacity. It does not prevent hydrogen embrittlement and equipment failure.

Zinc Chelate provides a water soluble form of Zinc over a wide pH range: 7–13.

- The Zinc ion is loosely bonded in the Chelate and is readily available to react with Sulfide in the mud
- It does not have an adverse effect on mud properties (as Zinc Carbonate does)
- It does not settle out in brines or low carrying capacity fluids
- Treatment rate at 1–10 kg/m^3.
- 3 kg/m^3 Zinc Chelate will remove 200 ppm Sulfide. Determine the concentration of Sulfides with the GGT and add the required concentration of Zinc Chelate to the mud.

HSW 705 is an amine based product soluble in water. It is used to remove H_2S from WBM. The product is a flammable liquid with flash point of 40°C.

- 1 L/m^3 HSW 705 will remove 100 ppm H_2S

HSO 600 is an amine based product soluble in oil. It is used to remove H_2S from OBM. The product is a flammable liquid with flash point of 52°C.

- 1 L/m^3 HSW 705 will remove 170 ppm H_2S.

Each product, HSW 705 or HSO 600:

- Quickly and permanently removes the H_2S with no pH restriction
- Does not form solid products when reacting with H_2S
- Does not have effect on rheological and filtration properties.